## "AN INVESTIGATION ON THE SYNTHESIS AND CHARACTERIZATION OF NOVEL POLY (PARA AMINO BENZOIC ACID) IRON - GRAPHENE OXIDE COMPOSITE"

### **PROJECT IN CHEMISTRY**

Submitted to St. Mary's College (Autonomous), Thoothukudi, in partial fulfillment for the award of the Degree of **Bachelor of Science** in Chemistry.

#### **Project Done By**

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# DECLARATION

We hereby declare that the project entitled "An Investigation on the Synthesis and Characterization of Novel Poly (p-aminobenzoic acid) Iron – Graphene oxide Composite" submitted to St. Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the Degree of Bachelor of Science is our original work and that, it has not previously formed the basis for the award of any degree, Diploma or similar title.

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APRIL,2023

Thoothukudi.

#### CERTIFICATE

This is to certify that the project in chemistry entitled "An Investigation on the Synthesis and Characterization of Novel Poly (para amino benzoic acid) Iron – Graphene Oxide Composite" is submitted to St. Mary's College (Autonomous), Thoothukudi, in partial fulfillment for the award of the degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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#### **INTRODUCTION**

#### 1. Composites

Composite materials are materials formed by combining two or more materials with different properties to produce an end material with unique characteristics. These materials do not blend or dissolve together distinct within the final composite structure. Composite materials can be made to be stronger, lighter or more durable than traditional materials due to properties they gain from combining their different components. There are a lot of composites around you. Concrete is a composite. It's made of cement, gravel, and sand, and often has steel rods inside to reinforce it. Those shiny balloons you get in the hospital when you're sick are made of a composite, which consists of a polyester sheet and an aluminum foil sheet, made into a sandwich. Most primitive manmade composite materials were straw and mud combined to form building construction.

Most composites have strong, stiff fibres in a matrix which is weaker and less stiff. The objective is usually to make a component which is strong and stiff, often with a low density. Commercial material commonly has glass or carbon fibres in matrices based on thermosetting polymers, such as epoxy or polyester resins. Sometimes, thermoplastic polymers may be preferred, since they are moldable after initial production. There are further classes of composite in which the matrix is a metal or a ceramic. For the most part, these are still in a developmental stage, with problems of high manufacturing costs yet to be overcome. Furthermore, in these composites the reasons for adding the fibres (or, in some cases, particles) are often rather complex; for example, improvements may be sought in creep, wear, fracture toughness, thermal stability, etc[1].

The polymer composites made from polymers, or from polymers along with other kinds of material. But specifically, the fiber-reinforced composites are materials in which a fiber made of one material is embedded in another material.

Composite =Matrix phase +Dispersed phase

- Matrix phase is the primary phase having a continuous character.
- Matrix is usually more ductile and less hard phase.



#### **1.1 Classification of Composites**

On the basis of matrix phase, composites can be classified into metal matrix composites (MMCs), ceramic matrix composites (CMCs), and polymer matrix composites (PMCs). The classifications according to types of reinforcement are particulate composites (composed of particles), fibrous composites (composed of fibers), and laminate composites (composed of laminates). Fibrous composites can be further subdivided on the basis of natural/biofiber or synthetic fiber.

Biofiber encompassing composites are referred to as biofiber composites. They can be again divided on the basis of matrix, that is, nonbiodegradable matrix and biodegradable matrix. Bio-based composites made from natural/biofiber and biodegradable polymers are referred to as green composites. These can be further subdivided as hybrid composites and textile composites. Hybrid composites comprise of a combination of two or more types of fibers.[2]

#### 2. Ceramic matrix composite

Ceramic matrix composite (CMCs) is a special type of composite material in which both the reinforcement and a matrix material are ceramics. In some cases, the same kind of ceramic is used for both parts of the structure, and additional secondary fibers may also be included. Because of this, CMCs are considered a subgroup of both composite materials and ceramics.

#### 2.1 CMC REINFORCING MATERIALS

Typical reinforcing fiber materials include the following:

- Carbon, C
- Silicon Carbide, SiC
- Alumina, Al2O3
- Mullite or Alumina Silica, Al2O3-SiO2

The fibers can take many different forms, including the more traditional continuous fiber as well as short fibers, particles, whiskers, and nanofibers. These fibers all have a polycrystalline structure like traditional ceramics possess. The reason you do not see glass, organic, or metallic fibers is because

CMC fibers must remain stable at temperatures above 1,800°F. The reinforcing fibers are just a fraction of the thickness of a human hair – and in the case of nanofibers, are even tinier. They are often woven into a fabric or tape - like material for inclusion in a CMC part. In a typical CMC process, the fibers are coated with a material such as boron nitride and then passed through a matrix slurry bath, resulting in a prepreg tape or cloth. The majority of current CMC applications use short fiber, whisker, or continuous fiber reinforcement. The use of whiskers



and short fibers improve the CMC's resistance to crack propagation and its overall toughness but can result in catastrophic failure. Long, or continuous, fiber reinforcement provides better strengthening than whiskers or short fibers. The use of long fibers also results in better toughness because the fibers can hold the CMC together even after the ceramic matrix has begun to crack, significantly slowing down crack propagation.

#### 3. Metal matrix composite

Metal composite materials have found application in many areas of daily life for quite some time. Often it is not realized that the application makes use of composite materials. These materials are produced *in situ* from the conventional production and processing of metals. Here, the Dalmatian sword with its meander structure, which results from welding two types of steel by repeated forging, can be mentioned. Materials like cast iron with graphite or steel with a high carbide content, as well as tungsten carbides, consisting of carbides and metallic binders, also belong to this group of composite materials. For many researchers the term metal matrix composites is often equated with the term light metal matrix composites (MMCs). Substantial progress in the development of light metal matrix composites has been achieved in recent decades, so that they could be introduced into the most important applications. In traffic engineering, especially in the automotive industry, MMCs have been used commercially in fiber reinforced pistons and aluminum crank cases with strengthened cylinder surfaces as well as particle-strengthened brake disks. These innovative materials open up unlimited possibilities for modern material science and development; the characteristics of MMCs can be designed into the material, custom-made, dependent on the application. From this potential, metal matrix composites fulfill all the desired conceptions of the designer. This material group becomes interesting for use as constructional and functional materials, if the property profile of conventional materials either does not reach the increased standards of specific demands, or is the solution of the problem. However, the technology of MMCs is in competition with other

modern material technologies, for example powder metallurgy. The advantages of the composite materials are only realized when there is a reasonable cost – performance relationship in the component production. The use of a composite material is obligatory if a special property profile can only be achieved by application of these materials. The possibility of combining various material systems (metal – ceramic – nonmetal) gives the opportunity for unlimited variation. The properties of these new materials are basically determined by the properties of their single components.

#### 4. Polymer Matrix Composites

Most commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredient. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, polyether ether ketone and others. The reinforcement materials are often fibers but can also be common ground minerals. The various methods described below have been developed to reduce the resin content of the final product. As a rule of thumb, hand lay up results in a product containing 60% resin and 40% fiber, whereas vacuum infusion gives a final product with 40% resin and 60% fiber content. The strength of the product is greatly dependent on this ratio. PMCs are very popular due to their low cost and simple fabrication methods. Use of nonreinforced polymers as structure materials is limited by low level of their mechanical properties, namely strength, modulus, and impact resistance. Reinforcement of polymers by strong fibrous network permits fabrication of PMCs, which is characterized by the following:

- a) High specific strength
- b) High specific stiffness
- c) High fracture resistance
- d) Good abrasion resistance

- e) Good impact resistance
- f) Good corrosion resistance
- g) Good fatigue resistance
- h) Low cost

Polymer matrix composite materials are widely used in biotechnology and medicine. Polymeric biomaterials have several advantages such as elasticity, resilience and ease of manufacturing. Also, these materials have a number of disadvantages: reduced strength, deformation and degradation over time.

#### 4.1 Factors Affecting Properties of PMC

Interfacial adhesion the behavior of a composite material is explained on the basis of the combined behavior of the reinforcing element, polymer matrix, and the fiber/matrix interface. To attain superior mechanical properties the interfacial adhesion should be strong. Matrix molecules can be anchored to the fiber surface by chemical reaction or adsorption, which determine the extent of interfacial adhesion. The developments in atomic force microscopy (AFM) and nano indentation devices have facilitated the investigation of the interface. The interface is also known as the mesophase.

# **4.2** Shape and Orientation of Dispersed Phase Inclusions (Particles, Flakes, Fibers, and Laminates)

Particles have no preferred directions and are mainly used to improve properties or lower the cost of isotropic materials. The shape of the reinforcing particles can be spherical, cubic, platelet, or regular or irregular geometry. Particulate reinforcements have dimensions that are approximately equal in all directions. Large particle and dispersion-strengthened composites are the two subclasses of particle-reinforced composites. A laminar composite is composed of two-dimensional sheets or panels, which have a preferred high strength direction as found in wood. The layers are stacked and subsequently cemented together so that the orientation of the high strength direction varies with each successive layer.

#### 4.3 Properties of Particle-Reinforced Metal Matrix Composites

Particle-reinforced metals are a particularly important class of metal matrix composites for engineering applications. There are a wide range of materials that fall in this category. A number of them have been used industrially for many years. An important example is a material consisting of tungsten carbide particles embedded in a cobalt matrix which is used extensively in cutting tools and dies. This composite, often referred to as a cermet, cemented carbide, or simply but incorrectly "tungsten carbide," has much better fracture toughness than monolithic tungsten carbide, which is a brittle ceramic material. Diamond particles embedded in a cobalt matrix, commonly called polycrystalline diamond, are used in rock drill bits and cutting tools. Particle-reinforced metals are now widely used in electronic and photonic thermal management and packaging applications. This is a major growth area, and new materials are continually emerging. Another commercial metal matrix composite, tungsten carbide particlereinforced silver, has been used as a circuit breaker contact pad material [3]. Here, the composite provides good electrical conductivity and much greater hardness and wear resistance than monolithic silver, which is too soft to be used in this application. Ferrous alloys reinforced with titanium carbide particles, discussed in the next section, have been used for many years in industrial applications. Compared to the monolithic base metals, they offer greater wear resistance and stiffness and lower density.

#### 5. GRAPHENE

Graphene as new material, due to its unique and novel properties has attracted extensive attention and in-depth research in the scientific community. Graphene, as a covalently bonded monolayer of carbon atoms with a hexagonal structure, is currently the thinnest material found in the world, and also makes it one of the world's best in terms of its properties. Graphene, with this special structure, contains rich and novel physical phenomena, which make it show many excellent properties such as ultra-high carrier mobility, good thermal conductivity, excellent mechanical modulus, breaking strength, and also a superior gas barrier, high transparency, and high specific surface area. Moreover, based on these extraordinary properties, graphene showed great potential application prospects and market value in different fields such as transportation, high-frequency electronic devices, flexible display, electrochemical biosensor, new energy battery, supercapacitor, aerospace, biomedical, etc.





Graphene can also be used as an ideal nanofiller to reinforce the properties of composites, thus providing a broader application space for composite materials. Even a small amount of graphene addition to composite tends to increase the mechanical, electrical, and processing properties. Hence, the addition of graphene into polymer composite has shown improvements of properties compared to pure polymer, significant changes in the mechanical, electrical, and thermal properties were proven, more than in the case of other materials. The polymer nanocomposites modified by graphene can be used in construction, automobile, aerospace, electronic, and medical applications, etc. The interaction between fillers and the polymer matrix at the interface has great importance for the performance of composites. As graphene is hard and very costly to produce, needs a lot of energy, and is difficult to control structure, coupled with other materials especially polymers, different alternatives were found by using modified graphene, such as graphene oxide (GO) and reduced graphene oxide (RGO) etc. provided more options which are considered easy to produce and showed a great improvement when combined with polymers. Generally, modified graphene coupled with polymers and polymer composites can be possibly reached easily using various methods [4].

Moreover, composite materials can be applied for producing materials with good tribological, electrical, and mechanical properties. Remarkably, compared with pure polymers, the addition of graphene derivative shows a great change in properties of the composite materials and proved to be suitable as alternatives to use under harsh conditions, especially corrosive and friction materials. In particular, high quality graphene nanofiller within polymer composites brought useful materials for technological applications and play a crucial benefit to the economy of different aspects. Graphene polymer composites have shown several advantages. Graphene provides new ways and opportunities for the preparation of lightweight, anti-corrosion, low friction. low-cost, high-performance, and multi-functional nanofiller/polymer composite materials. Therefore, this review studied and highlights the preparation, properties, use and applications, challenge, and future prospects for graphene based polymer composites. The preparation methods of graphene/polymer composites mainly include

- solution mixing method
- melt mixing method
- in-situ polymerization method.

**Solution mixing** involves dissolving graphene and polymer in appropriate solvent, obtaining uniform mixed solution by ultrasonic or violent stirring, and then obtaining the graphene polymer composite by removing solvent or precipitation. Solution mixing is a common method for preparing the graphene/ polymer composites. This method is simple, direct, does not require complex equipment, and can be prepared in large quantities, which can be widely used in industrial production. A variety of graphene/polymer composites were prepared by using this method, such as, polystyrene/ exfoliated graphite nanoplate composites, polycarbonate/graphene composite, polyvinylpyrrolidone/zeolite composite, etc.

**Melt blending** is the mixing of filler and polymer matrix at a relatively high temperature. Through strong mechanical stirring, the filler is evenly dispersed in the matrix, which enhances the interface bonding between filler and matrix. This blending method is appropriate for the mixture of thermally reduced graphene or exfoliated graphite and thermoplastic polymer. Compared with solution blending, melt blending shows a great advantage for large-scale industrial production, effectively avoiding the use of solvents, thus meeting the requirements of economy and environmental protection. Melt blending cannot achieve good spreading of fillers in the matrix like solution blending, and higher shear stress may affect the size and morphology of graphene sheets, which are connected to the properties of graphene and composite materials.

**Insitu polymerization** methods generally involve the mixing of nanomaterial in a neat monomer (or multiple monomers) or a solution of monomer, followed by polymerization in the presence of the dispersed nanomaterial. Different polymers composites were obtained with this method, including polypropylene/graphene oxide, polyurethane/graphene oxide, polyvinylidene fluoride/graphene. In situ polymerization is a kind of polymerization method by mixing polymer monomer solution and graphene solution, adding a certain catalyst, and polymerization under appropriate conditions [5].



#### Graphene/polymer composites preparation methods

It should be noted that the mixing order, proportion, and concentration of graphene and monomer solution have an important influence on the polymerization. Some examples are polyester/reduced graphene oxide composites, polyimide/graphene oxide, polyurethane/ graphene oxide/epoxy nanocomposites, and graphene-phenol formaldehyde.

# 5.1 Elements involving in the development of graphene into polymer nanocomposites Graphene structure

Graphene is a monolayer with carbon atoms connected by sp2 hybridization and has a honeycomb two-dimensional grid structure with a monolayer thickness of 0.35 nm. Graphene can produce different shapes of sheets accordingly; it can be further coated into zerodimensional fullerenes (a), curled into one-dimensional carbon nanotubes

(b), and stacked into three-dimensional graphite.

Nariman Yousefi et al examined the ultra-large graphene oxide effect on nanocomposite. Hence, the lateral size of the flakes plays a significant role in controlling the microstructure and properties of graphene-based materials. Herein, reducing the size distribution of graphene sheets tends to improve the properties of macroscopic graphene materials. Different sizes of graphene nanosheets have their advantages. Large nanosheets of graphene have higher electrical conductivity compared to that of small nanosheets. Graphene with ultra-small size nanolayer constitutes a novel material suitable for biological applications. Furthermore, the graphene size of nanosheets affects the electrical conductivity of

nanocomposites and thermal increase proportionally with flakes size of graphene.

#### 5.2 Preparation Methods and Mechanisms of Graphene composites

Graphene has been commonly used to enhance the properties of polymers and has shown noteworthy results. Different methods have been used in the preparation of graphene polymer composites, as mentioned above and each has advantages well as disadvantages for the formation of final materials; for example, in the case of melt blending it is difficult to disperse graphene, and graphene oxide and some chemically modified graphene may degrade during the melting process which affects material composites. Moreover, each method has shown great enhancement properties of composites and improves the graphene polymer composites applications. Controlling graphene contents, concentration, and stability during composites formation affects the final materials where different properties can be adjusted. Selecting a suitable method also is essential for producing composites with excellent properties. Hence, the lateral size of modified graphene should be controlled and other factors such as temperature, humidity, and time duration for experiments.



Fig. Graphene structure

The arrangement of graphene in polymers is somewhat related to the properties of composite materials, when the filler is arranged along the strain direction, the reinforcement is higher. Graphene is showed to be a good nanofiller. Organized alignment of polymer matrices can produce improved properties, more than that of randomly graphene distribution into composites. Graphene with ultra-large nanosheets was highly aligned with polyurethane nanocomposites and showed great improvements in electrical conductivity.

#### 5.3 Graphene and polymer matrix interaction

The aggregation and orientation of graphene, the inadequate dissemination of graphene in nanocomposites, and the loss of surface layer caused by insufficient interaction between polymer and graphene will have a negative impact on the expected properties of the composites. Thence, the final product to some extent depends on the processing techniques. Moreover, aligning graphene platelets among nanocomposites should increase the Young's modulus, as compared to randomly pointed sampling. The interface structure of graphene filler

and polymer composites is very important because it determined the properties of composites. Low tensile and low elongation properties of a material are caused by the poor interaction between the polymer matrix and graphene of the materials. In turn, an improved mechanical characterization of nanocomposites is a result of strong interfacial interaction.

#### **5.4 Graphene Polymer Composite Properties**

Graphene has high elastic modulus and good electrical conductivity; these properties rendered it preferable in the preparation of new polymer composites. Graphene has a high potential for improving the properties of polymer matrix composites under very low load. The advantages of graphene polymer composites are: it improves thermal conductivity, tensile strength, electrical conductivity, wear-resistance, and elastic modulus. It is a promising multifunctional material to use in different areas. There are several types of polymers used as matrix materials, such as epoxies, phenolics, polyethylene, polypropylene, polyimide, polyester; polyurethane, etc., which show outstanding mechanical, tribological, and thermal properties.

#### LITERATURE SURVEY

Mercy O. Bamigboye et.al synthesized Cu (II), Mn (II), Ni (II) complexes of mixed amodiaquine and para aminobenzoic acid 2020 [6]. In 2020 a novel electrochemical immunosensor for aflatoxin B1 based on Au nanoparticles-poly 4-aminobenzoic acid supported graphene was carried out [7]. Tailored cellulose nanocrystals as a functional ultraviolet absorbing nanofiller of epoxy polymers was carried out by Hongfei shao et.al in 2019 [8]. Porous polydopamine and para-aminobenzoic acid complex membrane formed by electrochemical co deposition/degradation was studied by Hongfei shao et.al in 2017 [9]. Para -amino benzoic acid doped micro-grooved carbon fibers to improve strength and biocompatibility of PLA-PEG was carried out in 2016 [10]. Para amino benzoic acid-derived self-assembled biocompatible nanoparticles for efficient delivery of siRNA was carried out by Teegala lakshminarayan reddy et.al in 2015 [11]. Xiao lia et.al done the Electro polymerization of 4-aminobenzoic acid containing nano-Au deposited on carbon paste electrode for determination of acetaminophen in 2012 [12]. Electrochemical sensor based on a poly (para-aminobenzoic acid) film modified glassy carbon electrode for the determination of melamine in milk was performed by Ya Ting Liu et.al in 2011 [13]. Raed Rahal et.al synthesized the para-amino benzoic acid -TiO<sub>2</sub> Hybrid nanostructures of controlled functionality by an aqueous one-step process in 2010 [14]. Dipankar Ghosh et.al found out a graphene oxide - 4 amino benzoic acid nanosheet as effective drug delivery system to treat drug resistant bacteria in 2010 [15].

#### **OBJECTIVE AND SCOPE**

Para-amino benzoic acid (PABA) is often used in sunscreen products. PABA is sometimes called vitamin Bx, but it is not a true vitamin. PABA has been used to improve discoloration in skin and hair ease digestion. It has been taken as a pill, powder, or extract. Graphene has a unique hexagonal network plane structure as well as excellent physical, mechanical, and chemical properties. It is an ideal inorganic filler. Graphene is functionalized and then compounded with a polymer matrix to obtain materials with excellent properties (mechanical, thermal, etc.) The increased surface-to-volume ratio of graphene also means that its properties are better reflected in the composite. Composite materials having long-term durability for continuous purposes are desirable and cost-effective. Since the interface has a significant role in property enhancement, new characterization techniques for interface will bring new opportunities. Graphene has wide potential applications in energy-related systems, mainly because of its unique atom-thick two-dimensional structure, high electrical or thermal conductivity, optical transparency, great mechanical strength, inherent flexibility, and huge specific surface area. For this purpose, graphene materials are frequently blended with polymers to form composites, especially when fabricating flexible devices. Graphene/polymer composites have been explored as electrodes of supercapacitors or lithium ion batteries, counter electrodes of dye-sensitized solar cells, transparent conducting electrodes and active layers of organic solar cells, catalytic electrodes, and polymer electrolyte membranes of fuel cells.

Here an attempt is made to synthesis of poly (para-amino benzoic acid) Iron-Graphene composite by chemical oxidation method. The polymer prepared was then characterized using the following techniques

- UV- Visible Spectrometer
- IR Infrared Spectroscopy

17

#### **EXPERIMENTAL METHOD**

#### **Chemicals required:**

- Para amino benzoic acid-5.15g
- ♣ Ferric Chloride-1.22 g
- ♣ Graphene Oxide-0.29 g
- ✤ Potassium persulphate-13.5 g
- 🖊 1 M HCL

#### **Procedure:**

Poly (para-amino benzoic acid)iron-graphene oxide composite was synthesized by chemical polymerization method using 13.5 g of potassium per sulphate as the oxidizing agent. For this 1 M HCL was taken in a 250 ml round bottom flask. To this 5.15 g of para amino benzoic acid was added and shaken uniformly using a magnetic stirrer. Now potassium persulphate was added allowed to stirred for a while. Then 1.22g of ferric chloride and 0.29 g of graphene oxide was added and the entire mixture was stirred for 3 hours. As the polymerization was initiated the colour of the solution turned to dark brown. It was then kept overnight in the refrigerator. The dark brown precipitate formed was then dried.





#### **RESULTS AND DISCUSSION**

#### **UV-Visible Spectra:**



For recording the UV-Vis absorption spectra, a computer controlled JascoV-500 Double beam spectrophotometer was used. UV-Visible spectra of Poly (para amino benzoic acid) Iron-Graphene oxide composite is as shown in Fig 1. UV-Visible spectra of p-aminobenzoic acid reported earlier shows a peak at 355nm [16] and in the prepared composite it appears around 380 nm. This is attributed to the  $\pi$ - $\pi$ \*transition for the benzenoid ring, the band at around 376nm for quinoid rings and around 580nm for polaronic transition due to the emeraldine state of the polymer. The maximum absorption peak of iron composite according to literature is 510 nm [17]. Hence the peak at 450nm indicates the incorporation of iron in the polymer matrix, this red shift might be due to the incorporation of both the metal oxide and graphene into the polymer matrix. Introduction of the absorption peak in the UV

spectra of graphene oxide according to the literature is at 200-235nm [18]. In the above figure the peak at 250nm indicates the presence of Graphene. This absorption peak is attributed to the  $n-\pi^*$  transition of C-O bonds. The absorption peak at 230nm is due to the  $\pi-\pi^*$  transition of an aromatic C-C ring.



FTIR Spectra of Poly (para amino benzoic acid) Iron-Graphene oxide composite

The FT-IR spectra were recorded using a SHIMADZU instrument. The FTIR spectra (Fig.2) shows the following peaks for PPABA namely a band at 3569.13cm<sup>-1</sup>(N-H stretching), 3121cm<sup>-1</sup>(O-H stretching), 1685.50 cm<sup>-1</sup>(C=O stretching), 1400.34cm<sup>-1</sup> (Stretching of aromatic ring), 1286.72 cm<sup>-1</sup> (C-H stretching), 1017.03cm<sup>-1</sup> (aromatic C-H plane bending), 775 cm<sup>-1</sup> (C-H out of plane bending and confirms 1,4 disubstituted benzene ring). According to literature the well-defined peak of Fe is observed at 577cm<sup>-1</sup> and 631cm<sup>-1</sup>. Comparing the FTIR of the monomer and the polymer composite the peak at 620.66cm<sup>-1</sup> and 538.93cm<sup>-1</sup>corresponds to the Fe. Characteristic peaks for CO bonds can be seen in the GO spectra at approximately 1230–1215 cm<sup>-1</sup> and the peak corresponding to the hydroxyl (O–H) groups can be seen in the 4000–3000 cm<sup>-1</sup> range, according to literature. In the prepared composite Carboxyl or Carbonyl group of GO shows the peak at 1123.51 cm<sup>-1</sup> and the peak at 3690.45cm<sup>-1</sup>. The above stretching

values are appeared due to the incorporation of the metal oxide and graphene oxide in the polymer matrix.

#### CONCLUSION

- By chemical polymerization method Poly (Para amino benzoic acid)-Fe- Graphene oxide composite was prepared using potassium per disulphate as the oxidizing agent
- The polymer composite obtained was dark brown solid and was subjected to UV-visible and FTIR studies.
- UV-Visible spectra of the prepared polymer composite showed a broad peak at 450 nm and at 230nm due to the incorporation of the iron and graphene oxide in the polymer matrix.
- The FTIR spectra of the polymer composite showed a new band at 3892.88cm<sup>-1</sup> and at 3690.45cm<sup>-1</sup> in the polymer composite which is due to the incorporation of iron and graphene oxide in the polymer matrix.
- The novel composite prepared can have potential applications in microelectronics and solar cells as transparent conductive electrodes because of their excellent electrical properties and superior optical transparency

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# "Novel And Facile Synthesis of Poly(p-aminobenzoicacid)Palladium-Graphene Oxide Composite"

# **PROJECT IN CHEMISTRY**

ubmitted to St.Mary's College (Autonomous), Thoothukudi, in partial ilfillment for the award of the degree of Bachelor of Science in hemistry.

**Project done by** 

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2022-2023

# DECLARATION

We hearby declare that the project entitled "Novel and Facile Synthesis of Poly(paminobenzoicacid) Palladium-Graphene Oxide Composite" submitted to St.Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the degree of Bachelor of Science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

> J. Jesu Abhiya J. JESU ABHIYA

S. Mareeshwari

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P. Rahina P. RAHINA

April Thoothukudi.

### CERTIFICATE

This is to certify that the project in chemistry entitled "Novel and Facile Synthesis of Poly(p-aminobenzoicacid)Palladium-Graphene Oxide Composite" is submitted to St. Mary's College (Autonomous), Thoothukudi, in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

NAME

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EXAMINER

#### **INTRODUCTION**

#### 1. Composites

Composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface. The different systems are combined judiciously to achieve a system with more useful structural or functional properties nonattainable by any of the constituent alone. Composites, the wonder materials are becoming an essential part of today's materials due to the advantages such as low weight, corrosion resistance, high fatigue strength, and faster assembly. They are extensively used as materials in making aircraft structures, electronic packaging to medical equipment, and space vehicle to home building. The basic difference between blends and composites is that the two main constituents in the composites remain recognizable while these may not be recognizable in blends. The predominant useful materials used in our day-to-day life are wood, concrete, ceramics, and so on. Surprisingly, the most important polymeric composites are found in nature and these are known as natural composites. The connective tissues in mammals belong to the most advanced polymer composites known to mankind where the fibrous protein, collagen is the reinforcement. It functions both as soft and hard connective tissue.

Composites are combinations of materials differing in composition, where the individual constituents retain their separate identities. These separate constituents act together to give the necessary mechanical strength or stiffness to the composite part. Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk

properties significantly different from those of any of the constituents. Matrix phase is the primary phase having a continuous character. Matrix is usually more ductile and less hard phase. It holds the dispersed phase and shares a load with it. Dispersed (reinforcing) phase is embedded in the matrix in a discontinuous form. This secondary phase is called the dispersed phase. Dispersed phase is usually stronger than the matrix, therefore, it is sometimes called reinforcing phase.

#### **1.1 Classification of Composites**

On the basis of matrix phase, composites can be classified into metal matrix composites (MMCs), ceramic matrix composites (CMCs), and polymer matrix composites (PMCs). The classifications according to types of reinforcement are particulate composites (composed of particles), fibrous composites (composed of fibers), and laminate composites (composed of laminates). Fibrous composites can be further subdivided on the basis of natural/biofiber or synthetic fiber. Biofiber encompassing composites are referred to as biofiber composites. They can be again divided on the basis of matrix, that is, non-biodegradable matrix and biodegradable matrix. Bio-based composites made from natural/biofiber and biodegradable polymers are referred to as green composites. These can be further subdivided as hybrid composites and textile composites. Hybrid composites comprise of a combination of two or more types of fibers. [1]



#### **1.1.1 Polymer composites**

Polymers are well-known materials in advanced applications for many years. They are versatile materials and easy to be molded into any required application. However, there are a few aspects in the field of polymer to consider well, a single polymer cannot meet the requirements in advance applications. Therefore polymer composites attracted the attention of the world.

A composite consists of at least two parts, one is reinforcement and the second is the matrix. The composite may contain metals, ceramics, and other polymers as a matrix and as reinforcement. In polymer composite, thermosetting and <u>thermoplastic</u> resins have been used extensively as the matrix.

The <u>thermosets</u> are of low viscosity, while <u>thermoplastics</u> have the possibility of recycling and reuse. Essentially all commercially important polymers have advance applications. Polymer composites are a rapidly growing industry.[2]

3
In the 90s the term polymer composite material was extended to all systems with at least two components, one of which was organic. With very diverse properties (from good mechanical capacity and easily implementation to specific weight, very low thermal conductivity and electrical) polymeric materials have became indispensable and irreplaceable. The high diversity of polymer composites makes it impossible to treat these materials in a uniform manner. However, according to the literature, the main criteria for the classification of polymer composites are

#### i) The number of components:

Composite materials presuppose, in their structure, the existence of at least two components. Usually, the synthesis composite materials are limited to the use of 2-3 components. In composite structure, besides polymers, micro molecular substances can be included.

#### ii) Nature of components:

Depending on the nature of components, polymer composites can be systems of: polymerpolymer (synthetic polymer-synthetic polymer, natural polymer-synthetic polymer, and natural polymernatural polymer); polymer-inorganic compounds; polymer-organic compounds; polymer-metal.

#### iii) Macromolecular interactions system:

In terms of interactions between components, polymer composites can be: natural composites (inter polymeric complex) characterized by the fact that physical links (ionic, hydrogen, van der Waals, etc.) between components occur; chemical composites characterized by the fact that covalent bonds are established between compounds; physicochemical composites or interpenetrated networks (IPN) (Tang et al., 2008), partially interpenetrated (semi-IPN) or totally interpenetrated (full-IPN). In full-IPN polymer composites, the chains of one component (cross-linked or not by covalent bonds) are "fixed" in the reticular structure of the second component.

According to the state of the composite in its functional form: solid, quasi-solid (gel), liquid (composite solutions). According to the methods and processes for achieving mixtures at the molecular level, the mixing of two macromolecular compounds can be achieved through the following methods: melt mixing; solutions mixing; solution mixing and drying; solution mixing followed by freeze-drying, co-precipitation. The polymer materials class is very large and these materials can be classified in as

•Plastic materials (polyethylene, polypropylene, polyvinyl chloride, polystyrene, phenol, polyester etc.);

•Elastomers (natural rubber, butadiene styrene, silicone etc.); •Polymeric fibers (fabric polymeric fibers, aramid fibers); •coating materials (paints, lacquers, enamels etc.);

•Adhesives (polymeric adhesives, natural-glu adhesive, casein, rosin);

•Films (polypropylene, polyethylene, cellophane, cellulose acetate films);

•Sponge or foam (polyurethane, rubber, polystyrene, sponge polyvinyl chloride).[3]

#### **1.1.2 Graphene Polymer Composite**

Graphene due to its unique and novel properties has attracted extensive attention and indepth research in the scientific community. Graphene has a covalently bonded monolayer of carbon atoms with a hexagonal structure, is currently the thinnest material found in the world, and also makes it one of the world's best in terms of its properties. Graphene, with this special structure, contains rich and novel physical phenomena, which make it show many excellent properties such as ultra-high carrier mobility, good thermal conductivity, excellent mechanical modulus (1 TPa), breaking strength (125 GPa), and also a superior gas barrier, high transparency, and high specific surface area. Moreover, based on these extraordinary properties, graphene showed great potential application prospects and market value in different fields such as transportation, high-frequency electronic devices, flexible display, electrochemical biosensor, new energy battery, supercapacitor, aerospace, biomedical, etc. Graphene can also be used as an ideal nanofiller to reinforce the properties of composites, thus providing a broader application space for composite materials. Even a small amount of graphene addition to composite tends to increase the mechanical, electrical, and processing properties. Hence, the addition of graphene into polymer composite has shown improvements of properties compared to pure polymer, significant changes in the mechanical, electrical, and thermal properties were proven, more than in the case of other materials. The polymer nanocomposites modified by graphene can be used in construction, automobile, aerospace, electronic, and medical applications, etc. The interaction between fillers and the polymer matrix at the interface has great importance for the performance of composites. As graphene is hard and very costly to produce, needs a lot of energy, and is difficult to control structure, coupled with other materials especially polymers, different alternatives were found by using modified graphene, such as graphene oxide (GO) and reduced graphene oxide (RGO), etc. provided more options which are considered easy to produce and showed a great improvement when combined with polymers. Generally, modified graphene (GO,

RGO, etc) coupled with polymers and polymer composites can be possibly reached easily using various methods. Moreover, composite materials can be applied for producing materials with good biological, electrical, and mechanical properties. Remarkably, compared with pure polymers, the addition of graphene derivatives show a great change in properties of the composite materials and proved to be suitable as alternatives to use under harsh conditions, especially corrosive and friction materials. In particular, highquality graphene nanofiller within polymer composites brought useful materials for technological applications and play a crucial benefit to the economy of different aspects. Graphene polymer composites have shown several advantages. Graphene provides new ways and opportunities for the preparation of lightweight, anti-corrosion, low friction, low-cost, high-performance, and multi-functional nanofiller/polymer composite materials.[4]



a) Graphene oxide

b) reduced graphene oxide

#### 1.1.3 Graphene oxide

Graphene oxide has become one of the most promising materials. Graphene consists only of carbon atoms where every carbon atom is attached to three carbon atoms with sp2 hybridized orbitals making a honeycomb lattice. Graphene's rare properties make it a very promising material for a huge variety of applications, including field effect transistors (FETs), gas and biomolecules sensors, transparent conductive films (TCFs), and graphene batteries. Graphene oxide is a layered carbon structure with oxygen containing functional groups (=O, -OH, -O-, - COOH) attached to both sides of the layer as well as the edges of the plane. As with any 2D carbon material, GO can also have either single layer or multilayer structure. A structure with one layer is graphene oxide. Two layers of graphene oxide referred as a two-layered GO. GO with more than two layers or less than five layers is called few-layered graphene oxide, GO with five to ten layers is multilayered GO, and material with eleven or more layers is called graphite oxide. GO can be synthesized by the oxidation of graphite into graphite oxide followed by the exfoliation of this graphite oxide into GO. The properties of the material strongly dependent on the synthesizing method, which influences the resulting number and type of oxygen-containing groups in the formed GO. In contrary to graphene, GO is hydrophilic, and it is hence relatively simple to prepare a water or organic solvent based suspensions. Highly oxidized forms of GO are electric insulators with a bandgap of approximately 2.2 eV.

Due to the presence of various oxygen functionalities on the surface of GO, GO can be used as fluorographene, bromographene, graphene and many others. On the other hand, by thermal or chemical reduction of GO, thermally or chemically reduced graphene can be prepared interestingly, GO can also be used for advanced applications such as for drug delivery, in high temperature materials, or in construction materials. There are still some remaining issues that can be improved and more intensively. It is very important to develop novel methods of environmentally friendly low-cast large-scale synthesis of GO. Over the years, the structure of GO was studied in detail using several instrumental techniques: annular dark-field imaging, 13C and 1H NMR, ultra-high-resolution transmission electron microscopy, X-ray diffraction, and many others. Despite the numbers of attempts to reveal the structure of GO, a number of possibl6e structural models exist with no unambiguous one. The many reason for this is the complexity of the material and the originality of every sample with variable stoichiometry. Simplistically, graphene oxide is a monolayer sheet of graphite containing hydroxyl, carboxyl and epoxy oxygen groups on its basal plane and edges, resulting in a mixture of sp2 and sp3 hybridized carbon atoms.

Many models of graphene oxide have been developed based on a number of analyses and theoretical simulations. The first model was suggested by Hofmann and Rudolf in 1939, where a lot of epoxy groups were distributed randomly across the graphite monolayer. Then, in 1946, Ruess updated the model by incorporating hydroxyl groups and alternating sp2 hybridized carbons with those revealing sp3 hybridization. In 1998, Lerf and Kilnowski created a model that contains two different kinds of regions: regions with six membered aliphatic rings and regions with nonoxidized benzene aromatic rings. The size of the two regions is dependent on the level of material oxidation. The model is composed mainly of aromatic bodies, epoxide groups and double bonds. Wrinkling in the monolayer is caused by the slightly distorted tetrahedral configuration of hydroxyl groups attached to carbon atoms. The oxygen functional groups attached to carbon atoms. The oxygen functional groups are attached to the monolayer of carbon above and below, creating two layers of oxygen atoms with variable concentrations composed mainly of epoxide and hydroxyl groups that are very close to each other. All of oxygen functionalities, aromatic bodies and aromatic bodies and oxidized rings are distributed randomly across the carbon monolayer. The acidity of graphene oxide can be explained by the oxygen groups that are attached to the edges of the lattice, which are hydroxyl and carboxyl groups. This LK model has become one of the most acceptable and used models for moderately oxidized graphene oxide. [5]

#### **Synthetic Methods of Polymer composites**

#### a. Spray lay-up

Chopped fiber (glass) and resin + catalyst (i.e. polyester) mixed in a hand-held gun and sprayed directly into the mould or on to the structure. Gives a random 2-D fiber array.



#### b. Wet lay-up, Hand lay-up

Resins impregnated by hand (using rollers or brushes) into fibers (generally in the form of woven cloth). Only suitable for low-viscosity resins (may be warmed). Left to cure at room temperature.





# c. Vacuum bagging

An extension of (b), but quality improved by applying hydrostatic (air) pressure through a flexible membrane before and during curing. Mould may be heated if the process is used to make finished goods; less easily done in the field for on-site repairs. The material may be supplied in the form of pre-preg

# d. Filament winding

Generally used for hollow (circular or oval sectioned) components, though large curved sheets can also be made by carving these up after winding. Fiber tows are passed through a resin bath before being wound onto a mandrel in a variety of orientations.

#### e. Pultrusion

It Can be used either to process fiber bundles in a form which can be used for subsequent layup processes (pre-pregs, avoiding the need to deal with resin separately at this stage), or can be used to produce composite material in final form.

#### f. Resin transfer moulding (RTM)

Fiber cloth stacked up as a perform in a closed cavity mould, resin injected (if under vacuum, process known as Vacuum Assisted RTM), component cured in mould[6]

#### **Characteristics of polymer composite**

- ✤ Lightweight,
- ✤ High stiffness,
- ✤ High strength along the direction of their reinforcements,
- ✤ Good abrasion resistance,
- ✤ Good corrosion resistance



#### **Examples of Applications**

#### **Transportation vehicles:**

Polymer matrix composites find many uses in automotive, aerospace, and marine applications. Some examples of these uses are provided below

# Automotive vehicles:

Examples of polymer matrix composite use include tires and various belts and hoses as well as polymer matrix composite components in automotive bodies. Some very expensive sports cars, such as Bugatti, use carbon fiber reinforced polymer matrix composite as the main material of construction of the body of the car.

#### Aerospace vehicles

Polymer matrix composites are also used in aircraft tires and interiors. Of even greater value, however, is the ability of polymer matrix composites to help satisfy the relentless drive in the aerospace industry to enhance performance while reducing weight.

#### Marine vehicles:

Polymer matrix composites find many uses in marine vehicles. Fiberglass boats are among the most familiar examples since fiberglass is a composite where a matrix polymer is reinforced by glass fibers which may be arranged randomly, or as a chopped strand mat, or as a woven fabric. The growing use of lighter, stiffer, and stronger carbon fibers instead of glass fibers is an emerging trend in boatbuilding

#### Medical devices:

- Polymers and composites are essential components of many medical devices and applications. Some examples of these uses are provided below. Polymer matrix composites are used as components in a wide range of medical devices; such as MRI scanners, C scanners, X-ray couches, mammography plates, tables, surgical target tools, wheel chairs, and prosthetics.
- Polymer matrix nanocomposites containing carbon nano tubes or TiO<sub>2</sub> nano tubes reduce the healing time of broken bones by acting as a "scaffold" which guides the growth of replacement bone.
- The potential uses of nanocomposites in diagnostics and therapy are being explored. For example, the combination of magnetic nano particles and fluorescent nano particles in nano composite particles that are both magnetic and fluorescent appears to make a tumor easier to see during MRI tests performed prior to surgery and may also help the surgeon to see the tumor better during surgery.

#### **Industrial equipment:**

Polymer matrix composites are used in a vast range of industrial equipment. They are used as the main material of construction, or as components of equipment, or in some instances both as the main material of construction and as components. The uses of equipment in which polymer matrix composites are incorporated span almost all industries.[7]

#### LITERATURE SURVEY

The method of synthesis and structure of Graphene oxide, characterization techniques, and physiochemical properties was carried out in 2021 [8]. A novel poly (para aminobenzoic acid-co-4,4-diaminodiphenyl sulfone), i.e, PABA-co-DDS, was synthesized by simple electro plolymerization processes by Fatemeh Ganjeizadeh Rohani etal in 2019(Journal of Materials Science, Materials in Electronics) [9]. In 2017, Jan Kalembkiewicz etal studied the complexes of aminobenzoic acid, it have been characterized in terms of their biological activity and applications as medicals, hybrid organic-inorganic materials, luminescent materials, green corrosion inhibitors, catalysts and magnetic materials [10]. N.I.Zaaba etal synthesized graphene oxide (GO) using a modified Hummer's method, and then blended it into polyvinyl chloride (PVC) and amino-functional PVC (PVC-4ABA) matrices in 2016(advances in material and processing technologies conference) [11]. Lei shang etal prepared porous PdCu alloy nanoparticles by chemical dealloying with acetic acid in 2014(ACS Applied materials & interfaces) [12]. Three kinds of polymers, poly (p-aminobenzoic acid) (PPA), poly (maminobenzoic acid) (PMA), and poly (o-aminobenzoic acid) (POA), were prepared by oxidizing p-, m-, and o-aminobenzoic acid with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in acidic solution, respectively in 2013 by Puhong wen etal in Journal of nanomaterials [13].

#### **OBJECTIVE AND SCOPE**

Para Aminobenzoic acid is a vitamin like substance and a growth factor required by several types of micro organisms. In bacteria, PABA is used in the synthesis of the vitamin folic acid. PABA is often used in sunscreen products. The shift or moment of the electrons closely matches the frequency of UVB light, absorbing the light energy and releasing it as heat and or longer wavelength of light. Pd is used in catalytic convertors for automobiles, in fuel cells to generate power, in jewellery dental fillings and electronic component. Pd and Pt nanoparticles are broadly used as catalyst, as drug, drug carrier and in cancer treatment.

One of the main advantage of graphene oxide is that it is dispersible to water. This makes it possible to use solution based processes. The materials are used in sensors, biosensors, electrochemistry, chromatography and in the sample preparation techniques. Chemical and electrochemical sensors containing graphene materials are useful devises for detecting some chemical and biochemical compounds.

Here an attempt is made to synthesis of poly (para-amino benzoic acid) Palladium-Graphene oxide composite by chemical oxidation method. The polymer prepared was then characterized using the following techniques

- UV- Visible Spectrometer
- IR Infrared Spectroscopy

#### **EXPERIMENTAL METHOD**

#### **Chemicals Required:**

- Para Aminobenzoic acid 1.03 g
- Palladium Chloride 0.443 g
- Potassium per sulphate 6.758 g
- Graphene oxide 0.29 g
- 1N HCl -250ml

#### Procedure

Poly(p-aminobenzoicacid) palladium-Graphene oxide was synthesized by chemical polymerization method using potassium persulphate as the oxidizing agent. For this, 250ml 1N HCL was taken in a 500 ml beaker. To this 5.15g of p-aminobenzoic acid was added and then 6.75 g of potassium persulphate was added allowed to stirred for a while and then 0.443 g of palladium chloride was added followed by 0.29 g of graphene oxide and shaken uniformly using a magnetic stirrer. Now, the entire mixed was stirred for 3 hours. As the polymerization was initiated the colour of the solution turned to dark brown. It was then kept overnight in the refrigerator. The brown coloured precipitate obtained was then dried.



#### **RESULTS AND DISCUSSION**



UV-Visible Spectra of Poly (p-aminobenzoic acid) Pd-graphene oxide composite:

UV visible spectra of poly (p-aminobenzoic acid) reported earlier shows a peak at 355 nm [14] and in the prepared composite it is appears around 400 nm. This is attributed to the  $\pi$ - $\pi$ \*transition for the benzenoid ring. The absorption peak at 268- 270 nm[15] is due to the presence of Palladium according to the literature. In the above figure the peak at 300nm indicates the incorporation of Palladium in the polymer matrix. Introduction of the absorption peak in the UV spectra of graphene oxide according to the literature is at 200-235nm[16]. In the above figure the peak at 250 mm indicates the presence of graphene oxide, this absorption peak is attributed to the  $n - \pi^*$  transition of C-O bonds. The absorption peak at 230 nm is due to the  $\pi - \pi^*$  transition of an aromatic C-C ring.

#### FTIR spectra of Poly (p-aminobenzoic acid) Palladium-graphene oxide composite:

The infrared spectra of a number of cis and trans palladium (II) complexes of the type PdL2Cl2 have been recorded from 600 to 250 cm-1.

The FTIR spectrum of GO shows a broad peak appeared at 3429 cm-1 in the high frequency area attributed to the stretching mode of O-H bond, reveals the presence of hydroxyl groups in graphene oxide. The band observed at 1720 cm-1 was assigned to the carboxyl group. The sharp peak found at 1615 cm-1 is a resonance peak that can be assigned to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide. The peak at 1356 cm-1 arises from C-OH group. The peak at 1225 cm-1 denotes C-O-C stretching and the peak at 1056 cm-1 corresponds to the vibrational mode of the C-O group.



The FTIR spectra shows the following peaks for PABA namely a band at 3674.29 cm<sup>-1</sup> (N-H Stretching), 3116.60 cm<sup>-1</sup> (O-H Stretching), 1685.99 cm<sup>-1</sup> (C=O), 1607.81cm<sup>-1</sup> (quinoid C=C stretching), 1401.18 cm<sup>-1</sup> (Stretching of aromatic ring), 1293.08 cm<sup>-1</sup> (C-H stretching), 1109.87 cm<sup>-1</sup> (N=Q=N stretching Q= quinoid ring), 948 cm<sup>-1</sup> (aromatic C-H in plane bending), 857.01 cm<sup>-1</sup> and 771.53 cm<sup>-1</sup> ( C-H out of plane bending and confirms 1,4 disubstituted benzene ring). According to literature the well-defined peak of palladium is absorbed around 600 to250cm<sup>-1.</sup> comparing the FTIR of the monomer and polymer composite the peak at 556.28 cm<sup>-1</sup> correspond to the Pd. According to the literature the FTIR shows a broad peak appeared at 4000-3000 cm<sup>-1</sup> in the high frequency area attributed to the stretching mode of O-H bond, reveals the presence of hydroxyl groups in graphene oxide. In the composite a broad peak reveals the hydroxyl group at 3778.89 cm<sup>-1</sup>.

#### CONCLUSION

- By chemical polymerization method Poly (p-aminobenzoic acid) Palladium-graphene oxide was prepared
- The polymer composite obtained was dark brown solid and was subjected to UV visible and FTIR
- > In the polymer/metal/graphene composite there is broad peak around 400 nm attributed to the  $\pi$ - $\pi$ \*transition for the benzenoid ring, the peak at 300nm indicates the incorporation of Palladium in the polymer matrix and the peak at 250 mm indicates the presence of graphene oxide
- FTIR of the polymer/metal/graphene oxide composite showed a new peak at 3674.29cm<sup>-1</sup> in the polymer/graphite composite is due to the incorporation of graphite in the polymer matrix, peak at 556.28 cm<sup>-1</sup> correspond to the Pd
- One of the main advantage of graphene oxide is that it is dispersible to water. This makes it possible to use solution based processes. The materials are used in sensors, biosensors, electrochemistry, chromatography and in the sample preparation techniques. Chemical and electrochemical sensors containing graphene materials are useful devices for detecting some chemical and biochemical compounds.

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# "AN INVESTIGATION ON THE SYNTHESIS AND CHARACTERISATION OF POLY( PARA AMINO BENZOIC ACID) RUTHENIUM – GRAPHENE OXIDE COMPOSITE"

# **PROJECT IN CHEMISTRY**

ubmitted to St. Mary's College (Autonomous), Thoothukudi, in partial ulfilment for the award of the Degree of **Bachelor of Science** in Themistry.

Project done by

C.Mutharasi

Nirmala Kujur

R.Shiva Sankari



St. Mary's College (Autonomous) (Re-accredited with 'A<sup>+</sup>'Grade by NAAC) Thoothukudi-628001 2022-2023

# DECLARATION

We here by declare that the project entitled "An investigation on the Synthesis and Characterisation of Poly (p-Aminobenzoic acid) Ruthenium – Graphene Oxide Composite'' submitted to St. Mary's College (Autonomous), Thoothukudi , affiliated to Manomaniam Sundaranar University, for the Degree of Bachelor of Science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

C.Mutharasi

N*irma*le Nirmala Kujur

Shiva Sankani R.Shiva Sankari

April, 2023 Thoothukudi.

# CERTIFICATE

This is to certify that the project in Chemistry entitled "An investigation on the Synthesis and Characterisation of Poly (p-Aminobenzoic acid) Ruthenium – Graphene Oxide Composite" is submitted to St.Mary's College (Autonomous), Thoothukudi, partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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EXAMINER

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PRINCIPAL St. Mery's College (Autonomous) Thosthukndi - 628 001.

#### **INTRODUCTION**

# **1. POLYMER COMPOSITE**

A composite is a material made from, at least two or more materials with significantly different chemical and physical properties. When combined, they form another material that has properties different from the individual components. The constituents retained their identities in the composites; that is, they do not dissolve or other merge completely into each other, although they act in concert. The composites are one of the most widely used materials because of their adaptability to different situations and their relatives of combination with other materials to serve specific purpose and exhibit desirable properties. The main advantages of composite materials are their high strength and stiffness, combined with low density, when compare with bulk matter.

#### **1.1 COMPONENTS**

Components are made up of two types

- Fibers
- ✤ Matrix

#### FIBERS

Fibers can be control materials the properties of composite materials. Fiber such as Carbon, aramid, polyethylene, glass, carbon fiber, or Kevlar. At the same time, a matrix is what holds the fibers together.

# MATRIX

The matrix is usually a thermostate such as epoxy resin, polydicyclopentadiene, or polyimide. To make the material of the matrix stronger, the fibers are embedded into the matrix.

This is one of the most common types of composite materials called fiber-reinforced composites.



#### MATRIX

# **1.2 PROPERTIES OF POLYMER COMPOSITES**

- Good corrosion resistance
- > Light weight
- Good abrasion resistance
- High strength along the direction of their reinforcements
- ➢ High stiffness
- ➢ Faster assembly
- > The individual characteristics of the fiber material
- > The individual characteristics of the polymer matrix material
- > The ratio to which the fiber and the polymer matrix are combined.

#### **1.3 FACTORS THAT DECIDE THE PERFORMANCE OF POLYMER COMPOSITES**

The geometry and the orientation of the fiber materials inside the polymer composite. The performance of the polymer composites is usually called the mechanical properties of the composite materials. The mechanical properties are the most important physical and chemical properties.

Factors that influence the mechanical properties of the composites:

- ➢ Size
- ≻ Type
- Concentration dispersion of reinforcing agent(filler)
- > The interfacial tension between the matrix and filler.

# **1.4 CLASSIFICATION OF POLYMER COMPOSITE**

Polymer composites are classified into two distinct level:



# The first level of classification

- Metal matrix composites
- ✤ Organic matrix composites
- ✤ Ceramics matrix composites.

#### The second level of classification

- Fibers Reinforced Components (F.R.C.s) are further divided into fibers containing continuous and discontinuous fibers
- Laminar composites and Particulate composites
- Polymer composite materials
- ✤ Metal matrix composites.

# **1.5 MATRIX COMPOSITES (MMCs)**

Metal matrix composites are high strength, fracture toughness and stiffness are offered by metal matrix then those offered by their polymer counterparts they can withstand elevated temperature in corrosive environment. MMCs are widely used in engineering application where the operating temperature lies in between 250 to 750°C.

Matrix materials: Steel, aluminum, titanium, copper, magnesium and super alloys.

#### **PROPERTIES OF MMCs**

- Higher strength-to-density ratios
- Higher stiffness- to- density ratios
- Better fatigue resistance
- > Better elevated temperature properties, higher strength and lower creep rate
- Low coefficient of thermal expansion
- Better wear resistance.

#### **ADVANTAGES OF MMCs**

- ➢ Higher temperature capability
- ➢ Fire resistance
- Higher transverse stiffness and strength
- ➢ No moisture absorption

- ➢ Higher electrical and thermal conductivities
- Better radiation resistance
- ➢ No outgassing.

# **DISADVANTAGES OF MMCs**

- Higher cost of some material systems
- Relatively immature technology
- Complex fabrication methods for fiber- reinforced system
- ➢ Limited service experience.

# **1.6 APPLICATICATIONS OF METAL MATRIX COMPOSITES**

Aluminum-based matrix composites are widely seen in the aerospace and automotive industries. Fiber-based titanium composites are used in developing the structures of the aircraft.

Continuous fibers: Boron, silicon, carbide, graphite, Alumina, alumina-silica

Whiskers: Silicon carbide Silicon carbide, boron carbide

Particulates: Silicon carbide, boron carbide

• Titanium-based composites are used for manufacturing missile and aircraft structures, whose operating speeds are very high. The main advantage of titanium- based composites is that they are highly reactive

Continuous fiber: Silicon carbide, coated boron

Particulates: Titanium carbide

• Magnesium-matrix composites have lower thermal conductivity and are used actively in the space industry

Continuous fiber: Graphite, alumina

Whiskers: Silicon carbide

Particulates: silicon carbide, boron carbide

• Super alloys are commonly used for the manufacture of turbine blades as they operate at higher speeds and temperatures

Whiskers: Tungsten(2)

#### 2. ORGANIC OR POLYMER MATRIX COMPOSTES

The polymer matrix composite is described as a composite material that contains some polymer in the form of either fibers or powder. Polymer matrix composites are also known in short as PMC's.

The fibers in Polymer matrix composites are embedded in the organic polymer matrix. This kind of polymer is used to enhance the properties of the materials. Its applications range from gadget components to automotive accessories. The most common type of polymers that are used as composites is either elastomers, thermosetting polymers, or thermoplastic polymers.

In polymer matrix composites, polymer is used matrix phase, whereas, organic, inorganic or hybrid materials are used as reinforcement phase. Polymer matrix composites have several advantages over metal and ceramic matrix composites, such as low density, high extensibility, high shock absorption capacity, low cost for fabrication etc.

Therefore, polymer matrix composites are more popular than metal and ceramic matrix composite. Nowadays fiber reinforced polymer composites materials used more than 90% of the total composites.

The polymer matrix composite is a lightweight and corrosion resistive element of very high strength and is commonly used in manufacturing automobile parts, airplane parts, and many others. It is also having a low cost and simple manufacturing process.

6



# Advantages of the Polymer matrix composites

- Attractive optical properties
- Lesser specific weight
- ➢ High material stability against corrosion
- Economic mass production
- ➢ Ease of shaping
- Good electrical insulation
- ➢ Good thermal insulation.

# The main disadvantages of Polymer Matrix Composites (PMC) are

- ➢ Low thermal resistance
- ➢ High coefficient of thermal expansion.

# Properties of Polymer matrix composites (P.M.C.'s)

**Matrix:** This polymer is in the continuous phase. This is the weak link in the structure of the P.M.C.

**Reinforcement:** This part can either be carbon fiber, quartz, basalt, or glass. This is the main load-bearing element, and it is in the discontinuous phase.

**Interphase:** This part is where the load transmission takes place between the matrix phases and the reinforcement

# 3. CLASSIFICATION OF POLMER COMPOSITE:

Following are the various types of polymer matrix composites:

- > Thermoset
- > Thermoplastic
- ➢ Elastomers

#### THERMOSET

Thermoset is a polymer made up of a combination of heavily branched molecules. It has the property of undergoing chemical reactions by the action of heat, light, catalyst, and others. It is made by mixing two components, resin, and hardener. The molecular structure of thermoset or thermosetting plastic is shown as

Crosslink



The diagram represents the molecular structure of the thermoset having cross-links.

# THERMOPLASTIC

Thermoplastic is described as a polymer material made by individual molecules in a linear structure without any chemical linkage between them. The molecular weight of thermoplastic

is high, and it is moldable at room temperature. Thermoplastic can be easily recycled. The molecular structure of thermoplastic mole is shown as:



The diagram represents the molecular structure of the thermoplastic having no cross-links.

# 4. Ceramic Matrix

 Materials having ceramic as a matrix material in composites is called as Ceramic Matrix Composite (CMC).

# **PROPERTIES OF CMC:**

# **Tensile & Compressive Behaviour**

No sudden failure in CMC as like in ceramics. Certain amount of elongation in CMC improves the tensile and compressive property.

# **Fracture Toughness**

> It limits to ceramics, but for CMCs fracture toughness increases due to reinforcement

# **Fatigue Resistance**

Fatigue occurs due to cyclic loading, in case of CMCs cracks arrested by reinforcement so higher fatigue resistance.

# **Thermal Response**

➢ It Can withstand high temperature

# **Chemical inertness**

- Ceramic do not react with chemicals
- Corrosion resistance

# **Advantages of CMCs**

- Excellent wear and corrosion resistance in a wide range of environment and temperature.
- ➢ Higher strength to weight ratio
- ➢ Higher strength retension at elevated temperature
- ➤ Higher chemical stability
- > Non catastrophic failure
- ➢ High hardness
- ➢ Light weight.

# **Disadvantages of CMCs**

- CMCs are designed to improve toughness of monolithic ceramics, the main disadvantages of which is brittleness
- High processing temperature results in complexity in manufacturing and hence expensive processing.
- Difference in the co-efficiency of thermal expansion between the matrix and the reinforcement lead to thermal stresses on cooling from the processing temperatures.

# **Application of CMCs**

Cutting tools
- ➤ Aerospace
- Jet Engine
- ➢ Burner
- ➢ Turbine Blade
- ➢ Hot Fluid Channel.

#### **Types of Fiber Reinforced Polymer (FRP)**

- 1. Glass Fiber Reinforced Polymer (GFRP)
- 2. Carbon Fiber Reinforced Polymer (CFRP)
- ➢ 3. Aramid Fiber Reinforced Polymer (AFRP)

#### 1. Glass Fiber Reinforced Polymer (GFRP)

- Glass fibers are basically made by mixing silica sand, limestone, folic acid and other minor ingredients. The mix is heated until it melts at about 1260°C.
- The molten glass is then allowed to flow through fine holes in a platinum plate. The glass strands are cooled, gathered and wound. The fibers are drawn to increase directional strength. The fibers are then woven into various forms for use in composites.
- Based on a aluminium lime borosilicate composition, glass produced fibres are considered as the predominant reinforcement for polymer matrix composites due to their high electrical insulating properties, low susceptibility to moisture and high mechanical properties.
- Glass is generally a good impact resistant fibre but weighs more than carbon or aramid.
   Glass fibres have excellent characteristics equal to or better than steel in certain forms.



#### 2. Carbon Fiber Reinforced Polymer (CFRP)

- Carbon fibers have a high modulus of elasticity, 200-800 GPA. The ultimate elongation is 0.3-2.5 % where the lower elongation corresponds to the higher stiffness and vice versa.
- Carbon fibers do not absorb water and are resistant to many chemical solutions. They withstand fatigue excellently and neither corrode nor show any creep or relaxation.



- 3. Aramid Fiber Reinforced Polymer (AFRP)
  - Aramid is the short form for aromatic polyamide. A well-known trademark of aramid fibers is Kevlar but there does exist other brands as well such as Twaron, Technora and SVM.
  - > The of the fibers are 70-200 GPa with an elongation of 1.5-5% depending on the quality.

Aramid has fracture energy and is therefore used for helmets and bullet-proof garments.

They are sensitive to elevated temperatures, moisture and ultraviolet radiation and therefore not widely used in civil engineering applications. Finally, Aramid fibers do have problems with relaxation and stress corrosion(4).



#### LITERATURE SURVEY

Nafees Ahmad carried out the preparation and properties of 4-aminobenzoic acid-modified polyvinyl chloride/titanium dioxide and PVC / TiO2 based nanocomposites membranes was done in 2022 [5]. E. Igberase etal., performed the enhanced heavy metal ions adsorption by 4-aminobenzoic acid grafted on chitosan /epichlorohydrin composite: Kinetics, isotherms, thermodynamics and desorption studies done in 2019 [6]. Fabrication of p-aminobenzoic acid grafted carbonyl iron /polyindole composite particles and their magnetorheological response was performed in 2018[7]. Lite Yang etal., report that a novel quercetin electrochemical sensor based on molecularly imprinted poly (para-aminobenzoic acid) on 3D Pd nanoparticles-porous graphene-carbon nanotubes composite was performed in 2017 [8]. An Investigation on 4-Aminobenzoic acid Modified was done by Ayesha Kausar ashees Polyvinyl chloride/ Graphene Oxide and PVC/Graphene Oxide was based Nanocomposite Membranes was done in 2015 [9]. Hindawi journal discovered that the synthesis and Visible Photocatalytic Activities of Poly (aminobenzoic acid)/ TiO2 Nanocomposites was done in 2013[6]. Electro-polymerization of 4-aminobenzoic acid was done by J. Iranian Chem. Res containing nano- Au deposited on carbon paste electrode for determination of acetaminophen was done in 2013[10]. Langmuir journal found that covalent Modification of a Glassy Carbon Surface by 4-Aminobenzoic Acid and Its Application in Fabrication of a Polyoxometalates-Consisting Monolayer and Multilayer Films was studied in 2000[11].

#### **OBJECTIVES AND SCOPE**

Ruthenium based nanocomposites have been widely studied for the improvement of the electrochemical performances as electrode materials for supercapacitors of next-generation super capacitors and super capatteries. Graphene oxide can be used in electronic devices, energy storage devices, (bio)sensors, biomedical applications, supercapacitors, membranes, catalysts, and water purification. As an electronic device, GO is used in field-effect transistors (FETs) as chemical sensors and biosensors and in light-emitting diodes (LEDs) as a transparent electrode .

Here an attempt is made to synthesis of poly (para-amino benzoic acid) Ruthenium-Graphene oxide composite by chemical oxidation method. The polymer prepared was then characterized using the following techniques

- UV- Visible Spectroscopy
- IR Infrared Spectroscopy

#### **EXPERIMENTAL METHOD**

#### **CHEMICALS USED**

*	p-amino benzoic acid	- 4.12 g
*	1N HCl	- 250ml
*	Potassium Per Sulphate	- 13.52 g
*	Ruthenium Trichloride Hydrate	- 0.05g
*	Graphene Oxide	- 0.09g

#### PROCEDURE

Poly (p-aminobenzoic acid)Ruthenium-graphene oxide composite was synthesized by chemical polymerization method in acid medium using potassium per sulphate as an oxidizing agent . About 250ml of 1N HCl is taken in 400 ml beaker, and 4.12g of p-aminobenzoic acid was added and shaken uniformly using a magnetic stirrer. To the above solution 13.52 g of potassium per sulphate, 0.05 g of ruthenium trichloride and 0.09 g of graphene oxide was added. The magnetic stirrer was continued for 3 hours to complete the reaction, then kept the content in refrigerator overnight. The brown coloured precipitate obtained was filtered using air suction pump and dried.



Before

After

#### **RESULTS AND DISCUSSION**



For recording the UV-Vis absorption spectra, a computer controlled JascoV-500 Double beam spectrophotometer was used. UV-Visible spectra of Poly (para amino benzoic acid) ruthenium-Graphene oxide composite is as shown in Fig 1. UV-Visible spectra of poly (p- aminobenzoic acid) reported earlier shows a peak at 355 nm and in the prepared composite it appears around 300 nm. This is attributed to the  $\pi$ - $\pi$ \*transition for the benenoid ring, the band at 375 nm for polaronic transition due to the emeralidine state of the polymer. Another maximum absorption peak is observed at 390 - 450nm. The maximum absorption peak of ruthenium composite according to literature is 400nm [12]. Hence this peak indicates that incorporation of ruthenium in the polymer matrix. Introduction of the absorption peak in the UV spectra of graphene oxide according to literature is at 200-235 nm [13]. In the above figure the peak at 250nm indicates the presence of graphene. This absorption peak is attributed to the n- $\pi$ \* transition of C-O bonds The absorption peak at 230 nm is due to the  $\pi$ - $\pi$ \* transition of an aromatic C-C ring.

#### FTIR Spectra of Poly (para amino benzoic acid) Iron-Graphene oxide composite



The FT-IR spectra were recorded using a SHIMADZU instrument The characteristic bands and their assignment of peaks of p-aminobenzoic acid were already studied by Inomato & Moriwaki. N-H stretching appeared at 3443,3343cm<sup>-1</sup>, hydrogen bonded-OH stretch appeared at 3200-2500 cm<sup>-1</sup>, aromatic -CH stretch absorption band at 3040cm<sup>-1</sup>. Conjugated -CO stretching observed at 1670 cm-1. N-H deformation appeared at 1620cm-1.C··· C stretching observed at 1594-1500cm<sup>-1</sup>.C-O and C-N stretch and O-H deformation is at 1320-1280cm<sup>-1</sup>. Out of plane bending C-H (P-Substituted benzene) absorption band at 837cm<sup>-1</sup>.

The FTIR spectra of GO show a strong peak around 1621 cm<sup>-1</sup> À1 due to the aromatic C-C . They also exhibit a peak at 1735 cm-1 À1 due to the C=O stretching of COOH groups

as well as peaks due to carboxy C-O (1420 cm<sup>-1</sup>), (827 cm<sup>-1</sup>), and O-H deformation (1048 cm<sup>-1</sup>) groups.

The FTIR spectra of Poly (para amino benzoic acid) Ruthenium-Graphene oxide composite shows the following peaks for PPBA namely a band at 3370 cm<sup>-1</sup> (N-H stretching), 2800 cm<sup>-1</sup>(O-H) stretching, 1689cm<sup>-1</sup> (C=O), 1593 cm<sup>-1</sup> (quinoid C=C stretching), 1515cm-1 (benzenoid C=C stretching , 1401cm<sup>-1</sup> ( stretching of aromatic ring), 1263cm<sup>-1</sup> (C-H stretching), 1176 cm<sup>-1</sup> (N=Q=N stretching Q= quinoid ring), 1044 cm<sup>-1</sup> and 845 cm<sup>-1</sup> ( aromatic C-H in plane bending) , 845cm<sup>-1</sup> and 770 cm<sup>-1</sup> (C-H out of plane bending and confirms 1,4 disubstituted benzenr ring). However, characteristics peaks for CO bonds can be seen in the GO spectra at approximately 1401cm<sup>-1</sup> 1263 cm<sup>-1</sup>, 1401 cm<sup>-1</sup>, 1176 cm<sup>-1</sup> (from carbonyl or carboxyl). In addition, the peak corresponding to the hydroxyl (H-H) groups can be seen in the 3160-3687cm<sup>-1</sup> range. The new peak observed at 1689.80 cm<sup>-1</sup> is due to the incorporation of ruthenium in the polymer matrix. The polymer shows the absorption band at 1044.31cm<sup>-1</sup> and 3687.32cm<sup>-1</sup> is an inductive of stretching vibration in hydroxyl of Graphene oxide. Absorption band at 1593.19 cm<sup>-1</sup> evidence to C-C stretching of PABA. The polymer shows absorption band 1263 cm<sup>-1</sup> which confirms the C-O and C-N and OH stretching of PABA.

Comparing the FTIR of the monomer and the polymer ruthenium composite the new bond observed at 1689.80 cm<sup>-</sup> due to the incorporation of ruthenium in the polymer matrix. The polymer shows the absorption band at 1044.31cm and 3687.32 is an inductive of stretching vibration in alkoxy or epoxy and hydroxyl of Graphene oxide. Absorption band at 1593.19cm evidence to C-C stretching of PABA. The polymer shows absorption band 1263cm which confirms the C-O and C-N and OH stretching of PABA.

#### **CONCLUSION:**

- By chemical polymerization method Poly (p-aminobenzoic acid) Ruthenium-Graphene oxide composite was prepared.
- The polymer composite obtained was dark brown powder and was subjected to UV visible and FTIR studies.
- ► In UV a peak around 300 nm is attributed to the  $\pi$ - $\pi$ \*transition for the benenoid ring, the band at 375 nm for polaronic transition due to the emeralidine state of the polymer. Another maximum absorption peak is observed at 390 - 450nm indicates that incorporation of ruthenium in the polymer matrix, the peak at 250nm indicates the presence of graphene. This absorption peak is attributed to the n- $\pi$ \* transition of C-O bonds The absorption peak at 230 nm is due to the  $\pi$ - $\pi$ \* transition of an aromatic C-C ring.
- ➤ In FTIR , the new peak observed at 1689.80 cm<sup>-1</sup> is due to the incorporation of ruthenium in the polymer matrix and the new peak observed at 3687.32cm<sup>-1</sup> is due to the incorporation of graphene oxide in the polymer matrix.
- Ruthenium (Ru) complexes have gained significant interest in energy conversion applications owing to its attractive opto-electronic properties such as good photostability, excellent light harvesting capability and efficient charge transport behaviour and Graphene is a rising-star of two dimensional material made up of single sheet of hexagonally packed carbon atoms with attractive properties such as large surface area, high intrinsic mobility, better optical transparency and thermal stability which further turn it as an impressive candidate for variety of applications including ultracapacitors, sensors, photocatalysis, actuators, fuel cells and solar cells etc. The large surface area and active edges associated with the two dimensional reduced

graphene oxide (rGO) sheets offer several advantages to incorporate various organic or inorganic moieties to develop hybrid nanocomposites for optoelectronic applications In particular, the covalent functionalization of rGO or graphene sheet have attracted numerous attentions in polymer solar cells (PSCs) technology.

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# Facile One Pot Synthesis of Au-Ru-Pt Nanoparticle and Evaluation of their Antibacterial and Antioxidant Activities

Project in chemistry

ibmitted to St. Mary's college (Autonomous) in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry

Done By

T. Muthu Nageshwari

S. Nandhini

M. Sumaiah



# ST. MARY'S COLLEGE (AUTONOMOUS) RE-ACCREDITED WITH "A<sup>+</sup>" GRADE BY NAAC THOOTHUKUDI-628001 2022-2023

## DECLARATION

We hereby declare that the project entitled "A Facile One Pot Synthesis of Au-Ru-Pt Nanoparticle and Evaluation of their Antibacterial and Antioxidant activities" submitted to St.Mary's College(Autonomous),Thoothukudi, Affilated to Manomaniam Sundranar University for the degree of Bachelor of Science is our original work and that, it has not previously formed on the basis of the award of any degree or similar title.

# 1. ata afij.

T. Muthu Nageshwari

5. Nardhini S. Nandhini

M. Lunyah

M. Sumaiah

April 2023 Thoothukudi

## CERTIFICATE

This is certify that project in chemistry "A Facile One Pot Synthesis of Au-Ru-Pt Nanoparticle and Evaluation of their Antibacterial and Antioxidant activities" submitted to St.Mary's college (Autonomous), Thoothukudi in partial fulfilment for the award of the degree of Bachelor of Science in Chemistry and is a record of the work done by following students during the year 2022-2023.

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S.NO	CONTENT	PAGE NO
1	INTRODUCTION	1-22
2	LITERATURE SURVEY	23-26
3	EXPERIMENTAL DETAILS	27-32
4	RESULT AND DISCUSSION	33-39
5	CONCLUSION	40
6	REFERENCE	41-43

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# CHAPTER-I INTRODUCTION

Nanotechnology is associated with nano-meter sized objects. Living organisms are made up of cells. These cell parts, however, are nano sized. Nanotechnology basically deals with design, production and characterization on nano sized particles. Nano sized particles are basically small objects that act as a whole unit in accordance with their transport and properties. Fine particles have the range of 100-2500nm and ultrafine particles have the size of 1- 100nm. They can also be designed to improve the pharmacological and therapeutic effects of the drugs. They also have a very high surface area and they permit many functional groups to be adhered to them which in turn, can bind to tumor cells. They have proven to be an excellent replacement for radiation and chemotherapy as they can easily assemble in the micro environment of the tumor.

Recent studies have developed a number of nano-sized particles such as metals, semiconductors and polymeric particles utilized in molecular imaging and particulate delivery vehicles. Polyethleneimine liposomes, silica nanoparticles, micelles and chitosans play an important role in drug delivery with minimized side effects. They have also been utilized as anticancer agents. So, basically, nanotechnology deals with construction of artificial cells, enzymes and genes or repair in the synthesis of protein. we discuss the synthesis, types, applications, advantages and limitations of nanoparticles.

Nanoparticles offer better advantages over other carrier systems. A major advantage of nanoparticles which makes them an efficient delivery system is their submicron size which makes

extravasations possible and occlusion of terminal blood vessels. In addition, high density of therapeutic agent can often be encapsulated, dispersed or dissolved in these nanoparticles, which

in turn depends on the preparation process to yield different properties and release characteristics of the entrapped agent. Though liposomes have been used as potential carriers with properties including protecting drugs from degradation, targeting to site of action and reduction in toxicity or side effect. More over drug delivery systems designed as liposomes cannot be used for controlled release of drug because of leakage of drug entrapped inside liposomes. On the other hand, polymeric nanoparticles offer some specific advantages of increasing the stability of drugs/proteins and possess useful controlled release properties. Other features of nanoparticles include low number of excipients used in their formulations, simple procedure for preparation, high physical stability, and the possibility of sustained drug release that may be suitable in the treatment of chronic diseases. By varying the polymer composition of the particle and morphology, one can effectively tune in a variety of controlled release characteristics, allowing moderate constant doses over prolonged periods of time. Further, the nanoparticle system was used for various routes for administration including oral, nasal, parenteral, ophthalmic application. Oral delivery of small drugs molecules can also be achieved which otherwise would not be available as injectable such as anticancer agents. Also, the nanoparticles are good candidates to be shown as adjuvant for vaccines and advantageous features of nanoparticles include increased interaction of drug molecules with epithelial cells can be achieved leading to maximal absorption of the drug molecule.

#### **1.1. Types of Nanoparticles**

#### 1.1.1. Carbon-based nanomaterials:

Generally, these NMs contain carbon, and are found in morphologies such as hollow tubes, ellipsoids or spheres. Fullerenes (C60), carbon nanotubes (CNTs), carbon nanofibers, carbon black, graphene (Gr), and carbon onions are included under the carbon-based NMs category. Laser ablation, arc discharge, and chemical vapor deposition (CVD) are the important production methods for these carbon-based materials fabrication.

#### 1.1.2. Fullerence:

Fullerenes are an allotropic modification of carbon, often termed as a molecular form of carbon, or carbon molecules. Fullerenes were discovered in 1985 by H.W. Kroto, R.F. Curl and R.E. Smalley who were later awarded with the nobel prize for chemistry in 1996. The fullerene family includes a number of atomic C n clusters (n > 20), composed of carbon atoms on a spherical surface. Carbon atoms are usually located on the surface of the sphere at the vertices of pentagons and hexagons. In fullerenes, carbon atoms are usually present in the sp2-hybrid form and linked together by covalent bonds. Fullerene C60 is the most common and best-investigated fullerene. The spherical molecule is highly symmetric and consists of 60 carbon atoms, located at the vertices of twenty hexagons and twelve pentagons . The diameter of fullerene C60 is 0.7 nm .



Fig.1.1.Diagrammatic Representation of Fullerence

#### 1.1.3. Carbon nanotubes (CNTs)

Among other carbon-based nanomaterials, CNTs are one of the carbon allotropes with exceptional properties suitable for technical applications. They were discovered in 1991 by the Japanese researcher S. Iijima. Carbon nanotubes are characterized by cylindrical structures with a diameter of several nanometers, consisting of rolled graphene sheets. Carbon nanotubes may vary in length and diameter, chirality (symmetry of the rolled graphite sheet) and the number of layers. According to their structure, CNTs may be classified into two main groups: (i) single-walled nanotubes (SWCNTs), (ii) multi-walled nanotubes (MWCNTs). Some researchers additionally isolate double-walled carbon nanotubes (DWCNTs) as a separate class of CNTs. Generally SWCNTs have a diameter around 1–3 nm and a length of a few micrometers. Multi-walled CNTs have a diameter of 5-40 nm and a length around 10 µm. However, recently synthesis of CNTs with a length of even 550 mm has been reported. The structure of CNTs leads to exceptional properties with a unique combination of rigidity, strength and elasticity compared with other fibrous materials. For instance, CNTs exhibit considerably higher aspect ratios (length to diameter ratios) than other materials, and larger aspect ratios for SWCNTs as compared with MWCNTs due to their smaller diameter. Additionally, CNTs show high thermal and electrical conductivity compared to other conductive materials. Electrical properties of SWCNTs depend on their chirality or hexagon orientation with respect to the tube axis. Accordingly, SWCNTs are classified into three sub-classes: (a) armchair (electrical conductivity > copper), (b) zigzag (semi-conductive properties) and (c) chiral (semi-conductive properties). By contrast, MWCNTs consisting of multiple carbon layers, frequently with variable chirality, can exhibit extraordinary mechanical properties instead of outstanding electrical characteristics.

#### 1.1.3.1. Single-walled carbon nanotubes (SWNTs):

Single-walled carbon nanotubes (SWNTs) are a special class of carbon materials known as onedimensional materials. They consist of sheets of graphene, rolled up to form hollow tubes with walls one atom thick. Due to its chemical structure and dimensional constraints, this material exhibits exceptional mechanical, electrical, thermal, and optical properties. As such, carbon nanotubes have become of great interest for both stand-alone studies and for use in composite materials.



Fig.1.2.Diagrammatic representation of Single walled carbon Nanotubes

#### 1.1.3.2. Multi-walled carbon nanotubes (MWCNTs):

Multi-walled carbon nanotubes (MWCNTs) are a special form of carbon nanotubes in which multiple single-walled carbon nanotubes are nested inside one another. Although MWCNTs are still classed as a 1-dimenional form of carbon, the unique properties that are seen within singlewalled and double-walled carbon nanotubes are not as prominent. The reason for this is the higher probability of defects occurring. These disadvantages are offset by the increased dispersability of MWCNTs, and the reduced cost in synthesis and purification of these materials.



#### 1.1.4. Graphene:

Graphene is a two-dimensional allotropic form of carbon, formed by single layers of carbon atoms . In graphene, carbon atoms exhibit sp2-hybridization connected by  $\sigma$ - and  $\pi$ -bonds in a twodimensional hexagonal crystal lattice with a distance of 0.142 nm between neighboring atoms of carbon hexagons. Graphene also represents a structural element of some other carbon allotropes, such as graphite, carbon nanotubes and fullerenes. Theoretical studies on graphene began a long time before the real material samples were obtained. The Canadian theoretical physicist P. R. Wallace first explored the theory of graphene in 1947, while the first graphene samples were described 57 years later (in 2004) by A. Geim (Dutch-British physicist) and K. Novoselov (Russian-British physicist), awarded with a nobel prize in 2010.



### Graphene

Fig.1.4.Digrammatic Representation of Graphene

#### 1.1.5. Organic-based nanomaterials:

These include NMs made mostly from organic matter, excluding carbon-based or inorganic-based NMs. The utilization of noncovalent (weak) interactions for the self-assembly and design of molecules helps to transform the organic NMs into desired structures such as dendrimers, micelles, liposomes and polymer NPs.

#### **1.1.6.** Composite-based nanomaterials:

Composite NMs are multiphase NPs and NSMs with one phase on the nanoscale dimension that can either combine NPs with other NPs or NPs combined with larger or with bulk-type materials (e.g., hybrid nanofibers) or more complicated structures, such as a metal-organic frameworks. The composites may be any combinations of carbon-based, metal-based, or organic-based NMs with any form of metal, ceramic or polymer bulk materials.

#### 1.1.7.Inorganic-nanoparticles:

Inorganic nanoparticle has been developed the role based upon their unique physical properties and particularly in biotechnology. Based upon these two factors of inorganic nanoparticles they have certain physical properties that mainly include size dependent optical, magnetic, electronic, and catalytic properties. Bio related application are involved for the preparation of these interesting nanoparticles like iron oxides, gold, silver, silica, quantum dots etc. Novel physical properties mainly related because of their size approaches nanometer scale dimension.

#### 1.1.8.Polymeric-nanoparticles

Polymeric nanoparticle it is also a type of nanoparticle. In the recent year polymeric nanoparticle has a tremendous development in the field of research. The dispersion of preformed polymers and the polymerization of monomers are two strong strategies mainly involved for preparation. 10 - 1000 nm it is the range of size involved with solid particles.

#### 1.1.9.Solid-lipid-Nanoparticles

For controlling the drug delivery in 1990s Solid lipid nanoparticles played a dominant role. There are certain alternate carrier systems to emulsions, liposomes and polymeric nanoparticles as a colloidal carrier system. Liposomes are one of the methods based upon the different types of nanoparticles. Structure of liposomes consists of one or more phospholipid bilayers and they are sphere-shaped vesicles to carry compound of interest. Today liposomes have been useful in the field of reagent and tool in various scientific disciplines. Since many features involved in liposome they made their own way in the market. Cosmetic and pharmaceutical industries numerous molecules act as a carrier, and in the field of Food and farming industries liposomes involved in encapsulation to grow delivery system that can entrap unstable compound.

#### 1.1.10.Nanocrystal

A nanocrystal is a type based upon material particle having at least one dimension smaller than 100 nanometres and mainly composed of atoms in either a single or poly-crystalline arrangement.

Nanocrystals are aggregates of around hundreds or thousands of molecules that combine in a crystalline form, composed of pure drug with only a thin coating comprised of surfactant or combination of surfactants.

#### 1.1.11.Dendrimers

Dendrimers arise from two Greek words: Dendron meaning tree and Meros meaning part. Structure of dendrimers has a well-defined size, shape and defined molecular weight and also Dendrimers are hyperbranched, globular, monodisperse, three dimensional nanoscales synthetic Polymers. Molecular chemistry and polymer chemistry both exhibit well-defined characteristics features of Dendrites.

#### **1.2.** Characterisation of nanoparticles

Nanoparticles are generally characterized by their size, morphology and surface charge, using such advanced microscopic techniques as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The average particle diameter, their size distribution and charge affect the physical stability and the in vivo distribution of the nanoparticles. Electron microscopy techniques are very useful in ascertaining the overall shape of polymeric nanoparticles, which may determine their toxicity. The surface charge of the nanoparticles affects the physical stability and redispersibility of the polymer dispersion as well as their in vivo performance.

#### **1.2.1.Particle-size**

Particle size distribution and morphology are the most important parameters of characterization of nanoparticles. Morphology and size are measured by electron microscopy. The major application of nanoparticles is in drug release and drug targeting. It has been found that particle size affects

the drug release. Smaller particles offer larger surface area. As a result, most of the drug loaded onto them will be exposed to the particle surface leading to fast drug release. On the contrary drugs slowly diffuse inside larger particles. As a drawback. smaller particles tend to aggregate during storage and transportation of nanoparticle dispersion. Hence, there is a compromise between a small size and maximum stability of nanoparticles. Polymer degradation can also be affected by the particle size. For instance, the degradation rate of poly (lactic-co-glycolic acid) was found to increase with increasing particle size in vitro.

#### 1.2.2.Dynamic-lights-scattering(DLS)

Currently, the fastest and most popular method of determining particle size is photon-correlation spectroscopy (PCS) or dynamic light scattering (DLS). DLS is widely used to determine the size of Brownian nanoparticles in colloidal suspensions in the nano and ubmicron ranges. Shining monochromatic light (laser) onto a solution of spherical particles in Brownian motion causes a Doppler shift when the light hits the moving particle, changing the wavelength of the incoming light. This change is related to the size of the particle. It is possible to extract the size distribution and give a description of the particle's motion in the medium, measuring the diffusion coefficient of the particle and using the autocorrelation function. The photon correlation spectroscopy (PCS) represent the most frequently used technique for accurate estimation of the particle size and size distribution based on DLS.

#### **1.2.3.Scanning-Electron-Microscope**

Scanning electron microscopy (SEM) is giving morphological examination with direct visualization. The techniques based on electron microscopy offer several advantages in morphological and sizing analysis; however, they provide limited information about the size distribution and true population average. For SEM characterization, nanoparticles solution should

be first converted into a dry powder, which is then mounted on a sample holder followed by coating with a conductive metal, such as gold, using a sputter coater. The sample is then scanned with a focused fine beam of electrons. The surface characteristics of the sample are obtained from the secondary electrons emitted from the sample surface. The nanoparticles must be able to withstand vacuum, and the electron beam can damage the polymer. The mean size obtained by SEM is comparable with results obtained by dynamic light scattering. Moreover, these techniques are time consuming, costly and frequently need complementary information about sizing distribution.

#### **1.2.4.Transmission-Electron-Microscope**

TEM operates on different principle than SEM, yet it often brings same type of data. The sample preparation for TEM is complex and time consuming because of its requirement to be ultra-thin for the electron transmittance. The nanoparticles dispersion is deposited onto support grids or films. To make nanoparticles withstand the instrument vacuum and facilitate handling they are fixed using either a negative staining material, such as phosphotungstic acid or derivatives. uranyl acetate, etc, or by plastic embedding. Alternate method is to expose the sample to liquid nitrogen temperatures after embedding in vitreous ice. The surface characteristics of the sample are obtained when a beam of electrons is transmitted through an ultra-thin sample, interacting with the sample as it passes through Atomic force microscopy Atomic force microscopy (AFM) offers ultra-high resolution in particle size measurement and is based on a physical scanning of samples at sub-micron level using a probe tip of atomic scale. Instrument provides a topographical map of sample based on forces between the tip and the sample surface. Samples are usually scanned in contact or noncontact mode depending on their properties. In contact mode, the topographical map is generated by tapping the probe on to the surface across the sample and probe hovers over the conducting surface in non-contact mode. The prime advantage of AFM is its ability to image nonconducting samples without any specific treatment, thus allowing imaging of delicate biological and polymeric nano and microstructures. AFM provides the most accurate description of size and size distribution and requires no mathematical treatment. Moreover, particle size obtained by AFM technique provides real picture which helps understand the effect of various biological condition

#### **1.2.5. Surface Charge**

The nature and intensity of the surface charge of nanoparticles is very important as it determines their interaction with the biological environment as well as their electrostatic interaction with bioactive compounds. The colloidal stability is analyzed through zeta potential of nanoparticles. This potential is an indirect measure of the surface charge. It corresponds to potential difference between the outer Helmholtz plane and the surface of shear. The measurement of the zeta potential allows for predictions about the storage stability of colloidal dispersion. High zeta potential values. either positive or negative, should be achieved in order to ensure stability and avoid aggregation of the particles. The extent of surface hydrophobicity can then be predicted from the values of zeta potential. The zeta potential can also provide information regarding the nature of material encapsulated within the nanocapsules or coated onto the surface.

Generally, biologically-derived chemicals or natural product extracts obtained from bio-renewable sources with their promising reducing, stabilizing and capping potentials can be deployed for the greener production of mono- and multi-metallic NPs. However, there are still some important challenging issues persist, including the exact mechanisms for NP formation, limitations to scale up and the reproducibility of procedures. Plant-mediated systems for the synthesis of mono/bi/trimetallic NPs. Generally, biologically-derived chemicals or natural product extracts obtained from bio-renewable sources with their wires, rods, and alloys exploit the chemical constituents and ingredients of various plant systems, such as flavonoids, phenolic acid,

glycosides, terpenoids, enzymes, proteins, vitamins, carbohydrates, alkaloids, and antioxidants (as capping, stabilizing, and reducing agents).

The earliest example of using plant-based systems for the biosynthesis of mixed metal NPs dates back to 2007 by Haverkamp et al. They have fabricated Au-Ag-Cu alloy NPs (~5-50 nm) using Brassica juncea seeds via an in vivo approach Au/Pt/Ag trimetallic NPs have been produced via a facile, and environmentally friendly method by applying aqueous extract of Lamii albi flos. Additionally, Au-ZnO-Ag trimetallic NPs (~20 nm) have been bio-prepared using the extract of Meliloti officinalis. In another study, a reliable procedure was reported for the biosynthesis of Cu/Cr/Ni trimetallic oxide nanomaterials by applying Froriepia subpinnata and Eryngium campestre (aqueous leaf extracts) under mild temperature conditions. These NPs exhibited superb antibacterial activities versus E. coli and Staphylococcus aureus. The optimized conditions for E. campestre leaf extract were 3 min reaction time, at 34 <sup>0</sup>C and metal salt-to leaf extract ratio of 2.38 with 73% yield. The corresponding value for F. subpinnata leaf extract was 3 min at  $40^{\circ}$ C, and the ratio of metal salt to leaf extract was 1.07; 72% of the conversion of salt into trimetallic oxide. NPs was evaluated by modeling software. Alloy-like Ag-Au-Pd trimetallic NPs (~8-11 nm) have been green-fabricated in 10 min under ambient conditions by using extracts from Aegle marmelos (leaf extract) and Syzygium aromaticum buds, by altering the composition of phytochemicals. These NPs exhibited promising catalytic activities for the glucose oxidation procedure, and demonstrated efficient antibacterial activities against Gram-negative bacteria, such as E. coli; high catalytic activity was presumably because of electronic charge transfer influence from the neighboring elements in trimetallic NPs which performed an important function.

#### 1.2.6. Microwave (MW)-Assisted Synthesis

MW-assisted synthesis have some important advantages, including rapid/uniform heating, energy savings, no selective heating of the surface remarkable yield in shorter synthesis time, high purity of synthesized NPs and small narrow particle size distribution. In one investigation, the formation, characterization, and synergistic antimicrobial activity of Au/Pt/Ag trimetallic NPbased nano-fluids have been reported. These trimetallic nano-fluids were fabricated via a greener MW-mediated successive chemical reduction technique. Additionally, the MW irradiation method facilitated the fabrication of trimetallic nanocomposites and nanotubes. As a result, high-resolution scanning electron microscopy (HRSEM) images indicated that these particles were close to nanocomposite (Ag-Pt) and nanowire (Au) structures (length = 792 nm and width = about 99 and 51 nm. Additionally, HRSEM images of the fabricated Au-Pd-Pt trimetallic NPs revealed them to be of uniform nanotube shapes, length, and width of the nanotube being ~141 nm and 152 nm, respectively. In another study, the authors reported on eco-friendly production of a Au/Pt/Ag trimetallic nanocomposite (~20–51.3 nm) by trisodium citrate-assisted reduction of ions under MW heating conditions the fabricated nanocomposites comprised gold nanowires and silver/platinum bimetallic NPs. The surface-enhanced Raman scattering (SERS), accomplished via the addition of 7-azaindole to trimetallic nanocomposites, and higher Pt content found on the surface. It appears that the fusion of these three NPs into a single object would help improve the consistent localization of surface plasmon absorption. The main advantageous feature of the trimetallic NPs is that there is suitable charge separation, as demonstrated in the heterostructure of matter, thus avoiding the charge recombination and rendering them as a promising alternative for photodegradation of organic contaminants. Additionally, these nanomaterials showed suitable adsorption ability and, consequently, they can be applied for the purification of wastewater laden with pharmaceutical wastes, especially antibiotics. In one investigation, MW-assisted synthesis of La/Cu/Zr trimetallic NPs was accomplished and the ensuing nano-scaled material was deployed as a suitable nano photocatalyst for removing the antibiotic, ampicillin, from an aqueous medium; the feasibility of ampicillin adsorbed on La/Cu/Zr trimetallic NPs demonstrated that the adsorption was accompanied with spur-of-the-moment photodegradation. Au/Pt/Ag trimetallic NPs have been produced via a facile, and environmentally friendly method by applying aqueous extract of Lamii albi flos. Additionally, Au- ZnO -Ag trimetallic NPs (~20 nm) have been bio-prepared using the extract of Meliloti officinali]. In another study, a reliable procedure was reported for the biosynthesis of Cu/Cr/Ni trimetallic oxide nanomaterials by applying Froriepia subpinnata and Eryngium campestre (aqueous leaf extracts) under mild temperature conditions. Alloy-like Ag-Au-Pd trimetallic NPs (~8-11 nm) have been green-fabricated in 10 min under ambient conditions by using extracts from Aegle marmelos (leaf extract) and Syzygium aromaticum buds, by altering the composition of phytochemicals. These NPs exhibited promising catalytic activities for the glucose oxidation procedure, and demonstrated efficient antibacterial activities against Gramnegative bacteria, such as E. coli; high catalytic activity was presumably because of electronic charge transfer influence from the neighboring elements in trimetallic NPs which performed an important function.



Fig.1.5.Diagrammatic Representation of Microwave Assisted Synthesis

#### 1.2.7. Ultrasonic-Assisted Synthesis

Sonochemical synthesis approach has been applied for facile fabrication of the trimetallic Pt-Au-Ru nanostructures with remarkably porous structures encompassing perpendicular pore channels. The prepared trimetallic nanocrystals with the augmented atomic ratio demonstrated superb electrocatalytic operations for oxidation of formic acid (the mass and specific activities are 1044.1 mA mg/1 and 14.5 mA cm2, accordingly), 4.1 and 2.2 times more than attained from commercial Pt/C. It should be noticed that electrocatalytic activity and resiliency are important criteria for the electrocatalyst evaluations. It was reported that an electrocatalyst with improved durability showed considerable long duration, which is vital for industrial applications.



Fig.1.6. Digrammatic Representation of Ultrasonic Assisted Synthesis

#### **1.2.8.Laser Abilation Synthesis**

Laser ablation synthesis in liquid solution is a green method for the synthesis of micro- and nanostructure directly from bulk materials, and is considered a green technique for producing trimetallic NPs without using any surfactant or addition of chemicals. This method is environmentally friendly and cost effective, and can produce high-purity nanomaterials with no further contaminations although controlling the size distribution, agglomeration, and crystal structure are difficult. Indeed, the precise quantitative analyses of the effects of pressure, temperature, and concentration of the ablated materials and concentration of the species in solution are vital for controlling the structure/phase of the final products. In one study, trimetallic (Al2O3@AgAu) NPs were synthesized using nanosecond pulse laser ablation in deionized water. Two-step laser ablation methodology was approved for the fabrication of these trimetallic NPs; a silver or gold target was ablated in colloidal solution of -alumina NPs synthesized by pulse laser ablation. These NPs showed high catalytic performance and were utilized for the catalytic reduction of 4-nitrophenol to 4-aminophenol. It was revealed that the catalytic efficiency of trimetallic NPs was significantly improved as they completed the catalytic reaction in only five seconds. In another study, Al@Al2O3@Ag@Au and Al@Al2O3@AgAu triple-layered core-shell
or alloy nanostructures were synthesized by a two-step laser ablation technique. The preparative method included temporal separations of Al, Ag, and Au deposition for step-by-step generation of triple-layered core-shell structure. To produce Al@Ag NPs, silver was ablated for about 40 min in aluminum NP colloidal solution; aluminum get oxidized simply in water to generate alumina, the prepared structure thus possessed a core-shell Al@Al2O3 configuration. These Al@Al2O3 particles served as seeds for the incoming energetic silver particles to produce multilayered Al@Al2O3@Ag NPs. Then, the silver target was substituted by gold, and the ablation was performed to generate Al@Al2O3@Ag@Au core-shells or Al@Al2O3@AgAu alloy.



Fig.1.7.Diagrammatic Representation of Laser Abilation Synthesis

#### 1.2.9. Sustainable Synthesis Using Oleo Polyol Reagents

The utilization and improvement of novel and greener preparation protocol for the nanostructures preparation with controlled size and/or shape by sustainable reagents has been exemplified by oleo polyol and related polymers in recently wherein novel Sr0.3Mg0.7Fe2O4 (SMF) trimetallic nanocubes were prepared via a solvent-less, cost effective oleo polyol reagents; the ensuing mesoporous trimetallic nanocubes exhibited excellent activities for wastewater treatment, and the removal of organic pollutants (Congo red) Three models (Freundlich, Temkin,

and Langmuir) were utilized to study the adsorption isotherm and it was found that the magnetic SMF nanocubes with a large surface area (21.85 m2g $\square$ 1) was able to efficiently adsorb Congo red (>90% within 30 min).



Fig.1.8.Diagrammatic Representation of Sustainable Synthesis using oleo polyol Reagents

#### 1.2.10.Chitosan

Chitosan is a naturally-occurring polysaccharide polymer with high biodegradability, significant biocompatibility, and nontoxicity which can be employed for synthesizing metallic NPs. For instance, chitosan was employed as a capping agent for fabrication of trimetallic Au-Pd-Ag with good stability; chitosan-Pd2+ and chitosan-Ag+ complexes were reduced on the surface of gold NPs. The NPs showed remarkable potentials as adsorbent for removing acid orange 7 from wastewater with maximum adsorption efficiency (~71.42 mg); the maximum adsorption (90%) was detected under acidic pH.



Fig.1.9.Stabilisation of Nanoparticles using chitosin

#### 1.2.11. Glycine

Glycine was employed as a size-controlling agent for the surfactant-free one-pot production of ultrasmall homogeneous trimetallic Pt-Ni-Cu NPs (~2–5 nm). In this study, the synthetic significance of the water existing in the latter solvent system in promoting metal reduction was demonstrated, resulting in the production of a starting nanomaterial of about 5 nm. Additionally, the application of glycine can help stabilize the prepared ultra-small NPs with a suitable level of tenability and can be employed to control the size and morphology of the alloyed nanomaterials. Subsequently, compared with the commercially-available platinum black, the prepared NP showed significantly improved quality activity for the electrooxidation of ethanol.

#### **1.3.** Applications of Trimetallic NPs

Sensing Applications: Cu-Au-Pt trimetallic NPs with intense plasmonic absorption in the near-infrared fluorescence imaging (NIR-I) bio-window (~650–950 nm) and significant catalytic activity were fabricated for biosensing and theranostics applications, considering the potential

combination of various enzyme-related reactions and different molecular recognition devices. By harnessing the catalytic characteristics of Cu/Au/Pt NPs, a sensitive colorimetric sensing technique was developed for the precise evaluation of glucose. Additionally, an innovative theranostic probe was produced by these thiolated aptamer-coated trimetallic NPs, which could achieve visual, sensitive, and selective analysis, and remarkable photothermal demise of target cancer cells. In another study, the nanocomposite sensor (based on Au-Ag-Pd NPs) which was uniformly capped by electro-pretreated GO has been fabricated and applied for the simultaneous determination of ascorbic acid, dopamine, acetaminophen, and tryptophan. This nanocomposite electrode can be practically employed for the analysis/determination of these substances in real samples of human blood serum. Interestingly, Pd-Cu-Au trimetallic nanomaterials with good stability were synthesized by the simple one-pot method, and exhibited potential as temperature sensors for sensitive detection of changes in fluorescence intensity (in about 4-95°C temperature range), because of their unique optical characteristic. Additionally, the trimetallic NPs showed significant catalytic operation for peroxidase-like enzymes; they could catalyze 3.3'.5.5'tetramethylbenzidine (TMB) promptly in the presence of H<sub>2</sub>O<sub>2</sub> and oxidatively convert it to a visible blue product (ox TMB). Thus, these trimetallic NPs can be employed as colorimetric platform for detection of  $H_2O_2$  (0.1–300 \_M, LOD = 5 nM) and glucose (0.5–500 \_M, LOD = 25 nM).

#### **1.3.1.**Cancer Therapy and Diagnosis

In addition to the available therapeutic options, cancers are still considered as foremost diseases causing enormous human mortality. Thus, the treatment and diagnosis of cancers in early stages are vital, and in this regard, trimetallic NPs show promising potentials and should be emphasized by researchers in the field. Additionally, developing sensitive, fast, and affordable electrochemical immunosensors for detecting cancer biomarkers (vital in primary diagnosis of cancers for better managements and treatment) is a challenging issue.

#### 1.3.2. Active Food Packaging

Due to poor mechanical and barrier characteristics of biopolymers, their applications are restricted in food packaging. Therefore, the incorporation of innovative NPs into biopolymers may improve these characteristics. Trimetallic NPs (like Au-Fe-Ag and Fe-Ag-Pt) can act as promising antimicrobial agents for food packaging applications. however, limited data are available on the passage of NPs into human organs and also their toxicity analyses in this field of science. Innovative synthesis of trimetallic NPs and their incorporation into biopolymers are expected to improve the shelf life of foods, including preserved food, vegetables, fruits, cooked meat, fish, processed foods, cakes, bread, fermented milks, and dairy foods. However, evaluations regarding the toxicity issues of such ensued nanocomposites used for food packaging should be considered systematically and critically before production, supply, and distribution of the product; the risk assessments and safety aspects of the complex NPs should be added to the priority for research.

#### 1.3.3. Removal of Antibiotics and Organic Pollutants

MOFs, metal-organic frameworks, are an emerging and fascinating class of porous hybrid organicinorganic materials prepared from metal ions or clusters and organic ligands linked by coordinating bonds, and have promising potential for sensing, gas storage, and catalysis. The suitable compatibility of these hybrid materials with different metal ions can produce homogeneous multimetallic spinels with unique characteristics attributable to both the MOFs and the metal ions with promising functionalities. In one investigation, magnetic NiCo/Fe3O4-MOF-74 was prepared by applying a precursor trimetallic NiCoFe-MOF-74. It exhibited significant stability, remarkable magnetism and active metal sites with respect to the original MOF. It showed suitable enrichment ability to remove antibiotics, like tetracycline (about 94.1% within 5 min, reusable five times without significant loss), which was more than NiCoFe-MOF-74. The open metal sites to generate a stable metal-ligand with the antibiotic molecules make it a suitable framework for prompt removal of antibiotics from water at a low cost and with high efficiency. Fe-La-Zn@GO trimetallic nanocomposite (~17 mm) and Fe-La-Zn trimetallic NPs (~19 mm) have been employed as photocatalysts for removal of organic pollutants. They were investigated for sunlight-induced phenylhydrazine photodegradation, and by applying Fe-La-Zn trimetallic NPs (optical band gap of about 2.73 eV) and Fe-La-Zn@GO trimetallic nanocomposite (band gap of about 2.30 eV), the reduction of 52 and 57.91% was obtained, accordingly. The photocatalytic activity of the MWsynthesized La/Cu/Zr/carbon quantum dots trimetallic nanocomposite was explored for removing persistent pollutants, including ampicillin antibiotic and malachite green dye, up on visible light exposure. Consequently, ampicillin antibiotic 96% and malachite green 86% have been destroyed in four hours of photo-irradiation via adsorption in dark followed by a photocatalysis and coupled adsorption/photocatalysis procedure. The adsorption of antibiotics and dyes occurred on the trimetallic nanocomposite's surface. The photocatalysis procedure involved in the production of electron-hole pairs on light irradiation of the trimetallic nanocomposite, which reacted with water molecules to generate super oxide and hydroxyl radicals causing contaminant (like dyes or antibiotics mineralization.

#### CHAPTER-II

## LITERATURE SURVEY

Trimetallic oxide Cu/Cr/Ni nanoparticles (NPs) using the aqueous leaf extracts of Eryngium campestre (E. campestre) and Froriepia subpinnata (F. subpinnata) as bio-reducing and capping agents. The effect of several parameters including incubation time, incubation temperature, and precursor salt to plant extract ratio was investigated in order to optimize trimetallic oxide Cu/Cr/Ni NP production. The trimetallic oxide NPs produced in their optimum condition using the two leaf extracts as well as by their 50:50 mixture and were characterized by UV-vis spectroscopy, FTIR, EDX, XRD, FESEM, and TEM analyses. The modeled experimental optimization for E. campestre leaf extract was found as time of 3 min, temperature of 34 °C and metal salt-to leaf extract ratio of 2.38 with predicted response of 73.17%. The corresponding values for F. subpinnata leaf extract including time of 3 min, temperature of 40 °C and metal salt-to leaf extract ratio of 1.07; while 72.22% conversion of metal salts into trimetallic oxide NPs was predicted by experimental design software. Antibacterial activity of the NPs was studied by determining the minimum inhibitory and bacterial concentrations on two pathogenic bacteria, namely, Gram -ve Escherichia coli PTCC1112, and Gram +ve Staphylococcus aureus PTCC1270. The results evidenced the bacterial growth inhibition effect of the trimetallic oxide NPs [1]. The synthesis and traits of trimetallic (CuZnFe) oxide nanoparticles (NPs) using X-ray diffraction, high-resolution transmission electron microscopy, and energy dispersive x-ray spectroscopy. We evaluated the antibacterial activity of these NPs against gram-negative Escherichia coli and gram-positive Enterococcus faecalis and then compared it to that of their pure single-metal oxide components CuO and ZnO [2] and We colloidal trimetallic (Ni-Cu)@Ag core@shell nanoparticles (NPs) without stabilizing materials.

Experimental evidence was found for the successful synthesis of these NPs using X-ray diffraction (XRD), optical spectroscopy, and high-resolution transmission electron microscopy (HRTEM). The presence of core metals (Ni and Cu) was confirmed by elemental analysis using a total reflection X-ray fluorescence (TXRF) analysis. In addition, the absorption spectra of the prepared samples exhibited broad bands compared to the bands of the monometallic NPs, indicating the formation of a core-shell nanostructure. The antibacterial activity of the trimetallic NPs was evaluated against three Gram-negative (Pseudomonas aeruginosa, Escherichia coli, and Salmonella) and two Gram-positive (Streptococcus and Staphylococcus aureus) bacteria on Mueller–Hinton agar. These NPs showed high inhibition of bacterial growth at the low sample concentrations used in this study compared to other nanomaterials. One of the interesting results of the current study is that the inhibition zone of Pseudomonas aeruginosa as a resistant bacterium was high for most NPs. These results make the prepared samples promising candidates for antibiotic material applications[3]. Synthesis method of PdCuAu Nanoparticles (PdCuAu NPs) prepared directly in aqueous solution. PdCuAu NPs have Attracted much attention owing to their unique synergistic electronic effect, optical And catalytic performance. As temperature sensor, PdCuAu NPs are sensitive to the Fluorescence intensity change in the temperature range of 4– 95°C, which is due To its unique optical properties. The prepared PdCuAu NPs have excellent catalytic Performance for peroxidase-like enzymes. It can catalyze TMB rapidly in the presence Of hydrogen peroxide and oxidize it to visible blue product (oxTMB). Based on its unique Peroxidase-like properties, this study used PdCuAu NPs colorimetric platform detection Of hydrogen peroxide and glucose. The linear ranges of hydrogen peroxide and glucose Were 0.1– 300µM and 0.5-500µM, respectively, and the detection limits (LOD) were 5 And 25 nM, respectively. This simple and rapid method provides a good prospect for the Detection of H2O2

and glucose in practical applications.[4] A facile room temperature one-pot synthesis of trimetallic porous Au@Pd@Ru nanoparticles (Au@Pd@RuNPs) has been developed. The trimetallic nanoparticles have been prepared by the successive sacrificial oxidation of cobalt nanoparticles (CoNPs). The average particle size of Au@Pd@RuNPs is 110 nm. The porous nature and the presence of Au, Pd and Ru have been confirmed via TEM, FE-SEM and EDS analyses. The trimetallic nanoparticles have shown excellent catalytic activity towards the reduction of pnitrophenol and efficient degradation of various azo dyes. This has been further extended towards the removal of colour from waste water via the catalytic degradation of azo dyes. Moreover, the produced amine can be eliminated from the waste water via its sorption on an industrial solid waste dolochar. [5] Recently reported patents and experimental articles on the synthesis, properties, and main applications of coreshell nanoparticles, containing iron or its oxides and gold, as well as trimetallic systems on their basis, are reviewed. These nanostructures were obtained by a series of methods, including reduction in reverse micelles, decomposition of organometallic compounds, electron-beam, laser and  $\gamma$ -irradiation, sonolysis and electrochemical methods. (Fe or FexOy)/Au nanoparticles are subject to be functionalized with organic moieties, may expand their main applications, which consist of catalysis, biological and biomedical uses. [6] In the present work & nanoparticles were synthesised for the first time using phytochemical extracts from Flacourtia indica leaves and applied in the photocatalytic degradation of Congo Red in the presence of Light Emitting Diode warm white light. The photocatalytic degradation was optimized with respect tonanoparticle dosage, initial Congo Red concentration, and degradation time. The optimum conditions for nanoparticle synthesis was pH 9, leaves extracts of F. indica dosage 4 g 100 mL-1, Zirconia, Cerium and Zinc metal ion concentration 0.05 mg/L and metal ion to plant volume ratio of 1:4. The leaves extract dosage, pH and metal concentration had the most significant effects on

the synthesis of the nanoparticles. The nanoparticles followed type III physisorption adsorption isotherms with surface area of 0.4593 m3g-1, pore size of 6.80 nm, pore volume 0.000734 cm and average nanoparticle size 0.255 nm. A degradation efficiency of 86% was achieved and the optimum degradation conditions were 0.05 g/L of nanoparticle dosage, 10 mg/L initial Congo red concentration, and 250 minutes irradiation time. [7-10]. Multimetallic nanoparticles (NPs) have extraordinary properties and therefore, drew the attention regarding their synthesis and applications in the form of bi and tri metallic nanoparticles. Bimetallic (BNPs) and trimetallic nanoparticles (TNPs) are gaining enormous attention than that of monometallic nanoparticles. Both NPs can be synthesized by different methods such as microwave, selective catalytic reduction, micro-emulsion, co-precipitation and hydrothermal etc. Using physical and chemical methods have more disadvantages such as production of toxic byproduct, use of excess energy and additional use of stabilizer. [11- 13].

The main objectives of the present investigation is

- ✤ To synthesize trimetallic nanoparticle of Au-Pt-Ru by chemical reduction method
- ✤ To characterize the formed nanoparticle by UV-Vis and FT-IR spectral studies.
- ◆ To study the antibacterial and antioxidant property of trimetallic nanoparticle.

#### CHAPTER-III

# EXPERIMENTAL DETAILS

#### **3.1. Chemicals Required**

- Auric Chloride [AuCl<sub>3</sub>)]
- Potassium tetrachloroplatinate K<sub>2</sub>[PtCl<sub>4</sub>]
- Ruthenium(lll)chloride hydrate [RuCl<sub>3</sub>.H<sub>2</sub>0]
- Potassium Bromide [KBr]
- Polyvinylpyrrolidone [C<sub>6</sub>H<sub>9</sub>NO]<sub>n</sub>
- Ascorbic acid [C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>]
- Hydrochloric Acid [HCl]

#### 3.2.Synthesis of Trimetallic Nanoparticle

Trimetallic nanoparticle of Au-Pt-Ru was prepared by mixing of 0.001M AuCl<sub>3</sub> and 0.001M of K<sub>2</sub>PtCl<sub>4</sub> and 0.01M of RuCl<sub>3</sub>. To this solution 0.01 M HCl, 0.6mg of KBr and 0.2g of PVP and 1.8g of Ascorbic acid were added and mixed evenly. The solution is kept in the water bath at 95<sup>o</sup>c with continuous stirring for 2 hours. The colour of the solution changes to purple. The colour change indicates the formation of trimetallic nanoparticles. The primary product Au-Pt-Ru is stored in the refrigerator and sent for further characterisation.



Fig.3.1. Au-Ru-Pt Trimetallic Nanoparticle

#### **3.3.** Ultraviolet–visible spectroscopy

Ultraviolet–visible spectroscopy is absorption or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

• Solutions of transition metal ions can be coloured (i.e., absorb visible light) because d electrons within the metal atoms can be excited from one electronic state to another. The

colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulphate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption ( $\lambda_{max}$ ).

- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.
- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.



Fig.3.2. Schematic diagram of UV- visible spectrophotometer

#### 3.4. Infrared Spectroscopy

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the transition energy of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the

atoms, and the associated vibronic coupling. In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighbourhood of the equilibrium molecular geometry, the resonant frequencies are associated with the normal modes corresponding to the molecular electronic ground state potential energy surface. The resonant frequencies are also related to the strength of the bond and the mass of the atoms at either end of it. Thus, the frequency of the vibrations is associated with a particular normal mode of motion and a particular bond type. Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO<sub>2</sub> concentrations in greenhouses and growth chambers by infrared gas analysers. It is also used in forensic analysis in both criminal and civil cases, for example in identifying polymer degradation. It can be used in determining the blood alcohol content of a suspected drunk driver.IR-spectroscopy has been successfully used in analysis and identification of pigments in paintings and other art objects such as illuminated manuscripts. A useful way of analysing solid samples without the need for cutting samples uses ATR or attenuated total reflectance spectroscopy. Using this approach, samples are pressed against the face of a single crystal. The infrared radiation passes through the crystal and only interacts with the sample at the interface between the two materials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.Infrared spectroscopy is also useful in measuring the degree of polymerization in polymer manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics:<sup>[8]</sup> for example. infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc. Another important application of Infrared Spectroscopy is in the food industry to measure the concentration of various compounds in different food products. The instruments are now small, and can be transported, even for use in field trials.IR spectroscopy is often used to identify structures because functional groups give rise to characteristic bands both in terms of intensity and position (frequency). The positions of these bands are summarized in correlation tables as shown below.



Fig.3.3. Diagrammatic Representation of position of Absorption Band

#### 3.5 Antibacterial activity and Antioxidant activity

Currently, throughout the globe, the emergence of bacterial resistance to the available antibiotics is a major health concern. Therefore, there is a need for the antibiotic agent that can kill pathogenic bacteria which show resistance to the available drugs. The NPs have small size with high surface area compared to the bigger molecules and therefore possess strong antibacterial activities. The NPs have dose-dependent membrane permeation and inhibit the synthesis of bacterial proteins by disturbing the cell membrane. Different metallic NPs such as gold, iron, silver, and metal oxide NPs such as iron oxide, cobalt oxide, and copper oxide showed significant antibacterial activities. The AgNPs are the main interest not only in biomedical industries but also in food industries because of its potential antimicrobial behaviour. Cobalt and cobalt oxide NPs also possess potential antibacterial activity similar to silver nanoparticles. Antioxidant activity Oxidative metabolism is a key process for the survival of cells. However, this process has some side effects as they produce free radicals and reactive oxygen species. When these free radicals are

produced in the body in the excess amount they can inundate the enzymes such as catalases, peroxidase, and superoxide dismutase and lead to lethal cellular effects by oxidizing cellular proteins, membrane lipids, DNA enzymes, and influence signaling pathways of the cell leading to termination of cellular respiration. Oxidation affects food as well, which is one of the main causes of chemical spoilage that affects flavour, texture, nutritional value, and safety of food. Different types of natural and synthetic antioxidants are available to limit the side effects of oxidation.

## CHAPTER-IV

# RESULTS AND DISCUSSION

#### 4.1. UV Visible Spectroscopy

Fig 4.1. presents the UV–Vis spectra of the synthesized trimetallic nanoparticles, depicting a sharp maximum absorption band at 259 nm. The strong peak at 259 nm indicates the complete reduction of Pt ions as reported earlier by sheny at al., [14]. Gold nanoparticles exhibit a distinct optical feature commonly referred to as localized surface plasmon resonance (LSPR), that is, the collective oscillation of electrons in the conduction band of gold nanoparticles in resonance with a specific wavelength of incident light. LSPR of gold and ruthenium nanoparticles results in a broad absorbance band in the visible region at 580 nm [15].



Fig. 4.1. UV-Visible spectrum of Au-Ru-Pt trimetallic nanoparticle

#### 4.2. FTIR Spectroscopy



Fig.4.2. FTIR Spectrum of Au-Ru-Pt trimetallic nanoparticle

Fig.4.2. presents the FTIR spectra of Au–Ru-Pt nanoparticles synthesized using ascorbic acid and PVP as size reducing agent and capping agent. The broad peak at 3411 cm<sup>-1</sup> was observed for the O–H bond vibrations of the hydroxyl group. The weak peaks at 2108 cm<sup>-1</sup> is associated with CH<sub>2</sub>-group stretching vibrations of PVP. The peak at 1636 cm<sup>-1</sup>corresponds to the conjugated carbonyl groups present in ascorbic acid. The C-H bending and CH<sub>2</sub>wagging were observed at 1400 cm<sup>-1</sup> and 1164 cm<sup>-1</sup> respectively. The peak present at 1037 cm<sup>-1</sup>, 878 cm<sup>-1</sup>,424 cm<sup>-1</sup>confirms the formation Au [16], Pt [17] and Ru [18] nanoparticle.

#### Antibacterial activity

Antibacterial activity assay was done by disc diffusion method (Kirby& Bauer, 1966). The test bacteria was inoculated in peptone water and incubated for 3 - 4 hours at  $35 \,^{\circ}$ C. Mueller hinton agar plates was prepared and poured in sterile petriplates. 0.1 ml of bacterial culture was inoculated on the surface of Mueller hinton agar plates and spread by using L-rod. The inoculated plates was allowed to dry for five minutes. The disk loaded with samples concentration 1000 µg/ml was placed on the surface of inoculated petriplates using sterile technique. The plate was incubated at

37 °C for 18-24 hours. The plate was examined for inhibitory zone and the zone of inhibition was measured in mm.





Bacteria: Staphylococcus aureus



Bacteria: Bacillus subtilis



## Bacteria: Bacillus cereus



Bacteria: Pseudomonas aeruginosa



Bacteria	Inhibition zone in mm		
	Ab Ampicillin	Au-Ru-Pt	
E.coli	14	11	
Staphylococcus	12	12	
aureus			
Bacillus	11.5	10	
subtilis			
Bacillus cereus	16	10.5	
Pseudomonas	12	9	
aeruginosa			

The Inhibition Zone of Au-Ru-Pt trimetallic nanoparticle for *Staphylococcus aureus* bacteria is higher than a *E.Coli, Bacillus subtiles, Bacillus cereus, Pseudomonas aeruginosa*.

#### Total Antioxidant Activity (TAA) by Phosphomolybdenum assay

TAA was estimated by phosphomolybdenum assay (Prieto et al., 1999). Sample of concentration 1000  $\mu$ g/ml were taken in individual test tubes and made upto 1 ml using distilled water and 2 ml of Molybdate reagent solution (0.6 M sulfuric acid, 28 mM sodium phosphate and 4 mM ammonium molybdate). The test tubes were incubated at 95°C for 90min. After incubation, the tubes were cooled to room temperature for 20-30 min and the absorbance of the reaction mixture was measured at 695nm.. Ascorbic acid was used as the positive reference standard

% Antioxidant activity = Abs sample/ Abs Std \* 100



Sample	Absorbance at 695 nm	%Antioxidant activity
concentration		
µg/ml		
Ascorbic	1.95	
acid		
Au-Ru-Pt		
200	0.15	7.69
400	0.30	15.38
600	0.42	21.54
800	0.92	47.17
1000	1.50	76.92

Table 1. Antioxidant activity



#### CONCLUSION

- Au-Ru-Pt nanoparticles was successfully synthesised by Chemical Reduction Method
- The UV visible spectrum of Au-Ru-Pt nanoparticles shows an absorption band in the region of 259 nm, which originates primarily from the absorption and scattering of UV radiation by Au-Ru-Pt nanoparticles
- In the Au–Ru-Pt nanoparticles the broad peak at 3411 cm<sup>-1</sup> was observed for the O-H bond vibrations of the hydroxyl group. The weak peaks at 2108 cm<sup>-1</sup> is associated with CH<sub>2</sub>-group stretching vibrations of PVP. The peak at 1636 cm<sup>-1</sup>corresponds to the conjugated carbonyl groups present in ascorbic acid. The C-H bending and CH<sub>2</sub>wagging were observed at 1400 cm<sup>-1</sup> and 1164 cm<sup>-1</sup> respectively. The peak present at 103cm<sup>-1</sup>,878cm<sup>-1</sup>,424 cm<sup>-1</sup> confirms the formation Au-Ru-Pt nanoparticle.
- The Inhibition Zone of Au-Ru-Pt trimetallic nanoparticle for *Staphylococcus aureus* bacteria is higher than a *E.Coli, Bacillus subtiles, Bacillus cereus, Pseudomonas aeruginosa*.
- The formed trimetallic nanoparticle shows very good antioxidant property.

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# Synthesis and Characterization of Ru/Polyaniline Core–Shell Nanocomposite

**Project in Chemistry** 

Submitted to St. Mary's College(Autonomous) in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry

DONE BY

S.Annite Bency

# **M.Anto Maria Sherena**

**P.Antony Mera** 



## ST.MARY'S COLLEGE(AUTONOMOUS)

# **RE-ACCREDITED WITH "A<sup>+</sup>" GRADE BY NAAC**

## THOOTHUKUDI-628001

2022-2023

# DECLARATION

We hereby declare that the project entitled "Synthesis and Characterization of Ruthenium/Polyaniline Core-Shell Nanocomposite" submitted to St.Mary's College (Autonomous), Thoothukudi, affliated to Manonmaniam Sundaranar University, for the degree of Bachelor of Science is our original work and that, it has not previously formed on the basis of the award of any degree or similar title.

S. Annite Bancy

S.Annite Bency

M. Anto Maria Sherena M.Anto Maria Sherena

P. Antony Mera . P.Antony Mera

April 2023

THOOTHUKUDI

# CERTIFICATE

This is to certify that project in chemistry "Synthesis and Characterization of Ruthenium/Polyaniline Core-Shell Nanocomposite" submitted to St.Mary's College (Autonomous), Thoothukudi in partial fulfillment for the award of the degree of Bachelor of Science in Chemistry and is a record of the work done by following students during the year 2022-2023.

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I. NO.	CONTENT	PAGE NO
1	INTRODUCTION	1
2	LITERATURE SURVEY	20
3	EXPERIMENTAL DETAILS	26
4	RESULT AND DISCUSSION	31
5	CONCLUSION	38
6	REFERENCE	39

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In recent times, Core-Shell Nanoparticles (CSN) have received increased attention owing to their interesting properties and broad range of applications in catalysis, biology, materials chemistry and sensors. By rationally tuning the cores as well as the shells of such materials, a range of core–shell nanoparticles can be produced with tailorable properties that can play important roles in various catalytic processes and offer sustainable solutions to current energy problems.

Core-shell type nanoparticles are a type of biphasic materials which have an inner core structure and an outer shell made of different components. These particles have been of interest as they can exhibit unique properties arising from the combination of core and shell material, geometry, and design . Additionally, they have been designed so that the shell material can improve the reactivity, thermal stability, or oxidative stability of the core material or to use an inexpensive core material to carry a thin, more-expensive shell material . Various synthetic methods for preparing different classes of CSNs, including the Stöber method, solvothermal method, one-pot synthetic method are briefly mentioned here. The roles of various classes of CSNs are exemplified for both catalytic and electrocatalytic applications, including oxidation, reduction, coupling reactions[1,2].



Based on the structural configuration, core-shell NPs can be classified in to following categories

- (A) Core shell nanoparticles
- (B) Core double-shell particles or core multi-shell nanoparticles
- (C) Polyhedral core-shell nanoparticles
- (D) Core porous-shell nanoparticles
- (E) Hollow-core shell nanoparticles or single-shell nanoparticles
- (F) Hollow-core double-shell nanoparticles
- (G) Moveable-core shell nanoparticles
- (H) Multi-core shell nanoparticles
- (I) Irregular shape core shell nanoparticles
- (J) Rod core shell nanoparticles



Schematic (A–J) different structure of core shell nanoparticles

#### 1.1. CORE :

It is the main functional component. It is 0-3D material. By coating the core material, the reactivity and thermal stability can be modified, which increases the stability and dispersibility of the core particle. Core moiety remains in unaggregated form as they are encapsulated by the surfactant.

#### **1.2.SHELL:**

It acts as a physical barrier between the optically active core and the surrounding medium, thus making the core less sensitive to environmental changes, surface chemistry, and Photo-oxidation. It helps in improving the property of the core.

#### **1.3.SYNTHESIS OF CORE-SHELL NANOPARTICLE**

#### **1.3.1.STOBER PROCESS**

The Stöber process is a chemical process used to prepare silica (SiO<sub>2</sub>) particles of controllable and uniform size for applications in materials science. It was pioneering when it was reported by Werner Stöber and his team in 1968, and remains today the most widely used wet chemistry synthetic approach to silica nanoparticles. It is an example of a sol-gel process[3].

#### **1.3.2. SOLVOTHERMAL PROCESS**

Solvothermal synthesis is a method of producing chemical compounds, in which a solvent containing reagents is put under high pressure and temperature in an autoclave. Many substances dissolve better in the same solvent in such conditions than at standard conditions, enabling reactions that would not otherwise occur and leading to new compounds or polymorphs. Solvothermal synthesis is very similar to the hydrothermal route; both are typically conducted in a stainless steel autoclave. The only difference being that the precursor solution is usually non-aqueous[4].

Solvothermal synthesis has been used to prepare Metal-organic frameworks (MOFs)[5], titanium dioxide and graphene, carbon spheres, chalcogenides and other materials[6].

#### **1.3.3. ONE POT SYNTHESIS**

One-pot synthesis is an efficient and simple approach for the construction of nanoscale organic/inorganic hybrid functional materials. In this process, a direct reaction in one step is used for the preparation of inorganic parts while the organic component works as surface capping material or template. Generally, the organic component plays a capping role and does not participate in any reaction[7].



Figure 1.3.3 One Pot Synthesis

#### **1.3.4. SONO-SYNTHESIS OF CSN**

A core-shell nanocomposite (CdS/TiO<sub>2</sub>) was synthesized at relatively low temperature (70 °C) with small particle sizes (~11 nm). First, Cadmium Sulfide (CdS) nanoparticles were prepared by a combination of ultrasound and new micro-emulsion (O/W) without surfactant. Then the synthesized CdS was easily combined with Titanium Dioxide (TiO<sub>2</sub>) under sonication. The formation of uniform surface layer of TiO<sub>2</sub> with depths of 0.75– 1.1 nm on the CdS led to an increase of particle size. Ultrasonic irradiation can control the hydrolysis and condensation of Titanium tetra-isopropoxide (TTIP) and the formation of TiO<sub>2</sub> shell around the CdS core. This technique avoids some of the problems that exist in conventional microemulsion synthesis such as the presence of different additives and
calcinations. It was found that nanocomposite particles extend the optical absorption spectrum into the visible region in comparison with pure  $TiO_2$  and pure CdS. In addition, a larger depth of  $TiO_2$  led to a red-shift of the absorption band in nanocomposite. The characterization of nanocomposites has been studied by HRTEM, TEM, XRD, EDAX, BET and, UV–vis.

#### **1.3.5. CHEMICAL VAPOUR DEPOSITION METHOD**

Copper-carbon nanowires (NWs) or nanorods (NRs) with outer diameters between 30 and 90 nm and lengths ranging from 700 nm up to 10 µm have been prepared with high yield via chemical vapor deposition (CVD) method followed by thermal decomposition of copper(II)-acetylacetonate. The morphology and microstructure of the Cu-C NWs/NRs were characterized by scanning electron microscopy (SEM) and tunnelling electron microscopy (TEM), which suggest that these as-grown copper cores with graphite carbon encapsulated inside showed one tip closed and another tip open-ended. The X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) analysis data indicate that the Cu-C NWs/NRs are free of any contamination, while the electron diffraction (ED) analysis revealed the NWs/NRs to be single crystals. Raman spectra of the deposits obtained with increasing reaction temperature show the transformation tendency from graphite carbon to amorphous carbon. The nanowire/rod growth mechanism has also been discussed. Moreover, Cu-C NWs/NRs are transformed into empty carbon nanotubes with Cu nanoparticles attached to the end after a thermal treatment above 800°C. This conversion process is of great importance for reuse and recycling of nanomaterials.



Figure 1.3.5 Chemical Vapour Deposition Method

5

#### **1.3.6. CHEMICAL REDUCTION METHOD**

There are many ways to form Copper–silver core–shell (Cu-Ag) nanoparticles such as electroplating, electroless plating, vacuum process, sputtering etc. In this paper, a simple chemical reduction method was used to synthesize Cu-Ag nanoparticles using polyvinyl pyrrolidone (PVP) as an efficient protective agent in a one-step process. Ascorbic acid( $C_6H_8O_6$ ) and sodium borohydride (NaBH<sub>4</sub>) are chosen as the reducing agents, due to their non toxicity and easy availability. Cu-Ag nanoparticles powders prepared by this method easily disperse and hardly oxidize even after a long time.



**Figure 1.3.6 Chemical Reduction Method** 

# 1.4.EVOLUTION OF CORE SHELL NANOPARTICLE

#### **1.4.1. FLUROSCENT AND SILICA CSN**

The fluorescent nanoparticles include a core comprising a fluorescent silane compound and a silica shell on the core. The core of the nanoparticle can comprise, for example, the reaction product of a reactive fluorescent compound and a co-reactive organo-silane compound, and the shell can comprise, silica forming compound can be formed. The silica forming compound can produce one or more layers of silica, such as from 1 to about 20 layers, and various desirable shell characteristics, such as shell layer thickness, the ratio of the shell thickness to the core thickness or diameter, silica shell surface coverage of the core, porosity and carrying capacity of the silica shell, and like considerations. The synthesis of the

fluorescent monodisperse core-shell nanoparticles is based on a two-step process. First, the organic dye molecules, tetramethyl rhodamine isothiocyanate (TRITC), are covalently conjugated to a silica precursor and condensed to form a dye-rich core. Second, the silica gel monomers are added to form a denser silica network around the fluorescent core material, providing shielding from solvent interactions that can be detrimental to photostability. By first forming a dye-rich core enables the incorporation of various classes of fluorophores which cover the entire UV-Vis absorption and emission spectrum. The amount of reagents used in the synthesis of the different core-shell architectures in terms of dye placement, i.e. compact core, expanded core, and homogenous, have been kept identical to generate precise structure property correlations. However, the order in which the reagents are reacted that resulted in the forming the core-shell architecture varies. Therefore, the chemical environment around the dye molecules in each architecture is different with respect to the silica matrix density and presence of organic moieties which has significant effects on the photophysical particle properties. For the synthesis of the compact core-shell nanoparticle, the dye precursor was added to a reaction vessel that contains appropriate amounts of ammonia, water and solvent and allowed to react overnight. The dye precursor was synthesized by addition reaction between TRITC and 3aminopropyltriethoxysilane (APTES) in molar ratio of 1:50, in exclusion of moisture. After the synthesis of the dye-rich compact core was completed, tetraethyl orthosilicate (TEOS) was subsequently added to grow the silica shell that surrounded the core. The synthesis of the expanded core-shell nanoparticle was accomplished by co-condensing TEOS with the aforementioned dye precursor and allow the mixture to react overnight. After the synthesis of the expanded core was completed, additional TEOS was added to grow the silica shell that surrounded the core.

#### **1.4.2. MAGNETIC IRON OXIDE CSN**

Magnetic iron oxide nanoparticles (MIONPs) are also attractive nanoparticles with an excellent magnetic property that is suitable for application in biomedical approaches. Although MINPs are easily oxidized with air, similar to gold nanoparticles (GNPs), their surface can be modified to provide better stability than the naked form. Various types of inorganic coatings, such as metal substance, silica, sulfide, metal oxide, and nonmetal material, can be used for coating the surface of MIONPs. Besides these inorganic materials, MIONPs can also be indirectly or directly coated with organic materials. The common organic materials that have been used to coat the surface of MIONPs are dextran, starch, polyethylene glycol (PEG), poly(D, 1-lactide), and polyethyleneimine. In general, after coating MIONPs with these materials, they can be further modified with designed molecules. It is commonly known that there are three popular forms of MINPs: hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). Their morphology relies on an iron oxide precursor with other processes such as nucleation, growth, and adsorption, which cause more difficulty in controlling the shape and size of MIONPs than gold nanoparticle synthesis. Nevertheless, different shapes and sizes of MIONPs can be prepared through various techniques, such as hydrothermal synthesis, thermal decomposition, coprecipitation, and Sono chemical synthesis. The aggregation is an important factor on synthesis of MIONPs. Different techniques for MIONP synthesis were reviewed. As mentioned previously, it is important to make MIONPS stable against aggregation stimulated by the magnetic field and biological fluid. To overcome this aggregation problem, controlling electrostatic and steric repulsions is a key factor. Therefore many approaches of surface coatings have been applied to increase the stability of MIONPs. However, the coating effect on magnetic property and biocompatibility of MIONPs needs to be taken into consideration[8].

#### **1.4.3. POROUS CORE SHELL NANOPARTICLES**

The porous hydrophilic core/hydrophobic shell nanoparticles were first prepared by coaxial electrospray method in the present study, and the most outstanding advantages of electrospray are rapid and efficient with the features of preparation of solid nanoparticles in one step and high enantiomeric excess (EE) (nearly 100%). And the ultrahigh EE of porous core/shell nanoparticles prepared with different poly(methyl methacrylate) PMMA concentrations was observed. While, the LC of porous core/shell nanoparticles decreased from to 10.43% to 3.73% with the increased PMMA concentrations. Electrospray has the potential to prepare the high drug loaded particles because of the ultrahigh entrapment efficiency. However, the maximum loading capacity of MTZ(Metronidazole) was 10.43% in the present study, which was due to the limited solubility of MTZ in dichloromethane. In addition, the size of core/shell nanoparticles increased from 58.3 to 389.7 nm with the PMMA concentrations that increased from 1% to 4%, and the trends could be explained by the fact that the increase of polymer concentration is thought to increase the resistance of the solution to be separated into droplets, leading to an increase of particle size. Meanwhile, the values of PDI were smaller than 0.300, indicating a narrow particle size distribution, and the porous ERS(eudragit RS 100)/PMMA core/shell nanoparticles displayed negative zeta potential ranging from - 9.39 to - 23.09 mV. Furthermore, the BET surface area of nanoparticles decreased from 30.06 to 5.89  $m^2/g$  with the increased PMMA concentrations from 1% to 4%, which may be due to the increase of particle size. And the maximum surface area of produced porous ERS/PMMA nanoparticles was approximately  $30 \text{ m}^2/\text{g}$ , doesn't display a large surface area. The reason probably resulted from the core-shell structure of porous nanoparticles[9].

#### 1.4.4. CORE -SHELL(CS)PLASMONIC NANOPARTICLE

CS nano particles allows to tune plasmonic resonance in a wide range of wavelength.

- Metal core show significant impact on the optical and fluorescence emission properties of optically active insulating shell material.
- The metal core can be made from noble plasmonic metals such as Au, Ag and Cu with shapes that include nanosphere, triangles, cubes, prisms and nanorods.



Figure 1.4.4 Plasmonic Nanoparticle

#### **1.5.TYPES OF CORE-SHELL NANOPARTICLES**

- ✓ Inorganic and Inorganic CSN
- ✓ Inorganic and Organic CSN
- ✓ Organic and Inorganic CSN
- ✓ Organic and Organic CSN

#### **1.5.1.INORGANC AND INORGANIC CSN**

The most basic advantages of the silica coating compared with other inorganic (metal or metal oxide) or organic coatings are as follows:

It reduces the bulk conductivity and increases the suspension stability of the core particles.

- In addition, silica is the most chemically inert material available; it can block the core surface without interfering in the redox reaction at the core surface.
- Silica coatings can also be used to modulate the position and intensity of the surface plasmon absorbance band since silica is optically transparent. As a result, chemical reactions at the core surface can be studied spectroscopically.

Gold coating on any particles enhances many physical properties, such as the chemical stability by protecting the core material from oxidation and corrosion, the biocompatibility, the bio affinity through functionalization of amine/thiol terminal groups, and the optical properties. Other shell metals such as Ni,Co,Pd,Pt and Cu are also important for some specific applications in the field of catalysis, solar energy absorption, permanent magnetic properties etc .Similar to the size-dependent color of pure gold nanoparticles, the optical response of gold nano shells depends dramatically on the relative size of the core nanoparticle as well as the thickness of the gold shell. By varying the relative core and shell thicknesses, the color of such gold nano shells can be varied across a broad range of the optical spectrum spanning the visible and the near-infrared spectral regions. Semiconductor Core/Shell Nanoparticles- particles are used for medical or bioimaging purposes, enhancement of optical properties, light emitting devices, nonlinear optics, biological labelling, improving the efficiency of either solar cells or the storage capacity of electronics devices, modern electronics field applications.

#### **1.5.2. INORGANIC AND ORGANIC CSN**

Inorganic/organic core-shell nanoparticles are made of metal, a metallic compound, metal oxide, or a silica core with a polymer shell or a shell of any other high density organic material.

One example is the fact that the oxidation stability of the metal core is increased when otherwise the surface atoms of the metal core can be oxidized to the metal oxide in a normal environment. In addition, they exhibit enhanced biocompatibility for bio applications. The polymer-coated inorganic materials have a broad spectrum of applications, ranging from catalysis to additives, pigments, paints, cosmetics, and inks. In many applications, the particles are coated to stabilize them in the suspension media, and the stability of such a colloidal suspension depends mainly on the attractive and repulsive forces between the particles. Magnetic nanoparticles with any polymer coating are used mainly for magnetic recording, magnetic sealing, electromagnetic shielding, MRI, and especially in the biological field for specific drug targeting, magnetic cell separation, etc. Dextran, a polysaccharide polymer composed of exclusively R-D-glucopyranosyl units with varying degrees of chain length and branching, is also widely used as a shell coating. Dextran is used as a polymeric shell because of its high biocompatibility. It in turn increases the biocompatibility of the magnetic nanoparticles to the extent. Side-chain-functionalized dextran coated ultrasmall superparamagnetic iron oxides (USPIO) show a prolonged blood residence time, which allows these USPIO particles to access the macrophages located in deep pathological tissues (such as lymph nodes, kidney, brain, osteoarticular tissues, etc.). Dextran-coated Fe nanoparticles are also used for labelling red blood cells (RBC) in cell separation studies using high gradient magnetic chromatography (HGMC). The most common polymers used as organic coatings on silica cores are poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(3- amino phenylboronic acid) and poly(vinyl chloride) (PVC) conductive polymers such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh), Natural polymers such as cellulose. Polymer-coated AgCl nanoparticles are useful for sensor applications.

- Polymer-coated CaCO3 shows improved mechanical properties as a filler material and is useful in different applications.
- Polystyrene-coated CaCO3 is widely used in the manufacture of paint, paper, rubber, plastics, etc. It was found that instead of pure CaCO3, a poly(butylene tetra phthalate)
   (PBT) coating on stearic acid-modified CaCO3 improves the mechanical, thermal, and structural properties of the CaCO3.
- The tensile strength of stearic acid-modified CaCO3 increases from 56 to 58.9 MPa because of the PBT coating; 80% weight fraction of the overall material

#### **1.5.3. ORGANIC AND INORGANIC CSN**

The shell can also be made from different materials, such as metals, metal oxides, metal chalcogenides or silica. The inorganic material, especially a metal oxide coating on an organic material, is beneficial in several aspects, such as increased strength of the overall material, resistance to oxidation, thermal and colloidal stability, and abrasion resistance. At the same time, these particles also show polymeric properties such as excellent optical properties, flexibility, and toughness, and in addition they can improve the brittleness of the inorganic particles. Another interesting application of these types of particles is for the synthesis of hollow inorganic particles by using an organic material as the sacrificial core.

#### **1.5.4. ORGANIC AND ORGANIC CSN**

In this category, both the core and shell particles are made of a polymer or another organic material. These classes of particles are known as "smart particles" and have a wide range of applications in different fields, such as drug delivery, biosensing, chemical separation, biomaterials, and catalysis. The advantages of having a polymer coating on another polymer is to modify the physical properties of the overall material, such as toughness or the glass transition temperature. The glass transition temperature is an important characteristic of a polymer because below this temperature polymers are in what is called a "glassy state". When the temperature of the material crosses the glass transition temperature, the mechanical properties of the polymers change from those of a glass (brittle) to a rubber (elastic) material. For example, a polymer coating on a polymer with a different  $T_g$ (glass transition temperature) is used to modify latexbased paints. Polymer/polymer core/shell particles are also extensively used for controlled drug release applications in in vivo systems because of their good biodegradable and drug encapsulation property. Poly(D,L-lactic-co-glycolic acid) (PLGA) is a biodegradable organic polymer with a high capacity for encapsulating hydrophobic drugs. C-dots coated with a polymer are promising as tools for sensing and imaging subcellular agents because they can be delivered into the cell cytoplasm.

#### **1.6.CHARACTERISTICS OF CORE-SHELL NANOPARTICLES**

#### **1.6.1. ELECTRONIC PROPERTIES**

The understanding of the electronic properties of nanomaterials has attracted a great deal of interest over the past decade. While the electronic structures of atoms, molecules and single crystalline bulk materials have been well established, there was limited knowledge regarding the electronic structures of nanoscale counterparts until recently. It is predicted, in both theoretical and experimental papers, that metal semiconducting nanoparticles in the size range of 1-10 nm can display unique quantum effects, leading to properties that are different from those of bulk metals. As the particle size decreases below the Bohr radius of the semiconductor material, the electron becomes more confined in the particle. This leads to an increase in the band gap energy and the valence and conduction bands break into quantized energy levels. For example, this figure shows the effect of changing the particle size of Cd-Se nanoparticles. The

band gap emission shown is observed to shift through the entire visible region, from red emission for the largest particles, to blue emission for the smallest clusters. The significance of nanoscale quantum confinement of the electrons provides visualization of the shift in the characteristics of the material depending on the size of the nanoparticles. These effects have been reported to create novel applications that have been used over the past decade[10].



Figure 1.6.1 The effect of changing the particle size

#### **1.6.2. OPTICAL PROPERTIES**

Optical properties of SiO<sub>2</sub>-Pd and SiO<sub>2</sub>-Pt core–shell nanoparticles (NPs) are investigated experimentally and theoretically, combined with a systematic comparison with those of traditionally investigated SiO<sub>2</sub>-Au NPs. Theoretical calculations show that both the plasmon hybridization effect and the retardation effect influence the spectral peak position of all three kinds of core–shell NPs. These two effects compete with each other. Plasmon hybridization is a dominant influence in the case of a thinner shell, whereas the retardation effect becomes more important when the shell becomes thicker. As a result, the dipolar plasmon band reveals an initial blue shift, and then red shift, with the increase of shell thickness. Furthermore, the influences of core size and shell material on the competition are discussed. Finally, the relative strengths of absorption and scattering associated with the localized surface plasmon resonance (LSPR) of the three kinds of core–shell NPs are investigated. For SiO<sub>2</sub>-Pd and SiO<sub>2</sub>-Pt NPs, extinction is found to be dominated by absorption when shell thickness is less than  $\sim 20$  nm, and a crossover from absorption dominance to scattering dominance takes place with the further increase of shell thickness. In contrast, scattering is always the main decay process for SiO<sub>2</sub>-Au NPs, which contribute more than 90% intensity of the extinction despite the shell thickness.



Figure 1.6.2 Optical Properties

#### **1.7. APPLICATION OF CORE-SHELL NANOPARTICLE**

Nanomaterials can occur naturally, be created as the by-products of combustion reactions, or be produced purposefully through engineering to perform a specialised function. Due to the ability to generate the materials in a particular way to play a specific role, the use of nanomaterials spans across a wide variety of industries, from healthcare and cosmetics to environmental preservation and air purification. The healthcare field, for example, utilises nanomaterials in a variety of ways, with one major use being drug delivery. One example of this process is whereby nanoparticles are being developed to assist the transportation of chemotherapy drugs directly to cancerous growths, as well as to deliver drugs to areas of arteries that are damaged in order to fight cardiovascular disease. Carbon nanotubes are also being developed in order to be used in processes such as the addition of antibodies to the nanotubes to create bacteria sensors. In aerospace, carbon nanotubes can be used in the morphing of aircraft wings. The nanotubes are used in a composite form to bend in response to the application of an electric voltage. Applications are being developed to use the nanowires -

zinc oxide nanowires - in flexible solar cells as well as to play a role in the treatment of polluted water. In the cosmetics industry, mineral nanoparticles – such as titanium oxide – are used in sunscreen, due to the poor stability that conventional chemical UV protection offers in the longterm. Just as the bulk material would, titanium oxide nanoparticles are able to provide improved UV protection while also having the added advantage of removing the cosmetically unappealing whitening associated with sunscreen in their nano-form. The sports industry has been producing baseball bats that have been made with carbon nanotubes, making the bats lighter and therefore improving their performance. Further use of nanomaterials in this industry can be identified in the use of antimicrobial nanotechnology in items such as the towels and mats used by sportspeople, in order to prevent illnesses caused by bacteria. Nanomaterials have also been developed for use in the military. One example is the use of mobile pigment nanoparticles being used to produce a better form of camouflage, through injection of the particles into the material of soldiers' uniforms. Additionally, the military have developed sensor systems using nanomaterials, such as titanium dioxide, that can detect biological agents. The use of nano-titanium dioxide also extends to use in coatings to form self-cleaning surfaces, such as those of plastic garden chairs. A sealed film of water is created on the coating, and any dirt dissolves in the film, after which the next shower will remove the dirt and essentially clean the chairs. Controlling the size, shape and material of the nanoparticle enables engineers to design photovoltaics (PV) and solar thermal products with tailored solar absorption rates. Absorption of solar radiation is much higher in materials composed of nanoparticles than in thin films of continuous sheets of material. The Sol-Gel process is a method for producing solid material from nanoparticles. While it is generally viewed as a relatively new industrial technology, it is used extensively in a number of industries, such as abrasive powder manufacture, coatings production and optical fibres.

#### **1.7.1.ELECTRICAL AND MAGNETIC APPLICATION**

Inorganic–organic core/shell nanoparticles are also widely investigated for their electrical and magnetic properties. The most used bulk materials for magnetic applications are Fe<sub>3</sub>O<sub>4</sub>[11,12] and MnFe<sub>2</sub>O<sub>4</sub>[13], while for electrical applications we have TiO<sub>2</sub>- SnO<sub>2</sub>, Ag, Au, S, BaTiO<sub>3</sub>, and ZnO. Coating materials used for nanoparticles include polystyrene (PS), polyaniline (PA), oleic acid, graphene, polyvinylpyrrolidone (PVP), polyvinyl acetate (PVA), paraffin, poly(3,4-ethylenedioxythiophene) (PEDOT), hyperbranched aromatic polyamide (HBP), poly(methyl methacrylate) (PMMA), polyethylene-based and polystyrene-based polymers and polyisobutylene. These kinds of materials have peculiar properties that enable them to be used in displays, batteries, optical sensors and magnetic imaging.

#### **1.7.2.WASTEWATER TREATMENT APPLICATIONS**

Pd nanoparticles in an apricot kernel shell substrate using Salvia hydrangea extract as an organic reducing agent and proved their catalytic activity for reduction of organic dyes, 4nitrophenol (4-NP), methyl orange (MO), methylene blue (MB), rhodamine B (RhB), and Congo Red (CR) at room temperature. In addition, it was found that the Pd NPs/Apricot kernel shell can be recovered and reused several times without significant loss of catalytic activity[14]. Moustakas, N. G. et al[15]. have synthesised inorganic–organic core–shell titania nanoparticles for efficient visible light activated photocatalysis. The modified TiO<sub>2</sub> (m-TiO<sub>2</sub>) nanostructure covered with a shell of carbonaceous type material, which acts as a highly efficient visible light sensitiser, was synthesised using the gel combustion method. The photocatalytic performance of the m-TiO<sub>2</sub> powder was tested for the degradation of methylene blue (MB) azo dye under UVA (350–365 nm), visible (440–460 nm) and daylight (350–750 nm) illumination. The visible light activation of the material is due to the formation of monolayers of carbonaceous species which cover the  $TiO_2$  core anatase nanoparticles. The particles size is 3–10 nm.

Application of core-shell(cs) plasmonic nanoparticle are

- Solar cell
- ✤ Sensing
- ✤ SERS
- Photo thermal ablation
- Drug delivery
- Photo catalysis

#### CHAPTER-II

#### **2.1.CORE SHELL NANOPARTICLES:**

Core – shell nanoparticles are a class of nanostructured materials. They have interesting properties and broad range of application in catalysis, biology, material chemistry and sensors. By rationally tuning the cores as well as shells of such materials, range of core -shell nanoparticles can be produced with tailorable properties that can play important roles in various catalytic process. Having multifunctional and synergistic physiochemical properties depending on the choice of the two components posses the properties of both core and shell materials. Since core and shell differs rom the intrinsic properties of both materials, both core and shell have different geometries, chemical composition and dimensions. Thus, functional materials with novel properties can be synthesized by using various combinations of core shell materials.

#### 2.2. ANILINE-PLATINUM CSN

The Platinum-aniline complex was successfully synthesized by irradiating an ultrasound to the hexachloro platinic acid and aniline monomer mixture. The highly viscous nature of aniline leads to reproducible hexagonal plate like Pt-aniline complex crystals[18]. The chemical composition of the Pt-aniline complex was identified as  $[PtCl_2(C_6H_5NH_2)_2]$  with the help of NMR, XPS, HR ESI-MS, and TGA analyses. Furthermore, the Pt-aniline hexagonal plates were sintered at various temperatures like 400 °C, 500 °C, and 700 °C for an hour.



Figure 2.2 Aniline-Platinum CSN

#### 2.3. ANILINE -GOLD CSN

Nano structural gold/polyaniline core/shell composite particles on conducting electrode Indium tin oxide (ITO)were successfully prepared via electrochemical polymerization of aniline based on 4-aminothiophenol (4-ATP) capped Au nanoparticles. The new approach to the fabrication includes three steps: preparation of gold nanoparticles as core by pulse electrodeposition; formation of ATP monolayer on the gold particle surface, which served as a binder and an initiator; polymerization of aniline monomer initiated by ATP molecules under controlled voltage lower than the voltametric threshold of aniline polymerization, which assured the formation of polyaniline shell film occurred on gold particles selectively. Topographic images were also studied by Atomic force microscopy (AFM), which indicated the diameter of gold nanoparticles were around 250 nm. Coulometry characterization confirmed the shell thickness of polyaniline film was about 30 nm. A possible formation mechanism of the Au/polyaniline core-shell nanocomposites was also proposed. The novel as-prepared core-shell nanoparticles have potential application in constructing biosensor when bioactive enzymes are absorbed or embedded in polyaniline shell.



Figure 2.3 Aniline-Gold CSN

#### 2.4.ANILINE-IRON CSN

The synthesis of monodispersed core-shell composites of silica-modified magnetic nanoparticles and conducting polyaniline by self-assembly and graft polymerization. Magnetic ferrite nanoparticles (Fe3O4) were prepared by coprecipitation of Fe<sup>+2</sup> and Fe<sup>+3</sup> ions in alkaline solution, and then silananized. The silanation of magnetic particles (Fe3O4@SiO2) was carried out using 3-bromopropyltrichlorosilane (BPTS) as the coupling agent. Formation mechanism of the core-shell structured nanocomposites and the effect of modified magnetic nanoparticles on the electro-magnetic properties of the Fe<sub>3</sub>O<sub>4</sub>@SiO2/PANI nanocomposites are also investigated. This method provides a new strategy for the generation of multi-functional nanocomposites that composed of other conducting polymers and metal nanoparticles.

#### 2.5.ANILINE -SILICA CSN

Highly conductive silica/polyaniline (PANi) core/shell nanoparticles (NPs) were synthesized in various diameters (from 18 to 130 nm) using self-stabilized dispersion polymerization. The polymerization was carried out in an aqueous/organic liquid system at -30 °C. In this system, the organic phase plays a key role in directing para-direction oriented polymerization of the PANi on the surface of silica NPs. Because of its para-direction polymerized structure, the synthesized silica/PANi core/shell NPs exhibited enhanced electrical conductivity compared (25.6Scm<sup>-1</sup>) with NPs (1.4Scm<sup>-1</sup>) prepared by homogeneous polymerization.

In this series, increased para-coupling along the polymer backbone was elucidated using several characterization techniques, including Fourier transform infrared (FTIR), X-ray diffraction (XRD), and nuclear magnetic resonance (NMR) spectroscopy.



#### 2.6.ANILINE-METHYL METHACRYLATE CSN

Semi-conducting poly(n-methylaniline) (PNMA)-coated poly(methyl methacrylate) (PMMA) composite nanoparticles were synthesized using cross-linked and grafted PMMA particles as a core, and then, the PNMA shell was coated via chemical oxidative polymerization on the surface of modified PMMA nanoparticles. Their electro responsive electrorheological characteristics when dispersed in silicone were confirmed under applied electric fields using a rotational rheometer, focusing on their viscoelastic response. Using a frequency sweep test, the frequency dependence of both the storage and loss moduli was confirmed to increase upon increasing the electric field, with a stable plateau regime over the entire angular frequency range.

#### 2.7.RUTHENIUM-PLATINUM CSN

Ruthenium–platinum (Ru–Pt) core–shell nanoparticles, with a crystalline and amorphous Ru core of the same diameter and diverse Pt shell thicknesses, are prepared and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), highangle annular dark-field scanning transition electron spectroscopy (HAADF-STEM), and CO tripping voltammetry. The well-defined heterostructured Ru–Pt interface and anisotropic growth of the Pt shell on the crystalline Ru core (Ru-Pt) were observed, while the amorphous Ru core induces a partial alloy at the Ru–Pt interface and isotropic growth of the Pt shell. The core–shell structure also results in an apparent down-shift of the d-band centre of Pt, which dissipates much faster on the amorphous Ru core than on crystalline ones, as demonstrated by the XRD and CO desorption potential. The two sets of core–shell nanoparticles show that a volcano-shape dependence of the catalytic activity on the thickness of the Pt shell and the crystalline Ru core markedly enhanced the catalytic performance and stability toward electrooxidation of formic acid and ethanol, which is ascribed to the lattice strain of the Pt shell, downshift of the d-band centre, the weakened CO adsorption, and thus alleviated poisoning.

#### **2.8.RUTHENIUM-NICKEL CSN**

Core-shell nanoparticles of Ru–Ni in the size range of 5–10 nm were synthesized by a single-step spray-pyrolysis process. Ruthenium chloride (RC) and Nickel chloride (NC) were dissolved in water and used as a feed stream through an ultrasonic atomizer. (RC/NC) ratio was varied from 1:1 to 5:1 at various operating temperatures ranging from 500 °C to 1000 °C. Smooth core-shell nanoparticles were formed when the RC/NC ratio was 3:1 and 5:1 at 800 °C and 600 °C. A mechanism leading to the formation of such morphologies was proposed and was compared with the experimental results. It was found that as the RC/NC ratio in the precursor increased, temperatures of 500 °C generated core-shell nanoparticles. RC/NC ratio of 1:1 at low temperatures of 500 °C generated core-shell nanoparticles which are concentric rings. No core-and-shell morphologies were observed at temperatures higher than 800 °C. Once the core-shell particles are formed, the temperature can be varied in the range of 200 °C to cause a geometry change from core-and-shell to spherical nanoparticles.

#### **2.9.RUTHENIUM-BARIUM CSN**

A low-temperature ammonia synthesis process is required for on-site synthesis. Barium-doped calcium amide (Ba-Ca(NH<sub>2</sub>)<sub>2</sub>) enhances the efficacy of ammonia synthesis mediated by Ru and Co by 2 orders of magnitude more than that of a conventional Ru catalyst at temperatures below 300 °C. Furthermore, the presented catalysts are superior to the wustitebased Fe catalyst, which is known as a highly active industrial catalyst at low temperatures and pressures. Nanosized Ru–Ba core–shell structures are self-organized on the Ba-Ca(NH<sub>2</sub>)<sub>2</sub> support during H<sub>2</sub> pre-treatment, and the support material is simultaneously converted into a mesoporous structure with a high surface area (>100 m<sup>2</sup> g<sup>-1</sup>). These selforganized nanostructures account for the high catalytic performance in low-temperature ammonia synthesis[16].

#### 2.10.RUTHENIUM-SELEIUM CSN

Ruthenium-Selenide nanomaterial with ordered mesoporous structure (P-RuSe<sub>2</sub>) employing KIT-6 silica as the template. The composition and structure of P-RuSe<sub>2</sub> were fully characterized. Further, its peroxidase-like activity was investigated.P-RuSe<sub>2</sub> possessed excellent peroxidase-mimicking activity, which catalysed the oxidation of peroxidase substrates, including 3,3',5,5'-tetramethylbenzidine, *o*-phenylenediamine, and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) in the presence of H<sub>2</sub>O<sub>2</sub>. Moreover P-RuSe<sub>2</sub> exhibited higher peroxidase like activity when compared with several representative nanozymes as well as bulk RuSe<sub>2</sub>. To demonstrate its potential applications, the colorimetric detection systems for H<sub>2</sub>O<sub>2</sub> and glucose were successfully constructed based on P-RuSe<sub>2</sub> nanozyme[17].

The main objectives of the present investigation is

- ✤ To synthesize Ru core by chemical reduction method.
- To prepare Ru-polyaniline core Shell nanocomposite by oxidative polymerisation using potassium perdisulphate.
- ◆ To characterize the formed composite by UV-Vis and FT-IR spectral studies.
- ✤ To study the surface morphological behaviour by SEM Analysis.

### CHAPTER-III EXPERIMENTAL DETAILS

#### **3.1. CHEMICALS USED:**

- ✓ Aniline
- ✓ Ruthenium chloride trihydrate
- ✓ Sodium borohydride
- ✓ Polyvinyl pyrrolidone
- ✓ Ascorbic acid

#### 3.2. Synthesis of Ru/polyaniline core-shell nanocomposites

#### 3.2.1. Preparation of Ru core

Ruthenium core is prepared by chemical reduction method using sodium borohydride as reducing agent and PVP as caping agent. Ascorbic acid is added inorder to have scavenging property. 0.01M Ruthenium chloride trihydrate and ammonium hydroxide are mixed separately. To the solution 1g of Ascorbic aid and PVP were added. 0.01M solution of sodium borohydride is poured slowly into the stirring solution kept in the water bath. The formed ruthenium core nanocomposite is kept in a refrigerator.

#### 3.2.2. Synthesis of Ru/ Polyaniline Core Shell nanocomposite

Aniline is polymerised using potassium perdisulphate as oxidizing agent in 0.1M HCl. The concentration of monomer and oxidizing agent was kept as 0.01 M. The reaction mixture is stirred in a magnetic stirrer for 10 mins. After 10 minutes the core ruthenium nanocomposite is added and continuously stirred for 3 hours. During stirring the colour of the solution will be changed from blue to dark blue and finally to green colour. The solution is kept in a refrigerator for 24 hours for the completion of the reaction. The formed composite is filtered in suction washed with water and finally dried in room temperature. Green coloured ruthenium-aniline core shell nanocomposite is used for further characterisation studies.



Fig.3.1. Ru/ Polyaniline Core Shell nanocomposite

#### **3.3. Ultraviolet-visible spectroscopy**

The typical ultraviolet-visible spectrophotometer consists of a light source, monochromator, and a detector. The light source is usually a deuterium lamp, which emits electromagnetic radiation in the ultraviolet region of the spectrum. A second light source, a tungsten lamp, is used for wavelengths in the visible region of the spectrum. The monochromator is a diffraction grating; its role is to spread the beam of light into its component wavelengths. A system of slits focuses the desired wavelength on the sample cell. The light that passes through the sample cell reaches the detector, which records the intensity of the transmitted light I . The detector is generally a photomultiplier tube, although in modem instruments photodiodes are also used. In a typical double-beam instrument , the light emanating from the light source is split into two beams, the sample beam and the reference beam. When there is no sample cell in the reference beam, the detected light is taken to be equal to the intensity of light entering the sample Io.

The sample cell must be constructed of a material that is transparent to the electromagnetic radiation being used in the experiment. For spectra in the visible range of the spectrum, cells composed of glass or plastic are generally suitable. For measurements in the ultraviolet region of the spectrum, however, glass and plastic cannot be used because they absorb ultraviolet radiation. Instead, cells made of quartz must be used since quartz does not absorb radiation in this region. The instrument design just described is quite suitable for measurement at only one wavelength. If a complete spectrum is desired, this type of instrument has some deficiencies. A mechanical system is required to rotate the monochromator and provide a scan of all desired wavelengths. This type of system operates slowly, and therefore considerable time is required to record a spectrum.

A modern improvement on the traditional spectrophotometer is the diode-array spectrophotometer. A diode array consists of a series of photodiode detectors positioned side by side on a silicon crystal. Each diode is designed to record a narrow band of the spectrum. The diodes are connected so that the entire spectrum is recorded at once. This type of detector has no moving parts and can record spectra very quickly. Furthermore, its output can be passed to a computer, which can process the information and provide a variety of useful output formats. Since the number of photodiodes is limited, the speed and convenience described here are obtained at some small cost in resolution.

#### **APPLICATION OF UV-VIS SPECTROSCOPY:**

#### • Detection of impurities

UV spectroscopy is one of the bast methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.

28

#### • Structure elucidation of organic compound

From the location peaks and combination of peaks, it can be concluded that whether the compound is saturated or unsaturated, hetero atoms are present or not.

#### • Chemical kinetics

Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

#### • Detection of functional group

This techniques is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.



Figure 3.3 Working of UV Spectrometer

#### **3.4.Infrared spectroscopy**

Infrared radiation with matter by absorption, emission, or reflection. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms. It can be used to characterize new materials or identify and verify known and unknown samples. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. Infrared spectroscopy gives information on molecular vibration or more precisely on transitions between vibration and rotational energy level in molecules. This information is of immense help to organic chemists because it can be directly related to molecular structure. Absorption of radiation in the infrared region results in the excitation of bond deformations, either stretching or bending. Various stretching and bending vibrations occur at certain quantized frequencies. When infrared light of that frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration is increased. An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared radiation absorbed. The material under study is usually in the form of a solid, a neat liquid or a solution. Sometime, however, a compound in the gas or vapour phase is studied. Under these condition, in addition to changes in vibrational energy, simultaneous change in rotational energy can occur and consequently some fine structure may be observed on the vibration band.

The normal range of an infrared spectrum, used by organic chemists for structural work, extends from  $4000cm^{-1}$ to  $667cm^{-1}$ . The shorter wavelength region (12500-4000 $cm^{-1}$ ) is referred to as near infrared region and contains absorption bands due to harmonic overtones of fundamental bands and combination bands. The region extending from  $667cm^{-1}$ to  $50cm^{-1}$  is referred to as far infrared region. The normal and far infrared region contains absorptions due to fundamental harmonic and combination bands. The use of linear -in -frequency instruments results in a considerable expansion of the high frequency end of the infrared region, resulting in an increased ability to resolve bands and defined their position. The position of absorption in the spectrum is usually expressed in terms of wave number ( $cm^{-1}$ ) of the absorbed light. The infrared spectrum is the simplest, most rapid and often most reliable means for assigning a compound to its class. It can also provide a variety of information on structure, symmetry, purity, structural and geometrical isomers and hydrogen bonding[18].



IR INSTRUMENTATION

### CHAPTER-IV

### RESULTS AND DISCUSSION

#### 4.1. UV-Visible Spectroscopy



Figure 4.1 UV -Visible behaviuor of Ru/Polyaniline nanocomposite

The UV–Visible absorption spectra of polyaniline (Fig. 4.1) generally depend on the level of doping, extent of conjugation, nature of the polymer and solvent. The UV-Visible spectrum of the composite exhibit two sharp bands at 236 nm and 420 nm attributed the incorporation of Ru nanoparticle and  $\pi$ – $\pi$ \* transitions in the aromatic rings of Polyaniline. The absorption bands around 600–650 nm correspond to the intramolecular electronic transitions between quinoid and benzenoid units. The characteristic low wavelength polaron bands around 400–440 nm due to the conductive form of polyaniline[19].

#### 4.2. FTIR Spectroscopy



Figure 4.2 FT-IR- Visible behaviuor of Ru/Polyaniline nanocomposite

The FT-IR spectral analysis of composite has revealed that the vibrational peaks at 3685 cm<sup>-1</sup> correspond to NH stretching vibrations, while the CH stretching vibrations are observed around 3168 cm<sup>-1</sup>. The characteristic vibrations around 1576 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> indicated the signatures of the PANI backbone, arising due to the stretching modes of the quinoid and the benzenoid rings. The peaks around 1294 cm<sup>-1</sup> are due to the strong aromatic CN stretching vibrations in PANI. In the lower frequency regions, the peaks at around 1100–1160 cm<sup>-1</sup> are due to the aromatic CH in-plane deformation. The peak at 1017 cm<sup>-1</sup> is attributed to C–N stretching mode for benzenoid ring, and the peak at 800 cm<sup>-1</sup> is assigned to the plane bending vibration of C–H, which is formed during protonation. The peak at 510 cm<sup>-1</sup> is due to the incorporation Ruthenium core inside the polyaniline matrix[20,21].

#### CONCLUSION

1 . Ru/polyaniline core-shell nanocomposite was successfully synthesized by chemical reduction method

2. The UV-visible spectrum of Ru/Polyaniline core-shell nanocomposite has two sharp bands at 236 nm and 420 nm attributed the incorporation of Ru nanoparticle and  $\pi -\pi^*$  transitions in the aromatic rings of Polyaniline.

3.In the FT-IR spectrum of Ru/polyaniline core shell nanocomposite the vibrational peaks at 3685 cm<sup>-1</sup> coresspond to NH stretching vibrations, while the CH stretching vibrations are observed around 3168 cm<sup>-1</sup>. The characteristic vibrations around 1576 cm<sup>-1</sup> and 1400cm<sup>-1</sup> indicating the signatures of the PANI backbone, arising due to the stretching modes of the quinoid and the benzenoid rings. The peaks around 1294 cm<sup>-1</sup> are due to the strong aromatic CN stretching vibrations in PANI. In the lower frequency regions, the peaks at aroun.d 1100–1160 cm<sup>-1</sup> are due to the aromatic CH in-plane deformation. The peak at 1017 cm<sup>-1</sup> is attributed to C–N stretching mode for benzenoid ring, and the peak at 800 cm<sup>-1</sup> is assigned to the plane bending vibration of C–H, which is formed during protonation . The peak at 510 cm<sup>-1</sup> is due to the incorporation Ruthenium core inside the polyaniline matrix.

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# Chemical Polymerization of Poly(aniline-co-3anisidine)/chitosan composite and its characterization

#### **Project in Chemistry**

Submitted to St. Mary's college(Autonomous) in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry

DONE BY

### M.Sakthi Priya

A.Sudharsini

S.Swetha @ Kiruba



### ST.MARY'S COLLEGE(AUTONOMOUS)

### **RE-ACCREDITED WITH "A<sup>+</sup>" GRADE BY NAAC**

#### THOOTHUKUDI-628001

2022-2023

### DECLARATION

We hereby declare that the project entitled "Chemical Polymerisation of poly(aniline-co-3-anisidine)/chitosan composite and its characterisation" submitted to St.Mary's college(Autonomous), Thoothukudi, affliated to Manonmaniam Sundaranar University, for the degree of Bachelor of Science is our original work and that, it has not previously formed on the basis of the award of any degree or similar title.

M. Sakthi priya M.Sakthi Priya

A. Budhansini A.Sudharsini

Ø. Quetha @ kiruba S.Swetha @ Kiruba

April 2023 THOOTHUKUDI

## CERTIFICATE

This is certify that project in chemistry "Chemical Polymerisation of poly(aniline-co-3-anisidine)/chitosan composite and its characterisation" submitted to St.Mary's college (Autonomous), Thoothukudi in partial fulfilment for the award of the degree of Bachelor of Science in Chemistry and is a record of the work done by following students during the year 2022-2023.

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SI. NO.	CONTENT	PAGE NO
1	INTRODUCTION	1-15
2	LITERATURE SURVEY	15-19
3	EXPERIMENTAL DETAILS	19-22
4	RESULT AND DISCUSSION	22-24
5	CONCLUSION	24-25
6	REFERENCE	25-32

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11

# CHAPTER-I INTRODUCTION

Nanocomposites are composites which has at least one phases in which it shows dimensions in the nanometre range (1nm = 10-9 m). Nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations which are not found in conventional composites. The general understanding of these properties is yet to be reached, even though the first inference on them was reported as early as 1992.Nanocomposite material is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm or structure having nano- scale repeat distance between different phases that make up the material. Nanocomposite materials are seen in nature too, for example in the structure of the abalones shell and bone as dimensions reach the nanometer level, interactions at the phase interfaces become largely improved, and this is important to enhance materials properties. Discovery of carbon nanotubes (CNTs) in 1991 and their subsequent use to fabricate composites exhibiting some of the unique CNT related mechanical, thermal and electrical properties added a new and interesting dimension to this area. Nanocomposite systems, including those reinforced with CNTs. Conducting polymer-based composites were novel materials with less than decade of history. In the case of biodegradable polymer-based nanocomposites, recent developments in preparation, characterization and properties, including crystallization behavior.

The nanoparticle includes the particles which having size between 1 and 100 nm. These particles have different properties at their atomic level due to their nanoparticles size. This

change in nanoparticles properties is beneficial in many fields. Numbers of developments have been made since then in the field of nanotechnology. They attract much attention because of their potential applications in many fields including optics, electrics, magnetism, ceramics, and catalysis. Nanoparticles can be classified as metal nanoparticles, non-metal ceramic nanoparticles, semiconductor nanoparticles, and a well-known type is carbon nanoparticles and Nanocomposite can be classified on the basis of their dispersed matrix and dispersed phase materials. Nanoparticles have those chemical and physical properties which makes them very different from that of the corresponding bulk materials due to their small size and large surface to volume ratio. Hence nanocomposite is to use building blocks with dimensions in nanometer range to design and create new materials with unprecedented flexibility and improvement in their physical properties. Nanocomposites are those composites in which one phase has nanoscale morphology like nanoparticles, nanotubes, or lamellar nanostructure. To overcome the limitation of different engineering materials now-a-days, nanocomposites are emerged to provide beneficial alternatives. The properties of the so-called found not only depended on the properties of their originals, but also crucially on their interfacial and morphological characteristics. So, we cannot ignore the fact that sometimes it also happened that the newly generated property in the material is unknown to the parent constituent materials.

Nanocomposites have three main classifications based on their matrix phase. They are metal matrix nanocomposite MMNC, ceramic matrix nanocomposite CMNC, and polymer matrix nanocomposite PMNC.





Fig.1.1. classification of nanocomposites based on matrix metal

## 1.1.Matrix Nanocomposites (MMNC)

- Metal matrix composites (MMCs), like other composites, are made up of at least two physically and chemically different phases that are dispersed in such a way that they provide properties that neither of the separate phases can provide. In power transmission lines a composite made from Al matrix reinforced with a continuous A1<sub>2</sub>O<sub>3</sub> fiber, the cutting tools and oil drilling inserts are made up from cobalt (Co) particulate and tungsten carbide (WC), and a composite made by reinforcing A1 matrix with SiC particle used in automotive, thermal management and aerospace applications are just a few examples.
- These nano composite MMNC are made up of a ductile alloy or metal matrix with nanosized reinforcing material. These materials have ceramic and metal properties, such as toughness and ductility, high modulus and strength. As a result, these nanocomposites are highly suited for the creation of materials with high service temperatures and shear/compression strengths. They offer significant potential for usage in a multitude of disciplines, including the automotive and aerospace industries, and also in structural material manufacture.

## **1.2.Polymer Matrix Nanocomposites (PMNC)**

• The most common type of nanocomposite is PMNC, which consist of isolated nano scale particles evenly distributed in a polymer in an ideal situation. The polymer matrix is used to disperse agglomerated nanoparticles in reality. Functional nanocomposites with better physical properties open up new possibilities in micro-optics, electronics, energy conversion, and storage. In the majority of cases, the filler load correlates with the change in the sought characteristic. Due to shape or molding constraints, large solid loading is limited by composite flow characteristics, as a result a property modification. Before the formation of process of the composites the rheological properties should be

measured using different tests to estimate the correct shear rate and temperature. Their rheological behaviour is determined by the surface area and the ensuing large polymer-filler interfacial layer.

 Polymer nanocomposites have opened a new horizon for a potential class of hybrid materials by introducing particle nanofiller into polymer matrices to improve the properties of neat polymers. During the last decade, polymer nanocomposites have gained a lot of attention and curiosity all around the world. The sol–gel process looks to be the most promising method among the fabrication methods for polymer nanocomposites. At the molecular or near molecular level, the nanoparticles were dispersed before being combined with the polymer gel.

## 1.3. Ceramic Matrix Nanocomposites (CMNC)

- Ceramic matrix nanocomposites (CMNC), particularly the aluminum oxide (Al<sub>2</sub>O<sub>3</sub>)/silicon carbide (SiC) system, have a lot of potential. All the investigation has proven that the addition of low volume fraction (10%) of SiC with a specific size for Al<sub>2</sub>O<sub>3</sub> matrix gives good improvement in the properties of matrix. The crack-bridging role of nanosized reinforcements has been used in certain research to explain this toughening mechanism. As a result of incorporating high-strength nanofibers into ceramic matrices, innovative nanocomposites with superior failure and high toughness characteristics have been developed in comparison to rapid failures of ceramic materials.
- The preparation of ceramic matrix nanocomposites has been described using a variety of approaches. Conventional powder method; Vapor techniques (CVD and PVD); Spray pyrolysis; Polymer precursor route; and Chemical methods, which include the colloidal and precipitation procedures, template synthesis, and sol-gel process are the most prevalent methodology utilized for micro composites. The sol-gel process can be

affected by a wide range of factors which permit control of the structure and chemical properties of the final material, such as solvent type, time, pH, water/metal ratio, precursor, and so on.

Nanocomposites are further classified into polymer based & non polymer based Nanocomposites and are classified based on metal Nanocomposite.



Fig.1.2. Classification of Nanocomposites based on Metal Nanocomposites

## 1.4. Polymer based nanocomposites

- Polymeric nanocomposites (PNCs) are important materials for industrial as well as research purposes and are used widely in packaging, energy, safety, transportation, electromagnetic shielding, defense systems, sensors, catalysis, and information industry. PNCs could resolve several problems and daily challenges of the real world, conferring great future potential to these materials. PNCs are designed based on the principle of size and surface area being associated with much higher reactivity.
- When inorganic phases in organic/inorganic composites become nanosized, they are called nanocomposites. Organic/inorganic nanocomposites are generally organic polymer composites with inorganic nanoscale building blocks. They combine the advantages of the inorganic material ,for example rigidity, thermal stability and the organic polymer, for example flexibility, dielectric, ductility, and processability.

Moreover, they usually also contain special properties of nanofillers leading to materials with improved properties.

- Layered silicates consist of two-dimensional (2D) layers of two fused silicate tetrahedral sheets with a dimension of approx. 1 nm thick and 100 nm to 1000 nm long and with an edge-shared octahedral sheet of metal atoms such as Mg or Al. The gap between the two sheets is called the gallery, which is normally filled with cations to counterbalance the excess of negative charges. Prior to being used in the polymer, the cations in the layered silicate galleries need to be replaced by organic cations with a long organic chain, such as alkyl ammonium ions, so that the layered silicates can be dispersed in the polymer either in the form of intercalated and/or exfoliated structures depending on the interactions between the polymer and the layered silicates. Furthermore, a nanoscale design of surfaces and layers is often necessary to optimize the interfaces between different material classes (e.g., compound semiconductors on silicon wafers), and to obtain the desired special properties.
- The commonly used layered silicates for the preparation of polymer-layered silicate (PLS) nanocomposites belong to the family of 2:1 layered or phyllosilicates. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm to several microns or larger, depending on the particular layered silicate.

## 1.5. Non polymer based nanocomposites

• Bimetallic nanoparticles being investigated in detail in the form of either of alloy or core-shell structures due to their improved catalytic properties and advancement in

optical properties related to individual and differentiate metals. They can be characterized by:

- Super plasticity
- Lower melting points
- Increased strength and hardness
- Improved magnetic properties
- Increased electrical resistivity, etc.
- Ceramic-based nanocomposites are defined as ceramic composites with more than one solid phase, in which at least one of the phases has dimensions in the nanoscale range (<50–100 nm). In these types of composites, both the phases have combined magnetic, chemical, optical, and mechanical properties, for example hydroxyapatite/titania nanocomposites. These can be characterized by:</li>
  - Better toughness
  - Increased ductility
  - Increased strength and hardness
- Ceramic/ceramic nanocomposites which can be used in the area of artificial joint implants for fracture failures and it could promptly reduce the cost of surgery and would extend the mobility of the patient. The life spam would increase by 30 years, if the use of zirconia-toughened alumina nanocomposite implants is used effectively. The other example of ceramic/ceramic nanocomposites are calcium sulfate-biomimetic apatite nanocomposites.

## **1.2. Structure and Properties of Nanocomposites :**

The structure of nanocomposites consists of the matrix material containing the nanosized reinforcement components in the form of particles, whiskers, fibres, nanotubes, etc. Various techniques have been employed to characterize the nanocomposites, including atomic force

microscopy (AFM), scanning tunnelling microscopy (STM), Fourier transformed infrared spectroscopy (FTIR), X ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), scanning and transmission electron microscopy (SEM/TEM), etc. Simultaneous small angle X ray scattering (SAXS) and X ray diffractometry (XRD) studies have been recently used for quantitative characterization of nanostructures and crystallite structures in some nanocomposites. Briefly, the density of single walled carbon nanotubes is less than one sixth of that of steel while the density of multi walled carbon nanotubes is one half of that of Al. Tensile strengths of single walled carbon nanotube and multi walled carbon nanotubes are reported to be in a range much higher than of high strength steel, while Young's modulus values are comparable to those of diamond. They exhibit tremendous resilience, in that they can sustain bending to large angles and restraightening without damage, in which they differ from the plastic deformation of metals and the brittle fracture of carbon fibres. Similarly, theoretical thermal and electrical conductivities are comparable with that of diamond, with an almost negligible thermal expansion coefficient. They also exhibit high thermal stability both in air and in vacuum, compared to the lower values obtained for metal wires in microchips, and high parallel and perpendicular magnetic susceptibilities. Some of the applications,

- Nanocomposites may provide many benefits such as enhanced properties, reduction of solid wastes and improved manufacturing capability, particularly for packaging applications.
- One of the leading in nanocomposites application areas is the automotive sector, with striking impact due to improved functionalities such as ecology, safety, comfort, etc.
   Details on the commercial usage of nanocomposites in automotives and future developments in this sector are now available.

- There are reports on the current use of a number of nanocoatings in different parts of Audi, Evobus and Diamler Chrysler automobiles, as well as ongoing trials on fuel cells, porous filters (foams) and energy conversion components, which include nanoTiO<sub>2</sub>containing paints.
- Light weight bodies made of metal- or polymer-based nanocomposites with suitable reinforcements are reported to exhibit low density and very high strength (e.g. carbon Bucky fibers). Also, two-phase heterogeneous nanodielectrics, generally termed dielectric nanocomposites, have wide applications in electric and electronic industries.
- Metal and ceramic nanocomposites are expected to generate a great impact over a wide variety of industries, including the aerospace, electronic and military, while polymer nanocomposites major impacts will probably appear in battery cathodes, microelectronics, nonlinear optics, sensors, etc.

## **1.3.** PolyAniline (PANI)

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. Among all the conducting polymers, polyaniline is known for it's

- $\checkmark$  Ease of synthesis
- ✓ Environmental stability and
- $\checkmark$  Easy to dope by protonic acids.

Polyaniline is well- known as an environmentally stable and highly tunable conducting polymer, which can be produced as bulk powder, cast films, or fibers. This, in conjunction with the feasibility of low- cost, large- scale production, makes it an ideal candidate for various applications. The term Polyaniline corresponds to a class of polymers having up to 1000 repeat units (also called mers). Much of the structural characterization of polyaniline has taken place

in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.

Polyaniline is a typical phenylene based polymer having a chemically flexible -NHgroup in a polymer chain flanked either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of monomeric aniline molecule. The protonation and deprotonation and various other physico-chemical properties of polyaniline is due to the presence of the -NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization. There are many levels of polymer structure, and one can categorize the levels loosely using terms used to describe protein structure. The primary structure describes the connectivity of the atoms. The secondary structure describes the three dimensional shape due to short range non- bonded interactions, such as backbone twisting. The tertiary structure describes the shape, also called conformation, of the polymer chains due to long-range non- bonded interactions, which may be interchain or intrachain. The term quaternary structure could be used loosely to describe the polymer in terms of degree of order, for example crystalline, semicrystalline, or amorphous. Morphology is defined as the study of the form. However, when applied to polymers, morphology generally describes the threedimensional chain conformation and the relationship between chains, as well as the aggregates. Furthermore, morphology includes the physical appearance of polymer particles such as rice grains, spheres, tubules, and fibrils. Polyaniline exists in four main oxidation states viz.

- Leucoemeraldine base,
- Emeraldine base
- Emeraldine salt and

• Pernigraniline,

## **1.4. PANI Derivatives**

The presence of non-hydrogen substituents, on the ring or nitrogen atom, has a dramatic effect on the polymer properties. In general, the solubility increases and the conductivity decrease. In terms of solubility, the increase depends on the nature of the substituents. For example, alkyl and alkoxy substituents result in increased solubility in organic solvents, whereas hydroxyl, carboxylic and sulfonic groups result in increased solubility in water. It is believed that the decrease in conductivity is a result of two factors: the difference in both size and electronic character of the non- hydrogen substituents. In addition, the electronic nature of the substituents can also affect the conductivity. Some substituents, such as carboxylic or sulfonic moieties, if substituted on the ring impart a very interesting property to the polymer.

## **1.5. Synthesis of Polyaniline**

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either electrochemically or chemically. Electrochemical methods tend to have lower yields than chemical yields.

## • Chemical Synthesis

Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium peroxo-di-sulfate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. In the review article by Gospodinova et al. [5] they had reported that the propagation of polymer chains proceeds by a redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of monomer to the

chain end. The high concentration of a strong oxidant,  $(NH_4)_2S_2O_8$ , at the initial stage of the polymerization enables the fast oxidation of oligo and polyaniline, as well as their existence in the oxidized form.

$$Ar-NH_{2} \xrightarrow{Ar-NH_{2}} Ar-NH-Ar-NH_{2}$$

$$Ar-NH-Ar-NH_{2} \xrightarrow{Ar-NH_{2}} Ar-NH-Ar-NH_{2}$$

$$Ar-NH-Ar-NH_{2} \xrightarrow{Ze, -2H^{+}} Ar-NH-Ar-NH-Ar-NH_{2}$$

$$Ar-NH-Ar-NH_{2} \xrightarrow{Further Oxidative} Coupling Polyaniline$$

#### Fig.1.3. Formation of polyaniline

#### • Electrochemical Synthesis

The electrochemical preparation of conducting polymer dates back to early attempts of Dall'olio and coworkers [6], who obtained "pyrroleblack" as it was called at that time, on electrochemical oxidation of pyrrole in aqueous sulphuric acid as a powdery, insoluble ppt on a platinum electrode. Electrochemical polymerization is regarded as a simple and novel method for synthesis of conducting polymers. The beauty of this method is that polymerization in suitable electrolytic medium gives directly the directly doped polymer as a flexible freestanding film. In this method, films are produced on the electrochemical deposition of metal. The first electrochemical synthesis of polyemeraldine salt was reported by Letheby [7] in the year 1862. In the year 1962 Mohilner et al [8] reported the mechanistic aspects of aniline oxidation. Major interest in the electrochemistry of polyaniline was generated only after the discovery that aromatic amine, pyrrole, thiophene, furan, indole and benzene can be polymerized anodically to conducting film. Electrochemically prepared polyaniline is the preferred method to obtain a clean and better ordered polymer thin film.

#### 1.6. Recent trends in the field of conducting polymers

Recent research was carried out that the major target of conductive polymer technology development has been to combine the electrical and optical properties of conducting materials with the mechanical and processability properties of commodity bulk polymers. Polyaniline was synthesized at  $-15^{\circ}$ C using a polyethylenglycole / ice bath and doped with Fe<sup>3+</sup> ions. Polyaniline films (tenths of mm) were prepared by the gravity method. The dried films were exposed to UV (300nm <l< 500nm, 10mW/cm2), up to 25 min. The conduction mechanism vs. the exposure time was analyzed by resistively measurements and Mossbauer spectroscopy. The chemical polymerization of aniline was carried out in media containing different linear dicarboxylic acids with the use of oxidants such as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KIO<sub>3</sub> and FeCl<sub>3</sub>. The highest yield and the conductivity was observed with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. The yield and the conductivity of the polyaniline (PAn) synthesized were observed to decrease in the order of oxalic acid> malonic acid> succinic acid> glutaric acid> adipic acid> phthalic acid. Contact molding and other related techniques of imprint lithography have recently received much attention as inexpensive and versatile methods for the replication of sub-100 nm features. They recently reported the use of contact molding for the accurate replication of structures as small as 60 nm. In this technique, they employed an inexpensive, reusable stamp is to mold a photopolymer resin. The resin, then cured in contact with the stamp resulting in a highly reproducible positive copy of the stamp. Advances in conducting electroactive polymers (CEPs) have driven the design of novel chemical and biochemical sensors. The redox properties of CEPs have been intensely studied for more than two decades with emphasis on their synthesis and characterization. Little attention has been paid to the importance of mechanism in sensor designs. They considered that, in order to design robust and stable sensors, it was

important to understand how the polymer structure, morphology, adhesion properties and microenvironment affect sensor performance. Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and therefore should yield many interesting physicochemical properties and useful applications.

## 2.2.POLY-3-ANISIDINE (P3A):



*3*-Anisidine one of the three isomers of anisidine. Among the substituted PANI derivatives, poly(o-anisidine) can be easily synthesized either chemically or electrochemically with higher processability and solubility as compared with. Researchers also reported the synthesis Poly o-anisidine nanoparticles /metal oxide nanocomposites and found that conductivity increases in case of metal oxide nanocomposites. The synthesis of aniline/*o*-anisidine copolymer was described enzymatically oxidative polymerization of aniline (An) and *o*-anisidine (As) using poly(sodium 4-styrene sulphonate) (SPS) as a template.



Scheme of homopolymerisation of poly-3-anisidine

## CHAPTER-II

## LITERATURE SURVEY

Zhaoqian jing, shiwel cao, ting yu, and jing hu[57] determined that the variation in ph remove the affected aniline. At this alkaline condition aniline are more susceptible and are removed by ozonation which results in more hydroxyl radical production .The results of GC-MS indicate the production of many intermediates produced during ozonation process are more degradable than aniline. Therefore, the ozonzation process such organic compounds like aniline could be integrated with biological processes for further removal.

Naveen kumar chaturvedi and Surjit Singh Katoch demonstrate that aniline ant its derivatives including 2-methoxyaniline and 4-methoxyaniline which are produced commonly and discharge in waste stream. Due to the toxicity and effects on human and aquatic species, the compound containing wastewater must be treated prior to disposal. In order to eliminate these compounds from wastewater, several technology are identified. Physical and biological treatment are effective but have more limitations and these limitations are overcome easily b AOPs which is more cost efficient but effective in removal of aniline. Hydroxyl radical degrade almost many organic contaminants to carbondioxide and water. Advanced oxidation process like photo – Fenton with UV degrades organic contaminates more efficient than solar fenton oxidation. AOPs can be applied to wastewater containing aniline and it's derivatives.[58]

Azza M.Mazrouaa, M.Yahia Abed, N.A. Mansour and M.G.Mohamed[59] determined that a poly-o-anisidine nanoparticles wass prepared in presence of cationic surfactant like Ndodecyloxycarbonylmenthyl-N-triethanol ammonium chloride. FTIR spectra of pure Paly-Oanisiidine and the nanoparticles in POA in presence of CuO, Zno, Tio2 and Ag2O were determined. The transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA) were studied. It was found that the influence of the inorganic nanoparticles is very complicated in thermogravimetric analysis. The antimicrobial activities of the synthesized compounds were evaluated; it was found that the POA/Ag2O nanocomposite microspheres have good effects on the sulfate it has capacity in reduction of bacteria than POA nanoparticles. The electrical measurement declare that the polu o-anisidine nanoparticles was improved by adding metal oxides which converted the polumer nanoparticles was improved by adding metal oxides which converted the polumer nanoparticles from insulator behaviour 10-16(S/cm) to semiconductor behaviour 10-11(S/cm) in case of POA/Ag<sub>2</sub>O snf 10-12(S/cm) in case of POA/ZnO. Also the conductivity was increased by increasing in the temperature.

Manglik Neetika, jain Rajini, pramod k Singh,B Bhattacharya, Vijay Singh and SK Tomar provide an overview in a series of self-doped, doped, and undoped forms of polyabiline(PANI), poly(o-anisidine), and poly[anilie-ci-(o-anisidine)] were synthesized using an oxidizing agent KIO3 it, give a better yield. The solubility and electrochromic properties of PANI, poly(o-anisidine), and poly[aniline-co-(o-anisidine)] in these form were characterized by method such as FTIR spectroscopy, UV spectroscopy, and electrical conductivity measurements. The presence of the OCH3 group facilitated the torsional angle between aniline and o-anisidine rings and resulted in better electrochromic properties than those of PANI. With a substituted-OCH3 group, the solubility of poly(o-anisidine) was increased in common organic solvents and the conductivity decreased with increase in the side group. The solubility of PANI in the doped form was less. The solubility of PANI in the doped form was less. The solubility of PANI in the doped form was less. The solubility of PANI in the doped form was less. The solubility of poly[aniline-co-(o-anisidine)] and poly(o-anisidine) dropped to zero. The self-doped and doped forms of poly[aniline-co-(o-anisidine)] appeared to be less conductive but had improved optical properties with respect to PANI.[60]

M. A. del Valle [61] Soto provide an overview the electro-synthesis of some oligomers of aniline and also an o-anisidine has been accomplished. Along with a non-quantifiable amount of oligomers, the characterisation proved that, the obtained products are correspond to aniline & o-anisidine (o-ANS) trimer.Some suitable experimental conditions show obtention of oligomers of electroactive species, e.g. aniline and oANS. This method allows controlling of the length of the oligomer chain as a function of the starting unit employed. Thus a simple and cheap method has been developed for the obtainment of oligomer materials. Using the optimum working conditions, is applicable to any electroactive monomer unit.

Pedro Henrique Cury Camargo, Kestur Gundappa Satyanarayana and Fernando Wypych nanocomposite are suitable material for the demand arising from scientific and technological advances. There are different types of nanocomposites and some of the nanopomposites are challenging for the researchers to overcome the difficulty. They offer improved performance over monolithic and microcomposite counterparts. Unique properties such as very high mechanical properties for loading of reinforcements, gas barrier and flame related properties, for many potential applications and hence the market for these materials have been projected in various sectors. Therefore all the three types of nanocomposites provide an opportunities and rewards creating new world wide interest in these new materials.[62]

Chitosan is a linear polysaccharide composed of randomly distributed  $\beta$ -(1 $\rightarrow$ 4)linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, such as sodium hydroxide. Chitosan has a number of commercial and possible biomedical uses. It can be used in agriculture as a seed treatment and biopesticide, helping plants to fight off fungal infections. In winemaking, it can be used as a fining agent, also helping to prevent spoilage. In industry, it can be used in a self-healing polyurethane paint coating. In medicine, it is useful in bandages to reduce bleeding and as an antibacterial agent; it can also be used to help deliver drugs through the skin.



Fig.2.1. Molecular Structure of Chitosan

The main objectives of the present investigation is

- ✤ To synthesize the copolymer of Poly(aniline-co-3-anisidine)/chitosan in acidic medium
- ✤ To characterize the formed composite using UV-Vis and FT-IR.

## 3.1. Chemicals used:

- ✓ Aniline
- ✓ 3-anisidine
- ✓ Potassium perdisulphate
- ✓ 1M Hydrochloric acid
- ✓ Chitosan

## 3.2. Synthesis of Poly(aniline-co-3-anisidine)/Chitosan composite

Poly(aniline-co-3-anisidine)/chitosan was synthesized by polymerization of aniline and o-anisidine in the presence of hydrochloric acid and Potassium perdisulphate as an oxidant by chemical oxidative polymerization method. 150ml of 1M HCl, and 6.6 ml of aniline and 8.3 ml of O-anisidine were taken in a 400 ml conical flask and stirred using a electromagnetic stirrer. Then 10 g of  $K_2S_2O_8$  (potassium perdisulphate) was added into the above solution. After 15 minutes during polymerisation process 5g of Chitosan was added. The stirring was continued for 2 hours to ensure the completion of the reaction. The composite obtained was filtered, washed successively by distilled water until the wash solution turned colourless. The material was collected and dried at room temperature.



Fig.3.1. Poly(aniline-co-3-anisidine)/Chitosan composite

#### 3.3. UV-Vis spectroscopy

The UV-Visible of the samples were studied using JASCO V- 530 spectrophotometer using a 1 cm quartz cuvette filled with the samples. Molecules containing  $\pi$ -electrons or nonbonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

## **3.4. FT-IR spectroscopy**

FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. Fourier transform infrared spectroscopy is preferred over dispersive or filter methods of infrared spectral analysis for several reasons:

• It is a non-destructive technique

- It provides a precise measurement method which requires no external calibration
- It can increase speed, collecting a scan every second
- It can increase sensitivity one second scans can be co-added together to ratio out random noise
- It has greater optical throughput
- It is mechanically simple with only one moving part

In this study FT-IR characterization was done by using perkin-Elmer 1650 FT-IR spectrophotometer using KBr technique.

## CHAPTER-IV

## 4.1. UV-Visible Spectral bahaviour

The band present at 900 nm is due to the shifting of electron from benzenoid ring to quinoid ring. The sharp band present at 310 nm is due to chitosan present in the composite. [63]. The band at 410 nm is due to  $\pi^* \leftarrow \pi$  transition in polaron/bipolaron states and the peaks present around 300 nm is due to  $\pi^* \leftarrow \pi$  transition of the benzenoid rings [64]. This clearly indicates that the polymer is in its emeraldine salt form [65].



Fig.4.1 UV -Visible Spectral Behaviour of Poly(aniline-co-3-anisidine)/Chitosan composite

## 4.2. FTIR Spectral behaviour

The broad band appears at  $3165 \text{ cm}^{-1}$  was due to the -OH group present in chitosan. The absorption bands at 2925, 1110, and 616 cm <sup>-1</sup>, were attributed to the vibrations of N–H, Ph– NH and C–N in the aniline unit [66] of polyaniline. In the region below 2000 cm <sup>-1</sup> the spectrum exhibits two main bands, with maxima situated at 1621 and 1400 cm <sup>-1</sup>, assigned to quinonoid

and benzenoid ring stretching vibrations, respectively [67,68]. Additional bands at 1017cm<sup>-1</sup> could be assigned to vibrations of the C–O–C bonds of the ether group [69] and aromatic C–O [70] respectively. The band characteristic of the electrically conductive form of doped polyanilines is observed at 1110 cm<sup>-1</sup> is attributed to the stretching of the C – N<sup>+•</sup> polaron structure, formed as a result of the acid doping of the emeraldine base (EB) form of polyaniline [71].



Fig.4.2. FTIR Spectral Behaviour of Poly(aniline-co-3-anisidine)/Chitosan composite

## Conclusion

- Poly(aniline-co-3-anisidine)/Chitosan composite was synthesized by chemical oxidative method using potassium perdisulphate in acid medium.
- The band present at 900 nm is due to the shifting of electron from benzenoid ring to quinoid ring. The sharp band present at 310 nm is due to chitosan present in the composite. [63]. The band at 410 nm is due to π\*←π transition in polaron/bipolaron states and the peaks present around 300 nm is due to π\*←π transition of the benzenoid rings.
- In FTIR spectroscopy the broad band appears at 3165 cm<sup>-1</sup> was due to the -OH group present in chitosan. The absorption bands at 2925, 1110, and 616 cm<sup>-1</sup>, were attributed to the vibrations of N–H, Ph–NH and C–N in the aniline unit [66] of polyaniline. In the region below 2000 cm<sup>-1</sup> the spectrum exhibits two main bands, with maxima situated at 1621 and 1400 cm<sup>-1</sup>, assigned to quinonoid and benzenoid ring stretching vibrations, respectively [67,68].
- The band characteristic of the electrically conductive form of doped polyanilines is observed at 1110 cm<sup>-1</sup> is attributed to the stretching of the C N<sup>+•</sup> polaron structure, formed as a result of the acid doping of the emeraldine base (EB) form of polyaniline [71].

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# Study of adsorption of zinc and lead ions by aberrant Polyindole/agar-agar composite

**Project in chemistry** 

Submitted to St. Mary's College (Autonomous), Thoothukudi in partial

fulfilment for the award of the degree of Bachelor of Science in Chemistry.

Project done by

Arockia Smilin. B

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St. Mary's College (Autonomous), Thoothukudi (Re-accrediated by 'A+' Grade by NAAC Thoothukudi- 628001. 2022-2023

## DECLARATION

We hearby declare that the project entitled, "study of adsorption of zinc and lead by aberrant polyindole/agar-agar composite" submitted to St. Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the Degree of Bachelor of science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

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April 2023 Thoothukudi

## CERTIFICATE

This is to certify that project in chemistry entitled "study of adsorption of zinc and lead by aberrant polyindole/agar-agar composite" is submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

iii

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# CONTENT

CHAPTER	TITLE	PAGE NO
.I	INTRODUCTION	1
II	LITERATURE REVIEW	7
III	SCOPE	10
IV	EXPERIMENTAL SECTION	12
V	RESULTS AND DISCUSSION	15
VI	CONCLUSION	19

#### **1.1 INDOLE**

Indole is an aromatic heterocyclic organic compound. The name indole is a portmanteau of the words indigo and oleum since indole was first isolated by treatment of the indigo dye with oleum. It has a bicyclic structure consisting of a sixmembered benzene ring fused to a five-membered nitrogen-containing pyrrole ring. It is also known as benzo pyrrole. Indole is a popular component of fragrances and the precursor to many pharmaceuticals. Indole is a solid at room temperature. It occurs naturally in human feces and has an intense fecal odor. At low concentrations, however, it has a flowery smell and is a constituent of many perfumes [1].



Figure 1.1 Structure of indole

Indole undergoes electrophilic position substitution, mainly at 3. Substituted indoles structural elements are of the tryptophanderived tryptamine alkaloids, which include the neurotransmitter serotonin and the hormone melatonin, well the naturally as as occurring dimethyltryptamine and psilocybin. Other indolic compounds include the plant hormone auxin [2].

#### **1.2 POLYINDOLE**

Indole monomer in a reaction medium with a suitable oxidizing agent and dopant can be polymerized. Different research groups employed various oxidizing agents, reaction medium, and dopants for successful synthesis. Other parameters like concentrations of reagents, reaction temperature, reaction time and preparatory methods, also determine the percentage of product formation [3].

Polybenzopyrrole is a polymer of indole and synthesized by emulsion polymerization, oxidative chemical polymerization, electrochemical polymerization, microwave-assisted polymerization, etc. Polyindole and its variants stand out due to their photocatalytic characteristics, as well as their great heat and chemical durability and cation exchange capabilities [4].



Figure 1.2 Polyindole

#### **1.3 BIOPOLYMER**

Biopolymers are organic substances present in natural sources. The term biopolymer originates from the Greek words bio and polymer, representing nature and living organisms. Large macromolecules made up of numerous repeating units are known as biopolymers. The biopolymers are biocompatible and biodegradable, making them useful in different applications, such as edible films, emulsions, packaging materials in the food industry, drug transport materials, medical implants like medical implants organs, wound healing, tissue scaffolds, dressing materials in pharmaceutical industries. Plants, animals, microorganisms, and agricultural wastes are examples of natural biological sources of biopolymers [5].

Biopolymers can be classified into three groups: Polysaccharides made of sugars, Proteins made of amino acids and nucleic acids made of nucleotides. Based on application, biopolymers can be classified as bioplastics, biosurfactant, biodeteregent, bioadhesives, biofloculant and so on [6].

#### **1.4 APPLICATIONS OF BIOPOLYMERS**

Biopolymers, due to its biocompatible and biodegradable nature, can be used to improve the performances of other biologically active molecules in a product [7].

#### 1.5 AGAR AGAR

Agar is a polysaccharide-based hydrocolloid seaweed with significant gelling ability. It is a gel-forming polysaccharide that produces D-galactose when hydrolyzed with acid. The chemical structure of agar comprises its components namely agarose and agaropectin. The structure and relationship between these two polysaccharides are quite complex and decide the gelling ability of agar [9].

#### **1.6 PROPERTIES**

The most important characteristics of agar are the following.

1. Its great gelling power in an aqueous environment allows it to form gels which are more resistant than those of any other gel-forming agent. 2. The simple water solution has a very good gelling power. There is no need to add reagents to produce gelation, such as potassium or calcium. High sugar concentrations or an acid environment are not needed.

3. It can be used over a wide range of pH, from 5 to 8, and in some cases beyond these limits.

4. It withstands thermal treatments very well, even above 100°C which allows good sterilization.

5. A 1.5% aqueous solution gels is between 32°C-43°C and does not melt below 85°C. This is a unique property of agar.

6. Agar gives gels without flavour and does not need the additions of cations with strong flavours, it can be used without problems to gel food products with soft flavours.

7. It assimilates and enhances flavours of products mixed with it and acts as a fragrance-fixer permitting their long term fixation.

8. Its gel has an excellent reversibility allowing it to be repeatedly gelled and melted without losing any of the original properties.

9. Transparent gels that are easily coloured can be obtained whose refractive index can also be easily increased by adding sugar, glucose, glycerine, etc., given them an attractive brightness.

10. The gel is very stable, not causing precipitates in the presence of certain cations as happens to alginates with calcium [10].

#### **1.7 STRUCTURE**

The agar was considered to have just sulphate semiester group along with a few galactoses' hydroxyl group in a single unitary structure. Then agaropectin and agarose were the two distinct polysaccharides that were found in the agar. Gel forming attributes of agar is determined by the relative hydrophobicity of the basic repeating unit, the alternating 1, 3-linked b-D-galactopyranose and 1,4linked 3,6-anhydro-a-L-galactopyranose or agarobiose, and its substitution by hydrophobic and polar groups. In 1938, the presence of 3-6 anhydro-Lgalactose in the agar molecule was also discovered along with some agarobioses. Agar gels form when a helical structure of agar polysaccharides is possible and the helices may unite [11].



Figure 1.3 Structure of Agar-agar

#### **1.8 USES OF AGAR AGAR**

#### i) In Nanotechnology

Agar is also used in nanoparticle films as a packaging material. The melanin nanoparticle was integrated into the agar film to create a fully functional packaging film. Agar agar nanocomposite films with UV-light barrier characteristics, antimicrobial activities, and enhanced film properties have a great potential for use in active food packaging to ensure food safety and extend shelf life of packed foods [12].

#### ii) In food application

90 % of the extracted agar is utilised in culinary items as a thickener and stabiliser in baked goods, a gelling agent in meats and fish items, and a texture improver in various dairy products such as yoghurt and cheese. Agar can be utilized as a binder for brown rice from corn and red bean flour since it is easier to extract than other binders such as gum or carrageen [13].

#### iii) Pharmaceutical application

Agar-Agar is primarily used in pharmaceuticals as a gelation, stabilization, and thickening agent. Agar-agar is also commonly used for purgative purposes and as a surgical aid. Agar-based products like as composite hydrogels, nanocomposite films, and other materials finds application in the pharmacological industry [14].

Dedhila Devadathan et.al. synthesized ZnO/MgO nanocomposite using chemical oxidation method. The synthesized materials were characterized using XRD and UV/Vis absorbance spectroscopy. The study investigates the applicability of polyindole based ZnO/MgO nanocomposite for the removal of Pb(II) heavy metal ion. Proper tuning can increase the removal efficiency of polyindole based ZnO/MgO nanocomposite and can be made a good candidate for the removal of lead ions [15].

Liming Xu et.al. prepared high-quality polyindole in neutral solvents by electrochemical method. Due to the coordination interaction between indole and  $MoS_2$ , the oxidation potential of indole in this medium was reduced to 0.5 V from 0.75 V determined in acetonitrile/LiClO<sub>4</sub>. The results of thermal analysis indicated that the PIn/MoS<sub>2</sub> nanocomposite had an improved thermal stability relative to PIn and MoS<sub>2</sub> nanosheets. Moreover, the specific capacitance of PIn/MoS<sub>2</sub> nanocomposite was 8.3 times higher than that of PIn prepared acetonitrile/LiClO<sub>4</sub> [16].

Dedhila Devadathan, Baiju V, Raveendran R synthesized polyindole based metal oxide nanocomposites through chemical oxidation method. For comparative study, the counterparts, polyindole was synthesised through chemical oxidation method and the metal oxides were synthesised through chemical coprecipitation method. Structural studies were done using XRD. The study confirms that the polyindole based metal oxide nanocomposites samples prepared showed antibacterial agent activity. The results suggest that proper tuning can make them good antimicrobial agents [17].

Ibtisam Abbasi discovered that synthesized MPIn exhibits a bathochromic when compared to initially researched polyindoles of a different variety. Results reveal that polyindoles have luminescence properties due to their coiled geometry. [18]. Samia M. Mokhtar et.al found a copolymer of indole with chitin and chitosan was prepared by two techniques, chemically using potassium persulphate as an initiator. The grafted samples show a higher chelation capacity towards cation ions of Cu<sup>2+</sup>, Ni<sup>2+</sup> and Co<sup>2+</sup>. The thermogravemitric analysis of grafted samples showed an improvement in the thermal stability. These composites different effects against a diverse range of organisms comprising some Gram-positive, Gram-negative bacteria and fungi. Also a weak antimicrobial activity was shown against the other organisms [19].

Harish Mudila, Parteek Prasher, Mukesh Kumar, Anil Kumar, M. G. H. Zaidi, Amit Kumar, found that Polyindole-based hybrid composites are being recognized as a promising candidate to be used in energy storage. This assessment recapitulates the position of Polyindole and its hybrid composite to be used as energy harvest material [20].

P. C. Pandey and R. Prakash done the electrochemical synthesis of polyindole upon anodic oxidation of indole in dichloromethane containing 0.1 M tetrabutylammonium perchlorate. The air-stable polyindole films were obtained by sweeping the potential between -0.2 and 1.0 V vs Ag/AgCl as well as at constant potential. The conductivities of such films were found to lie in the range 0.1-1 S cm<sup>-1</sup>. The electrochemically produced polyindole was studied as active material for secondary batteries in aqueous electrolyte. This battery showed good reversibility and good coulombic efficiency [21].

Danhua et.al. found a ternary single-walled carbon nanotubes/RuO<sub>2</sub>/polyindole nanocomposite was fabricated by the oxidation polymerization of indole on the prefabricated SWCNT/RuO<sub>2</sub> binary nanocomposites. The electrochemical results demonstrated that the symmetric supercapacitor used SWCNT/RuO<sub>2</sub>/PIn as electrodes

presented 95% retention rateafter 10000 cycles, superior capacitive performance of 1203Fg<sup>-1</sup> at 1 A<sup>0</sup>/g, and high energy density of 33 Wh/kg at 5000 W/kg. The high capacitance performance of SWCNT/RuO<sub>2</sub>/PIn nanocomposite was mainly ascribed to the beneficial cooperation effect among components [22].

Karthikeyan. P, Rajavel. R, synthesized Poly(indole-5-carboxylic acid) by electrochemical polymerization technique from different concentration of poly(indole-5-carboxylic acid) using lithium per chloride as oxidation agent at different scan rate. The corrosion protection performance of low nickel stainless steel specimens coated with 0.1 M concentration of PICA was investigated in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium using potentiodynamic polarization and electrochemical impedance spectroscopic methods. Electrochemical corrosion tests and surface analysis results evidently showed that PICA coating served as a stable mass matrix on LN SS against corrosion. It was also revealed that the coating of PICA at 0.1V scan rate with 0.1M indole-5-carboxylic acid exhibited the best corrosion resistance among all concentrations [23]. Polyindole based nanocomposites were observed to be a potential biomaterial against the multi-drug resistant microbes. They can be used as an alternative to antibiotics and antifungal drugs. Another concern is at the development of an economical as well as an ecofriendly method for the synthesis of polyindole based nanocomposites. However, nowadays more and more researchers are coming up with some innovative green synthetic strategies, which may give progress to the field of polyindole based nanocomposites for biomedical applications. Many polyindole derivatives have been prepared till now, in regards to the antimicrobial activity of indole monomer, some them shows fungicidal activity [25].

Safe drinking water is a significant, but simple indicator of development. Nanotechnology has shown promising developments in providing safe drinking water through effective purifying mechanisms. Developing various nanocmposites with functional materials which can scavenge various toxic metals like arsenic, lead need to be developed. In this context polyindole along with any biopolymer can be used as a adsorbent for the purification of impure water. These composites can absorb heavy metals and also organic dyes from water [8].

#### **OBJECTIVES**

- ✓ To synthesize polyindole/agar agar composite by oxidative polymerization of indole in alcohol medium in the presence of agar-agar
- ✓ To confirm its absorption properties using UV- Visible DRS Spectroscopy
- ✓ To confirm the formation of polyindole composite by Fourier transform infrared spectroscopy
- ✓ To study the adsorption capacity of the composite by zinc using EDTA titration method.
- ✓ To study the adsorption capacity of the composite by lead using EDTA titration method.

#### **4.1 CHEMICALS REQUIRED**

Indole of analytical grade was purchased from Sisoo Research Laboratories Pvt (98% pure), Ethyl alcohol, Potassium persulphate was purchased from Isochem laboratories Angamaly Kochi, Starch .

#### 4.2 Synthesis of polyindole/Agar-agar composite

About 0.02 mol of indole was taken in a 400ml beaker. To this 10 ml of ethyl alcohol is added. It was then diluted to 100 ml and placed on the magnetic stirrer and allowed to stir for 10 minutes. Then 2 g of potassium persulphate dissolved in 50 ml of water was added in drops with constant stirring. A slow colour change is noted. Then it was allowed to polymerize on the magnetic stirrer for 3 hours. The polyindole thus formed was allowed to settle for one day by refrigerating the solution for complete polymerization. The precipitate was filtered at the suction pump, washed with water for 5 to 6 times and dried between Whatmann filter papers. It was then dried for a week.

#### **4.3 FT-IR SPECTROSCOPY**

Infrared spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. The frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

FTIR spectra were recorded for polyindole/Agar-agar composite using Nicolet Si5 spectrometer using KBr pellets in the range of 4000 - 400 cm<sup>-1</sup>

#### 4.4 UV-Visible DRS spectral analysis

UV-Visible spectra were recorded using Jasco V-630 spectrophotometer for the polyindole/Agar -agar composite solution in the range of 200-900 nm.

#### **4.5 Adsorption Studies**

#### 4.5.1 Preparation of standard zinc sulphate solution

A standard solution of about 0.01M zinc sulphate solution was prepared in a 100 mL standard measuring flask using distilled water. It was shaken well for uniform concentration.

#### 4.5.2 Preparation of standard lead nitrate solution.

A standard solution of about 0.01M lead nitrate solution was prepared in a 100mL standard measuring flask using distilled water. It was shaken well for uniform concentration.

#### 4.5.3 Preparation of disodium salt of ethylene diamine tetra acetic acid solution

A disodium salt of ethylene diamine tetra acetic acid solution of 0.01M was prepared in a 100ML standard measuring flask using distilled water and shaken well to achieve uniform concentration.

#### 4.5.4 Adsorption of zinc and lead ions

About 0.01g of polyindole composite was taken in a clean beaker. About 20mL of 0.01M standard zinc sulphate solution was pipetted out into the beaker. It was then stirred in a magnetic stirrer for about 30 minutes and kept aside for 10 minutes. Then the solution was then filtered using a filter paper and the filtrate was collected.

Similarly adsorption for lead ions were also conducted.

#### 4.5.5 Estimation of adsorbed zinc using titration

Burette was filled with EDTA solution. The filtered solution after adsorption was taken in a conical flask and 5mL of ammonium chlorideammonium hydroxide buffer of pH 10 was added. A pinch of eriochrome black T indicator was added. It was then titrated against EDTA taken in the burrette. The end point was the colour change from wine red to blue. At this point the reading on the burette was noted. From this burette reading the volume of zinc adsorbed can be found.

#### 4.5.6 Estimation of adsorbed lead ions using titration

The filtered solution was taken in a conical flask. The burette was filled with EDTA solution. To the solution in the flask 2.5g of hexaammine was added and 2 drops of xylenol orange indicator was added. It was then titrated against EDTA. The end point was the colour change from red to lemon yellow. The burette reading at this point was noted. The burette reading gives the volume of lead that is adsorbed.

#### **5.1 UV-Visible DRS Studies**

UV-Visible spectrum of polyindole/agar agar composite is given in figure 5.1. UV Spectra shows two peaks in 296nm and a broad peak at 442nm. Normally for polyindole there is a absorption peak at 220 to 300 nm [28]. The peak displayed at 296nm is due to the conjugation of benzene ring in the polyindole unit. A broad band in the range of 430 to 500nm with the peak at 442nm is due to the  $\pi$ - $\pi$ \* transition of other aromatic rings [29]. This band also indicates the extend of conjugation between the rings making the flow of charge of easy. There is no specific peak for agar-agar [30].



Figure 5.1 UV-Visible spectrum of Polyindole/Agar-agar composite

#### 5.2 FT-IR studies of the composite.

The FT-IR spectra of polyindole/Agar-agar composite is given in figure 5.2. The peak at  $1110 \text{ cm}^{-1}$  is due to the vibration of the C-N bond present in the polyindole ring. The peak at  $1457 \text{ cm}^{-1}$  is due to the stretching mode of benzene ring [31]. The vibrations of benzene ring is present at 1045 cm<sup>-1</sup> and C-H stretching vibrations is

present at 740 cm<sup>-1</sup>. The pyrrole ring stretching vibration is at 1360cm<sup>-1</sup> [32]. The broad band at 3121 cm<sup>-1</sup> is due to –OH stretching.

The peak at 744 cm<sup>-1</sup> shows the benzene ring, which is not involved during the polymerization of indole molecule. The peaks observed at 1457 cm<sup>-1</sup> are due to the C-H stretching vibrations. The peaks observed at 1334 cm<sup>-1</sup> and 1100 cm<sup>-1</sup> indicate the stretching mode of pyrrole ring and vibration mode of C-N bond. The peak at 3390 cm<sup>-1</sup> is due to the N–H stretching confirming that the nitrogen atom containing moiety is not involved in the polymerization sites[33]. It is also observed that the presence of band at 931 cm<sup>-1</sup> and 1043 cm<sup>-1</sup> shows the presence of 3, 6-anhydrogalactose bridges of agar-agar [34].



Figure 5.2 FT-IR spectrum of polyindole/Agar-agar composite

#### Adsorption studies.

Adsorption of zinc and lead ions by the composite was studied by EDTA titration method.

Weight of ZnSO <sub>4</sub> taken for 100r	nl = 0.281g
Weight of ZnSO <sub>4</sub> for 1ml	= 0.00281g
Weight of ZnSO <sub>4</sub> for 17.7ml	= 0.0497g
161.47g of ZnSO <sub>4</sub> contains	= 65.38g of Zn
∴0.0497g of ZnSO4 contain	= 65.38 x 0.0497/ 161.47
	= 0.0201g of Zn

Weight of PbNO<sub>3</sub> taken for 100ml = 0.33g

Weight of PbNO <sub>3</sub> for 1ml	= 0.0033g

Weight of PbNO<sub>3</sub> for 18.1ml = 0.0597g

331.2g of PbNO<sub>3</sub> contains 207.2g of lead

 $\therefore 0.0597$ g of PbNO<sub>3</sub> contains = 207.2 x 0.0597/331.2

= 0.0373g of Pb



The amount of zinc adsorbed is 0.0201g by 0.01g by the composite and the amount of lead adsorbed is 0.0373g by 0.01g by the composite. The adsorption capacity (mg/g) is the amount of the molecule adsorbed (the adsorbate) per unit mass of the adsorbent. The adsorption capacity of the composite is high and hence it adsorbed zinc and lead.

Polyindole/Agar-agar composite was prepared by the oxidative polymerization of indole in the presence of oxidizing agent. The synthesized composite has very good adsorption property. This adsorption property of polyindole composite is proved by its titration against EDTA solution. It adsorbed zinc ions and lead ions from the salt solution. This study can be further extended to other metals also and this composite can be used for the purification of unclean water.

The metal ions of wastewater adhere to the surface of nanoporous adsorbents, which has a high surface area due to its porosity. The adsorption process could be selective for one or more metals than others.

Among zinc and lead, lead is more adsorbed by polyindole composite than that of zinc. Hence this can be used to remove the heavy metal zinc and lead from the waste water. The adsorbent removed heavy <u>metal</u> <u>ions</u> effectively from solution medium in the order of lead > zinc.

Lead is much softer than zinc with a Mohs hardness scale rating of 1- 2 compared to zinc's rating of 2 - 3. Moreover lead is much denser than zinc. The tendency to coordinate with the composite is greater for lead than zinc. Hence lead and zinc coordinates with the composite and easily removed from the waste water.

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# Removal of Lead and Zinc ions from solution using novel polyindole/starch composite

**Project in chemistry** 

Submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the degree of **Bachelor of Science** in Chemistry.

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St. Mary's College (Autonomous), Thoothukudi (Re-accrediated by 'A+' Grade by NAAC) Thoothukudi- 628001. 2022-2023

#### DECLARATION

We hearby declare that the project entitled "Removal of Lead and Zinc ions from solution using novel polyindole/starch composite" submitted to St. Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the Degree of Bachelor of science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

L. Antony Rathina Sugura L.Antony Rathina Suguna

A·Ceenithai

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A. Helen Busaan Motha A.Helen Susaan Motha

April 2023 Thoothukudi

# CERTIFICATE

This is to certify that project in chemistry entitle "Removal of Lead and Zinc ions from solution using novel polyindole/starch composite" is submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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# ACKNOWLEDGEMENT

We express our first and fervent thanks to GOD ALMIGHTY for giving an opportunity to devote ourself for this work.

We would like to deeply express our sincere thanks to the secretary **Rev Dr. Sr. C. SHIBANA**, for providing infra structural facilities. We thank our principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE** and our Head of the Department **Mrs. RANI JEYAMARY**, Associate Professor, Department of Chemistry, for providing us necessary arrangements for the successful completion of our project.

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iv

# CONTENTS

CHAPTER	TITLE	PAGE
		NO.
I.	Introduction	1
Π	Literature Review	7
III	Scope	10
. IV	Experimental	12
	Section	
V	Results And	15
	Discussions	
VI	Conclusions	19

### **1.1 INDOLE**

Indole with a molecular formula  $C_8H_7N$  is a non-basic nitrogenous heterocyclic organic compound. It is also known as benzopyrrole. It was first isolated in 1866 and commonly synthesized from phenylhydrazine and pyruvic acid. It is a planar molecule with 10 electrons. Indole is a colourless solid with a pleasant fragrance in highly dilute solutions. Its melting point is 52.5°C. It is mostly soluble in alcohol, benzene. It mainly occurs in some flower oils such as jasmine, orange, in coal tar and in fecal matter. It is mainly used in perfumes. Indole can be polymerized with selective oxidising agent such as FeCl<sub>3</sub>, CuCl<sub>2</sub> or KIO<sub>3</sub> [1, 2].

#### **1.2 SYNTHESIS OF INDOLE**

Indole is synthesized by an organic reaction called Fischer-Indole synthesis which is carried by an acid catalyst which convert phenyl hydrazine and an aldehyde or ketone to an indole. By the acid catalysed reaction of the hydrazine with the carbonyl, the cycle starts with the formation of phenyhydrazone [3].



Figure 1.1 Structure of indole

#### **1.3 POLYINDOLE**

Polyindole is a conducting polymer with a structure consisting of fused pyrrole and benzene ring. It is very well known for its good redox activity. Compared to polyaniline and polypyrrole it is very well known for its excellent thermal stability and corrosion protection. Mainly polyindoles are synthesized by chemical oxidative polymerization and electrochemical polymerization. Owing to the unique physical and electrochemical properties, polyindole has gained marvellous consideration of the researchers, in the past years. Polyindole, and its composites, have found significant importance in many fields such as sensors, supercapacitors, batteries and anticorrosion. The major reasons for its applicability are its excellent mechanical stability, reasonably good electro-activity, optical properties [4]. Polyindole can be synthesized by chemical oxidative polymerization using citric acid as a dopant [5].



**Figure 1.2 Structure of Polyindole** 

#### **1.4 APPLICATIONS OF INDOLE**

1. Indoles have a wide range of applications for the treatment of viral and microbial infections, depression, hypertension, inflammation and migraine.

2. Indole nucleus is present in tryptophan, an amino acid. This makes it prominent in neurotransmitters, indole alkaloids, and plant hormones, which are called auxins.

3. The most common auxin found in plants is indole-3- acetic acid and is used in horticulture.

4. Indole has several biological applications, due to its several properties, like, it being antimicrobial, antioxidant, analgesic, anticancer, anti-inflammatory, diuretic, antitumor, anti-HIV, antiviral, and its cardiovascular effects [6].

#### **1.5 BIOPOLYMERS**

Biopolymers are polymeric biomolecules having a long chain of monomeric units which are covalently joined together. Polynucleotides, polypeptides, and polysaccharides are the major class of biopolymers. Biopolymers have a complex molecular assembly leading to a well-defined three-dimensional structure. These polymers are solutions to the problems created by plastics. These polymers have a potential application in various fields of industry such as biomedical, water treatment, energy storage, food industry, sensing, coatings, etc. Protein, Starch, Cellulose, DNA, RNA, Lipids, Collagen, Carbohydrates are the examples of biopolymers [7].

#### **1.6 STARCH**

Starch is a semi-crystalline polymer composed of amylose and amylopectin molecules. The primary carbohydrate used for energy storage in plants is starch, the equivalent of glycogen in animals.

Both starch and glycogen are polymers of glucose, with different glycosidic linkages between glucose monomers and different degrees of branching. Amylose is a linear polymer composed of (1–4)-linked  $\alpha$ -D-glucopyranosyl units while amylopectin is a very large molecule made up of (1–4)-linked  $\alpha$ -D-glucopyranose chains with a-(1– 6) branches. Starch is one of the most abundant natural polymers and it is cheap and degradable. Nano and micro structured fibers when dispersed in the polymer matrix, improve its tensile strength and flexibility [8].

#### **1.7 SIGNIFICANCE**

The significance of starch in plants and humans are undeniable. While plants consider it as a storage of energy, humans need it as a vital part of their diet and also for various commercial products. Starch and its derivatives have already been explored in various applications like in the manufacture of paper, textiles and adhesives. Their biodegradable and renewable nature make them an environmental friendly alternative to the use of synthetic additives in many other products, including plastics, detergents, pharmaceutical tablets, pesticides, cosmetics, and even oil-drilling fluids [8].

#### **1.8 CHEMICAL PROPERTIES**

The chemical properties of starch are dependent on the reactivity of starch

which is a function of the polyhydroxyl functional groups in the constituent glucose monomers. The hydroxyl groups at position C-2, C-3 and C-6 which are free from the glycosidic bond linkages and pyranose ring formation, are usually free for substitution reactions involving either the attached hydrogen or the entire hydroxyl group. While the -OH at C-6 is a primary alcoholic hydroxyl group, those at C-2 and C-3 are secondary alcoholic hydroxyl group. Hence, starch can undergo hydrolytic cleavage of its chains at the glycosidic bonds [9].



**Figure 1.3 Structure of starch** 

#### **1.9 APPLICATIONS OF STARCH**

#### i) Bioplastics

Starch is an important natural polymer to make bioplastics. With water and plasticisers such as glycerol, starch can be processed into so-called "thermoplastic starch" using conventional polymer processing techniques such as extrusion, injection molding and compression molding [10]. Since materials based on only native starch
have poor processibility, mechanical properties and stability, more commonly modified starches are used and starch is combined with other polymers [11].

#### ii) Adhesives

Starch is used in the manufacture of various adhesives or glues for bookbinding, wallpaper adhesives, paper sack production, tube winding, gummed paper, envelope adhesives, school glues and bottle labeling. Starch derivatives, such as yellow dextrins, can be modified by addition of some chemicals to form a hard glue for paper work, some of those forms use borax or soda ash, which are mixed with the starch solution at 50–70 °C to create a very good adhesive. Sodium silicate can be added to reinforce these formula [11].

#### iii) Other uses

- Starch is mainly used to size cotton based yarns. Modified starch is also used as textile printing thickener.
- In oil exploration, starch is used to adjust the viscosity of drilling fluid, which is used to lubricate the drill head and suspend the grinding residue in petroleum extraction.
- Starch is also used to make some packing peanuts, and some drop ceiling tiles.
- In the printing industry, food grade starch is used in the manufacture of anti-setoff spray powder used to separate printed sheets of paper to avoid wet ink being set off [11].
- For body powder, powdered corn starch is used as a substitute for talcum powder, and similarly in other health and beauty products.
- Starch is used to produce various bioplastics, synthetic polymers that are biodegradable. An example is polylactic acid [11].

Anjitha Thadathil, Hareesh Pradeep, Deepak Joshy, Yahya A. Ismail and Pradeepan Periyat (2022) synthesized two main types of N-containing conducting polymers, namely, polypyrrole and polyindole, and analyzed their binary and ternary nanocomposites in the treatment of contaminants, sensing, and green chemistry. Also they found out different strategies for the versatile property improvement of these conducting polymers with unique applications [12].

Begum et.al. synthesized a polyindole hybrid material by in situ chemical oxidative polymerization and explored the efficiency of a novel activated carbon incorporated polyindole composite for adsorptive removal of Malachite Green dye from aqueous solution. The characteristics of the polyindole composite were determined using Fourier-transform infrared spectrometer, X-ray diffraction, SEM, energy dispersive X-ray spectroscopy and UV spectroscopy [13].

Ping Wang, Carlos R. Arza and Baozhong Zhang found out that indole can be used as a new sustainable aromatic unit for polyesters. A series of new polyesters were synthesised by the polycondensation of an indole-based dicarboxylate and five potentially bio-based diols. The new polyesters are amorphous, have superior thermal quality, and can form clear transparent films [14]. Hareesh Pradeep et.al. found that several polyindole based nanocomposites were found to exhibit the ability to release reactive oxygen species and hence they show excellent antimicrobial properties. The features of polyindole can be fine-tuned to make them potential alternatives to antibiotics and antifungal medicines [15].

P. Rejania and B. Beenab found that manganese oxide polyindole hybrid structures have optical properties.  $Mn_2O_3$  nanoparticles were prepared by the sol-gel method and characterized by XRD, scanning electron microscope and infrared spectroscopy. The hybrid manganese oxide polyindole structure was obtained by the addition of polyindole on the surface of  $Mn_2O_3$  [16].

Harish Mudila, Parteek Prasher, Mukesh Kumar, Anil Kumar, M. G. H. Zaidi Amit Kumar found that polyindole-based hybrid composites can be used as energy harvest materials because of their low electrical and electrochemical conductivity, high redox activity, tunable electrical conductivity, significant thermal stability, slow degradation rate, and possible blending property [17].

Carlos R. Arza and Baozhong Zhang, found the synthesis and characterization of new indole-based dicarboxylate monomers with only aromatic ester bonds can improve the thermal stability and glass transition temperature of the resulting polyesters [18]. Chhattise et. al. found the catalytic performance of polyindole as a heterogeneous catalyst by the synthesis of 3,3'-arylmethylene-bis-1H-Indole derivatives using various substituted aldehydes and indole under reflux reaction condition with good to excellent yield. The synthesized polymer was well characterized by various spectroscopic techniques like FT-IR, XRD and FESEM [5].

T. Anjitha, T. Anilkumar, G. Mathew, M. T. Ramesan found that the Polyindole/ZnFe<sub>2</sub>O<sub>4</sub> nanocomposites can be considered as a potential candidate for the applications in sensors and nanoelectronic devices [19].

Polyindole find many applications in the electrical field, medicinal field, textile industry, waste water treatment etc. Several studies on polyindole revealed that they could be used as promising candidates for applications such as supercapacitors, batteries, electrochromic devices, sensors, electrocatalysis, catalysis, and anticorrosion. They are found be an excellent source of storage devices due to their remarkable electrical properties [17]. It is used in the manufacture of many drugs namely serotonin, vinblastine, indomethacin, fendosal, melatonin, and others. Polyindole- based nanocomposites are used as potential antimicrobial agents. They are useful in developing biopolyesters [14, 18]. Incorporating biopolymer to polyindole makes the polymer backbone more stable. Also this polyindole composites are better compounds than ordinary polymers. Therefore starch is is used to prepare composite with polyindole which makes the composite more stable This composite can be used for various applications. This composites have various binding sites. So it can easily coordinate metals and it can remove heavy metals from solutions. Also polyindole composites can remove harmful organic dyes from water. This property can be used in the purification process.

#### **OBJECTIVES**

- To synthesize polyindole-starch composite by oxidative polymerization of indole in ethanol.
- ✤ To confirm its absorption properties using UV- Visible DRS Spectroscopy
- To confirm the formation of polyindole composite by Fourier transform infrared spectroscopy
- To study the adsorption property of the composite by zinc using EDTA titration method using eriochrome black indicator.
- To study the adsorption property of the composite by lead using EDTA titration method using xylenol orange indicator.

#### **4.1 Chemicals required**

Indole of analytical grade was purchased from Sisoo Research Laboratories Pvt (98% pure), Ethyl alcohol, Potassium persulphate was purchased from Isochem laboratories Angamaly Kochi, Starch .

#### 4.2 Procedure

About 0.02 mol of indole with 10mL of ethyl alcohol was taken in a beaker and the solution was diluted to 100ml. The solution was then stirred with a magnetic stirrer for 10 minutes. Then starch of about 2 weight percentage of indole was added and stirred for 20 minutes. About 2g of Potassium persulphate was dissolved in 50ml of water and was added to the above solution in drops. A slow change of colour was noted. It was further stirred for 3 hours and refrigerated for 24 hours for the completion of polymerization. The solution was filtered at the suction pump using whattmann filter paper and washed well with water. The precipitate was then dried and collected.

#### 4.3 FT-IR SPECTROSCOPY

#### **UV Spectral analysis**

UV-Vis spectroscopy also known as electronic spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample. UV-Visible spectra were recorded using Jasco V-630 spectrophotometer for the polyindole/starch composite solution in the range of 200-900 nm.

#### **FT-IR Spectral Analysis**

Infrared spectroscopy is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. FTIR spectra were recorded for polyindole/starch composite using Nicolet Si5 spectrometer using KBr pellets in the range of 4000 - 400 cm<sup>-1</sup>

#### **ADSORPTION STUDIES**

#### 4.5.1 Preparation of standard zinc sulphate solution

A standard solution of about 0.01M zinc sulphate solution was prepared in a 100 mL standard measuring flask using distilled water and shaken for uniform concentration.

#### 4.5.2 Preparation of standard lead nitrate solution

A standard solution of about 0.01M lead nitrate solution was prepared in a 100mL standard measuring flask using distilled water shaken well for uniform concentration.

#### 4.5.3 Preparation of disodium salt of ethylene diamine tetra acetic acid solution

A disodium salt of ethylene diamine tetra acetic acid solution of 0.01M was prepared in a 100ML standard measuring flask using distilled water.

#### 4.5.4 Adsorption of zinc and lead ions

About 0.01g of polyindole/starch composite was taken and mixed with 20mL of 0.01M zinc sulphate solution. It was then stirred in a magnetic stirrer for about 30 minutes and kept aside for 10 minutes. Then the solution was then filtered using filter paper.

About 0.01g of polyindole/starch composite was taken and mixed with 20mL of 0.01M lead nitrate solution . It was then stirred in a magnetic stirrer for about 30 minutes and kept aside for 10 minutes. Then the solution was then filtered using filter paper.

#### 4.5.5 Estimation of adsorbed zinc ions using titration

Burette was filled with EDTA solution. The filtered solution after adsorption was taken in a conical flask and 5mL of ammonium chloride ammonium hydroxide buffer of pH 10 was added. A pinch of eriochrome black T indicator was added and titrated against EDTA taken in the burette. The end point was the colour change from wine red to blue. Burette reading was noted.

#### 4.5.6 Estimation of adsorbed lead ions using titration

Burette was filled with EDTA solution . The filtered solution after adsorption was taken in a conical flask and 1.2g of hexamine buffer was added. A few drops of xylenol indicator was added and titrated against EDTA solution taken in the burette. The end point was the colour change from wine red to pale yellow. Burette reading was noted.

#### 5.1 UV-Visible DRS spectral analysis

UV-Visible spectrum of polyindole/starch composite is given in figure 5.1. UV-Visible spectrum shows three peaks in 244nm, 278nm and 372nm. Normally for polyindole there is a absorption peak at 220 to 300 nm [20]. The peak displayed at 278nm is due to  $\pi$ - $\pi$ \* transition in the benzenoid ring [20]. The peak occurred at 372nm, may be assigned to  $\pi \rightarrow \pi$ \* transition of the other aromatic C–C bonds and to n  $\rightarrow \pi$ \* transition [21]. Starch has absorption peak in the region 200nm to 250nm. The peak at 244nm is due to the presence of starch [22].



Figure 5.1 UV-Visible spectra of polyindole/starch composite

#### **5.2 FT-IR spectral studies**

The FT-IR spectra of polyindole/starch composite is given in figure 5.2. The peak 1110cm<sup>-1</sup> is due to the C-N stretching mode of the polyindole ring. The peak at 1401cm<sup>-1</sup> is due to the stretching mode of benzene ring [23]. The peak at 740 cm<sup>-1</sup> is due to the C-H stretching of the benzene ring which is not involved in polymerization. The pyrrole ring stretching vibration is at 1304cm<sup>-1</sup> [24]. The broad band at 3121cm<sup>-1</sup>

is due to -OH stretching. The peak at  $3383 \text{cm}^{-1}$  is due to the N–H stretching confirming that the nitrogen atom containing moiety is not involved in the polymerization sites. This indicates that the polymerization is happening through 2 and 3 positions of the monomers. The narrow peaks observed at  $1304 \text{cm}^{-1}$  and  $1100 \text{ cm}^{-1}$  indicate the stretching mode of pyrrole ring and vibration mode of C-N bond [25]. The peak at  $3126 \text{cm}^{-1}$  corresponds to the hydroxyl groups present in the starch. The peak at  $1008 \text{cm}^{-1}$  is due to the stretching of the C–O–C bond, present in starch [22].



Figure 4.2 FT-IR spectrum of polyindole/starch composite

#### **Adsorption studies**

Adsorption of zinc ions by the composite was studied by EDTA titration method.

Calculations

Weight of ZnSO <sub>4</sub> taken for 100ml	= 0.281g	
Weight of ZnSO <sub>4</sub> for 1ml	= 0.00281g	
Weight of ZnSO <sub>4</sub> for 18.4ml	= 0.0517g	
161.47g of ZnSO <sub>4</sub> contains 65.38g of Zinc		
∴0.0517g of ZnSO4 contains	= 65.38 x 0.0517/161.47	
	= 0.0209g of Zinc	
Weight of PbNO3 taken for 100ml	= 0.33g	
Weight of PbNO <sub>3</sub> for 1ml	= 0.0033g	
Weight of PbNO3 for 18.6ml	= 0.0613g	
331.2g of PbNO <sub>3</sub> contains 207.2g of Lead		
∴0.0610g of PbNO <sub>3</sub> contains	= 207.2  x  0.0613/331.2	
	= 0.0383g of Lead	



The 0.01g of polyindole-starch composite thus prepared adsorbs 0.02g of zinc ions and 0.03g of lead ions . Lead ions are adsorbed more than zinc ions. This may be due to high coordination capacity , differences in adsorbent properties such as structure , surface area , porosity functional groups . Recent advancements in adsorption also found that EDTA has high adsorption capacity. This is due to its chelating ability which can be used for effective lead removal from wastewater. Polyindole/starch composite was prepared by the oxidative polymerization of indole with starch in the presence of oxidizing agent. Adsorption is a technique that caters not only to the remediation of heavy metal from waste water, it is also ecofriendly with a low footprint. Addition of functional groups to biopolymer aids heavy metals scavenging from water. The synthesized composite has very good adsorption property and it adsorbed lead and zinc from the salt solution effectively. It adsorbed zinc only in small amounts eventhough the concentration of the composite is decreased .The composite acts as an adsorbent with high surface area for the adsorption of metals leading to the effective removal of heavy metals from waster water. This study can be further extended to other heavy metals like Fe, Cu, Cr, Mn, Cd, As, Ni etc. and the composite can also be modified for productive activity of adsorption.

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## A Study on chemical polymerization of Indole chitosan composite and its characterization

### **Project in chemistry**

Submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the degree of Bachelor of Science in Chemistry.

Project done by

D. Abi Rajaseeli

S. Abisha Evangelin

M. Anclin



St. Mary's College (Autonomous), Thoothukudi (Re-accrediated by 'A<sup>+</sup>' Grade by NAAC) Thoothukudi- 628001. 2022-2023

1

## DECLARATION

We hereby declare that the project entitled "A Study on chemical polymerization of Indole chitosan composite and its characterisation" submitted to St. Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the Degree of Bachelor of science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

Abi Rajereeli D. D. Abi Rajaseeli

Abisha Evangelin.s.

S. Abisha Evangelin

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M. Anclin

April 2023 Thoothukudi

### CERTIFICATE

This is to certify that the report of the project in chemistry entitled "A Study on chemical polymerization of Indole chitosan composite and its characterisation" is submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

Names D. Abi Rajaseeli S.Abisha Evangelin M. Anclin

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Examiners

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We express our first and fervent thanks to God Almighty for giving an opportunity to devote ourself for this work.

We would like to deeply express our sincere thanks to our Secretary for providing infra structural facilities. We thank our Principal Rev. Dr. Sr. A. S. J. Lucia Rose, our Head of the Department Mrs. Rani Jeyamary for providing us necessary arrangements for the successful completion of our project.

We wish to express our heartfelt thanks to our guide Dr. A. Parveen Sulthana for her valuable suggestions, gentle guidance, enthusiastic ideas, to carryout and complete our work perfectly. We thank all other faculty members of the department for their encouragement and support. We thank Dr. C.Vedhi, Assistant Professor, Department of Chemistry, V.O. Chidambaram College, Thoothukudi for rendering his valuable help to provide UV and IR spectral data.

Our sincere thanks to the non teaching staff of the department for their timely help.We express our love and gratitude to our friends and our family for the encouragement given to us.

# A Study on chemical polymerization of Indole chitosan composite and its characterization

S.No	Title	Page No
1	Abstract	1
2	Introduction	3
3	Objectives	17
4	Experimental Part	19
5	Results and Discussion	24
6	Conclusion	28
7	References	30



#### ABSTRACT

Indole has a bicyclic structure consisting of a six membered pyrrole ring. It is usually prepared from non-heterocyclic precursors by cyclisation reactions on suitable substituted benzenes. Polyindole based composite are used in energy storage field along with the conjugated organic polymers. They are affected with low electrical and electrochemical conductivity. Polyindole has to be synthesize in the presence of chitosan we get polyindole chitosan composite. Chitosan is a bioactive compound used for the preservation of food. It has some excellent properties such as biocompatibility, non-toxic and adsorption. It was characterized by various techniques such as UV, IR. Polyindole chitosan composite has to be characterized by UV and IR from the graph we have identify the absorption peak. It was discussed in various condition and we have done complexometric titration with EDTA using zinc and lead. From that we have to identify which metal is more adsorbed.

# INTRODUCTION

#### **INTRODUCTION:**

Heteroatoms constitute a very common fragment in a number of active pharmaceutical ingredients. According to statistics, more than 85% of all biologically-active chemical entities contain a heterocycle which is used in modern drug design. The increasing presence of various heterocycles in drugs is related to advances in synthetic methodologies, such as metal-catalysed cross-coupling and hetero-coupling reactions, that allow rapid access to a wide variety of functionalized heterocycles which have critical importance for medicinal chemists. It is possible to expand the available drug-like chemical space and drive more effective drug discovery programs. Medicinal chemistry is a chemistry-based discipline, involving aspects of biological, medical, and pharmaceutical sciences and concerned with the invention, discovery, design, identification, and preparation of biologically active compounds which helps in the interpretation of their mode of action and in the study of their metabolism. Nitrogen-based heterocyclic chemistry is an important and unique class among the applied branches of organic chemistry, with a significant amount of research dedicated to the development of novel molecules and composites.

Indole is an aromatic heterocyclic organic compound known as Benzo pyrrole. It has a bicyclic structure consisting of a six-membered benzene ring fused to a five-membered nitrogen containing pyrrole ring. Indole is solid at room temperature which occurs naturally in human feces and has an intense fecal odor. At very low concentrations it has a flowery smell and is a constituent of many flower scents and perfumes and also occurs in coal tar [1]. It occur both naturally and synthetically and exhibit a wide range of biological activity. They have been referred to as a 'privileged structure' because of their excellent binding ability with various receptors. This is the reason why indole derivatives have becomes structural motifis in many pharmaceutical and agrochemical products [2]. As an intercellular signal molecule, indole regulates various aspects of bacterial physiology, including spore formation, resistance to drugs, plasmid stability, bacterial physiology, biofilm formation and virulence [3]. With a few exception, such as those proceeding through functionalization of pyrroles and method that form both rings simultaneously, indole synthesis almost universally involve annelation of the five membered ring to an existing benzene ring bearing the appropriate functionality [4]. Besides medicinal or therapeutic activities., many proteins contain indole skeleton for example; tryptophan an essential aromatic amino acid in the human diet is a component of many structural or enzyme proteins. [5].

Indole is biosynthesized in the shikimate pathway via anthranilate. It is an intermediate in the biosynthesis of tryptophan where it stays inside the tryptophan synthase molecule between the removal 3-phospho- glyceraldehyde and the condensation with serine. When indole is needed in the cell it is usually produced from tryptophan by tryptophanase [6]. The Leimgruber-Batcho indole synthesis is an efficient method of synthesizing indole and substituted indoles. This method is high- yielding and can generate substituted indoles. This method is high- yielding and can generate substituted indoles. This method is especially popular in the pharmaceutical industry, where many pharmaceutical drugs are made up of specifically substituted indoles [7].



FIGURE 1



#### **FIGURE 2 INDOLE**

Polyindole is one of the rising conducting polymers finding application in energy sensors, corrosion protection, and catalysis. Polyindole and its composites of carbon are gaining enormous attention as electrodes in batteries and supercapacitors [8]. Synthesis of nanocomposites using conjugated polymers with metal had drawn much the attention nowadays due to their thermal and electrical properties. Polyindole-based rechargeable batteries have been reported for fast charging and discharging due to high electromotive force together [9]. Polyindole (PIN), a rising conducting polymer, is being explored and developed as a possible candidate for electrochromic devices, sensors, photocatalysis, electrocatalysis, anticorrosion, diodes, supercapacitors, batteries, and biological application [10]. Polyindole-based hybrid composites are being recognized as a promising candidate to be used in energy storage field along with other conjugated organic polymers. Major components affecting performance of polyindole and composites [11] are also studied. The present invention relates to a process for the preparation of polymers based on polyindoles by chemical polymerization of indole which relates to electroconductive compositions and have more applications [12]. Polyindole (PIN) is heteroatomic organic molecule which belongs to the fused-ring family and have emerged in the past several decades as promising materials due to their unique physical and electrochemical properties. Polyindole was successfully synthesized by chemical polymerization of indole [13]. Properties of PIN can be improved by mixing polymer with conducting metals, metal oxide, carbon nanocomposites and other materials. Polyindole nanocomposites (PNCs) were characterized through various spectral, thermal and electrical methods [14]. Polyindole-based hybrid composites are being recognized as a promising candidate to be used in energy storage field along with other conjugated organic polymers. Polyindoles themselves are affected with low electrical and electrochemical conductivity; nevertheless, high redox activity, tunable electrical conductivity, significant thermal stability, slow degradation rate, and possible blending property give them upper hand to be used as a good contender [15]. Synthesis of hybrid material based on polyindole (PIN) nanobrush modified with gold nanoparticles and its application towards electrooxidation of ethanol. For the characterization of PIN–Au composites, scanning electron microscopy and X-ray diffraction analyses were used [16].



FIGURE 3 POLYINDOLE

Chitosan is known as deacetylated chitin, a natural polycationic linear polysaccharide derived from partial deacetylation of chitin. Chitin is the structural element in the exoskeleton of insects, crustaceans is mainly crabs and shrimps, cell wall of fungi etc., The complexity of the chitin structure, difficulty in its extraction and insolubility in aqueous solution. Chitosan is composed of  $\beta$  (1-4)- linked D-glucosamine and N-acetyl-D- glucosamine randomly distributed within the polymer [17]. The cationic nature of chitosan is rather special, as the majority of polysaccharides are usually either neutral or negatively charged in an acidic environment. This property allows it to form electrostatic complexes or multilayer structures with other negatively charged synthetic or natural polymers [18]. The interesting characteristics of chitosan such as biocompatibility, non-toxicity, low allergenicity and biodegradability allow it be used in various application [19]. Besides, chitosan is reported to have biological properties, such as antitumour, antimicrobial and antioxidant activities. The degree of deacetylation which is described by the molar fraction of deacetylated units or percentage of deacetylation and the molecular weight of chitosan were found to affect these properties [20]. For instance it can be used in the water treatment, wound-healing materials, pharmaceutical excipient or drug carrier, obesity treatment and scaffold for tissue engineering. pharmaceutical as well as biomedical application of chitosan and its derivatives and significant development has been achieved [21]. Chitosan is the only polycation in nature and its charge density depends on the degree of acetylation and pH of the media. Chitosan oligomers are soluble over a wide range of pH range from acidic to basic ones. This lack of solubility at neutral and basic pH has hindered the use of chitosan in some application under neutral physiological conditions. This is reason why a great number of chitosan derivatives with enhanced solubility have been synthesized [22].

#### **BIOACTIVITIES OF CHITOSAN**

Many reports have shown that chitosan exhibited antimicrobial activity, but the actual mechanism has not yet been fully elucidated. Low molecular weight chitosan can penetrate bacterial cell walls, binds with the DNA and inhibit DNA transcription and mRNA synthesis while high molecular weight chitosan can bind to the negatively charged components on the bacterial cell wall [23]. It forms an impermeable layer around the cells

and changes cell permeability and blocks transport into the cell. The hydrophilicity and negative charge on the cell surface were higher on gram-negative bacterial cell walls than those of gram-positive bacteria [24]. Thus the gram-negative bacteria showed a stronger interaction with chitosan which result in stronger antibacterial activity against them. It was also reported that the amount of chitosan binding to the bacterial cell wall was dependent on the environment pH value, molecular weight and degree of acetylation of chitosan. Thus antibacterial activity against S. aureus but meager antibacterial activity against E.coli [25].

The effect of molecular weight and degree of acetylation of chitosan on its antifungal activity varies with the fungus. Chitosan was also found to exhibit antifungal activity against several phytopathogenic fungi such as Penicillium sp. in citrus fruit, Botrytis cinerea in cucumber plants [26]. Silver nanoparticles distributed superficially on and internally in chitosan spheres demonstrated as a macro porous feature and could find application such as fungicidal agents [27]. Chitosan and whey proteins chitosan films with quince and cranberry juice added for the potentially useful for increasing the shelf life of apples [28].

Chitosan and its derivatives exhibited antitumor activity in both invitro and in vivo models. The antitumor effect of chitosan derivatives was due to the increase in secretion of interleukin-1 and 2 which was caused maturation and infiltration of cytolytic T-lymphocytes [29]. Chitosan was involved in the direct killing of tumor cells by inducing apoptosis. Chitosan was shown to inhibit adhesion of primary melanoma A375 cells. Carboxymethylated chitosan protected the peripheral nerves and inhibited the apoptosis of cultured Schwann cells [30]. The degree of deacetylation and molecular mass of oligosaccharides, procured from the enzymatic hydrolysis high molecular weight chitosan affected by antitumor activity. [31].

Antioxidant are well- known for their beneficial effects on health. They protect the body against reactive oxygen species which exert oxidative damage to membrane lipids, protein and DNA. It proposed that mechanism is due to the reaction of unstable free radicals with amino and hydroxyl groups on the pyranose ring which can form stable radicals [32].

- Table salt product that contains small amount of chitosan might help lower blood pressure in people with high blood pressure.
- Taking chitosan by mouth while on a calorie restricted diet can improve weight loss in people who are overweight or obese, but only a very small amount.
- Applying a chitosan gel might help prevent scar tissue from forming in the sinuses after surgery [33].

Chitosan and its derivatives are recognized as versatile biomaterials because of their diverse bioactivities, non-toxicity, biocompatibility, biodegradability and low-allergenicity. They have superior physical properties such as high surface area, porosity, tensile strength and conductivity. In addition, they can be easily molded into different shapes and forms (films, fibers, sponges, beads, powder, gel and solutions) [34].

When the fungi are used to produce chitosan the alkaline treatment removes the protein and deacetylates chitin. When the shells of crustaceans are used as source of chitosan two pretreatment are required one to remove traces of organic materials and another to remove the calcium carbonate. Nowadays, there are chemicals and enzymatic methods to produce chitosan [35].

- Chitosan is a biodegradable natural polymer with many advantages such as nontoxicity, biocompatibility and biodegradability.
- It can be applied in many fields especially in medicine.

- As a delivery carrier it has great potential and cannot be compared with other polymers.
- This method is environmentally unfriendly due to the large amount of alkaline waste and organic material [36].



Chitosan ( $\beta$ -1, 4-poly-D-gucosamine)

#### **FIGURE 4 CHITOSAN**

#### **UV SPECTROSCOPY:**

UV- visible spectroscopy is a technique that measures the amount of light absorbed by a chemical substance. It is absorption spectroscopy or reflectance spectroscopy technique within the ultraviolet and visible regions of the electromagnetic spectrum. When continuous radiation is passed through a compound a portion of that compound is absorbed by the compound. The residual radiation after passing through a compound yields a spectrum with gaps in it due to absorption by the compound, this spectrum is called the absorption spectrum. Absorption of UV-Visible radiation results in the electronic transition of the compound. It is a quantitative technique used in the analytical chemistry to measure the amount of light absorbed by a substance. When the light falls upon a substance it absorbs and reflects a certain amount of radiation. The instrumentation of UV-Visible spectroscopy is called a UV-Visible spectrophotometer. The spectrophotometer has a key components namely light source, monochromator, sample area and detector. The UV range normally extends from 100 to 400nm, with the visible range from approximately 400 to 800nm. UV-Visible spectroscopy is used in a wide variety of applications and a UV-Visible spectrophotometer can be found in most laboratories. It can used for determine the purity or concentration of biological samples containing DNA or RNA. It finds application in characterizing the rate of a chemical reaction. Its measurement can be done in a short span of time, helping easy integration into experiments and data analysis is simple and requires less processing. Beer-Lamber Law is only obeyed when a single absorbing species is present in the solution. A sample containing multiple absorbing species cannot be used to determine concentration using absorbance. Micro spectrophotometry is the UV-Visible spectroscopy of microscopic samples, where an optical microscope is fitted with UV-Visible optics [37].



FIGURE 5 UV-SPECTROSCOPY

#### **IR SPECTROSCOPY:**

The IR spectroscopy theory utilizes the concept that molecules tend to absorb specific frequencies of light that are characteristic of the corresponding structure of the molecules. Infrared spectroscopy is the analysis of infrared light interacting with a molecule. This can be analyzed in three ways by measuring absorption, emission, reflection and it is used by chemists to determine functional groups in the molecules. The IR absorption range for covalent bonds is 600-4000cm-1. IR spectrometer consists of three basic components such as radiation source, monochromator and detector. The units of wavenumber used of wavenumber used in IR spectra are reciprocal centimeter spectra with the symbol cm-1. IR radiation consists of electromagnetic waves which oscillate with a frequency of  $3\times1011$  to  $4\times1014$  Hz. The corresponding wavelength range is 103 to  $0.78\mu$ m. IR spectroscopy can be used to analyze the structure and chemical composition of solid such as metals, minerals and polymers. An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis [38].



#### FIGURE 6 IR SPECTROSCOPY

Richard sundberg found that the potent biological activity of several indole derivatives and explains the structure of indole alkaloids. Monograph starts with an overview of the most important types of reactions of the indole ring on a mechanical basis. The author then proceeds to review the methods of synthesizing indoles and describes the oxidations and rearrangements of indole derivatives [39].
Imran Ali was done that among all the evaluated compounds, the chemotype 4chloro-N'-[(1-(2-morpholinoethyl)-1H-indol-3-yl) methylene] benzenesulfonohydrazide (5f) showed promising inhibition of both MCF-7 and MDA-MB-468 cancer cells with the respective IC50 values of 13.2  $\mu$ M and 8.2  $\mu$ M [40].

The aim of the research done by Kaptu, Tolga is to develop new synthetic methodologies leading to the synthesis of new derivatives of pyrimidoindole and quinoline, which have been found to show important biological activities. In this study, an indole derivative was used as a starting compound which was obtained using reaction of Fischer Indole cyclization reaction [41].

Raja Sudha and Shankar discovered by the significant spectral changes of Polyindole and ZnO nanocomposites reveal the strong interaction between Polyindole and ZnO nanoparticles. The structural morphologies of the ZnO, Polyindole, and Polyindole–ZnO are obtained from SEM [42].

P.Rejani and B. Beena is found that Manganese oxide/poly indole (Mn2O3/PIND) hybrid structures have been investigated for their optical properties. Mn<sub>2</sub>O<sub>3</sub> nanoparticles prepared by the sol-gel method and characterized by XRD, Scanning Electron Microscope (SEM). [43].

Siti suri Archad discovered Chitosan (CS) is a cationic polymer whereas saponin (SP) is classified as glycoside. In this study, a spherically-shaped CS-SP nanoparticle was synthesized and characterized [44].

Murat yanat, is found that properties of chitosan NPs can be tuned in such a way that they can serve as reinforcement elements in biodegradable plastics leading to much-needed improvements, and also as functional elements that make the application in food packaging with e.g., enhanced antimicrobial activity possible [45].

A.M. safer is done by chitosan nanoparticles are shaped into several pathways. The purpose of this article is to provide an overview of its antiviral application as a nanocarrier for antiviral medications, highlighting the benefits, limitations, and downsides. In this review, we will report the most recent COVID-19 vaccination advances [46].

Sunil Kumar discovered the indole derivatives have diverse biological activities and also behave an immeasurable potential to be explored for newer therapeutic possibilities as indole, Antiviral, Anti-inflammatory, Anticancer, Antimicrobial [47].

Indole based derivatives have potential as antibacterial against methicillin resistant slaphylococcus aureus. Indole derivatives constitute an important class of therapeutic agents in medicinal chemistry. It is used as dyes, pigments, plastics, fungicides, vitamin supplement, flavor enhances and perfumery. Indole is often described as having a sweet and floral odor typical as jasmine flowers. It also contributes to the flavor of food and aroma of perfumes. Therefore it is used as flavor enhancer and fragrance in the food and cosmetics industries. Indole containing compounds are the best used for their medicinal properties in the pharmaceutical industry. Although to a lesser degree the indole motif none the less appears in many significant products across the entire chemical industry. It promotes health outcomes in intestinal epithelial cells in human and rodents by preventing colitis induced by dextran sulphate sodium. Polyindole could be used in the manufacture of synthetic industrial materials in the commercial production of plastic, elastomers, man-made fibers, adhesives and surface coatings. A tremendous variety of polymers are used which is mainly used for the batteries, sensors, electrocatalysis, supercapacitors and anticorrosion. It is currently only a natural biopolymer to have a electrostatic charge which provide its bacteriostatic and

flocculating properties. It can be used in industries to replace the petrochemical based plastics. Polyindole based nanocomposites exhibit outstanding antimicrobial properties because of its promising capability to generate ROS and also used as drug delivery to improve absorption and it can effectively inhibit the microbial growth. Chitosan and its derived nanoparticles can be used as carrier materials for nano delivery systems and have many biomedical industry such as drug delivery, vaccine delivery, antibacterial agent and wound healing. Chitosan is a biodegradable natural polymer such as non-toxicity, biocompatibility. It can be applied in many fields, especially in medicine industry [48].

## **OBJECTIVES**

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- To synthesis the Polyindole chitosan composite
- To characterize its structure by IR and UV
- To study the adsorption studies as application

## **EXPERIMENTAL METHOD**

#### **EXPERIMENTAL METHOD**

#### **CHEMICALS REQUIRED:**

- Indole of analytical grade was purchased from Siscoo Research Laboratories private limited.
- > Potassium persulphate was from Isochem Laboratories Angamaly, Kochi.
- > EDTA was purchased from Edayar Kochi.
- > Zinc sulphate and Lead nitrate was purchased from Edayar, Kochi.
- > Hexamine was purchased from Isochem Laboratories Angamaly, Kochi.
- > Xylenol orange was purchased from Kochi.

#### **PROCEDURE:**

About 2g of indole is accurately weighed in a beaker, to this 10ml of alcohol is added and diluted to100ml. The above mixture is stirred for about 10 minutes using a magnetic stirrer. About 0.2g of chitosan is added and stirred it for 20 minutes. 2g of potassium persulphate dissolved in 50ml of water is added drop by drop. The colour changes after addition of potassium persulphate and stirred for 3 hours and kept in refrigerator for 24 hours. Now the solution is filtered at the suction pump using Whatman filter paper. The precipitate is kept at room temperature and dried it for a week and the yield is collected. Adsorption studies are carried out by standardizing the polyindole by complexometric titration using standard Zinc sulphate solution.

a) Preparation of standard zinc sulphate solution:

A standard solution of about 0.01M zinc sulphate solution was prepared in a 100ml in a standard measuring flask using distilled water. The solution is shaken well for uniform concentration.

b) Preparation of disodium salt of ethylene diamine tetra acetic acid solution:

A disodium salt of ethylene diamine tetra acetic acid solution of 0.01M was prepared in a 100ml standard measuring flask using distilled water. Then solution is shaken well for uniform concentration.

c) Adsorption:

About 0.01g of Polyindole composite was taken and mixed with 10ml of 0.01M zinc sulphate solution. It was kept in a magnetic stirrer for about 30 minutes. It kept aside for 10 minutes. Then the solution was filtered.

d) Estimation of adsorbed zinc using filtration:

The filterate solution after adsorption was taken in a conical flask. About 5ml of ammonium hydroxide buffer of pH 10 was added. A pinch of Erichrome black T indicator is added and titrated against EDTA taken in a burette. The end point is colour change from wine red to blue. The reading is noted.

21

Adsorption studies are carried out by standardizing the polyindole by complexometric titration using standard Lead nitrate solution.

a) Preparation of standard lead nitrate solution:

A standard solution of about 0.01M lead nitrate solution was prepared in a 100ml in a standard measuring flask using distilled water. The solution is shaken well for uniform concentration.

b) Preparation of disodium salt of ethylene diamine tetra acetic acid solution:

A disodium salt of ethylene diamine tetra acetic acid solution of 0.01M was prepared in 100ml standard measuring flask using distilled water. The solution is shaken well for uniform concentration.

c) Adsorption:

About 0.01g of polyindole composite was taken and mixed with 10ml of 0.01M of lead nitrate solution. It was kept in magnetic stirrer for about 30 minutes and kept as such for 10 minutes. Then solution is filtered.

d) Estimation of adsorbed lead nitrate using filtration:

The filterate solution is taken in a conical flask and 0.25g of hexamine buffer is added. Add 2 drops of xylenol orange indicator is added and titrated against EDTA taken in the burette. The end point is colour change from red to lemon yellow and the readings are noted.

#### **UV Spectral analysis:**

UV-Visible spectra were recorded using Jasco V-630 spectrophotometer for the Polyindole /Chitosan composite solution in the range of 200-900nm.

#### **FT-IR Spectral analysis:**

FT-IR spectra were recorded for Polyindole/Chitosan composite using Nicolet Si5 spectrometer using KBr pellets in the range of 4000-500nm.

# **RESULTS AND DISCUSSION**

#### **RESULTS AND DISCUSSION**

#### **UV-Visible Spectra analysis**

The UV-visible spectrum noted for the poly-indole is shown in Figure 1. The percentage absorption is higher on the lower wavelength side which is witnessed from the plot. The UV-visible spectrum of the prepared material shows absorption in the region of 220-300 nm [49]. The two different absorption peaks at 228 and 278 nm developed due to extensive chain length spreading of polymer. Band gap energy (E gap) values were obtained by linear regression of the absorption slope by extrapolating the tangent to the energy [(E = 1240.81/ $\lambda$ ) versus absorption curve. Polyindole displays a peak at 278 nm, which is because of  $\pi$ - $\pi$ \* transition. The band gap energy of polyindole value was found to be 4.4 Ev, which is a characteristic band of polyindole peak [50].



FIGURE 7 UV SPECTRA OF INDOLE CHITOSAN COMPOSITE

#### **FT-IR** spectra studies

The FT-IR spectrum recorded for the poly-indole is shown in Figure 2. The sharp band at 740 cm-1 is due to the characteristic out-of-plane deformation of the C-H bond in the benzene ring in indole molecule. The band at 1304 cm-1signifies the heterocyclic ring stretching modes and 1401 cm-1ascribed to characteristic stretching mode of benzene ring in polyindole [51]. The band present at 1701 cm-1 are attributed to -C-C- stretching modes and is also indicative of highly conductive nature of polyindole. The major band appears at 3390cm-1 indicates N-H stretching. The sharp band appears at about 3117 cm-1 for the bonded N-H stretch is absent, indicated a participation of nitrogen in polymerization which is a typical characteristic band of polyindole peak [52].



FIGURE 8 IR SPECTRA OF INDOLE CHITOSAN COMPOSITE

#### **ADSORPTION STUDIES:**

i) The amount of ZnSO<sub>4</sub> present is 0.00281g per mL. Hence in titration method we obtain 0.0466g of ZnSO<sub>4</sub> is present which corresponds to the titre value of 16.6ml.
161.47g of ZnSO<sub>4</sub> contains 65.38g of Zn, 0.0502g of ZnSO<sub>4</sub> contains, 0.018g of Zn

ii) The amount of PbNO<sub>3</sub> present is 0.0033g per mL. Hence in titration method we obtain 0.0558g of PbNO<sub>3</sub> is present which corresponds to the titre value of 16.9ml. **331.2g of PbNO<sub>3</sub> contains 207.2 g of Lead** 0.0558g of PbNO<sub>3</sub> contains, 0.034g of Pb



#### FIGURE 9 ADSORPTION ACTIVITY OF POLYINDOLE USING CHITOSAN

# CONCLUSION

#### **CONCLUSION:**

Indole is an aromatic heterocyclic organic compound with the molecular formula C<sub>8</sub>H<sub>7</sub>N. In the present study polyindole was synthesized in the presence of chitosan and the resulting biopolymer was characterized by various analytical techniques such as UV and IR. The adsorption behavior of polyindole for Zn and Pb was discussed under various conditions. The maximum adsorption capacities of Zn and Pb on polyindole were 16.6ml and 16.9ml respectively at pH 10 and 25°C. The Polyindole chitosan composite suggested that technologies capable of removing particles within the colloidal fraction have good potential to enhance metals removal from waste water.

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## Synthesis and Characterization of Polyindole Bovine Serum Albumin composite

Project in chemistry

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St. Mary's College (Autonomous), Thoothukudi (Re-accrediated by 'A<sup>+</sup>' Grade by NAAC) Thoothukudi- 628001. 2022-2023

i

### DECLARATION

We hearby declare that the project entitled "Synthesis and Characterization of Polyindole Bovine Serum Albumin composite" submitted to St. Mary's college (Autonomous), Thoothukudi, affiliated to Manonmaniam Sundaranar University, for the Degree of Bachelor of science is our original work and that, it has not previously formed the basis for the award of any Degree, Diploma or similar title.

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April 2023 Thoothukudi

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II

### CERTIFICATE

This is to certify that the report of the project in chemistry entitled "Synthesis and Characterization of Polyindole Bovine Serum Albumin composite" is submitted to St. Mary's College (Autonomous), Thoothukudi in partial fulfilment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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## ACKNOWLEDGEMENT

We express our first and fervent thanks to GOD ALMIGHTY for giving an opportunity to devote ourself for this work.

We would like to deeply express our sincere thanks to the secretary for providing infra structural facilities. We thank our principal Rev. Dr. Sr. A. S. J. Lucia Rose and our Head of the Department Mrs. Rani Jeyamary for providing us necessary arrangements for the successful completion of our project. We thank all other faculty members of the department for their encouragement and support.

We wish to express our heartfelt thanks to our guide Dr. A. Parveen Sulthana for her valuable suggestions, gentle guidance, enthusiastic ideas, to carry out and complete our work perfectly. We thank Dr. C.Vedhi, Assistant Professor, Department of Chemistry, V.O. Chidambaram College, Thoothukudi for rendering his valuable helped to analyze UV and IR spectral data.

Our sincere thanks to the non teaching staff of the department for their timely help.

We express our love and gratitude to our friends and our family for the encouragement given to us.

iv

Synthesis and Characterization of Polyindole Bovine Serum Albumin composite

T		
S.No	Title	Page No
1	Abstract	1
2	Introduction	3
3	Objectives	12
4	Experimental part	14
5	Result and Discussion	19
6	Conclusion	23
7	Reference	25

V

# ABSTRACT

#### Abstract :

Biopolymer is prepared by using Indole3-aceticacid with composite protein. Indole has a bicyclic structure, consisting of a six-membered ring fused to a five-membered nitrogen-containing pyrrole ring benzene. It is widely distributed in the natural environment and can be produced by variety of bacteria. In the present study the indole is polymerized by using 2g of indole-3-aceticacid dissolved in 100ml of water and addition of alcohol with constant stirring using magnetic stirrer. After 30 minutes potassium persulphate in water is added, the colour change taskes place. The mixture is kept in refrigerator for 24 hours and centrifuged. About 2g of centrifugate 10 ml of alcohol is added and dissolved in 100ml of water. 0.2g of Bovine Serum Albumin is added and placed in magnetic stirrer. After 30 minutes 2g of potassium persulphate is dissolved in 50 ml of water and added, the colour change takes place. After 3 hours the mixture is placed in a refrigerator for 24 hours. Then the precipitate is filtered and collected. Using titration method we have studied the adsorption of the polyindole using zinc and lead. The titration is done against EDTA using Eriochrome black-T as a indicator and using buffer. Hence we conclude that polyindole has a adsorption property in titration method.

# INTRODUCTION

#### **INTRODUCTION**

Indole is an aromatic, heterocyclic, organic compound with the formula  $C_8H_7N$ . It has a bicyclic structure, consisting of a six-membered ring fused to a fivemembered nitrogen-containing pyrrole ring[1]. Indole is widely distributed in the natural environment and can be produced by variety of bacteria. Some of the indole derivatives are known to play an important role in the vital activity of human and animals, namely the amino acid tryptophan [2]. The synthesis of indole derivatives due to the possibilities for the design of polycyclic structures by the incorporation of multiple heterocyclic scaffolds in an attempt to achieve chemical and biomedical relevance[3]. Indole is a solid at room temperature. It occurs naturally in human faeces and has an intense faecal odour. At very low concentrations, however, it has flowery smell, and is a constituent of many perfumes. Indole is a popular component of fragrances and the precursor to many pharmaceuticals. It also occurs in coal tar[4]. Indole is also known as benzopyrrole which contains benzenoid nucleus and has 10  $\pi$ -electrons (two from lone pair on nitrogen and double bonds provide eight electrons) which makes them aromatic in nature. Similar to the benzene ring, electrophilic substitution occurs readily on indole due to excessive  $\pi$ -electrons delocalization [5].

Indole is an important heterocyclic system that provides the skeleton to lysergic acid diethylamide (LSD), strychnine, and alkaloid obtained from plants. Physically, they are crystalline colorless in nature with specific odours. The addition of the indole nucleus to medicinal compounds that is biologically active pharmacophore made it an important heterocyclic compound having broad-spectrum of biological activities [6]. Due to this, researchers took interest to synthesize various scaffolds of indole for screening different pharmacological activities. Various natural compounds contain indole as parent nucleus for example tryptophan. Indole-3-acetic acid is a plant hormone produced by the degradation of tryptophan in higher plants. Derivatives of indole are of wide interest because of their diverse biological and clinical applications[7].



**Figure:1.1 Structure of Indole** 

Polyindole is synthesized from indole through chemical polymerization. It is a polymer of indole monomer, which has a fused aromatic molecular structure considering of a five-membered nitrogen containing pyrrole ring a six- membered benzene ring.

Conducting polymers are considered to be conducting in nature attributed to their rapid redox process which offers pseudo capacitance to be stored. However, these conducting polymers posses variability in their supercapacitor conductance as they swing in between their two forms, i.e.,conduction and insulation[8]. Polyindole based aqueous polymer, rechargeable battery has high electromotive force together with a high cycle property and it is capable of fast charging and discharging. The polymeric compound uses protons as charge carriers. The conductivity of a polymer can be improved greatly by doping with other ions[9].



Figure:1.2 Structure of Polyindole

Proteins are the most abundant and diverse from a functional point of view. From the hormones and enzymes that control metabolism, the framework forming collagen in bones, the contractile proteins in muscles, to the haemoglobin and albumin in the bloodstream and immunoglobulins fights infections, almost every life process relies on this class of molecules. Albumin is the most abundant protein in the vertebrate organisms (up to 40mg/ml) and the most prominent plasma protein (about 60% of the total protein content of plasma). It is one of the first discovered and most intensely studied proteins[10].

The BSA molecule consists of 583 amino acids, bounds in a single chain crosslinked with 17 cystine residues. Albumins are a group of acidic proteins which occurs plentifully in the body fluids and tissues of mammals and in some plant seeds. Bovine serum albumin (BSA) is a single polypeptide chain consisting of 583 amino acid residues, without carbohydrates[11]. When approaching the evaluation of small molecules affinity for albumins, bovine serum albumin(BSA) is usually selected as a relevant model, due to its structural similarity with human serum albumin(76%), its low cost and wide availability[12]. Serum albumin is conceived by the lives and soluble in water[13]. BSA nanoparticles can be prepared by three major methods including desolvation, emulsification, thermal gelation and recently nano spray drying, nab-technology and self-assembly techniques have also been used[14]. BSA is also used as a nutrient in cell and microbial culture. Bovine serum albumin (BSA) has been widely applied in drug delivery due to its low cost and tolerance, and simple preparation [15].

In the recent years, bioinorganic chemistry has provided numerous examples of structures with high affinity towards biomolecules, including nucleic acids and proteins, and showing real potential to be developed into therapeutic agents, fighting bacterial, viral and/or fungal infections targeting different types of tumours radiopharmaceuticals and superoxide dismutase and insulin mimics[16].



#### **Figure 1.3 structure of Bovine serum albumin**

The BSA interaction and binding ability of a large variety of mononuclear and polynuclear  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Pt^{2+}$  complexes with aromatic ligands (some of them bearing known pharmacologically active moieties) has been investigated [17]. Coordination compounds exhibit unique properties offering interesting opportunities in designing new pharmacologically active molecules, such as

adjustable ligand kinetics and redox activity and a large variety of geometries and coordination numbers offered by metal ions, resulting in high structural diversity [18]. As in the case of the interaction of metal complexes with other classes of biomolecules, it has been suggested that the planarity of the ligands coordinating the metal centre plays an important role in enhancing protein binding ability[19]. An interaction between BSA and metal complexes often leads to a perturbation of the secondary structure of the protein, by disrupting the disulfide bonds and leading to a partial loss of  $\alpha$ -helix conformation with the subsequent unfolding of the protein [20].

Paulo A.F.Pacheco and Maria M.M.Santos provide an overview of the indole-based compounds developed against important parasitic disease, namely malaria,trypanosomiasis and leishmaniasis, by focusing on the design, optimization and synthesis of the most revelant synthetic indole scaffolds recently reported. A concrete example is the spiroindolonecipargamin(91), an inhibitor of the plasmodium falciparum p-type ATPase, which has successfully completed phase II studies for malaria treatment.[21]

Ramitsingla, Arvind Negi, Virendrasingh showed that naturally occurring indole alkaloids were isolated and evaluated against different cancer cell lines where they revealed commendable anticancer activity. The indole scaffold is so versatile that it has shown diverse activities against the different targets in cancer[22].

Ming-zhi-zhang, Qiongcheng, Guang Fu-yang focused on the recent development of indole derivatives as anti-viral agents, drugs on market or compounds in clinical trials and promote the ideas of indole macrocycle and Bis(Tris) indole as novel lead structure might be exploited in the future[23].

Prakash Chhattise provide synthese of biologically active 3,3'arylmethylene bis-1-H indoles using polyindole as a heterogeneous catalyst has been

8

reported. The present protocol offers several advantages like short reaction time, high yield of the desired products, reusability of the catalyst, simple workup procedure and minimal use of toxic and hazardous chemicals compared to the traditional method of synthesis[24].

G. Rajasudha, P. Thangadurai, N. Boukos, V. Narayanan & A. Stephen lay out that Polyindole nanocomposite containing ZnO has been prepared by polymerization with different monomer concentrations. IR spectral measurements allow us to conclude that polymer nanocomposites has formed and also there is intermolecular interaction between the polyindole and ZnO nanoparticles[25].

Neeraj Gupta and Goyal found out that strong efforts to invent new catalysts. The combination of all strategies, in conjuction with other water mediated methologies, can deliver the libraries of indoles in water. Applying these routes to tryptophan derivatives will open up a way for the modification of amino acids through modification of indole nucleus in water[26].

Anjitha Thadathil, Hareesh Pradeep provided that the applications of polyindoles based nanocomposites remediates environmental problems to the tip of the iceberg. 3D materials and dendrimers support selectively and enhanced in mass transfer. Polyindole with nanobelts, nanorod, nanowire and nanofibers can able provide higher surface area, improved conductivities, continuous charge transfer compared to nanospheres[27].

Tlabo Caiphus Leboho provide one of the main groups of organic compounds containing nitrogen in both cyclic systems and straight chains in the alkaloids. Indole is perhaps the single most common hererocycle in all of chemistry and it is embodied in a myriad of natural products, pharmaceutical agents and a growing list of polymers[28].

9
Harish Mudila, M. G. H. Zaidi-Amit Kumar provide on Polyindolebased hybrid composites are being recognized as a promising candidate to be used in energy storage feld along with other conjugated organic polymers. Polyindoles themselves are affected with low electrical and electrochemical conductivity[29]

K. Giribabu, R. Manigandan, R. Suresh, L. Vijayalakshmi, A. Stephen, V. Narayanan work on Polyindole nanowires were synthesiszed by oxidative polymerization of indole using ammonium persulphate as oxidant. The structure of polyindole nanowires was confirmed by XRD, FT-IR spectroscopy[30].

Indole belongs to the top 10 of the most important organic chemistry scaffolds included in biochemicals, dyes, drugs, natural products, materials and agro chemicals. Indoles may promote good health and are being studied in the prevention of certain types of cancer, including breast cancer, prostate cancer and colon cancer. It is associated with several health benefits including arthritis relief, improved skin health, and bone loss prevention. It posses various biological activities, (i.e) antiviral, anti-inflammatory, anti cancer, anti HIV, anti oxidant, antimicrobial. Polyindole revealed that they could be used as promising candidates for applications such as supercapacitor, batteries, electrochromic devices, sensors, electrocatalysis, catalysis and anticorrosion. Smart polymeric system have extensively contributed to the agricultural industry by increasing the efficiency of pesticides, herbicides and fertilizers by facilitating controlled release systems and therefore, enabling lower doses to be used. A number of indole derivatives have important cellular functions, including neurotransmitters such as Serotonin. The antioxidant properties of BSA protein can also reduce cellular stress and damage.

# **OBJECTIVES**

### **OBJECTIVES :**

To synthesize the biopolymer using indole and bovine serum albumin composite.

To study the formation of polyindole composite using UV-visible spectroscopy and by infrared spectroscopy.

To study the adsorption property of the composite using EDTA titration method.

### **EXPERIMENTAL PART**

### **EXPERIMENTAL PART :**

### **Chemicals required :**

- Indole-3-acetic acid was purchased from Sisoo Research Laboratories.
- Potassium persulphate was purchased from Isochem laboratories
   Angamaly,Kochi
- ✤ Zinc sulphate was purchased from Edayar -Cochin.
- Lead Nitrate was purchased from Edayar-Cochin.
- Hexammine was purchased from isochore laboratories Angamaly ,kochi.
- Xylenol orange from Cochin. Bovine serum albumin was purchased from Angamaly, Kochi.

### Synthesis of Poly Indole :

### **Procedure:**

About 2g of Indole is taken in a 250 ml beaker. To this 10 ml of alcohol is added and dissolved in 100 ml of water. It is then placed in magnetic stirrer. After 30 minutes 2g of Potassium persulphate in 50ml of water is then added drop by drop the colour change takes place. After 3 hours the mixture is placed in a refrigerator for 24 hours. It is then filtered at the suction pump and washed with water and dried using filter paper.

### Synthesis of Poly Indole with Bovine serum albumin composite:

About 2g of Indole is taken in a 250ml beaker. To this 10ml of alcohol is added and dissolve in 100ml of water. About 0.2g of Bovine serum albumin is weighed and added. It is then placed in a magnetic stirrer. After 30 minutes 2g of Potassium persulphate is added drop by drop the colour change takes place. After 3 hours the mixture is placed in a refrigerator for 24 hours. It is then filtered at the suction pump and washed with water and dried using filter paper.

### **CHARACTERIZATION METHODS:**

### **UV-Visible Spectroscopy:**

UV-Visible Spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or bank sample. It is very useful to measure the number of conjugated double bonds and also aromatic conjugation within the various molecules. It is also distinguishes between conjugated and non conjugated systems; homoannular and Heteroannular conjugated dienes etc. For visible and ultra-violet spectrum, electronic excitations occurs in , the range of 200-800nm and involves the promotions of electrons to the higher energy molecular orbital.

### **IR Spectroscopy :**

Infra-red spectrum is an important record which gives sufficient information about the structure of compound. Unlike ultraviolet spectrum which comprises of relatively few peaks, this technique provides a spectrum containing a large numer of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of infra-red radiations(quantised) causes the various bands in a molecule to stretch and bend with respect to one another. An IR spectrum can be visualized in a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency, wavenumber or wavelength on the horizontal axis. IR-spectroscopy has been successfully used in analysis and identification of pigments in paintings and other art objects such as illuminated manuscripts.

### **Adsorption studies:**

### **Using Zinc Sulphate:**

#### i) Preparation of Standard Zinc Sulphate Solution:

A standard solution of about 0.01M Zinc Sulphate solution was prepared in a 100 mL standard measuring flask using distilled water and shaken for uniform concentration.

### **Using Lead Nitrate:**

### i) Preparation of Standard Lead Nitrate Solution:

A standard solution of about 0.01M Lead Nitrate solution was prepared in a 100mL standard measuring flask using distilled water and shaken for uniform concentration.

### ii) Preparation of disodium salt of ethylene diamine tetra acetic acid solution:

About 0.01M of Disodium salt of ethylene diamine tetra acetic acid solution was prepared in a 100ml standard measuring flask using distilled water.

### iii) Adsorption:

About 0.01g of polyindole composite was taken and mixed with 10ml of 0.01M Zinc Sulphate solution. It was then stirred in a magnetic stirrer for about 30 minutes and kept aside for 10 minutes. Then the solution was then filtered using filter paper.

### iv) Estimation of adsorbed Lead using titration:

The filtered solution after adsorption was taken in a conical flask and 1.2g of hexamine buffer of pH 4.8 was added. A pinch of xylene orange indicator was added and titrated against EDTA taken in the burette. The end point was the colour change from wine red to pale yellow. Burette reading was noted.

### **RESULTS AND DISCUSSION**

### **Results and Discussion:**

### **UV-Visible spectral analysis:**

Two peaks correspondingly at 295nm and 420 nm are seen in U.V spectra. The absorption peak at 220 to 300 nm [31] corresponds for polyindole and the peak at 292 nm is due to the  $\pi$ - $\pi$ <sup>\*</sup> transition in the aromatic ring [32]. U.V- Visible spectrum of polyindole with bovine serum albumin composite is given in figure 1.4.



Figure 1.4 UV-Visible spectra of indole protein composite

### **IR-Spectral studies:**

In IR spectra the peak at 1456 cm<sup>-1</sup> is due to characteristic stretching mode of benzene ring in polyindole. Due to stretching vibration of OH groups the band appears in 3600-3000cm<sup>-1</sup> region. The peak at 1110 cm<sup>-1</sup> is due to the C-N stretching mode of the polyindole ring. Due to the C-H stretching of the benzene ring a peak is seen at 740cm<sup>-1</sup> is which is not involved in polymerisation[33]. The IR-spectra of polyindole with bovine serum albumin composite is given in figure 1.5.



Figure 1.5 IR spectra of indole protein composite

### **Adsorption studies:**

i) The amount of ZnSO<sub>4</sub> present is 0.00281g per mL. Hence in titration method we obtain 0.0502g of ZnSO<sub>4</sub> is present which corresponds to the titre value of 17.9ml.
161.47g of ZnSO<sub>4</sub> contains 65.38g of Zn, 0.0502g of ZnSO<sub>4</sub> contains, 0.0203g of Zn Ii) The amount of PbNO<sub>3</sub> present is 0.0033g per mL. Hence in titration method

we obtain 0.0544g of PbNO<sub>3</sub> is present which corresponds to the titre value of 16.5ml. **331.2g of PbNO<sub>3</sub> contains 207.2 g of Lead** 0.0544g of PbNO<sub>3</sub> contains, 0.0340g of Pb



Figure 1.6 Adsorption of Zinc and Lead in the composite

# CONCLUSION

### **CONCLUSION:**

Polyindole- Protein composite was prepared by the polymerization of indole with Bovine serum albumin protein in the presence of oxidizing agent. The synthesized composite has very good adsorption property and it adsorbed zinc and lead ions from the salt solution. This study can be further extended to other metals also and this composite can be used for the purification of dirty water.

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### SILVER NANOPARTICLES LOADED ON SEA SHELL USING Alkanna tinctoria BARK EXTRACT AND ITS APPLICATIONS

Project in Chemistry Submitted to St.Mary's college (Autonomous) in partial ulfillment for the award of the Degree of **Bachelor of Science** in Chemistry Project done by **PON SHANTHINI . R SHALINI . M SPINOLA ROMY . A** 



St.Mary's college (Autonomous) (Re-acceredited with 'A+' Grade by NAAC) Thoothukudi-628001

### DECLARATION

We hereby declare that the project entitled "SILVER NANOPARTICLES LOADED ON SEASHELL USING Alkanna tinctoriaBARK EXTRACT AND ITS APPLICATIONS" submitted to St. Mary's College (Automonous), Thoothukudi affiliated to Manonmaniam Sundarnar University for the Degree of Bachelor of science is our original work and that it has not previously formed the basis for the award of any degree, Diploma or Similar title.

R. Pon Sh PonShanthini .R Shalini M

Shalini . M

A. grinola Romy Spinola Romy. A

April, 2023

Thoothukudi

### CERTIFICATE

This is to certify that the report of the project in chemistry entitled "SILVER NANOPARTICLES LOADED ON SEA SHELL SURFACE USING Alkanna tinctoria BARK EXTRACT AND ITS APPLICATIONS" is submitted to St. Mary's College (Autonomous), in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 202-2023.

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### ACKNOWLEDGEMENT

In the accomplishment of this project successful, many people have best owned upon us their blessings and the heart pledged support. We thank all the people who have been concerned with this project.

Primarily we would thank God for being able to complete this project with success. We express our thanks to our secretary **Sr.C. Shibana** for supporting us to finish the project. Then we would like to thank our principal **Dr. A.S.J. Lucia Rose**,

St. Mary's College (Autonomous), Thoothukudi for providing the facilities to carry out this project successfully. We would also like thank our HOD **Ms. Rani Jeyamary,** Associate Professor, Department of Chemistry, St. Mary's College (Autonomous), Thoothukudi.

We would like to express our special thanks of gratitude to our guide **Dr. G . Amala Jothi Grace,** Assistant Professor, Department of Chemistry, St. Mary's College (Autonomous), Tuticorin for their able guidance and support in completing my project.

Our sincere thanks to the **TEACHING** and **NON-TEACHING STAFF** of the department for their timely help.

### CONTENTS

CHAPTER	TITLE	PAGE NO
NO.		
CHAPTER I	INTRODUCTION	
1.1	ADVANTAGES OF	
	NANOPARTICLES.	
1.2	DISADVANTAGES OF	
	NANOTECHNOLOGY	
1.3	GREEN SYNTHESIS OF AGNPS	
1.4	ALKANA TINCTORIUS ROOT	
1.5	MARMOROFUSSUS	
	NICOBACTERIUM	
1.6	ANTIBACTERIAL ACTION OF AGNPS	
1.7	ANTIFUNGAL ACTION OF AGNPS	
1.8	DPPH	
1.9	HYDROGEN PEROXIDE	
CHAPTER II	STATE THE ART & SCOPE OF	
	WORK	
2.1	LITERATURE SURVEY	

2.2	SCOPE OF THE WORK	
2.3	OBJECTIVES OF THE WORK	
CHAPTER III	MATERIALS AND METHODS	
3.1	MATERIALS REQUIRED	

3.2	PROCEDURE	
3.3	METHODS	
3.3.1	UV SPECTROSCOPY	
3.3.2	INFRARED SPECTROSCOPY	
3.3.3	ATOMIC FORCE SPECTROSCOPY	
3.3.4	SACNNING ELECTRON	
	MICROSCOPT	
CHAPTER IV	RESULTS AND DISCUSSION	
4.1	CHARACTERISTICS OF	
	NANOPARTICLES	
4.1.1	ULTRA VIOLET SPECTRASCOPY	
4.2	ATOMIC FORCE MICROSCOPY	
4.3	APPLICATIONS OF SILVER NANOPARTICLES	
4.4	ANTIBACTERIAL ACTIVITY	

4.5	AGAR WELL DIFFUSION METHOD	
4.6	RESULTS	
4.7	ANTIFUNGAL ACTIVITY	
4.8	AGAR WELL DIFFUSION METHOD	
4.8.1	RESULTS	
4.9	HYDROGENPEROXIDESCAVENGING ASSAY	

### LIST OF TABLES

Table number	Contents	page number
4.1	SD Means of zone of inhibition obtained by sample G,H against Staphylococuss aurens and Pseudomonas aeruigunosa	
4.2	SD Means of zone of inhibition obtained by Asperigillus niger	
4.3	Absorbance of Silver nano particles at various concentration	
4.4	Percentage of inhibitions of synthesised the silver nano particles	
4.5	IC50 Value of tested sample:63.09 /ml	
4.6	Absorbance of silver nano particles at various concentration	
4.7	Percentage of inhibition of synthesised Silver nano particles	
4.8	IC50 Value of tested sample:69:39 /ml	

### LIST OF FIGURES

Figure number	Contents	Page number
1.5	Marmorofususnicobaricus	
3.1	Bark extract	
3.2	Residue from Alkana Tinctoria	
3.3	Residue from Alkana Tinctoria and Marmorofus Nicobaricus	
3.5	UV spectrometer	
3.6	IR spectrometer	
3.7	Atomic Force Microscopy	
3.8	Scanning Electron Microscopy	
4.1	UV Spectra of silver nano particles using Alkana tinctoria	
4.2	UV Spectra of silver nano particles using Alkana tinctoria and Marmorfusus Nicobaricus	
4.3	IR Spectra image ofsilver nano particles using Alkana tinctoria	
4.4	IR Spectra image of Silver nano particles using Alkana Tinctoria and Marmorfusus Nicobaricus	
4.5	Atomic Force Microscopy of silver nano particles using Alkana tinctoria	
4.6	Atomic force microscopy of silver nano particles using	

	alka noting toria and Marmofuses Nicobaricus	
4.11	Effect of sample G against Aspergillus niger	
4.12	Effec tof sample H against Aspergillus niger	
4.15	Hydrogen Peroxide Scavenging Assay G	
4.16	Concentration versus OD 2.30nm	
4.18	Hydrogen Peroxide Scavenging Assay H	

# **CHAPTER I**

## INTRODUCTION

### **1. INTRODUCTION**

The fabricated objects, ranging in size from 1 to 100 nm, are called nanoparticles. The global applications of metal nanoparticles are due to their myriad aberrant properties. Being the smallest particle of a bulk object, nanoparticles manifest enhanced properties as more atoms are present on their surfaces, with less coordination than the bulk material [1].

Nanotechnology has unlocked new opportunities in diverse sectorssuch as food packaging, the environment, animal husbandry, agriculture and healthcare, making it one of the most fascinating industrial phenomena of the modern era. It is an emerging tool with which to address the challenges of making technology more sustainable and eco-friendly, with an increasing range of application [2]. Silver nanoparticles have been widely used for antimicrobial, anticoagulant, anticancer, orthopedic and thrombolytic purposes and in drug delivery, medical devices, sensing and diagnostics, etc. The importance of AgNPs is due to their catalytic activity, optical and thermal properties, chemical stability, thermal stability and antimicrobial activity [3].

### 1.1Advantages of nanoparticles

To enumerate the advantages and disadvantages of nanotechnology, let us first run through the good things this technology brings:

- (i) Nanotechnology can actually revolutionize a lot of electronic products, procedures, and applications. The areas that benefit from the continued development of nanotechnology when it comes to electronic products include nano transistors, nano diodes, OLED, plasma displays, quantum computers, and many more.
- (ii) Nanotechnology can also benefit the energy sector. The development of more effective energy-producing, energy-absorbing, and energy storage products in smaller and more

efficient devices is possible with this technology. Such items like batteries, fuel cells, and solar cells can be built smaller but can be made to be more

effective with this technology.

- (iii)Another industry that can benefit from nanotechnology is the manufacturing sector that will need materials like nanotubes, aerogels, nano particles, and other similar items to produce their products with. These materials are often stronger, more durable, and lighter than those that are not produced with the help of nanotechnology.
- (iv)In the medical world, nanotechnology is also seen as a boon since these can help with creating what is called smart drugs. These help cure people faster and without the side effects that other traditional drugs have. You will also find that the research of nanotechnology in medicine is now focusing on areas like tissue regeneration, bone repair, immunity and even cures for such ailments like cancer, diabetes, and other life threatening diseases.

### **1.3 Green Synthesis of AgNPs**

Nanoparticles can be produced by physical, chemical and biological methods. Physical and chemical methods of synthesis pose a threat to environment due to the use of reducing and stabilizing agents that are known to be both toxic and non – biodegradable. Alternatively, biological synthesis or 'GREEN SYNTHESIS' of nanoparticles is considered a novel approach due to its numerous advantages such as eco-friendly nature, ease of production, feasible large scale synthesis and lack of requirement of harmful chemical agents.

Green synthesis of silver nanoparticles has gained much interest from chemist and researchers. In this concern Indian flora has yet to devilige in numerable sources of cost efficient non-hazardous reducing and stabilizing compounds utilized in preparing AgNPs (4).

Three important steps are required for the biosynthesis of AgNPs,

- i. Bio-reduction of silver ions,
- ii. Controlled growth of the crystals to nanoparticles
- iii. Stabilization of nanoparticles [5].

### **1.4** Alkanna tinctoria BARK

Botanical Name :AlkannaTinctoria

English Name : Alkanet

Tamil Name : VembalamPattai

Alkanet plant is a herb in the borage family, It has a dark red root of blackish appearance externally, but blue-red inside, with a whitish core. The root produces a fine red colouring material, which has been used as a dye in the Mediterranean region since antiquity.

*Alkanna tinctoria* commonly known as alkanet, bugloss, anchusa, Spanish bugloss, dyer's bugloss, orchanet, common alkanet and hoary puccoon is a plant in the Boraginaceae (Borage family) whose roots are used as a red dye. The plant is native in the Mediterranean region. The name Anchusa is derived from the Greek word anchousa which means paint, from the use of root as a dye. The root produces a fine red coloring material which has been used as a dye in the Mediterranean region since antiquity. The root as a dyestuff is soluble in alcohol, ether, and the oils, but it is insoluble in water. It is used to give color to wines and alcoholic tilnctures, to red vegetable oils and to varnishes .

### **1.5***Marmorofususnicobaricus*,

Kingdom:	Animalia
Phylum:	Mollusca
Class:	Gastropoda
Subclass:	Caenogastropoda
Order:	Neogastropoda
Family:	Fasciolariidae
Genus:	Marmorofusus



NICOBAR SPINDLE SHELL

### Common name : Nicobar spindle

It is a species of sea snail, a marine gastropod mollusc in the family Fasciolariidae, the spindle snails, the tulip snails and their allies. This species occurs in the Pacific Ocean off Japan, New South Wales, Australia, New Guinea, and Hawaii.

### **1.6 Antibacterial Action of AgNPs**

AgNPs are the most extensively used antibacterial nanoagent because of their wide-ranging antimicrobial effectiveness against several bacteria [6]. AgNPs intermingle via the bacterial cell envelope, yet the prime cellular target remains unknown. The combined effects of AgNPs along with antibiotics lead to increased antibacterial activity against drug-resistant bacteria [7]. The combined uptake of AgNPs and popular antibiotics such as kanamycin, tetracycline, enoxacin and neomycin led to the suppression of multiple-drug-resistant S. typhimurium bacterial growth; however, this synergistic effect is not observed in the case of penicillin and ampicillin [8].while kanamycin, ampicillinand chloramphenicol showed synergistic effects against various bacterial strains includingSt. mutans, St. aureus, Ent. faecium and E. coli [9]. Silver nanoparticles can also kill bacteria themselves, without the release of silver ions.After the attachment of AgNPs to the cell surface, they accumulate in the cell wall pits,which results in cell membrane disruption [10].

### **1.7Antifungal Action of AgNPs**

Studies have found that outbreaks caused by pathogenic fungi can be controlled by exploiting the fungicidal or fungistatic activity of nanoparticles [11]. Biosynthesized AgNPs stabilized with sodium dodecyl sulfate (SDS) exhibit good antifungal activity compared to fluconazole and are hostile towards phytopathogens such as Aspergilusniger, Trichophytonmentagrophytes, Fusariumsemitectum, Candida glabrata, Issatchenkiaorientalis, Phomaglomerata, Candida albicans and Phomaherbarum [12]. The

antifungal activity of Ag ions and AgNPs hostile to two plant pathogenic fungi (Bipolarissorokiniana and Magnaporthegrisea) was reported [13].

### **1.8 DPPH**

DPPH is a common abbreviation for the organic chemical compound 2,2-diphenyl 1 picrylhydrazyl. It is a dark-colored crystallinepowder composed of stable free radical molecules. DPPH has two majorapplications, both in laboratory research: one is a monitor of chemical reactions involving radicals, most notably it is a common antioxidant assay, and another is a standard of the position and intensity of electronparamagnetic resonance signals. DPPH is a well-known radical and a trap ("scavenger") for otherradicals. Therefore, rate reduction of a chemical reaction upon addition of DPPH is used as an indicator of

the radical nature of that reaction.Because of a strong absorption band centered at about 520 nm, theDPPH radical has a deep violet color in solution, and it becomescolorless or pale yellow when neutralized. This property allows visualmonitoring of the reaction, and the number of initial radicals can becounted from the change in the optical absorption at 520 nm or in theEPR signal

of the DPPH.

### 1.9 Hydrogen peroxide

Hydrogen peroxide is the simplest kind of peroxide available (oxygen-oxygen single bond). It is a colourless liquid and is used in aqueous solution for safety reasons. It acts as a bleaching agent and is alsomusedas disinfectant. Concentrated hydrogen peroxide is a very reactive oxygen species and is used as a propellant in rocketry. The chemicalformula for hydrogen peroxide is  $H_2O_2$ . It is often referred to as water with one more oxygen atom. It is acidic in nature and PH is about 4.5. It is 100 percent degradable compound.

**STATE OF THE ART & SCOPE OF THE WORK** 

### **CHAPTER II**

### 2.1 LITERATURE SURVEY

The synthesis of silver nanoparticles is very common due to their numerous applications in various fields. Silver nanoparticles have unique properties such as: optical and catalytic properties, which, depend on the size and shape of the produced nanoparticles. So, today the production of silver nanoparticles with different shapes which have various uses in different fields such as medicine are noted by many researchers. This article, is an attempt to present an overview of the shape-controlled synthesis of silver nano particles using various methods [14].

Silver nanoparticles were synthesised using clitoriaternatea and solanumnigrum. Further investigation of the shape and size of nanoparticle was done by X-ray diffraction and scanning electron microscopic studies. A silver nanoparticle at different concentration was assessed for its antibacterial effect against various nosocomial pathogens[15].

Green synthesis of silver nanoparticles (AgNPs) has gained much interest from chemists and researchers. In this concern, Indian flora has yet to divulge innumerable sources of costeffective non-hazardous reducing and stabilizing compounds utilized in preparing AgNPs. An efficient and sustainable route of AgNP preparation from 1 mM aqueous AgNO3 using leaf extracts of three plants, musabalbisiana (banana), azadirachtaindica (neem) and ocimumtenuiflorum (blacktulsi), well adorned for their wide availability and medicinal property was reported[16].

A novel approach for the green synthesis of silver nanoparticles using aqueous leaves extracts of catharanthusroseus (C. roseus) Linn. G. Don which has been proven active against malaria parasite plasmodium falciparum(P.falciparum) [17].

AgNPs proved to be effective as an antimicrobial agent even at a very low concentration and they inhibit the growth of antibiotic resistant bacteria. AgNPs interact with membrane proteins and DNA of bacteria, which have sulphur and phosphorous complex that have high affinity towards AgNPs [18] The anti-bacterial action of AgNPs is quite complex and not well studied. Its mechanism is only tentatively explained. The antimicrobial action of AgNPs can be categorized in two types: the inhibitory action and bactericidal action. In the former strategy bacterial cells are not killed but their division is prevented whereas in the later bacterial cells will die due to the action of AgNPs [19]..

DPPH is also reflected as a respectable moving model for peroxyl radicals. Antioxidant property is an important characteristic and greatly significant for natural life. Numerous biological roles of antioxidants are documented like anti-mutagenicity, anti-carcinogenicity and anti-aging among others. Previous reports suggested that protein from L. rubromaculata crab and Hemolymph showed DPPH scavenging activity. The influence of antioxidants on DPPH radical scavenging was due to their hydrogen giving facility [20].

Among various MNPs, silver (Ag) nanoparticles are widely studied because of their high conductivity, good light absorption, high sensitivity, resolution, antibacterial activity, and chemical stability. [21]

The synthesized nanomaterials, many analytical techniques have been used, including ultraviolet visible spectroscopy (UV-Vis spectroscopy), X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), dynamic light scattering (DLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and so on [22].

There is an inevitable and urgent need to develop antifungal agents, which should be biocompatible, non-toxic, and environmentally friendly. At this juncture, AgNPs play an important role as anti-fungal agents against various diseases caused by fungi. Nano-Ag showed potent anti-fungal activity against clinical isolates and ATCC strains of Trichophytonmentagrophytes and Candida species with concentrations of  $1-7 \mu g/mL$ . was reported byEsteban-Tejeda et al. [23] In recent years, metal and
metal oxides nanoparticles have gained extensive interest because of their wide application as catalyst in many reaction.[24]

Several routes such as thermal decomposition, sol-gel technique, sonochemical procedure, microwave irradiation, electrochemical method and precipitationpyrolosis were applied for the preparation of CuO nanoparticle.[25].

However, these methods usually have some disadvantages such as utilization of organic solvents, toxic and expensive reagents, complicated equipments and harsh reaction condition. The uses of plant extract as a reducing, chelating and capping agents can be beneficial for large scale synthesis of nanoparticles. [26].

Seashell as a natural ceramic has a layered brick-mortar architecture consisting of aragonite inorganic aragonite and organic bio polymer as the mortar. This combination seashell produces a unique composite with increasing in strength and toughness over their constituents.[27]

Among nanoparticles, CuO nanostructures have been widely studied due to their applications in various fields such as catalysis, batteries, semiconductors, super capacitors and photo deductors.[28].As compared to the XRD pattern of seashell some reflection XRD pattern of CuO seashell are in same position.[29].

Atomic Force Microscope (AFM) and Transmission Electron Microscope (TEM) analysis were used to characterize the size and size distributions of the metals NPs on the levels of triiodothyronine. [30, 31]. Metal nanoparticles have been known to be synthesized in glycerol within limited experimental conditions including high temperatures, alkaline pH conditions and the irradiance of ultraviolet light. Herein, we report that silver nanoparticles have been formed in glycerol under completely green conditions (e.g., room temperature, neutral pH conditions and without irradiance of ultraviolet light). [32] Iron oxide nanoparticles (NPs) have attracted much consideration due to their unique properties, such as super paramagnetism, surface-to-volume ratio, greater surface area and easy separation methodology. Various physical, chemical and biological methods have been adopted to synthesize magnetic NPs with suitable surface chemistry. [33].

Synthesis of nano particles by utilizing some of the green chemistry principles off a viable and sustainable approach for nanotechnology. Iron nano particles (Fe,NPs ) were synthesised using Artocarpusheterophyllus (Jackfruit) peel extract. The peel with its high antioxidant content serves as a potential source of valuable biomolecules which act as the bio-reductants, capping and stabilizing agent for green synthesis of nanoparticles.[34]..

Iron nanoparticles with strong redox and adsorption abilities have been applied in a range of different fields including medicine, sensing, catalysis, optics, electronics and environmental remediation. Iron nanoparticles have been experimentally proven effectively decrease the potential leachability of heavy metals via in situ immobilization and prevent transport of these heavy metals ilnto deeper soil layers, rivers and ground water. Nanotechnology is currently ja relatively mature remediation method for water pollution. However, soil complexity has limited using iron nanoparticles for soil remediation.[35]

Gold nanoparticles (AuNPs) are important components biomedical applications. AuNPs have been widely employed for diagnosatics and have seen increasing use in the area of therapeutics.AuNPs highlight a selection of recent applications of these materials inbionanotechnology.[36]..

Gold nanoparticles demonstrate special advantages in this field due to their unique properties ,small size and high surface area-to-volumeratio. These particles have been widely used in various biomedical applications and drug delivery systems due to their inert nature, stability, high dispersity,non-cytotoxicity and biocompatibility.[37].

Glyco-gold nanoparticles combine in a single entity the peculiar properties of gold nanoparticles with the biological activity of carbohydrates. The result is an exciting nanosystem, able to mimic the natural multivalent presentation of saccrahide moieties and to exploit the peculiaroptical properties of the metallic core. Recent advances on glycol-gold nanoparticle applications in different biological fields, highlightinnthe key parameters which inspire the glycol nanoparticle design.[38]..

The AuNPs have been successfully used in bioelectrochemistry and found to efficiently enhance interfacial electrochemical electron transfer of the metalloprotien yeast cytochrome c in homogenous solution. The synthesis has been extended successfully to direct use of starch-rich foods such as potato, carrotand onion to synthesize AuNPs.[39].Medicinal plants have been a part of our life since our presence and have been involved for various medicinal purposes since ancient times to the present medicinal plants, as Ayurveda medicine has been with great importance a system of medicine with historical routes in the Indian subcontinents and based on the belief that health and wellness depend on a delicate balance between mind and body.[40].

Alkana species are considered among the medicinal plants since they are known for their medicinal, pharmaceutical and other properties from ancient times and used for remedy of human health.[41]. The genus alkana is widely known for its medicinal and pharmaceutical properties, since ancient times, and depending chemical constituents of its plant parts. The most important part of the plant is the bark of the root which is containing dying substance.[42].

Alkana root tissues also contain resins, alkaloid, tannins and wax meanwhile the roots can be toxic then pyrrolizidine- alkaloid accumulates in their tissues . This compounds is a group of ester substances that have liver damaging effect. Some other compounds from alkanacappadocica that proven they are cytotoaxic effect.[43].

Alkana roots has been extensively used for diarrohea, anticancer and gastric ulcer treatments, in such case oral administration is recommended. Alkana root has also demonstrated radical

scavenging activity, suggesting potential anti-ageing effect, however diminutive clinical information is available.[44]).

The activity of leaves extract alkana species is not fully studied and needed to be explored. However, few studies showed the ability of alkana leaves to inhibit the growth of infectious human pathogens.[45].

Alkana root has antifungal activities and able to heal any diseases related to skin fungi such as phlegm, ringworm and eczema on your skin disorder.[46].

#### **2.2 SCOPE OF WORK**

Chemical method of synthesizing nanoparticles and green method of synthesizing nanoparticles were widely studied by the researchers. Among this, Green method of synthesis is very important due to its advantage in controlling particle size, morphology very effectively. This method also involve less time consuming process for getting the desired nanoparticle size. Hence for this investigation, Green method is chosen to synthesize nanoparticles.

Silver is mainly used for various applications. Silver, the basic element is one of the important metal. Silver is harder than gold and has excellent properties such as ductility and malleability. Also, silver has the highest electrical and thermal conductivity of all the metals and has the lowest contact resistance. In this investigation, we have synthesized Ag nanoparticles from Silver nitrate. Bark synthesis of nanoparticles is a greenery way and it's interesting applications of synthesized nanoparticles were studied . Anti-Bacterial, Anti-Fungal activities, DPPH scavenging effect and Hydrogen Peroxide scavenging effect shows the excellent application of Ag nanoparticles towards pharmaceutical applications.

#### **2.3 OBJECTIVES OF THE WORK**

The main objectives of this investigation are

- 1. To synthesize nanoparticles through Eco-Friendly Method.
- 2. To load sea shells on synthesised Nanoparticles.
- 3. To evaluate the presence of Metal Nanoparticles through various techniques such as

UV-visible spectroscopy, FTIR, AFM and XRD.

4. To study the surface morphology of nanoparticle.

5. 6. To study Anti-Bacterial, Anti-Fungal and Anti-Aging Applications of synthesised nanoparticles.

# **CHAPTER III**

# MATERIALS AND METHODS

#### MATERIALS AND METHODS

A brief outline of the materials and methods used in this in project work is present here.

#### **3.1 MATERIALS REQUIRED FOR SYNTHESIS**

- Marmofurous nicobaricus
- Alkana tinctoria
- Double distilled water
- Silver nitrate

Analar Silver nitrate (99.9%) was purchased from Merck

#### **3.1Instrumentation:**

- 1. Cooling Centrifuge
- 2. Muffle Furnace
- 3. Ultraviolet Spectroscopy
- 4. IR
- 5. AFM
- 6. XRD

#### **3.2 PROCEDUE**

#### **3.2.1 PREPARATION OF BARK EXTRACT**

*Alkanna tinctoria* was purchased from the local market, Thoothukudi. The bark was finely cut, washed with double-distilled water to remove any impurities. *About* 2 g of *Alkanna tinctoria* bark are weighed accurately. The extract is prepared by the addition of 100 ml of water in Erlenmeyer flask. It was then cooled to room temperature. The extract is filtered using Whatman no. 41 filter paper.



Alkanna tinctoria bark

**Bark Extract** 

FIGURE 3.1 Bark extract

3.2.2 SYNTHESIS OF NANOPARTICLES USING BARK EXTRACT OF ALKANA TINCTORIA



FIGURE 3.2 RESIDUE FROMALKANA TINCTORIA

To prepare Silver Nanoparticles, about 1mL of 20mM Silver nitrate was diluted to20mL with double distilled water and treated with 10mL of bark extract. The solution was exposed to sunlight. There was a visible colour change to brown.

# 3.2.3 SYNTHESIS OF NANOPARTICLES USING BARK EXTRACT OF ALKANA TINCTORIA AND MORMOFUROUS NICOBARIS

2g seashell powder of *Mormofurous nicobaricus* was dispersed in the extract of Silver Nitrate and *Alkanna tinctoria* bark and heated at 60° for 20 min. A dark brown precipitated was separated and centrifuged with 7000 rpm for 20 minutes, Thermal Decomposition was carried out at 300° C in the muffle furnace for 1 hour.



#### FIGURE 3.3 RESIDUE WITHALKANA TINCTORIAANDMOMOFROUS NICOBARIS

## **3.3 METHODS**

#### 3.3.1 UV SPECTROSCOPY

Ultraviolet-visible spectroscopy (UV)refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible spectral regions. Molecules containing bonding and non-bonding electrons (n electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals.



**FIGURE 3.5 UV Spectrometer** 

## 3.3.2INFRARED SPECTROSCOPY

An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis.



#### FIGURE 3.6 IR Spectroscopy

# 3.3.3ATOMIC FORCE MICROSCOPY ( AFM )

The AFM works much the same way a profilometer works only on a much, smaller scale: a very sharp tip is dragged across a sample surface and the change in the vertical position (denoted the "z" axis) reflects the topography of the surface. By collecting the height data for a succession of lines it is possible to form a three dimensional map of the surface features. The AFM has three major abilities force measurement, imaging, and manipulation. The Atomic force microscopy analysis using the Nanosurf easy2scanBT02218 is profilometer.



#### FIGURE3.7 AFM

#### 3.3. X-ray Diffractometer (XRD)



Figure 3.8 X-ray Diffractometer (XRD)

XRD measurements are used to identify the structure of the materials where it amorphous or crystalline. X-ray diffraction techniques are superior in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of materials largely depend on the crystal structures, therefore researchers are enthusiastic for analyzing the materials production.

The Scherrer equation for identifying of crystalline size of nanoparticles using the following equation.

$$D = \frac{0.89 \,\lambda}{\beta \cos \theta} (m)$$

Where  $\lambda$  is the wavelength of the x-ray,  $\theta$  is the Bragg diffraction and  $\beta$  is the FWHM.

#### 3.3.5 ANTIBACTERIAL ACTIVITY

#### PRINCIPLE

The antimicrobials present in the given sample were allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in millimeters.

#### MATERIALS REQUIRED

(*Staphylococcus aureus* – 902 and *Pseudomonas aeruginosa*-424) was purchased from MTCC, Chandihar, India. Nutrient Agar medium, Nutrient broth, Gentamicin antibiotic solution was purchased from Himedia, India. Test samples, petri-plates, test tubes, beakers conical flasks were from Borosil, India. Spirit lamp, double distilled water.

#### 1. AGAR- WELL DIFFUSION METHOD

#### a. Nutrient Agar Medium

The medium was prepared by dissolving 2.8 g of the commercially available Nutrient Agar Medium (HiMedia) in 100ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm petriplates (25-30ml/plate) while still molten.

#### b. <u>Nutrient broth</u>

Nutrient broth was prepared by dissolving 2.8 g of commercially available nutrient medium (HiMedia) in 100ml distilled water and boiled to dissolve the medium completely. The medium was dispensed as desired and sterilized by autoclaving at 15 lbs pressure (121°C) for 15 minutes.

#### PROCEDURE

Petri plates containing 20 ml nutrient agar medium were seeded with 24 hr culture of bacterial strains were adjusted to 0.5 OD value according to McFarland standard, (*Staphylococcus aureus*– 902 and *Pseudomonas aeruginosa*-424)Wells were cut and concentration of sample H, G and A(0.01) (500, 250, 100 and 50  $\mu$ g/ml) was added. The plates were then incubated at 37°C for 24 hours. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the wells.

Gentamicin antibiotic was used as a positive control. The values were calculated using Graph Pad Prism 6.0 software (USA). [47,48]

#### **3.3.6** ANTIFUNGAL ACTIVITY

#### PRINCIPLE

The anti-fungal agent present in the given sample was allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in millimeters.

#### MATERIALS REQUIRED

Potato dextrose agar medium, Amphotericin B antimycotic solution, test samples, test tubes, beakers conical flask, spirit lamp, double distilled water and petri-plates.

#### 1. AGAR- WELL DIFFUSION METHOD

#### c. Potato Dextrose Agar Medium

The potato dextrose agar medium was prepared by dissolving 20 gm of potato influsion, 2 gm of dextrose and 1.5 gm of agar in 100ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm petri plates (25-30 ml/plate) while still molten.

#### PROCEDURE

Petri plates containing 20ml potato dextrose agar medium was seeded with 72 hr culture of fungal strain (*Aspergillus niger*) wells were cut and different concentration of sample G, A(0.01) and H (500, 250, 100 and 50  $\mu$ g/ml) was added. The plates were then incubated at 28°C for 72 hours. The anti-fungal activity was assayed by measuring the diameter of the inhibition zone formed around the wells.

Amphotericin B was used as a positive control. The values were calculated using Graph Pad Prism 6.0 software (USA). [49,50]

#### **3.3.7. HYDROGEN PEROXIDE SCAVENGING ASSAY G and H**

#### **Principle :**

Hydrogen peroxide is a weak oxidizing agent and can inactivate a few enzymes directly, usually by oxidation of essential thiol (-SH) groups. Hydrogen peroxide can cross cell membranes rapidly, once inside the cell, H2O2 can probably react with Fe2+, and possibly Cu2+ ions to form hydroxyl radical and this may be the origin of many of its toxic effects. It is therefore biologically advantageous for cells to control the amount of hydrogen peroxide that is allowed to accumulate.

#### Material Required

Hydrogen peroxide solution and Sodium phosphate buffer.

#### Procedure

Ability of plant extracts to scavenge hydrogen peroxide was estimated according to the method reported by Ruch et al. with minor modification. A solution of hydrogen peroxide (43 mM) is prepared in phosphate buffer (1 M pH 7.4). Different concentration of sample G (500, 250, 100, 50 and 10  $\mu$ g/ml) was added to a hydrogen peroxide solution (0.6 ml, 43 mM). Absorbance of hydrogen peroxide at 230 nm was determined after 10 minutes against a blank solution containing phosphate buffer without hydrogen peroxide. Ascorbic acid was used as standard. The free radical scavenging activity was determined by evaluating % inhibition as above. % inhibition = [(Control- Test)/control] ×100. [51]

#### 3.3.8 DPPH Radical scavenging activity

The DPPH assay is popular in natural product antioxidant studies. One of the reasons is that this method is simple and sensitive. This assay is based on the theory that a hydrogen

donor is an antioxidant. It measures compounds that are radical scavengers. Figure below, shows the mechanism by which DPPH accepts hydrogen from an antioxidant. DPPH is one of the few stable and commercially available organic nitrogen radicals (1). The antioxidant effect is proportional to the disappearance of DPPH in test samples. Monitoring DPPH with a UV spectrometer has become the most commonly used method because of its simplicity and accuracy. DPPH shows a strong absorption maximum at 517 nm (purple). The color turns from purple to yellow followed by the formation of DPPH upon absorption of hydrogen from an antioxidant. This reaction is stoichiometric with respect to the number of hydrogen atoms absorbed. Therefore, the antioxidant effect can be easily evaluated by following the decrease of UV absorption at 517 nm.

#### **MATERIALS REQUIRED**

0.1mM DPPH solution, Ascorbic acid, Methanol

#### 0.1 mM DPPH Solution

Dissolve 39 mg of DPPH in 100 ml of methanol and store at -200 C until needed.

#### Ascorbic acid (Standard)

1mg/ ml of Ascorbic acid

#### Procedure

1. Briefly, prepare 0.1 mM of DPPH solution in methanol and add 100  $\mu$ l of this solution to 300  $\mu$ l of the solution of sample B at different concentration (500, 250, 100, 50 and 10  $\mu$ g/mL).

2. The mixtures have to be shaken vigorously and allowed to stand at room temperature for 30 minutes.

3. Then the absorbance has to be measured at 517 nm using a UV-VIS spectrophotometer. (Ascorbic acid can be used as the reference).

4.Lower absorbance values of reaction mixture indicate higher free radical scavenging activity.

5. The capability of scavenging the DPPH radical can be calculated by using the following formula.

6. DPPH scavenging effect (% inhibition) = [(absorbance of control- absorbance of reaction mixture)/absorbance of control] X 100

# **CHAPTER IV**

# **RESULTS AND DISCUSSION**

## **RESULTS AND DISCUSSION:**

# **4.1** Characteristics of silver nanoparticles

4.1.1 Ultraviolet spectroscopy



Figure 4.1 UV-Visible spectra of Alkanna tintcoria Bark

UV – Vis spectral analysis of Alkanna tintcoria bark was performed on JASCO, V-650

Spectrophotometer. The colour of the bark extract was found to be purple. A peak was observed around 270nm and 350nm for the bark shows the presence of organic molecules. A band around 270 and 35nm which assigned to transitions localised within C=C and C=O bonds.



FIGURE 4.2 UV- Spectra of Silver nanoparticles using Alkanna tinctoria Bark Extract

Silver Nanoparticles were synthesised using *Alkanna tinctoria* bark and the optical absorbance properties of the synthesized Au Nanoparticles were investigated using bark extract in the wavelength range 200-900 nm at ambient temperature. The nanoparticles formed very fast and it was clear from the colour of the gold solution from golden yellow to purple. Figure.4.2 indicates the UV –Visible diffuse

reflectance spectra of Ag Nanoparticles using extract of *Alkanna tincoria*. There is a strong absorption peak around 450nm which confirms the presence of Ag nanoparticles.



FIGURE 4.3 UV - Spectra of silver nanoparticles using Alkanna tinctoria loaded on

## Marmorfusus nicobsricus Sea Shell

Synthesised Silver Nanoparticles using bark extract were loaded on *Marmorfusus nicobsricus*. The optical absorbance properties were investigated in the wavelength range 200-900 nm at ambient

temperature. Figure.4.3 indicates the UV –Visible diffuse reflectance spectra of Ag Nanoparticles loaded on *Marmorfusus nicobsricus*. There is a strong absorption peak around 422nm which confirms the presence of Ag nanocomposites.

# 4.2 INFRARED SPECTROSCOPY:



Figure 4.4 Infrared spectra of Alkanna tintcoria bark

FT-IR spectra of bark extract were recorded to find out the presence of biomolecules present for the reduction and capping. Using KBr, the dried powder was made as pellets and the FT-IR spectra were recorded. Figure.4.4 shows the FT-IR spectra of the bark extract. The bark extract has peaks at 3125cm<sup>-1</sup>, 1638cm<sup>-1</sup> 1400cm<sup>-1</sup> and 1033cm<sup>-1</sup>.



FIGURE 4.5 IR - Spectra image of Silver Nanoparticles using Alkanna tinctoria bark

Ag nanoparticles show peaks at 3148 cm<sup>-1</sup>, 1580 cm<sup>-1</sup>, 1400 cm<sup>-1</sup>, 1115 cm<sup>-1</sup>, 1033 cm<sup>-1</sup> and at 822 cm<sup>-1</sup>.

The peak at 3154cm<sup>-1</sup>gets shifted to 3148cm<sup>-1</sup> in the spectra of Ag nanoparticles. This peak was observed due to the presence of -OH group which was responsible for the biogenic reduction. A peak was recorded around 1037cm<sup>-1</sup>. corresponds to the C-O stretching frequency of biocomponents.

From the results of FT-IR spectral data it was clear that the reduction of Au nanoparticles and its stabilisation was due to the presence of active biomolecules such as C-O and OH functional groups.



FIGURE 4.4 IR-Spectra Image of Silver Nanoparticles using ALKANA TINCTORIA loaded on

#### Marmorfusus nicobaricus Sea shell

Ag nanoparticles loaded on *Marmorfusus nicobaricus* Sea shell show peaks at 3125cm<sup>-1</sup>, 1670cm<sup>-1</sup>, 1495cm<sup>-1</sup>, 1399 cm<sup>-1</sup>, 1021cm<sup>-1</sup> and at 859cm<sup>-1</sup>.

The peak at 3148cm<sup>-1</sup>gets shifted to 3125 cm<sup>-1</sup> in the spectra of Ag nanoparticles loaded on *Marmorfusus nicobaricus* Sea shell. This peak was observed due to the presence of -OH group which was responsible for the biogenic reduction. A peak at 1670 cm<sup>-1</sup> was due to the presence C=O group. A peak was recorded around 1021cm<sup>-1</sup>. corresponds to the C-O stretching frequency of biocomponents.

From the results of FT-IR spectral data of the sea shell loaded nano particles, it was clear that the reduction of Ag nanoparticles and its stabilisation was due to the presence of active biomolecules.



# FIGURE 4.5 AFM Images of Ag Nanoparticles using ALKANA TINCTORIA



FIGURE 4.6 AFM Images of Ag Nanoparticles using Alkanna tinctoria loaded on

Mormofusus nicobaris

# **4.4 APPLICATIONS:**

# 4.4.1 ANTIBACTERIAL ACTIVITY:



Fig: 4.7 Effect of Ag nanoparticle against *Pseudomonas aeruginosa*.



Fig: 4.8 Effect of sample H against *Staphylococcus aureus*.



G 📕 g/m l

**Fig: 4.9 Effect of sample G against** *Pseudomonas aeruginosa* **Fig : 4.10 Effect of sample G against** *Staphylococcus aureus*.





# Table 4.1. SD± Means of zone of inhibition obtained by sample H, G against*Staphylococcus aureus* and *Pseudomonas aeruginosa*.

S. No	Name of the	Name of the test	of Zone of inhibition (mm) test						
	test organism	sample	SD ± Mear	SD ± Mean					
			500 μg/ml	250 μg/ml	100 µg/ml	50 μg/ml	РС		
1.	Staphylococcu s aureus	Н	7.5±0.7	6.5±0.7	5.25±0.35	4.25±0.35	16.5±0.7		
2.	Pseudomonas aeruginosa		9.5±0.7	7.5±0.7	5.5±0.7	4.25±0.35	14.5±0.7		
3.	Staphylococcu s aureus	G	8.5±0.7	7.5±0.7	5.25±0.35	4.25±0.35	15.25±0. 35		
4.	Pseudomonas aeruginosa		9.5±0.7	7.25±0.35	6.25±0.35	5.25±0.35	15.5±0.7		

# SD – Standard Deviation, \*Significance - p< 0.05

# **4.5. ANTIFUNGAL ACTIVITY:**



# Fig :4. 11.Effect of sample G against Aspergillus niger.

## Fig: 4.12.Effect of sample H against Aspergillus niger.



# Table 4.2. SD± Means of zone of inhibition obtained by sample G, H against Aspergillus niger.

S.N O	Name of the test organism	Name of the test sample	Zone of inhibition (mm) SD ± Mean				
			500 μg/ml	250 µg/ml	100 μg/ml	50 μg/ml	PC
1.	Aspergillus	G	7.5±0.7	6.5±0.7	4.25±0.3 5	4.25±0.3 5	13.5±0.7
2.	niger	Н	0	0	0	0	17.5±0.7

SD – Standard Deviation, \*Significance - p< 0.05

# 4.6. HYDROGEN PEROXIDE SCAVENGING ASSAY G

# A. OD Value at 230 nm

Control Mean OD value: 0.481

S. No	Tested sample concentration (µg/ml)	OD Valu triplicates	ue at 230 s)	nm (in
	Control	0.471	0.481	0.491
	500 µg/ml	0.116	0.129	0.134
	250 µg/ml	0.139	0.142	0.150
	100 µg/ml	0.171	0.179	0.266
	50 µg/ml	0.277	0.282	0.342
	10 µg/ml	0.376	0.373	0.480
	Ascorbic acid	0.087	0.083	0.085





Table <b>44</b> Percentage	of inhibition	of synthesised	Δσ	Nanonarticles
Table 4.4.1 Creenage	or minipition	of synthesiscu	пg	ranopar ticics

S. No	Tested sample concentration (µg/ml)	Percentage triplicates)	of inhibitic	on (in	Mean value
1	Ascorbic acid	81.91268	82.74428	82.32848	82.32848

2	500 µg/ml	75.88358	73.18087	72.14137	73.73527
3	250 µg/ml	71.10187	70.47817	68.81497	70.13167
4	100 µg/ml	64.44906	62.78586	44.69854	57.31116
5	50 µg/ml	42.41164	41.37214	28.89813	37.56064
6	10 µg/ml	21.82952	22.45322	0.2079	14.83021



Figure.4.14. Concentration Vs Percentage of Inhibition

Table.4.5	. IC50 V	Value of	tested	sample:	63.09	μg/ml
-----------	----------	----------	--------	---------	-------	-------

log(inhibitor) vs. normalized response	
Variable slope	
Best-fit values	
LogIC50	1.800
HillSlope	-2.094
IC50	63.09

Std. Error		
LogIC50		0.04820
HillSlope		0.5387
95% Confidence Intervals		
LogIC50		1.696 to 1.904
HillSlope		-3.257 to -0.9302
IC50		49.64 to 80.18
Goodness of Fit		
Degrees of Freedom		13
R square		0.9127
Absolute Sum of Squares		1993
Sy.x		12.38
Number of points		
Analyzed	3	15



500 μg/ml 250 μg/ml 100 μg/ml 50 μg/ml 10 μg/ml Control Std

Figure.4.15.Hydrogen Peroxide Scavenging Assay G

# 4.7. HYDROGEN PEROXIDE SCAVENGING ASSAY H

# A. OD Value at 230 nm

Control Mean OD value: 0.521

 Table.4.6. Absorbance of Ag Nanoparticles at various concentration

S. No	Tested sample concentration (µg/ml)	OD Value at 230 nm (in triplicates)				
	Control	0.510	0.525	0.530		
	500 µg/ml	0.134	0.123	0.121		
	250 µg/ml	0.199	0.191	0.172		
	100 µg/ml	0.174	0.171	0.286		
	50 μg/ml	0.384	0.306	0.378		
	10 µg/ml	0.423	0.425	0.525		
	Ascorbic acid	0.070	0.081	0.082		



Figure.4.16.Concentration Vs OD 230 nm

Table.4.7.Percentage	of inhibition	of synthesised	Ag	<b>Nanoparticles</b>
0			<u> </u>	

S. No	Tested sample concentration (µg/ml)	Percentage triplicates)	of inhibitio	on (in	Mean value
1	Ascorbic acid	86.5643	84.45298	84.26104	85.09277
2	500 μg/ml	74.28023	76.39155	76.77543	75.81574
3	250 μg/ml	61.80422	63.33973	66.98656	64.04351

4	100 µg/ml	66.60269	67.1785	45.10557	59.62892
5	50 µg/ml	26.29559	41.26679	27.44722	31.66987
6	10 μg/ml	18.80998	18.4261	0	12.41203



H **"**g/m l

# **Figure.4.17. Concentration Vs Percentage of Inhibition**

# Table.4.8. IC50 Value of tested sample: 69.39 µg/ml

log(inhibitor) vs. normalized response	
Variable slope	
Best-fit values	
LogIC50	1.841
HillSlope	-2.006
IC50	<mark>69.39</mark>
Std. Error	
LogIC50	0.05304
HillSlope	0.5349
95% Confidence Intervals	
LogIC50	1.727 to 1.956
HillSlope	-3.161 to -0.8509
IC50	53.30 to 90.33
Goodness of Fit	

Degrees of Freedom		13
R square		0.8912
Absolute Sum of Squares		2382
Sy.x		13.54
Number of points		
Analyzed	3	15

# 500µg/ml 250µg/ml 100µg/ml 50µg/ml 10µg/ml Control Std

Figure.4.18. Hydrogen Peroxide Scavenging Assay H



**CHAPTER V**
#### **CONCLUSIONS AND REFERENCES**

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### Alkanna tinctoria BARK EXTRACT MEDIATED GREEN SYNTHESIS OF GOLD NANOPARTICLES: CHARACTERISATION AND APPLICATIONS

Project in Chemistry Submitted to St. Mary's college (Autonomous) in partial fulfilment for the award of the Degree of **Bachelor of Science** in Chemistry

> Project done by MUTHU KAVITHA.M ROJA.V SHRUTHI.S. S



St. Mary's college (Autonomous) (Re-accredited with 'A+' Grade by NAAC) Thoothukudi-628001 2022-2023

#### DECLARATION

We hereby declare that the project entitled *Alkanna tinctoria* BARK EXTRACT MEDIATED GREEN SYNTHESIS OF GOLD NANOPARTICLES: CHARACTERISATION AND APPLICATION submitted to St. Mary's College (Autonomous) Thoothukudi affiliated to Manonmaniam Sundarnar University for the Degree of Bachelor of science is our original work and that it has not previously formed the basis for the award of any degree, Diploma or Similar title.

> Muthukavetha.M MUTHU KAVITHA.M

> > Roja·∨ ROJA.V

Shouth: S. S SHRUTHI.S. S

April, 2023

Thoothukudi.

#### CERTIFICATE

This is to certify that the report of the project in chemistry entitled *Alkanna tinctoria* BARK EXTRACT MEDIATED GREEN SYNTHESIS OF GOLD NANOPARTICLES: CHARACTERISATION AND APPLICATIONS is submitted to St. Mary's College (Autonomous), in partial fulfilment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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CHAPTER NO	TITLE	Page No
Chapter I	INTRODUCTION	
1.1	NANO PARTICLES	2
1.2	APPLICATIONS OF NANOMATERIALS	3
1.3	GREENSYNTHESIS	4
1.4	ANTIBACTERIAL	5
1.5	ANTIFUNGAL	6
1.6	DPPH	6
1.7	HYDROGEN PEROXIDE	6
1.8	ALKANNABARK (Alkanna tinctoria)	7
1.9	GOLD NANOPARTICLES	9
1.10	APPLICATIONS OF GOLD NANOPARTICLES	10
Chapter II	STATE OF THE ART & SCOPE OF THE WORK	
2.1	LITERATURE SURVEY	12
2.2	SCOPE OF THE WORK	15
2.3	OBJECTIVES OF THE WORK	17
Chapter III	MATERIALS AND METHODS	
3.1	MATERIALS REQUIRED FOR SYNTHESIS	18
3.2	INSTRUMENTATION	18
3.3	PROCEDURE	18
3.4	METHODS	22
3.4.1	UV - SPECTROSCOPY	22
3.4.2	INFRARED SPECTROSCOPY	23

3.4.3	ATOMIC FORCE SPECTROSCOPY	23
3.4.4	ANTI BACTERIAL METHOD	24
3.4.5	ANTIFUNGAL ACTIVITY	25
3.4.6	HYDROGEN PEROXIDE SCAVENGING ASSAY	26
3.4.7	DPPH	27
Chapter IV	<b>RESULTS AND DISCUSSION</b>	
4.1	CHARACTERISATION OF GOLD NANOPARTICLES	29
4.1.1	UV-VIS SPECTRAL ANALYSIS	29
4.1.2	INFRARED SPECTROSCOPY	30
4.1.3	ATOMIC FORCE MICROSCOPY	32
4.2	APPLICATIONS OF GOLD NANOPARTICLES	35
4.2.1	ANTIBACTERIAL ACTIVITY	35
4.2.2	ANTI FUNGAL ACTIVITY	37
4.2.3	HYDROGEN PEROXIDE SCAVENGING ASSAY	38
4.2.4	DPPH RADICAL SCAVENGING ACTIVITY	42
Chapter V	CONCLUSIONS	
5.1	CONCLUSIONS	44
5.2	REFERENCES	46
4.2.4 Chapter V 5.1 5.2	DPPH RADICAL SCAVENGING ACTIVITY         CONCLUSIONS         CONCLUSIONS         REFERENCES	42 44 46

#### LIST OF FIGURES

FIGURE NO.	CONTENTS	PAGE NO.
1.1	Au NP'S SYNTHESIZED WITH DIFFERENT SIZES	2
1.2	Alkanna tinctoria BARK	7
1.3	Alkanna tinctoria	8
1.4	MECHANISTIC APPROACH OF GREEN SYNTHESIS OF Au NANOPARTICLES	10
3.1	AURIC CHLORIDE SOLUTION	18
3.2	EXTRACT OF THE REDUCING AGENT Alkanna tinctoria bark	19
3.3	CHANGE IN PHYSICAL APPEARANCE OF REDUCING AGENT FROM PURPLE TO WINE RED	20
3.4	SYNTHESIS OF GOLD NANOPARTICLE	21
3.5	UV-VIS SPECTROMETER (UV-VIS)	22
3.6	INFRARED SPECTROSCOPY	23
3.7	ATOMIC FORCE MICROSCOPY (AFM)	23
4.1	UV-VISIBLE SPECTRAOF Alkanna tintcoria BARK	29
4.2	UV-VISIBLE SPECTRAOF GOLD NANOPARTICLES	29
4.3	INFRAREDSPECTRAOF Alkanna tintcoria BARK	30
4.4	INFRARED SPECTRAOFGOLD NANOPARTICLES	31

4.5	AFM SPECTRA OF Alkanna tintcoria BARK	32
4.6	AFM SPECTRA OFGOLD NANOPARTICLES + Alkanna tintoria bark	33
4.7	EFFECT OF Au NANOPARTICLES WITH Alkanna tinctoria bark extract AGAINST Pseudomonas aeruginosa	35
4.8	EFFECT OF Au NANOPARTICLES WITH Alkanna tinctoria bark extract AGAINST Staphylococcus aureus.	35
4.9	EFFECT OF Au NANOPARTICLES AGAINTS Aspergillus niger.	37
4.10	PERCENTAGE OF INHIBITION	39
4.11	CONCENTRATION VERSUS PERCENTAGE OF INHIBITION	40
4.12	SCAVENGING EFFECT OF H2O2	41
4.13	DPPH SCAVENGING EFFECT OF Au NANOPARTICLES	42
4.14	PERCENTAGE OF INHIBITION	43

#### LIST OF TABLES

TABLE NO.	CONTENTS	PAGE NO
1.1	SCIENTIFIC CLASSIFICATION	8
4.1	AFM data of gold nanoparticle mediated from <i>Alkanna tinctoria</i> bark	34
4.2	SD + /- MEANS OF ZONE OF INHIBITION OBTAINED BY Au NANOPARTICLES AGAINST Staphylococcus aureus AND Pseudomonas aeruginosa.	36
4.3	SD +/- MEANS OF ZONE OF INHIBITION OBTAINED BY Au NANOPARTICLES AGAINST <i>Aspergillus</i> <i>niger</i> .	37
4.4	ABSORBANCE OF Au NANOPARTICLES AT VARIOUS CONCENTRATION BY HYDROGEN PEROXIDE SCAVENGING EFFECT	38
4.5	PERCENTAGE OF INHIBITION OF HYDROGEN PEROXIDE	39
4.6	IC50 VALUE OF TESTED SAMPLE: 52.53 µg/ml	40
4.7	ABSORBANCE OF Au NANOPARTICLES AT VARIOUS CONCENTRATIONS BY DPPH SCAVENGING EFFECT	43
4.8	PERCENTAGE OF INHIBITION OF Au SYNTHESIZED NANOPARTICLES	43

#### ABSTRACT

Novel methods are used to synthesis nanoparticles due to its vast application. The aim of this study is to synthesis gold nanoparticles by green method. An aqueous bark of *Alkanna tinctoria* is used to prepare gold nanoparticles. Gold nanoparticles were characterised using UV-visible spectroscopy, Fourier transform infrared (FTIR)spectroscopy, atomic force microscopy (AFM), x-ray diffraction (XRD), UV- visible spectrum shows a peak around 520nm which confirms the presence of gold nanoparticle. The results of FTIR spectroscopy confirmed the bioactive molecule of the bark extract on gold nanoparticles XRD data clearly reveals the structure of gold nanoparticles. AFM results also reveal the presence of gold nanoparticles around 28nm. Antibacterial and Antifungal activities showed excellent inhibiting activity of gold nanoparticles. Hydrogen peroxide scavenging results also shows excellent property towards anti-aging application



# CHAPTER I

### INTRODUCTION

#### **1.1 Introduction**

Nanoparticles (NPs) are wide class of materials that include particulate substances, which have one dimension less than 100 nm at least and Undetectable by human eye (1). Depending on the overall shape these materials can be 0D, 1D, 2D or 3D (2). The importance of these materials realized when researchers found that size can influence the physiochemical properties of a substance e.g. the optical\_properties. A 20-nm gold (Au), platinum (Pt), silver (Ag), and palladium (Pd) NPs have characteristic wine-red colour, yellowish Grey, black and dark black colours, respectively.



Figure. 1 Au NPs synthesized with different sizes

#### **1.2 APPLICATIONS OF NANOMATERIALS**

- In healthcare field, for example, utilises nanoparticles in a variety of ways, withone major use being drug delivery. One example of this process is whereby nanoparticles being developed to assist the transportation of chemotherapy drugs directly to cancerous growth, as well as to deliver drugs to areas of arteries that are damaged in order to fight cardiovascular diseases. Carbon nanotubes are also being developed in order to be used in processes such as the addition of antibodies to the nanotubes to create bacteria sensors.
- In aerospace, carbon nanotubes can be used in the morphing of aircraft wings. The nanotubes are used in a composite form in response to the application of an electric voltage. Elsewhere, environmental preservation processes make use of nanomaterials. Applications are being developed to use the nanowires-zinc oxide nanowires-in flexible solar cells as well as to play a role in the treatment of polluted water.
- In the cosmetics industry, mineral nanoparticle such as titanium oxide are used in sunscreen due to the poor stability that conventional chemical UV protection offers in the long term. just as the bulk material would, titanium oxide nanoparticles are able to provide improved UV protection while also having the added advantage of removing the cosmetically unappealing whitening associated with sunscreen in their nano-form.
- The sports industry has been producing baseball bats that have been made with carbon nanotubes, making the bats lighter and therefore improving their performance. Further use of nanoparticles in this industry can be identified in the use of antimicrobial nanotechnology in terms such as the towel and mats used by the sports people in order to prevent illnesses caused by bacteria.

- The use in the military. One example is the use of mobile pigment nanoparticles being used to produce a better form of camouflage, through injection of the particles into the material of soldier's uniform. Additionally, the military have developed sensor systems. Using nanoparticles, such as titanium dioxide, that can detect biological agents.
- The use of nano-titanium dioxide also extends to use in coatings to form selfcleaning surfaces, such as those of plastic garden chairs. A seaked film of water is created on the coating, and any dirt dissolves in the film, after which the next shower will remove the dirt and essentially clean the chairs.
- Controlling the size, shape and material of the nanoparticle enables engineers to design photovoltaics and solar thermal products with tailored solar absorption rates. Absorption of solar radiation is much higher in materials composed of nanoparticles than in thin films of continuous sheets of materials.
- Green synthesis method principally produces nanoparticles using capping and reducing agents present in plant extract. Plant extract can be acquired from vegetative parts such as stem, leaves, bark and flowers. These parts are rich source of reducing agents such as membrane proteins, phenols, flavonoids and other secondary metabolites. In addition to this, plant extracts also contain capping agents such as extracellular tannic acids, peptides and enzymes. Biowaste, in the form of vegetable or fruit waste, has become a major environmental concern due to its improper disposal.

#### **1.3 Green Synthesis:**

To overcome the challenges in the conventional chemical synthesis method, an alternative approach to synthesize biocompatible NPs, termed "green synthesis", has evolved. It is an emerging branch of nanotechnology and has attracted huge attention among researchers and industries, as well as people concerned about environmental pollution and health hazards. Green synthesis techniques are important as they are an eco-friendly approach that involves the use of natural bioresources and avoids toxic chemicals to synthesize different types of NPs thegreen synthesis method offers the following advantages over the chemical methods:

- (i) Safety this method avoids the exposure of chemicals or their toxic byproducts, either during the NPs synthesis step or during their stabilization process
- (ii) **Cost-effective** no external stabilizing agent is required. AuNPs synthesized via green synthesis method are also reported to exhibit antibacterial, antifungal, anticancer, and anti-inflammatory properties, and antioxidant and catalytic activity due to the presence of phytochemicals from the bio extract. All these factors have rendered the green synthesis approach more rewarding than conventional methods.

#### **1.4 ANTIBACTERIAL**

Antibacterial usually refers to an antibiotic, a Principal type of antimicrobial agent used mainly against bacteria. It may kill or inhibit them. Antibacterial may also refer to Antiseptic, a principal type of antimicrobial agent used mainly against bacteria; it may kill or inhibit them Disinfectant, an agent to impair microbes in cleaning/sanitation, but not taken internally as medicine; it may kill or inhibit them Bactericide, an agent that kills bacteria populations Bacteriostatic agent, an agent that does not kill bacteria populations, but inhibits their growth

#### **1.5 ANTI FUNGAL**

An antifungal medication, also known as an anti-myotic medication, a pharmaceutical fungicide or fungistatic used to treat and prevent mycosis such as ringworm, candidiasis (thrush), serious systemic infections such 8 as cryptococcal meningitis, and others. Such drugs are usually obtained by a doctor's prescription, but a few are available over the counter (OTC).

#### **1.6 DPPH**

DPPH is a common abbreviation for the organic chemical compound 2,2diphenyl-1- picrylhydrazyl. It is a dark-coloured crystalline powder composed of stable free radical molecules. DPPH has two majora applications, both in laboratory research: one is a monitor of chemical reactions involving radicals, most notably it is a common antioxidant assay, and another is a standard of the position and intensity of electron paramagnetic resonance signals. DPPH is a well-known radical and a trap ("scavenger") for other radicals. Therefore, rate reduction of a chemical reaction upon addition of DPPH is used as an indicator of the radical nature of that reaction. Because of a strong absorption band centred at about 520 nm, the DPPH radical has a deep violet colour in solution, and it becomes colourless or pale yellow when neutralized. This property allows visual monitoring of the reaction, and the number of initial radicals can be counted from the change in the optical absorption at 520 nm or in the EPR signal of the DPPH

#### **1.7 HYDROGEN PEROXIDE**

Hydrogen peroxide is the simplest kind of peroxide available (oxygenoxygen single bond). It is a colourless liquid and is used in aqueous solution for safety reasons. It acts as a bleaching agent and is also used as disinfectant. Concentrated hydrogen peroxide is a very reactive oxygen species and is used as a propellant in rocketry. The chemical formula for hydrogen peroxide is H 2 O 2 It is often referred to as water with one more oxygen atom. It is acidic in nature and PH is about 4.5. Itis 100 percent degradable compound

#### **1.8** ALKANNABARK (Alkanna tinctoria)

*Alkanna tinctoria* commonly known as *Alkanna*, bugloss, anchusa, Spanish bugloss, dyer's bugloss, orchanet, common *Alkanna* and hoary puccoon is a plant in the Boraginaceae (Borage family) whose bark are used as a red dye. The plant is native in the Mediterranean region. The name Anchusa is derived from the Greek word anchousa which means paint, from the use of the bark as a dye



Figure 1.2 Alkanna tinctoria BARK

The bark produces a fine red coloring material which has been used as a dye in the Mediterranean region since antiquity. The bark as a dyestuff is soluble in alcohol, ether, and the oils, but is insoluble in water. It is used to give color to wines and alcoholic tinctures, to vegetable oils, and to varnishes. *Alkanna* bark contains a mixture of red pigments found in the bark at levels of up to 5% to 6%. These consist mainly of fat-soluble naphthazarin (5,8-dihydroxy-1, 4naphthaquinone) components, such as alkannin and related esters. The red pigments are soluble in fatty oils, which makes them useful for the detection of oily materials in microscopic powders during histological examination. Like some other members of the Borage family, pyrrolizidine alkaloids have been found in *Alkanna tinctoria*, but levels have not been determined. The alkannin esters of beta, beta-dimethyl acrylic acid, beta-acetoxy-isovaleric acid, isovaleric acid, and angelic acid has also been isolated from the bark.

#### Scientific Classification of Alkanna tinctoria



Figure 1.3 Alkanna tinctoria

#### Table 1.1 Scientific classification

Rank	Scientific Name & (Common Name)
Kingdom	Plantae (Plants)
Subkingdom	Tracheobionta (Vascular plants)
Infrakingdom	Streptophyta (land plants)
Superdivision	Spermatophyta (Seed plants)
Division	Magnoliophyta (Flowering plants)
Class	Magnoliopsida (Dicotyledons)
Subclass	Asteridae
Order	Lamiales
Family	Boraginaceae (Borage family)
Genus	Alkanna Tausch (alkanna)
Species	Alkanna tinctoria (L.) Tausch (alkanna)
Synonyms	Alkanna lehmannii (Tineo) A.DC.

#### **1.9 Gold Nanoparticles**

Gold is a D-block, Period 6 element. It is a soft metal that is often alloyed to give it more strength. It is a good conductor of heat and electricity. It is a good reflector of infrared and is chemically inert. The versatile surface chemistry of gold nanoparticles allows them to be coated with small molecules, polymers, and biological recognition molecules, thereby extending their range of application. The morphology of gold nanoparticles is spherical, and they appear as brown powder. Among nanoparticles, gold nanoparticles (Au NPs) have unique surface morphologies, stable nature and controlled geometry. Most Au NPs are used in sensing, electronics, data packing, molecular switches and light-harvesting assemblies. Au NPs are also used in detection, diagnosis and treatments of several diseases. Recently, different methods have been used to synthesize NPs such as physical (sonication, laser ablation and radiation), chemical (condensation, sol gel method and reduction.

#### **Turkevich method**

One of the most well-known techniques for the synthesis of AuNPs is based on the reduction of HAuCl4 by citrate in water, which was first designed by Turkevich in 1951. In this method, the HAuCl4 solution is boiled, and the trisodium citrate dihydrate is then rapidly added into the boiling solution under vigorous stirring. After a few minutes, the color of the solution changes from light yellow to wine red. This method results in AuNPs measuring about 20 nm in diameter. In this technique, citrate ions play a double role, as both stabilizing and reducing agents



Figure 1.4 Mechanistic approach for green synthesis of gold nanoparticles (Au NPs) 1.10 Application of Gold Nanoparticles:

In recent years, a dramatic surge has occurred in the field of nanotechnology, its applications ranging from medicine to engineering (101). The biocompatible nature of Au NPs makes them suitable for medical applications. Au NP conjugates are mostly used in the treatment of cancer, arthritis and antimicrobial therapies.

- Electronics Gold nanoparticles are designed for use as conductors from printable inks to electronic chips. As the world of electronics become smaller, nanoparticles are important components in chip design. Nanoscale gold nanoparticles are being used to connect resistors, conductors, and other elements of an electronic chip.
- 2) Photodynamic Therapy Near-IR absorbing gold nanoparticles (including gold nano shells and nanorods) produce heat when excited by light at wavelengths from 700 to 800 nm. This enables these nanoparticles to eradicate targeted tumors. When light is applied to a tumor containing gold nanoparticles, the particles rapidly heat up, killing tumor cells in a treatment also known as hyperthermia therapy.

- 3) Therapeutic Agent Delivery Therapeutic agents can also be coated onto the surface of gold nanoparticles. The large surface area-to-volume ratio of gold nanoparticles enables their surface to be coated with hundreds of molecules (including therapeutics, targeting agents, and anti-fouling polymers).
- 4) Sensors Gold nanoparticles are used in a variety of sensors. For example, a colorimetric sensor based on gold nanoparticles can identify if foods are suitable for consumption. Other methods, such as surface enhanced Raman spectroscopy, exploit gold nanoparticles as substrates to enable the measurement of vibrational energies of chemical bonds. This strategy could also be used for the detection of proteins, pollutants, and other molecules label-free.
- 5) **Probes** Gold nanoparticles also scatter light and can produce an array of interesting colors under dark-field microscopy. The scattered colors of gold nanoparticles are currently used for biological imaging applications. Also, gold nanoparticles are relatively dense, making them useful as probes for transmission electron microscopy.
- 6) **Diagnostics** Gold nanoparticles are also used to detect biomarkers in the diagnosis of heart diseases, cancers, and infectious agents. They are also common in lateral flow immunoassays, a common household example being the home pregnancy test.
- 7) Catalysis Gold nanoparticles are used as catalysts in a number of chemical reactions. The surface of a gold nanoparticle can be used for selective oxidation or in certain cases the surface can reduce a reaction (nitrogen oxides). Gold nanoparticles are being developed for fuel cell applications. These technologies would be useful in the automotive and display industry.

## CHAPTER II

**STATE OF THE ART &** 

**SCOPE OF THE WORK** 

#### 2.1 Literature Survey

Emerging use of Nanoparticles in diagnosis and treatment of breast cancer was reported by M.V.Yezhelyev et.al [1] and global cancer statistics was reported by Jamal A , et.al [2]. Discoveries in the past decade have demonstrated that the electromagnetic, optical and catalytic properties of noble-metal nanoparticles such as gold, silver and platinum are strongly influenced by shape and size. Biological properties of "naked" metal nanoparticles, written by Bhattacharya R, et.al. [3].

NPs could target at cornea, retina and choroid by surficial applications and intravitreal injection. A review on Silver nano – a trove for retinal therapies, written by Kalishwaralal .K,et,al [4].

Lara H.H, et.al reported the mode of antiviral action of silver nanoparticles against HIV-1[5]. Silver nanoparticles fabricated in Hepes buffer exhibit cytoprotective activities toward HIV-1 infected cells, was illustrated by Sun R, et.al [6]. Nanostructure materials for applications in drug delivery and tissue engineering, was shown by Goldberg M, et, al [7].

Block Copolymer Mediated Synthesis of Dendritic Platinum Nanoparticles, written by Wang L, et. al [8]. A facile method for the fabrication of well-dispersed mesoporous Pt nanospheres involves the use of a polymeric micelle assembly. Polymeric Micelle Assembly for the smart Synthesis of Mesoporous Platinum Nanospheres with Tunable Pore Sizes, written by Li Y, et.al. [9].

Malgras V, et,al. reported the Nanoarchitectures for Mesoporous Metal where the materials have been showcasing impressive enhancements of their electro chemical properties for further implementation, compared to their micro- and microporous counterparts [10].

Yin and co-workers [11] reported that large-scale and size-controlled silver NPs

could be rapidly synthesized under microwave irradiation from an aqueous solution of silver nitrate and trisodium citrate in the presence of formaldehyde as a reducing agent. Size and size distribution of produced silver NPs are strongly dependent on the states of silver cations in the initial reaction solution. Photochemically grown silver nanoparticles with wavelength-controlled size and shape, written by Callegari A et.al [12].

Biomimetic synthesis and patterning of silver nanoparticles was reported by NaikR,et.al [13]. Rapid synthesis of silver nanoparticles using dried medicinal plant of basil was reported by Ahmad N et.al [14]. Sivaraman S.K, et.al illustrated a green protocol for room temperature synthesis of silver nanoparticles in seconds [15].

A review on the biosynthesis of nanoparticles: technological concepts and future applications was written by Mohanpuria P, et.al [16]. Perumal-Samy R, et.al. did the Screening of 34 medicinal plants for antibacterial properties [17]. Studies on analgesic and anti-inflammatory activities of Vitexnegundo Linn, written by Telang R.S, et.al [18].

Larvicidal activity of few plant extracts against culexquinque-fasciatus and Anopheles stephensi, written by Pushpalatha E, et.al [19]. Investigation of the effect of pomegranate extract and monodisperse silver nanoparticles combination on MCF-7 cell line was reported by Sahin B, et.al.[20]. Green Synthesis, characterisation and application of nanoparticles was reported by Gaurav pal et al. [21].

Honey mediated green synthesis of nanoparticles provides a simple, cost effective, biocompatible, reproducible, rapid and safe method was done by Balasooriya et al. The special activity of honey functionalized nanoparticles may provide valuable end products with numerous applications in diverse fields [22].

The current generation is all about nanotechnology and nanoparticles. The field has

captured applications from daily life technological applications to armoires and space technology and from human cosmetics to medicine [14-16]. On the other hand, green-plant extraction method is a non-toxic and safe process [17-19]. Nowadays, these metal nanoparticles are used in shampoo, soap, cosmetics and toothpastes as well [20-22].

Henry G. Aritonang, Henry kolenang reported the synthesis of silver nanoparticles using aqueous extract of medicinal plant [23]. Mital et al., investigated the synthesis of silver nanoparticles using plant extract. Biomolecules present in plant extract used to reduce metal ions to nanoparticles in green synthesis process. They reported that the synthesis conducted at room temperature and pressure and easily scaled up [24].

Green synthesis of gold nanoparticles using plant extract as reducing agent was worked by pazelia and Raya czach. All GNPs prepared shows good bio compatibility and good stability for over three weeks was reported in this literature [25]. Synthesis of silver nanoparticles using buchu plant extract and their analgesic properties was confirmed by Herbert chiguvare et al.,[26].

RatiramGomaji et al reported the Ni NPs were obtained through a nickel salt with hydrazine hydrate at 80 C temperature by using ethylenediamine as protective [27]. New application of zinc oxide nanoparticles in the field of porous and nanometric materials prepared by non-conventional process was reported by meena et al., [28].

Shlomae et al reported the synthesis of copper nanoparticles using *Penicillium autantiogriseum*, *Penicillium citricum*, *Penicillium waksmanni*[29]. Biosynthesis of cadmium oxide nanoparticles using flowers extract of *Achillea wilhelmsii*as the reducing agents were reported by andeani et al [30]. Though there have been several studies reported on the biological synthesis of platinum nanoparticles using extracts from different plant

species [31-34].

The enzyme- based NPs biogenic synthesis is also a viable technique but is time consuming. Natural resources availability, tedious and costly purification, storage problems and sensitivity temperatures, strong acid and alkaline pH are the limiting factors [35,36]. Various techniques are available for the synthesis of nanofilms and nanowire [37-40]. Metal and metal oxide nanoparticles are used for antimicrobial activities drug delivery and cancer therapy [41-45]. Physical methods are expensive [46] and the by-products formed is useful in cosmetic and medical applications [47].

#### 2.2 Scope of the work

Chemical method of synthesizing nanoparticles and green method of synthesizing nanoparticles were widely studied by the researchers. Among this, green method of synthesis very important due to its advantage in controlling particle size, morphology very effectively. This method also involves less time-consuming process for getting the desired nanoparticle size. Hence for this investigation, green method is chosen to synthesize nanoparticles.

The synthesis of gold nanoparticles has received a considerable attention and has been focus of research due to their high chemical and thermal stability, fascinating optical, electronic properties and promising applications such as nanoelectronics, biomedicine, sensing and catalysis.

Different physical and chemical methods for gold nanoparticles synthesis are known but these methods are either expensive or not eco-friendly due to the use of hazardous chemicals, stringent protocols used during this process. Therefore, tremendous excitement in the study of gold nanoparticles synthesis by using biological systems. Microorganisms play a very important role in the eco-friendly and green synthesis of metal nanoparticles. This review contains a brief outlook of the bio- synthesis of gold nanoparticles using plant resource, their characterization and potential applications in various fields.

Gold is used for the biomedical and various applications. The work on Synthesize of Gold nanoparticles using the bark extract of Alkanna Tinctoria gives importance for reducing the hazardous chemical methods. In this investigation we have synthesized the Gold Nanoparticles from Auric chloride salt.

It is then characterized by UV- visible spectroscopy, IR spectroscopy and AFM to confirm the nature of gold nanoparticles. The applications of synthesized gold nanoparticles were studied: Anti-bacterial, Anti-fungal activities, DPPH scavenging activity and Hydrogen Peroxide scavenging activity shows the excellent applications of gold nanoparticles.

#### **2.3 OBJECTIVES OF THE WORK**

The main objectives of the study are:

- 1. To synthesize nanoparticles of Gold through Green synthesis method.
- 2. To utilize the bark extracts of Alkana Tinctoria for synthesizing nano particles.
- 3. To characterize the presence of Metal nanoparticles through various techniques such as UV- visible Spectroscopy, IR and AFM.
- 4. To study the surface morphology of gold nanoparticle.
- 5. To study the enormous applications of nanoparticles.
- 6. To identify the antibacterial, antifungal and DPPH activity.

### CHAPTERII

**MATERIALS AND METHODS** 

#### **3. MATERIALS AND METHODS**

A brief outline of the materials and methods used in this project work is

presented here.

#### **3.1Materials required for Synthesis:**

1. Bark of Alkanna tinctoria

2. Auric chloride salt (Analar Gold (III) Chloride was purchased from

Spincotech Private Limited )

#### **3.2Instrumentation:**

- 1. Cooling Centrifuge
- 2. Muffle furnace
- 3. Ultraviolet Spectroscopy
- 4. IR

5. AFM

#### **3.3 PROCEDURE:**

#### > Preparation of Auric chloride solution:

1mM Gold (III) Chloride was prepared using double distilled water.

It is shaken well for uniform concentration.



Figure 3.1 Auric chloride solution

#### > **Preparation** of bark extract: the reducing agent

*Alkanna tinctoria* was purchased from the local market, Thoothukudi. The bark was finely cut, washed with double-distilled water to remove any impurities. *About* 2 g of *Alkanna tinctoria* bark are weighed accurately. The extract is prepared by the addition of 100 ml of water in Erlenmeyer flask. It was then cooled to room temperature. The extract is filtered using Whatman no. 41 filter paper.



Figure 3.2 Extract of the reducing agent Alkanna tinctoria bark

About 20 ml of the bark extract is taken in a RB flask fitted with a water condenser. It is fitted in a clamp. Then it is heated in a water bath for 10-15 minutes. The extract is refluxed using 20 ml of the made-up Auric chloride solution in drops, added occasionally and let it reflux for few minutes. The reduction of extract is observed by the colour change from purple to wine red.


Figure 3.3 Change in physical appearance of reducing agent from Purple to Wine red

This physical change ensures the presence of Au nanoparticles. Then it is cooled for an hour. The extract obtained from refluxing is centrifuged using Cooling centrifuge to get precipitate of gold nanoparticle.

The precipitate is collected in a silicon crucible, this on heating in muffle furnace at 100 degrees Celsius for 45minutes we get solid gold nano particles.



Figure 3.4 Synthesis of Gold nanoparticle

#### **3.4 METHODS**

#### **3.4.1 UV SPECTROSCOPY:**



Figure 3.5 UV-VIS SPECTROMETER (UV-VIS)

Ultraviolet–visible spectroscopy (UV) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible spectral regions. Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of Ultraviolet or visible light to excite these electrons to higher antibonding molecular orbitals.

# **3.4.2 INFRARED SPECTROSCOPY:**



#### Figure 3.6 INFRARED SPECTROSCOPY

An infrared spectrophotometer is an instrument that passes infrared light through an organic molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis.

## 3.4.3 ATOMIC FORCE MICROSCOPY (AFM)



Figure 3.7 ATOMIC FORCE MICROSCOPY (AFM)

The AFM works much the same way a profilometer works only on a much, smaller scale: a very sharp tip is dragged across a sample surface and the change in the vertical position (denoted the "z" axis) reflects the topography of the surface. By collecting the height data for a succession of lines it is possible to form a three-dimensional map of the surface features. The AFM has three major abilities

- ➢ force measurement,
- ➢ imaging, and
- ➤ manipulation

The Atomic force microscopy analysis using the Nano surf easy2 scanBT02218 is a profilometer.

#### **3.4.4 ANTIBACTERIAL METHOD:**

#### AGAR WELL DIFFUSION METHOD

#### PRINCIPLE

The antimicrobials present in the given sample were allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in millimetres.

#### MATERIALS REQUIRED

(*Staphylococcus aureus* – 902 and *Pseudomonas aeruginosa*-424) was purchased from MTCC, Chandihar, India. Nutrient Agar medium, Nutrient broth, Gentamicin antibiotic solution was purchased from Himedia, India. Test samples, petri-plates, test tubes, beakers conical flasks were from Borosil, India. Spirit lamp, double distilled water.

#### **AGAR- WELL DIFFUSION METHOD**

#### a. Nutrient Agar Medium

The medium was prepared by dissolving 2.8 g of the commercially available Nutrient Agar Medium (HiMedia) in 100ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm Petri plates (25-30ml/plate) while still molten.

#### **b.** Nutrient broth

Nutrient broth was prepared by dissolving 2.8 g of commercially available nutrient medium (HiMedia) in 100ml distilled water and boiled to dissolve the medium completely. The medium was dispensed as desired and sterilized by autoclaving at 15 lbs pressure (121°C) for 15 minutes

#### PROCEDURE

Petri plates containing 20 ml nutrient agar medium were seeded with 24 hr culture of bacterial strains were adjusted to 0.5 OD value according to McFarland standard, (*Staphylococcus aureus* – 902 and *Pseudomonas aeruginosa*-424) Wells were cut and concentration of sample H, G and A (0.01) (500, 250, 100 and 50  $\mu$ g/ml) was added. The plates were then incubated at 37°C for 24 hours. The antibacterial activity was assayed by measuring the diameter of the inhibition zone formed around the wells. Gentamicin antibiotic was used as a positive control. The values were calculated using Graph Pad Prism 6.0 software (USA).

#### **3.4.5 ANTIFUNGAL ACTIVITY:**

#### AGAR WELL DIFFUSION METHOD

#### PRINCIPLE

The anti-fungal agent present in the given sample was allowed to diffuse out into the medium and interact in a plate freshly seeded with the test organisms. The resulting zones of inhibition will be uniformly circular as there will be a confluent lawn of growth. The diameter of zone of inhibition can be measured in millimetres.

#### **MATERIALS REQUIRED**

Potato dextrose agar medium, Amphotericin B antimycotic solution, test samples, test tubes, beakers conical flask, spirit lamp, double distilled water and petri-plates.

#### **AGAR- WELL DIFFUSION METHOD**

#### **Potato Dextrose Agar Medium**

The potato dextrose agar medium was prepared by dissolving 20 gm of potato infusion, 2 gm of dextrose and 1.5 gm of agar in 100ml of distilled water. The dissolved medium was autoclaved at 15 lbs pressure at 121°C for 15 minutes. The autoclaved medium was mixed well and poured onto 100mm petri plates (25-30 ml/plate) while still molten.

#### PROCEDURE

Petri plates containing 20ml potato dextrose agar medium was seeded with 72 hr culture of fungal strain (*Aspergillus Niger*) wells were cut and different concentration of sample G, A (0.01) and H (500, 250, 100 and 50  $\mu$ g/ml) was added. The plates were then incubated at 28°C for 72 hours. The anti-fungal activity was assayed by measuring the diameter of the inhibition zone formed around the wells. Amphotericin B was used as a positive control. The values were calculated using Graph Pad Prism 6.0 software (USA).

#### **3.4.6 HYDROGEN PEROXIDE SCAVENGING ASSAY:**

#### PRINCIPLE

Hydrogen peroxide is a weak oxidizing agent and can inactivate a few enzymes directly, usually by oxidation of essential thiol (-SH) groups. Hydrogen peroxide can cross cell

membranes rapidly once inside the cell, H2O2 can probably react with Fe2+, and possibly Cu2+ ions to form hydroxyl radical and this may be the origin of many of its toxic effects. It is therefore biologically advantageous for cells to control the amount of hydrogen peroxide that is allowed to accumulate.

#### **MATERIALS REQUIRED**

Hydrogen peroxide solution and Sodium phosphate buffer.

#### PROCEDURE

The ability of plant extracts to scavenge hydrogen peroxide was estimated according to the method reported by Ruch et al. with minor modification. A solution of hydrogen peroxide (43 mM) is prepared in phosphate buffer (1 M pH 7.4). Different concentration of sample A (0.01) (500, 250, 100, 50 and 10  $\mu$ g/ml) was added to a hydrogen peroxide solution (0.6 ml, 43 mM). Absorbance of hydrogen peroxide at 230 nm was determined after 10 minutes against a blank solution containing phosphate buffer without hydrogen peroxide. Ascorbic acid was used as standard. The free radical scavenging activity was determined by evaluating % inhibition as above.

% inhibition = [(Control-Test)/control]  $\times 100$ .

#### 3.4.7 DPPH RADICAL SCAVENGING ACTIVITY:

The DPPH assay is popular in natural product antioxidant studies. One of the reasons is that this method is simple and sensitive. This assay is based on the theory that a hydrogen donor is an antioxidant. It measures compounds that are radical scavengers. Figure below, shows the mechanism by which DPPH accepts hydrogen from an antioxidant. DPPH is one of the few stable and commercially available organic nitrogen radicals (1). The antioxidant effect is proportional to the disappearance of DPPH in test samples. Monitoring DPPH with a UV spectrometer has become the most commonly used method because of its simplicity and accuracy. DPPH shows a strong absorption maximum at 517 nm (purple). The color turns from purple to yellow followed by the formation of DPPH upon absorption of hydrogen from an antioxidant. This reaction is stoichiometric with respect to the number of hydrogen atoms absorbed. Therefore, the antioxidant effect can be easily evaluated by following the decrease of UV absorption at 517 nm



#### **MATERIALS REQUIRED:**

0.1mM DPPH solution, Ascorbic acid, Methanol 0.1 mM DPPH Solution Dissolve 39 mg of DPPH in 100 ml of methanol and store at -200 C until needed. Ascorbic acid (Standard) 1mg/ ml of Ascorbic acid Procedure 1 Briefly, prepare 0.1 mM of DPPH solution in methanol and add 100  $\mu$ l of this solution to 300  $\mu$ l of the solution of sample B at different concentration (500, 250, 100, 50 and 10  $\mu$ g/mL). 2 The mixtures have to be shaken vigorously and allowed to stand at room temperature for 30 minutes. 3 Then the absorbance has to be measured at 517 nm using a UV-VIS spectrophotometer. (Ascorbic acid can be used as the reference). 4 Lower absorbance values of reaction mixture indicate higher free radical scavenging activity. 5 The capability of scavenging the DPPH radical can be calculated by using the following formula. 6. DPPH scavenging effect (% inhibition) = [(absorbance of control- absorbance of reaction mixture)/absorbance of control] X 100

# **CHAPTER IV**

**RESULT AND DISCUSSION** 

#### **4. RESULT AND DISCUSSION**

#### 4.1 Characterization of Gold nanoparticles

#### 4.1.1 UV-Vis Spectral analysis



Figure 4.1 UV-Visible spectra of Alkanna tintcoria Bark

UV – Vis spectral analysis of *Alkanna tintcoria* bark was performed on JASCO, V-650 Spectrophotometer. The colour of the bark extract was found to be purple. A peak was observed around 350nm and 450nm for the bark shows the presence of organic molecules.



Figure 4.2 UV-Visible spectra of gold nanoparticles

Gold Nanoparticles were synthesised using *Alkanna tinctoria* bark the optical absorbance properties of the synthesized Au Nanoparticles were investigated using bark extract of in the wavelength range 200-900 nm at ambient temperature. The nanoparticles formed very fastand it was clear from the colour of the gold solution from yellow to purple. Figure.4.2 indicates the UV –Visible diffuse reflectance spectra of Au Nanoparticles using extract of *Alkannatincoria*. There is a strong absorption peak around 500nm which confirms the presence of Au nanoparticles.



#### 4.1.2 INFRARED SPECTROSCOPY

Figure 4.3 Infrared spectra of Alkanna tintcoria bark



Figure 4.4 Infrared spectra of gold nanoparticle

FT-IR spectra of bark extract and au nanoparticles were recorded to find out the presence of biomolecules present for the reduction and capping. The bark sample was used as such and the prepared nanoparticles were centrifuged using 7000 rpm for 15 min and its was dried. Using KBr the dried powder was made as pellets and the FT-IR spectra was recorded. Figure.4.3 shows the FT-IR spectra of the bark extract. The bark extract has peaks at 3125cm<sup>-1</sup>, 1638cm<sup>-1</sup> 1400cm<sup>-1</sup> and 1033cm<sup>-1</sup>. Au nanoparticles show peaks at 3125cm<sup>-1</sup>, 1637cm<sup>-1</sup>, 1400cm<sup>-1</sup> and 1037cm<sup>-1</sup>.

The peak at 1638cm<sup>-1</sup>gets shifted to 1637cm<sup>-1</sup> in the spectra of Au nanoparticles. This peak was observed due to the presence of carbonyl C=O group which shows the binding of biomolecules with the nanoparticles. The peak at 3125cm<sup>-1</sup>may be due to the presence of -OH group which was responsible for the biogenic reduction. A peak was recorded around 1037cm<sup>-1</sup>. corresponds to the C-O stretching frequency of biocomponents.

From the results of FT-IR spectral data it was clear that the reduction of Au nanoparticles and its stabilisation was due to the presence of active biomolecules such as C=O and OH functional groups.



#### 4.1.3 ATOMIC FORCE MICROSCOPY

Figure 4.5 AFM SPECTRA OF Alkanna tintcoria BARK AFM

topographical pictures of bark extract in Figure 4.5 shows the images of *Alkanna tinctoria* bark which shows the sponge like texture/structure



Figure 4.6 AFM spectra of Gold + Alkanna tinctoria Bark

AFM technique is the one of the best tools for measuring nano sized materials. This method analysis the particle surface using Tip, it is so high-pitched that as it is moved across something, the tip can feel the shape by measuring the forces between the atoms on the tip and the atoms on the objectAFM topographical pictures of Novel gold nano particles in Figure 4. 6.AuNPs were majorly equal in size, particles size range between 30 to 90 nm due to the metal covers or oversittingofeachtogether3-D images exhibits the brick like structure.

PARAMETERS	Gold nanoparticle
Area	2.5 to 39.4
Surface roughness	9.5 to 28.1
RMS valley	12.6 to 40.2
Valley	91.5 to 333.8
Highest Peak	58.4 to 181.4
Maximum valley depth	(-33.1) to (-152.4)
Surface to average mean valley	-18.6

# 4.2 APPLICATION OF GOLD NANOPARTICLES 4.2.1ANTIBACTERIAL ACTIVITY



Figure 4.7 Effect of sample A (0.01) against *Pseudomonas aeruginosa*.



Figure 4.8 Effect of sample A (0.01) against *Staphylococcus aureus*.

# Table 4.2 SD± Means of zone of inhibition obtained by sample

# A(0.01) against Staphylococcus aureus and Pseudomonas

# <u>aeruginosa.</u>

S.No	Name of the	Name of	Zone of inhibition (mm) SD ± Mean				
	test organism	the test sample	500 μg/ml	250µg/ml	100 μg/ml	50µg/ml	PC
1.	Staphylococcus aureus	A(0.01)	0	0	0	0	13.5±0.7
2.	Pseudomonas aeruginosa		4.25±0.35	0	0	0	16.5±0.7

SD – Standard Deviation, \*Significance - p < 0.05

Petri plates containing 20 ml nutrient agar medium were seeded with 24hr culture of bacterial strains *shows excellent inhibitory activity for Pseudomonas aeruginosa. Different* concentration of sample (500µg/ml, 250µg/ml,100µg/ml and 50µg/ml) added shows that 500µg/ml exhibits good inhibiting activity. Gentamicin antibiotic was used as a positive control.

#### 4.2.2 ANTIFUNGAL ACTIVITY



Figure 4.9 Effect of sample A(0.01) against Aspergillus niger.

# Table 4.3 SD± Means of zone of inhibition obtained by sample A

# (0.01) against Aspergillus niger.

S.NO	Name of the test organism	Name of the test	Zone of inhibition (mm) SD ± Mean				
sample		sample	500 μg/ml	250 μg/ml	100 µg/ml	50 μg/ml	PC
1.	Aspergillus niger	A (0.01)	11.5±0.7	5.5±0.7	0	0	16.5±0.7

SD – Standard Deviation, \*Significance - p < 0.05

Aspergillus niger was used to study the inhibitory effect of Au nano particles.at various concentrations. Using Potato dextrose agar medium, the antifungal activity of Au nanoparticles was

studied. The results show that at 500  $\mu$ g/ml, a high inhibitory activity was observed. Pathogens growth can be inhibited. Hence it can be used as excellent antifungal agent.

# 4.2.3 HYDROGEN PEROXIDE SCAVENGING ASSAY

# Table 4.4 ABSORBANCE OF Au NANOPARTICLES AT VARIOUSCONCENTRATION BY HYDROGEN PEROXIDE SCAVENGINGEFFECT

S. No	Tested sample concentration (μg/ml)	OD Value at 230 nm (In triplicates)		
1.	Control	0.301	0.314	0.335
2.	500 μg/ml	0.081	0.080	0.089
3.	250 μg/ml	0.094	0.116	0.116
4.	100 μg/ml	0.117	0.118	0.130
5.	50 μg/ml	0.138	0.141	0.162
6.	10 μg/ml	0.180	0.226	0.253
7.	Ascorbic acid	0.017	0.011	0.012

Control Mean OD value: 0.316



FIGURE	4.10	PERCE	NTAGE	OF	INHIB	ITION
IJOURL	1.10	LINCL	<b>THOL</b>			

S. No	Tested sample concentration (μg/ml)	Percentage of in	Mean value		
1.	Ascorbic acid	94.62025	96.51899	96.20253	95.78059
2.	500 μg/ml	74.36709	74.68354	71.83544	73.62869
3.	250 μg/ml	70.25316	63.29114	63.29114	65.61181
4.	100 µg/ml	62.97468	62.65823	58.86076	61.49789
5.	50 μg/ml	56.32911	55.37975	48.73418	53.48101
6.	10 μg/ml	43.03797	28.48101	19.93671	30.48523

log(inhibitor) vs. normalized response Variable		
Slope Post fit values		
Best-fit values		
LogIC50		1.720
HillSlope		-1.461
IC50		<mark>52.53</mark>
Std. Error		
LogIC50		0.07377
HillSlope		0.3594
95% Confidence Intervals		
LogIC50		1.561 to 1.880
HillSlope		-2.237 to -0.6846
IC50		36.40 to 75.82
Goodness of Fit		
Degrees of Freedom		13
R square		0.8722
Absolute Sum of Squares		2481
Sy.x		13.81
Number of points		
Analyzed	3	15

## Table 4.5 IC50 Value of tested sample: 52.53 $\mu g/ml$



A (0.01) **p**g/m l

#### FIGURE 4.11 CONCENTRATION VERSUS PERCENTAGE OF INHIBITION



## FIGURE 4.12 SCAVENGING EFFECT OF $\underline{H_2O_2}$

Inhibitory concentration at 50 percentage was found to be  $52.53\mu$ g/ml. Dose dependent increase in the antibacterial activity was observed. At higher concentration (500  $\mu$ g/ml), 74% excellent inhibition activity was observed

#### **4.2.4 DPPH RADICAL SCAVENGING ACTIVITY:**

# TABLE 4.7 ABSORBANCE OF Au NANOPARTICLES AT VARIOUSCONCENTRATIONS BY DPPH SCAVENGING EFFECT

S.NO	Tested Sample Concentration (µg/ml)	ABSORBANCE (517 nm)
1.	Control	0.494
2.	20 ml	0.329
3.	40 ml	0.331
4.	60 ml	0.420
5.	80 ml	0.478



#### FIGURE 4.13 DPPH SCAVENGING EFFECT OF Au NANOPARTICLES

TABLE 4.8 Percentage o	f Inhibition of	f synthesized Au	Nanoparticles
------------------------	-----------------	------------------	---------------

S.NO	Tested sample concentration (µg/ml)	Percentage of inhibition
1.	20	33.4
2.	40	32.99
3.	60	14.9
4.	80	3.23



#### FIGURE 4.14 PERCENTAGE OF INHIBITION

The scavenging effect of synthesized Au Nanoparticles were studied by measuring the absorbance. The results shows that at 80 ml the percentage of inhibition is good. This shows that the free radicals exist in our body will get scavenge using the Au Nanoparticles mediated *Alkanna tinctoria* bark extract. Hence it finds excellent application in anti-aging property.

# **CHAPTER V**

**CONCLUSION AND REFERENCE** 

#### CONCLUSION

Nanotechnology has the potential to revolutionize our lives. This is because it presents almost unlimited potential to make remarkable changes in virtually all fields ranging from medicine, computer technology, construction, environmental remediation, food industry, to new energy sources.

Despite presenting many potential benefits in many areas, nanotechnology of today is still in its infancy as just a few projects have been commercialized. Many are yet to undergo full lifecycle assessment. The number of nanotechnology innovations continues to rise. However, the same cannot be said of research about their potential effects on environment and biological systems.

As the world readily adapts to this new technology wave, concomitant effort should be directed to the understanding of their possible impacts. This is essential to ensure that nanomaterials do not become the new hazard of 21st century.

The long-long term sustainability of this new technology may depend on the establishment of its risks. Scientists are keen to introduce nanoparticles in every field of life, since it has various applications. Various methods such as physical, chemical and biological methods are available to synthesis Nanoparticles.

Green synthesis of Nanoparticles is an important method to synthesis, since it is highly efficient for the Fabrication of Nanoparticles at Nanoscale without affecting our Environment.

By Eco-Friendly Method, using *Alkanna tinctoria* Au Nanoparticles can be synthesized. This method of Biogenically synthesized Au Nanoparticles is characterized using UV-visible Spectra, IR Spectra. Also, the surface morphology of the Nanoparticles is confirmed by SEM and AFM techniques.

The Extract of *Alkanna tinctoria* is successfully employed for the preparation of Au Nanoparticles. The nanoparticles synthesized shows good absorbance around 523 nm.

The presence of Bio-active agents in the extract was confirmed from FTIR studies. The results of Atomic Absorption spectra showed the formation of Nanoparticles. Also, SEM images confirms the Flaky Nanoparticles. Anti-Bacterial and Anti-Fungal applications showed on Excellent percentage of inhibition at higher concentration. Hence this Au Nanoparticles is used for Anti-Bacterial and Anti-Fungal application. The scavenging effect of DPPH and Hydrogen Peroxide showed that the synthesized Nanoparticles can be employed for Anti-Aging application

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# A Comparative Study on Efficient Inhibition of Green

# Inhibitors for mild steel in acidic medium: A Sustainable and

# **Green** approach

**Project in Chemistry** 

Submitted to St. Mary's College (Autonomous) in partial

fulfillment for the award of the Degree of Bachelor of Science in

Chemistry

Project Done By

M.Gayathiri

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St. Mary's College (Autonomous)

(Re - accredited with 'A+' Grade by NAAC)

Thoothukudi – 628001

2022 - 2023

#### DECLARATION

We hereby declare that the project entitled "A Comparative study on efficient inhibition of green inhibitors for mild steel in acid medium: A sustainable and green approach" submitted to St. Mary's college (Autonomous) Thoothukudi affiliated to Manonmaniam Sundaranar university for the degree of bachelor of science is our original work and that is has not previously formed the basis for the award of

any degree diploma or similar title.

M.Gayathri M.Gayathri

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Thoothukudi. April, 2023

#### CERTIFICATE

This is to certify that the report of the project in chemistry entitle A COMPARTIVE STUDY ON EFFICIENT INHIBITION OF GREEN INHIBITORS FOR MILD STEEL IN ACIDIC MEDIUM: A SUSTAINABLE AND GREEN APPROACH submitted to St. Mary's College (Autonomous), in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 2022-2023.

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### CONTENTS

Chapter No.	TITLE	Page No.
	INTRODUCTION	
CHAPTER I		
1.1	CAUSE OF CORROSION	
1.0		2
1.2	IMPORTANCE OF CORROSION STUDIES	3
1.3	TYPES OF CORROSION	3
1.3.1	GENERAL CORROSION	4
1.3.2	STRESS CORROSIAN CRAKING	4
1.3.3	LOCALISED CORROSIAN	5
1.3.4	PITTING CORROSION	5
1.3.5	CREVICE CORROSION	6
1.3.6	INTER GRANULAR CORROSIAN	6
1.3.7	GALVONIC CORROSION	6
1.3.8	EROSION	7
1.3.9	WATERLINE CORROSION	7
1.4	METHODS OF CORROSION PROTECTION	8
1.4.1	APPLICATION OF PROTECTIVE COATINGS	8
1.4.2	POLARIZE OF SHIFT THE POTENTIAL OF THE METAL	9
1.4.3	CATHODIC PROTECTION	9
1.4.4	CORROSION INHIBITORS	9
1.5	CORROSION INIBITION OF MILD STEEL	10
1.5.1	CORROSION INHIBITION IN ACID SOLUTIONS	10
1.6	CORROSION MONITORING	11
1.7	FACTORS AFFECTING CORROSION	11
1.8	ADSORPTION AND INFLUENCE OF INHIBITION OF CORROSOION	12
1.9	ADSORPTION ISOTHERMS	13
1.10	BEHAVIOUR OF INHIBITORS IN ACID SOLUTION	13
CHAPTER II	STATE THE ART & SCOPE OF WORK	
2.1	LITERATURE SURVEY	15
2.2	SCOPE OF THE WORK	22

CHAPTER II	MATERIALS & METHOD	
3.1	COMPOSITION OF THE MILD STEEL SPECIMEN USED	23
3.2	INHIBITOR USED	24
3.3	COLLECTION OF FLOWERS	24
3.4	EXTRCTION OF FLOWER	24
3.4.1	Camelia sinensis (GREENTEA LEAVES)	25
3.4.2	Mimusops elengi(SPANISH CHERRY)	26
3.4.3	Nerium oleander(ARALI LEAVES)	27
3.5	EXPERIMENTAL PROCEDURES	28
3.5.1	WEIGHT LOSS MEASUREMENTS	28
3.6	KINETIC AND THERMODYNAMIC CONSIDERATION	29
3.7	ADSORPTION ISOTHERM	30
3.8	POTENTIODYNAMIC POLARIZATION MEASUREMENTS	30
3.9	ELECTROCHEMICAL IMPEDANCE MEASUREMENTS	31
3.10	FOURIER TRASFORM INFRARED SPECTROSCOPIC STUDIES	33
CHAPTER IV	RESULTS AND DISCUSSION	
4.1	WEIGHT LOSS MEASUREMENTS	34
4.1.1	THE EFFECT ON CHANGING CONCENTRATION OF ACID	34
4.1.2	EFFECT OF TEMPERATURE	43
4.2	ADSORPTION ISOTHEERM	46
4.3	ELECTROCHEMICAL MEASUREMENTS	52
4.3.1	POLISATION MEASUREMENTS	52
4.3.2	EIS MEASUREMENTS	56
4.4	FOURIER TRANSFORM INFRARED SPECTRAL RESULTS	60
4.4.1	FTIR STUDIES OF CAMELLIA SINENSIS	60
4.4 2	FTIR STUDIES OF NERIUM OLEANDER	61
4.4.3	FTIR STUDIES OF MIMUSOPS ELENGI	62
	CONCLUSION	64
	REFERENCES	65

## LIST OF TABLES

TABLE NO.	CONTENTS	PAGE NO.
3.1	COMPOSITION OF COMMERCIAL MILD STEEL	23
4.1	CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS CONCENTRATION OF <i>Mimusops elengi</i> EXTRACT WITH DIFFERENT ACID CONCENTRATION	35
4.2	CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS CONCENTRATION OF <i>Camellia sinensis</i> EXTRACT WITH DIFFERENT ACID CONCENTRATION	38
4.3	CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS CONCENTRATION OF <i>Nerium oleander</i> EXTRACT WITH DIFFERENT ACID CONCENTRATION	41
4.4	CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS CONCENTRATION OF Mimusops elengi (Spanish cherry) EXTRACT WITH HCI AT 303K	44
4.5	CONCENTRATION OF <i>Camelia Sinensis</i> EXTRACT WITH HCl AT 303K	45
4.6	CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS CONCENTRATION OF Nerium oleander (Arali leaves) EXTRACT WITH HCl AT 303K	45
4.7	POLARIZATION MEASUREMENTS FOR MILD STEEL CORROSION IN 1M HCI IN THE ABSENCE AND PRESENCE OF INHIBITOR	55
4.8	Electrochemical Impedance data for mild steel corrosion in 1M HCl in the absence and presence of inhibitor (ppm)	59

## LIST OF FIGURES

FIGURE NO.	CONTENTS	PAGE NO.
1.1	TYPES OF CORROSION	3
1.2	DIAGRAM OF WATER LINE CORROSION SETUP	8
3.1	ELECTROCHEMICAL WORKSTATION	31
3.2	INFRARED SPECTROSCOPY	33
4.1	VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF <i>Mimusops elengi</i> EXTRACT ON MILD STEEL IN 1M HCl CONCENTRATION	36
4.2	VARIATION OF INHIBITION EFFICIENCY WITH CONCENTRATION OF <i>Mimusops elengi</i> EXTRACT ON MILD STEEL IN 1M HCL SOLUTION	37
4.3	VARIATION OF CORROSION RATE WITH CONCENTRATION OF Mimusops elengi EXTRACT ON MILD STEEL IN 1.5M HC1 CONCENTRATION	37
4.4	VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Camellia sinensis EXTRACT ON MILD STEEL IN 1M HCI SOLUTION	39
4.5	VARIATION OF INHIBITION EFFICIENCY WITH CONCENTRATION OF <i>Camellia sinensis</i> EXTRACT ON MILD STEEL IN 1.5M HCl SOLUTION	40
4.6	VARIATION OF CORROSION RATE WITH CONCENTRATION OF 40 Camellia sinensis EXTRACT ON MILD STEEL IN 1.5M HCI CONCENTRATION	
4.7	VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Nerium oleander EXTRACT ON MILD STEEL IN 1M ACID SOLUTION	42
4.8	VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Nerium oleander EXTRACT ON MILD STEEL IN 1M ACID SOLUTION	42
4.9	VARIATION OF CORROSION RATE WITH CONCENTRATION OF Nerium oleander EXTRACT ON MILD STEEL IN 1.5M ACID SOLUTION	43
4.10	LANGMUIR ISOTHERM FOR <i>Mimusops elengi</i> (SPANISH CHERRY) AT 1M HCl AT ROOM TEMPERATURE	47
4.11	LANGMUIR ISOTHERM FOR <i>Mimusops elengi</i> (SPANISH CHERRY) IN 1.5M HCl AT ROOM TEMPERATURE	47
4.12	LANGMUIR ISOTHERM FOR <i>Mimusops elengi</i> (SPANISH CHERRY) IN 2M HCl AT ROOM TEMPERATURE	48

4.13	LANGMUIR ISOTHERM FOR Nerium oleander (ARALI LEAVES) LEAVES IN 1M HCI AT ROOM TEMPERATURE	48
4.14	LANGMUIR ISOTHERM FOR <i>Nerium oleander</i> (ARALI LEAVES) IN 1.5M HCI AT ROOM TEMPERATURE	49
4.15	LANGMUIR ISOTHERM FOR <i>Nerium oleander</i> (Arali leaves) IN 2M HCL AT ROOM TEMPERATURE	49
4.16	LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (Camellia sinensis) IN 1M HCL AT ROOM TEMPERATURE	50
4.17	LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (Camellia sinensis) AT 1.5M HCL AT ROOM TEMPERATURE	50
4.18	LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (Camellia sinensis) IN 2M HCL AT ROOM TEMPERATURE	51
4.19	TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCI	53
4.20	TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR <i>Camellia sinensis</i>	53
4.21	TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR <i>Nerium oleander</i>	54
4.22	TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR <i>Mimusops elengi</i>	54
4.23	TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH VARIOUS INHIBITORS	55
4.24	NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCI	57
4.25	NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR <i>Camellia sinensis</i>	57
4.26	NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR Nerium oleander	58
4.27	NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE INHIBITOR <i>Mimusops elengi</i>	58
4.28	NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITHOUT AND WITH INHIBITOR	59
4.29	FTIR ANANLYSIS OF Camellia sinensis	60
4.30	FTIR ANANLYSIS OF Nerium oleander	61
4.31	FTIR ANANLYSIS OF Mimusops elengi	62

# Abstract

Eco-friendly, inexpensive, green inhibitor is of greater interest in the corrosion inhibition. The extraction of various plants was used for the investigation. The inhibition performance of the various inhibitors such as *Camellia sinensis* (Green tea leaves), *Mimusops elengi* (Spanish cherry), *Nerium oleander* (Arali leaves) was studied in 1M, 1.5M, 2M HCl on Mild steel. The inhibition efficiency was analysed by electrochemical technique such as polarisation test and Electrochemical Impedance Spectroscopy. Corrosion inhibition was also studied from the usual weight loss method. The results depict that the increase in the concentration of inhibitor increases the inhibition efficiency of the extract. The adsorption of the inhibitor used on the mild steel surface was found to obey Langmuir adsorption isotherm.



## **1. INTRODUCTION**

Corrosion (irreversible process) is a natural process in which pure metal (unstable) except noble metals is converted into chemically stable compounds like oxides, sulphide, hydroxide, carbonates etc. or the process of slowly deterioration of the metal due to attack of atmospheric gases on the surface of metal resulting into the formation of more stable compounds such as oxides, sulphide, carbonates etc. is known as Corrosion. The most common corrosion is rusting of Iron (Fe2O3.xH2O).

### **1.1 CAUSE OF CORROSION**

Most of the metals found in nature are in the form of their compounds except the noble metals such as gold and platinum. This is due to the fact that the metals in their compound state are thermodynamically more stable than their elemental state (Vedavyasan, 2013). As most of the metals exists in the form of oxides so during their extraction into free state, a lot of energy is provided to them. This provided energy enables them to rebound back to their combined state when they are exposed to external environment like moisture, oxygen etc. For example: when iron is exposed to external conditions, it undergoes corrosion and produces brown colored hydrated ferrous oxide. This shows that corrosion is a process which is contrary to metal extraction.

Sometimes,

Sometimes, corrosion also takes place in essentially clean and unpolluted waters at a temperature of about 1300C on the product side. Such type of corrosion is classical hot spot corrosion (Charing& Lansing, 1982).

## **1.2 IMPORTANCE OF CORROSION STUDIES**

The importance of corrosion studies is two folds. The first is economic, including the reduction of material losses resulting from the wasting away or sudden failure of piping, tanks, metal components of machines, ships, hulls, marine, structures...etc. The second is conservation, applied primarily to metal resources, the world's supply of which is limited, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures.

## **1.3 TYPES OF CORROSION**

The various types of corrosion are classified into following categories as shown in Figure.1.1



Fig.1.1 Types of corrosion

## **1.3.1 GENERAL CORROSION**

It is also known uniform corrosion or dry corrosion; it is the type of corrosion which perishes the barren metal surface more or less, uniformly. It can also be defined as a type of corrosion which proceeds at same rate over the entire barren area. Oxygen acts as a foremost cause of this corrosion. The most common materials which show general corrosion are cast iron and steel. When they are exposed to moist atmosphere, they give rust-like appearance.



Where, A is any metal.

Experiments on the behavior of dry metals show that no corrosion occurs when they are kept over sulfuric acid and only show superficial corrosion when they are kept over water (Makhlouf et al. 2019).

## **1.3.2 STRESS CORROSION CRACKING**

Failure is due to the simultaneous influence of static tensile stresses and a corrosive environment and this is specific to a particular metal. The stresses may be internal such as those caused by cold work, welding, heat treatment or external forces caused by mechanical stresses set up by assembly practices.

## **1.3.3 LOCALIZED CORROSION**

Localized corrosion is quite different from general corrosion. General corrosion takes place at a relatively larger area whereas localized corrosion takes place comparatively at a smaller area (Michael & Pudji, 1996). This corrosion occurs when the small areas of a metal surface are corroded much easily as compared to the whole in a corrosive environment. These small areas are partially corroded from the metal surface due to the presence of corroding medium at a faster rate. The area with limited supply of oxygen becomes anode whereas the other with full supply becomes cathode. It is further of two types: (i) Pitting corrosion (ii) Crevice corrosion

## **1.3.4 PITTING CORROSION**

Pitting corrosion is a complex but important problem that is at the root of many corrosion failures. It has been studied in detail for many years, yet crucial phenomena remain unclear. In pitting corrosion, the surface of the metal is attacked in small-localized areas. Organisms in water or breaks in a passive film can initiate corrosion. In pitting corrosion very, little metal is removed from the surface but the effect is marked.

Pitting corrosion occurs mostly in solutions containing halide or oxyhalides. Chlorides, bromides and hypochlorite are the most aggressive anions. Fluoride, iodide and iodine containing anions were thought to be without pitting tendency. However, iodide ions were found to cause pitting corrosion in many cases. Solutions of certain oxidizing cations produce the worst pitting attack. Ferric, cupric and mercuric halides are the most aggressive of all pitting reagents. The non-oxidizing metal halides such as Al, Ca and Na cause pitting to a lesser degree.

## **1.3.5 CREVICE CORROSION**

Crevice corrosion is one of the major practical problems especially in marine applications (North & Macleod, 1987; Tan et al. 2001). It mainly affects Stainless Steels. Presence of chloride adds more difficulties while handling with crevice corrosion (Prawoto & Ibrahim, 2009; Davis et al., 2001; Tan et al., 2011). It is a restricted space corrosion to which the approach of working fluid from the corrosive environment to the space (crevices) is inadequate. The joint area has comparatively lower content of oxygen as compared to the outer area, so joint area acts as anode whereas the outer area acts as cathode. This corrosion is started by concentration gradients. The grouping up of chlorides ions inside a crevice will begin it. It occurs at comparatively lower temperature than pitting corrosion. Various factors that impact crevice corrosion are as follow.

i. The type of material i.e. alloy, metal.

ii. Geometric characteristics of crevices such as surface roughness

iii. Environmental conditions such as pH level, temperature, etc.

## **1.3.6 INTER GRANULAR CORROSION**

. Corrosion occurs at the grain boundaries due to a difference in potential between the anodic grain boundaries and the cathodic grains. "Sensitized" stainless steels, where carbides have been precipitated in the grain boundaries during improper heat treatment or in the heat-affected zone of a weld, are particularly susceptible to intergranular corrosion.

## **1.3.7 GALVANIC CORROSION**

Galvanic corrosion takes place between two different metals, or coatings, which are joined together in the presence of an electrolyte. Each metal has a potential different from any other metal when placed in an electrolyte. A series can be built up of all the metals relative to each other.

## **1.3.8 EROSION**

Due to the relative movement between the metal surface and corrosive fluid, the metal surface gets corroded. This is known as erosion. When the fluid contains solid particles that are harder than the affected metal surface, erosion will occur by the combined action of corrosion and abrasion whereas when the fluid contains the particles which are softer than the metal, erosion will occur by corrosion and attrition (Kumar et al. 2018). The rate of relative flow gives the idea about abrasion. The mechanism of chipping and cracking determines the cause of erosion, which occurs due to concurrent formation and removal of scale from the surface of material (Proton& Frey, 2016). The cavitation corrosion is the special form of erosion. The vapor bubbles in liquids near the metal surface form and collapse, thus giving rise to this corrosion. Some general techniques to restrict erosion are: Use harder materials (ii) Use lower velocity of the liquid.

## **1.3.9 WATERLINE CORROSION**

This type of corrosion occurs in the metallic tanks. When the tanks are partially filled with water, the area below the surface of water is poorly oxygenated and thus acts as anode whereas the area above the line of water has significant amount of oxygen and thus acts as cathode. The water line corrosion setup is represented in Figure. Thus, the area just below the level of water is corroded and the area above the level is protected.



Water line corrosion



FIG.1.2 DIAGRAM OF WATER LINE CORROSION SETUP

Mostly, marine engineers face this type of corrosion. It can be reduced by using anti fouling paints to some extent.

#### **1.4 METHODS OF CORROSION PROTECTION:**

#### **1.4.1 APPLICATION OF PROTECTIVE COATINGS:**

Metallic structures can be protected from corrosion in many ways. A common method involves the application of protective coatings made from paints, plastics or films of noble metals on the structure itself (e.g., the coating on tin cans). These coatings form an impervious barrier between the metal and the oxidant but are only effective when the coating completely covers the structure. Flaws in the coating have been found to produce accelerated corrosion of the metal.

#### **1.4.2 POLARIZE OR SHIFT THE POTENTIAL OF THE METAL:**

Another method of reducing corrosion is to polarize or shift the potential of the metal enabling it to act as a cathode (rather than an anode) in an electrochemical cell. One example is the galvanizing of steel with a coating of zinc. The iron and zinc then function as the electrodes of a cell. Zinc is the more readily oxidized metal of the pair and functions as the anode and corrodes, while the iron functions as the cathode. The zinc is used up and protection is effective as long as some zinc remains. Sacrificial anodes work on the same principal but use an external electrode made from a readily oxidized metal; this form of protection is commonly used on buried pipelines.

#### **1.4.3 CATHODIC PROTECTION:**

Cathodic protection using an impressed current derived from an external power supply is a related form of protection in which the metal is forced to be the cathode in an electrochemical cell. For example, most cars now use the negative terminal on their batteries as the ground. Besides being a convenient way to carry electricity, this process shifts the electrical potential of the chassis of the car, thereby reducing (somewhat) its tendency to rust.

#### **1.4.4 CORROSION INHIBITORS:**

Corrosion inhibitors can be added to solutions in contact with metals (e.g. inhibitors are required in the antifreeze solution in automobile cooling systems). These compounds can prevent either the anode or the cathode reaction of corrosion cells; one way that they can do this is by forming insoluble films over the anode or cathode sites of the cell. Examples of anodic inhibitors are sodium phosphate or sodium carbonate while zinc sulfate and calcium or magnesium salts act as cathodic inhibitors. New forms of paints are being developed which take advantage of similar properties. These paints promise to nearly eliminate corrosion in applications like painted car fenders, etc.

#### **1.5 CORROSION INHIBITION OF MILD STEEL:**

Mild steel is one of the most important metals widely used in different fields of industries, automobiles, engineering, submarine etc. However this metal is severely affected due to the environmental pollutant such as chlorate, sulphate, nitrate, phosphate etc. In order to overcome this problem, the use of inhibitor is one of the best methods to protect the metal against corrosion. Thus corrosion of mild steel and its inhibition in acid and other environments have more attention from numerous previous of investigators [1-4]. Most of the chemicals containing hetero atoms like oxygen, nitrogen and Sulphur are used as corrosion inhibitors which are very toxic to all living organisms even in very small concentration thereby green corrosion inhibitors are used nowadays which is biodegradable, nontoxic, eco- friendly and do not contain heavy metals.

#### **1.5.1 CORROSION INHIBITION IN ACID SOLUTIONS:**

Acid solutions are widely used in industry, where the most important fields of application are acid pickling, industrial acid cleaning and oil well acidizing. Because of general aggressively of acid solutions, the practice of inhibition is commonly used to reduce the corrosive attack on metallic materials. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, temperature and velocity of flow, the presence of dissolved organic and/or inorganic substances, and on the type of metallic material exposed to the action of acidic solution. Most of well-known acid inhibitors are organic compounds containing nitrogen, sulphate and oxygen.

#### **1.6 CORROSION MONITORING:**

A larger number of corrosion monitoring techniques exist. The following list details the most common techniques which are used in industrial applications:

- ✓ Corrosion coupons (weight loss measurements)
- ✓ Electrical Resistance (ER)
- ✓ Linear Polarization Resistance (LPR)
- ✓ Hydrogen penetration
- ✓ Electrochemical Impedance Spectroscopy (EIS)
- ✓ Non-Destructive Testing (NDT) techniques
- ✓ Analytical techniques

Electrochemical impedance spectroscopy forms the core of industrial corrosion monitoring system. These corrosion monitoring techniques have been successfully applied and are used in an increasing range of applications because

- > The techniques are easy to understand and implement.
- Equipment reliability has been demonstrated in the field environment over many years of operational application.
- Results are easy to interpret.
- Measuring equipment can be made intrinsically safe for hazardous area operation.
- Users have experienced significant economic benefit through reduced plant down time and plant life extension.

#### **1.7 FACTORS AFFECTING CORROSION**

The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are:

- Nature of the metal, nature of the environment and the corrosion products.
- Temperature.
- Concentration of electrolyte.
- Electrode potential.
- Aeration.
- Agitation.
- Hydrogen over voltage and pH of the electrolyte.

#### **1.8 ADSORPTION AND INFLUENCE OF INHIBITION OF CORROSION**

The ions and molecules of the inhibitor adsorb on the metal surface. This adsorption of ions and molecules at an electrified interface is of fundamental importance in all aspects of aqueous corrosion. Some researches [1] used the radioactive technique by using labeled thiourea(S35) and the adsorption of the inhibitor on iron was found to be uniform and about 90% adsorption occurred in 5-10 minutes.

Since the corrosion reaction is heterogenous the reaction sequence involves at least one surface step. Organic inhibitors presumably as not capable of oxidizing or precipitating the metal ion, but have the ability to adsorb and also alter either cathodic, anodic or both the reactions.

Most of the organic inhibitors such as the heterocyclic nitrogenous compounds were believed to be cathodic reaction. But it has been shown [2] that in some cases ( $\beta$  naphtha quinoline) anodic inhibition have also been observed.

As far as the inhibition process is concerned, it is assumed that the adsorption of the inhibitor at the metal solution interface is the first step in the mechanism of action of inhibitor in aggressive media. There are four type of possible adsorptions involving organic molecules at the metal solution interface [3-5].

- Electrostatic attraction between the charged molecules and the charged metal,
- Interaction of unshared electron pairs in the molecule with the metal,
- > Interaction of  $\pi$ -electrons with the metal and
- A combination of all the above.

#### **1.9 ADSORPTION ISOTHERM**

The adsorption isotherms are often shown to demonstrate the performance of organic adsorbenttype inhibitors and the surface coverage rates determined by the capacitance measurements give a good correlation with these plots. The three adsorption isotherms are the Langmuir, the Frumkin and the Temkin isotherms.

Frumkin isotherm,  $(\theta/1-\theta) \exp(-2f\theta) = Kads$ 

Temkin isotherm, exp  $(f\theta) = Kads$ 

Langmuir isotherm,  $\theta/1-\theta = A.C.e-Q/RT$ 

Where  $k_{ads}$  is the equilibrium constant of the inhibitors adsorption process, C is the inhibitor concentration,  $\Theta$  is the surface coverage, (1- $\Theta$ ) the vacant sites not occupied by the inhibitor, A is a constant dependent on the characteristics of the system of adsorption, Q is the heat of adsorption and f is the parameter related to the variation in adsorption energy with surface coverage.

#### **1.10 BEHAVIOUR OF INHIBITORS IN ACID SOLUTION**

The anodic and cathodic reactions involved in the corrosion of metal in acidic solution are

 $M \rightarrow Mn^+ + ne H^+ + e^- \rightarrow H$  $H + H \rightarrow H_2$ 

The adsorption inhibitor blocks either the anodic or cathodic reaction or both. The effect of the inhibitor may be due to changes in the electrical double layer by reducing metal reactivity or by the inhibitor participation in partial electrode or by formation of a physical barrier.

The adsorbed inhibitor may not cover the entire metal surface, but occupies sites which are electrochemically active and thereby reduce the extent of anodic o cathodic reaction or both. The corrosion rate will be decreased on proportion to the extent to which the electrochemically active sites are blocked by the adsorbed inhibitor [6].

In acid solutions, general corrosion can be prevented by using suitable concentrations of inhibitors. Some inhibitors used for the prevention of general corrosion might accelerate the hydrogen entry into the metal. In general, a good corrosion inhibitor is a compound which is capable of inhibiting both general corrosion and hydrogen entry into the metal.

## 2. LITERATURE SURVEY

The adsorption of natural corrosion inhibitors on metal surfaces is influenced by a number of factors including nature of metal, testing media, chemical structure of inhibitor, nature of substituents presents in the inhibitor, presence of additives, solution temperature, and solution concentration [7]. The use of corrosion retardants or inhibitors amongst many other techniques offers a versatile means of preventing or controlling corrosion. Several texts and articles have extensively discussed issues relating to corrosion control and protection (Fontana, 1987 and Al-Turkustani, et al.,[8]. These techniques include the use of appropriate metals and alloys, metal purification, use of non-metals, altering the environment, design techniques, cathodic and anodic protection, metallic coatings, organic coatings and use of inhibitors.

In the past two decades, the research in the field of "green" corrosion inhibitors has been directed toward the goal of using cheap, effective molecules of low or zero negative environmental impact. Therefore, the use of non-toxic inhibitors has also become one of the major selection requirements. Omanovic and Ghareba [9] introduce 12-aminododecanoic acid (AA) as a green corrosion inhibitor to carbon steel in CO<sub>2</sub>. Sethuraman and Kamal [10] found Spirulina platensis as green inhibitor for mild steel in HCl and media. They found that inhibition efficiency increased with increasing the inhibitor concentrations. saturated acidic medium also known as sweet corrosion.

Another single inhibitor investigation by Eddy and Odiongenyi [11] was conducted on mild steel immersed in sulphuric acid solution in the presence of ethanol extract of Heinsia crinatia. The techniques adopted in the study were weight loss, thermometric, hydrogen evolution and infrared spectroscopy for surface analysis. The IE of the extract varied with concentration of the extract, period of immersion and temperature. The extract is adsorbed impulsively on the surface of mild steel sample in accordance with Temkin and Frumkin adsorption isotherms. Raja and Sethuraman [12] worked on the use of Solanum tuberosum as an inhibitor of mild steel corrosion in acid media of HCl and sulphuric acid using weight loss and electrochemical techniques at temperatures of 303, 313 and 323 K. Result revealed mixed type inhibitor behavior and the interaction mechanism between metal and extract was best fitted to the Temkin isotherm.

Soror, [13] carried out a study on Medicago polymorpha roxb. Medipolymorphol, a new sterol isolated from the whole plant of Medicago polymorpha roxb was used as corrosion inhibitor for stainless steel (316) in 5% HCl at room temperature.

Recently, Omotosho and Ajayi [14] used the gasometric method to investigate the acid failure of aluminium alloy in 2 M hydrochloric (HCl) acid solution in the presence of Vernonia amygdalina extract. Metal coupons were immersed in test solutions of free acid and those containing extract volumes of 2, 3, 4 and 5 cm3 at ambient temperature for 30 minutes. The analysis of the result revealed that maximum IE was obtained when inhibitor quantity was 5 cm<sup>3</sup>.

The effectiveness of garlic extract to inhibit the bio-corrosion of carbon steel API 5L (CS) and stainless steel 316 (SS) in the presence of Bacillus Subtilis A1 and Streptomyces parvus B7 was estimated a by Punniya kotti Parthiban et al., [15]. This the first time garlic extract is proposed as a green corrosion inhibitor with biocidal activity to control bio corrosion in hypersaline corrosive environment containing microorganism.

Loto et al.,[16] showed the synergistic effect of Sage and Jojoba oil extract on the corrosion inhibition of low carbon steel was evaluated with potentiodynamic polarization resistance technique. The compound displays mixed inhibition behaviour and the mechanism of inhibition was determined to be through chemisorption absorption mechanism.

To evaluate the residual life and safe operation of metallic materials, it is crucial to accurately identify the intensity and depth of corrosion pits. Scanning acoustic microscopy (SAM) using tomographic acoustic microimaging (TAMI) under c-mode was employed to determine corrosion pit morphology and depth on aluminium alloy 7050, and the results were cross-checked by optical microscopy [17].

Zhao et.al [18] showed two chitosan derivatives are synthesized for the first time as green corrosion inhibitors for the carbon dioxide corrosion of P110 steel. The experimental results show that synthetic corrosion inhibitors CHC and CAHC are all good corrosion inhibitors for carbon dioxide corrosion inhibitors.

Corrosion and corrosion inhibition behaviors of steel Q-235 were studied in 7.5% NH<sub>4</sub>Cl solution with the newly synthesized inhibitor by potentiodynamic polarization. The results showed that inhibition efficiency above 90% is achievable at 298K with 0.5m ML<sup>-1</sup> inhibition concentration. It was seen from the EDS characterization of corroded steel surfaces that the HDIE retarded the corrosion by impeding the chloride attack[19].

corrosion inhibitors are chemicals that efficiently slow the rate of corrosion of metals and alloys when used in relatively low concentrations, particularly in cooling systems, storage vessels and boilers, oil and gas pipelines as well as in construction. Mild steel is an important construction material due to its outstanding mechanical characteristic and minimal costs in comparison to other materials[20].

Mildsteel like other alloys is susceptible to corrosion, thus the surface must be protected [21]. However, this operation needs to be controlled due to the extremely damaging corrosive effect of acids used such as hydrochloric acid. The acidizing process in general manufacturing cleaning techniques in petrochemical applications eliminates metal oxides and inorganic layer removals [22], thus mild steel corrosion is unavoidable but can be controlled [23].

The possibility of utilizing dextran as a green corrosion inhibitor for steel in strong acid environment was explore using weight loss, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM) and some other techniques. The effect of molecular weight, temperature, and modification on the inhibition efficiency of dextran was also studied. Results from all the applied techniques reveal that dextran exhibit moderate anticorrosion property toward St37-2 steel dissolution in 15% H<sub>2</sub>SO<sub>4</sub> solution [24]. Layered double hydroxide (LDH) has been widely developed in the field of corrosion and protection in recent years based on its unique characteristics including anion capacity, anion exchange ability, structure memory effect, and barrier resistance. This paper comprehensively reviews recent work on the preparations, properties of LDH in the forms of powder and film and their applications in different environments in corrosion and protection. Some novel perspectives are also proposed at the end of the review for future research in corrosion and protection field [25].

The inhibition properties of phytic acid (PA) on Q235 mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> was estimated using electrochemical techniques. Polarization results revealed PA to be a mixed-type inhibitor in 0.5 M H<sub>2</sub>SO<sub>4</sub>, with a more pronounced cathodic effect, while impedance results indicate adsorption of the PA species on the steel surface. The adsorption of PA followed the Langmuir adsorption isotherm. The mechanism of chemical adsorption is proposed on the basis of the trend of inhibition efficiency with temperature and the calculated values of the activation energy (E<sub>a</sub>) [26].

The anticorrosive effect of Veratrum root extract (VRE) as the inhibitor for copper corrosion in  $H_2SO_4$  solution was studied by electrochemical experiments and quantum chemistry calculation. The electrochemical experiments manifested that VRE exhibited good anticorrosion performance at a range of tested temperatures, which was further manifested by surface characterizations. When the concentration of VRE is 200 ppm, its anti-corrosion efficiency can reach 97%. Quantum chemical calculation was employed to manifest the mechanism of adsorption and the relationship between the electronic structure of inhibitors and their anticorrosion performance [27].

The inhibition efficiency (IE<sub>inh</sub> %) of the (2-aminobenzyl)triphenylphosphonium bromide (ABTPPB) environmental friendly inhibitor on mild steel (MS) corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at concentrations ( $10^{-5}$  to  $10^{-2}$  M) and temperatures (298 to 328 K) have been achieved using potentio static polarization (GP), electrochemical impedance spectroscopy (EIS), and

surface characterized via the scanning electron microscopy (SEM) with energy dispersive x-ray (EDX) spectroscopy, and atomic force microscopy (AFM). Both SEM-EDX and AFM analyses sustained the formation of protective layers of the ABTPPB molecules on the sample surface. Quantum chemical (QC) calculations were employed for computational calculations, and the acquired results were instigated to be reliable with the experimental findings [28].

The current investigation presents the corrosion activity of Armoracia rusticana root extract in 0.5 M H<sub>2</sub>SO<sub>4</sub> as a corrosive medium. Weight loss measurements, Tafel polarization and electrochemical impedance spectroscopy (EIS) measurements have been done to check the inhibition efficiency. Electrochemical examination and weight reduction estimations say that the root extract for Armoracia rusticana indicates the amazing inhibition efficiency up to 95.74% for mild steel at 100 mg/L concentration in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 298 K. The adsorption of the inhibitor obeys the Langmuir adsorption isotherm [29].

Corrosion inhibition ability of *Borassus flabellifer* coir dust thus extracted by water (BFDWE) and methanol (BFDME) against aluminium in 1 M H<sub>2</sub>SO<sub>4</sub> at 303–333 K has been examined using electrochemical, non-electrochemical, and microstructural analysis. The experimental results depicted that corrosion inhibition efficiency increases with addition of inhibitor content and it adversely decreases as a function of temperature. Potentiodynamic polarization results showed that BFDME and BFDWE perform as mixed-type inhibitors with notable cathodic nature [30].

The inhibitive action of Santolina *chamaecy parissus* extract as a natural inhibitor on corrosion of 304 stainless steel in 3.5% NaCl solution was investigated by potentiodynamic polarization, EIS, and SEM techniques. The results indicate that the extract shows mixed-type inhibition behaviour and inhibition efficiency of 86.9% was achieved. The corrosion rate decreased with increasing concentration

of extract and increased with the increase in temperature of the medium. Adsorption of the extract obeyed the Langmuir isotherm model [31].

Clotrimazole an antifungal drug was investigated for its corrosion inhibition action on zinc metal in 0.1 M HCl solution. Corrosion rate was determined by weight loss, potentiodynamic polarization and impedance spectroscopic techniques. Tafel polarization measurements showed that clotrimazole acts as mixed type of corrosion inhibitor and its adsorption on the zinc surface obeys Langmuir isotherm [32].

Failures of industrial boilers have been reported to be mainly due to water side corrosion and scaling. Boiler corrosion is due to highly alkaline or acidic conditions of the boiler water. The present work has been aimed at investigating the corrosion behaviour of T22 (2.25 Cr–1 Mo) boiler steel TIG weldments in neutral and alkaline media. The parent metal and weld root regions are chosen as regions of exposure for the study made at room temperature and at 100 °C. The results show that parent metal experiences higher corrosion rate than weld metal and thiourea as inhibitor is found unsuitable in NaOH medium [33].

Crab waste protein (CWP) has been extracted, characterized and examined as a green polymer inhibitor for carbon steel in 2 M H<sub>3</sub>PO<sub>4</sub> media by weight loss and electrochemical techniques. The inhibition of CWP accelerates by increasing the inhibitor content, but the temperature has hardly affected the inhibition efficiency. Thermodynamic data clearly show that the adsorption mechanism of CWP on the carbon steel surface in 2 M H<sub>3</sub>PO<sub>4</sub> solution is mainly physical adsorption. Moreover, the adsorption of the CWP molecules was found to follow a Langmuir adsorption isotherm. Results of potentiodynamic polarization measurements revealed that the CWP acts as a mixed-type eco-friendly inhibitor [34].

Mariana X. Milagre et. al [35] showed that the common mechanism of the AA2024 -T3 and AA2098 -T351 were investigated and compared using various electrochemical techniques in 0.005 mol  $L^{-1}$  NaCl solution. The severe type of corrosion in the AA2098 -T351 was intragranular attack (IGA)

although trenching and pitting related to the constituent particles were seen. Electrochemical techniques showed that the corrosion reaction in both alloys was controlled by diffusion. However, local electrochemical techniques were useful for the evaluation of the corrosion resistance of the alloys.

The use of human ethnic hair sample extract as corrosion inhibitors of mild steel (MS) in 1M H3PO4 medium by mass loss, Potentiodynamic polarization, Electrochemical Impedance Spectroscopy. The results showed that the corrosion inhibition efficiency increased with increasing the concentration of the inhibitor. The extract was a mixed type inhibitor with an optimum concentration of 0.040% v/v in potentiodynamic polarization. The adsorption characteristics of the inhibitors have been determined from the results [36].

The inhibition efficiency and adsorption characteristics of alkaloids, flavonoids and tannins extracts of *Mangifera indica* leaves in controlling corrosion of Zinc sheet in 5 M hydrogentetraoxosulphate (VI) acid solution has been evaluated by gasometric method. The formulation consisting of 2 g/L of extract offers 96.2%, 85.3% and 70.6% inhibition efficiencies (alkaloids, flavonoids and tannins respectively) at 300C to Zinc metal immersed in 5 M hydrogentetraoxosulphate (VI) acid solution. Judging from the trend in inhibition efficiency against temperature, it can be deduced that the adsorption process was physisoption being that corrosion rate increased while inhibition efficiency decreased with temperature [37].

#### 2.1 SCOPE OF THE PRESENT WORK:

Corrosion is widely used in industry to reduce the corrosion rate of different metals and alloys which are present in contact with aggressive environments. Many studies have been carried out to find suitable chemicals which may be very creatures and environments. It is very important to choose cheap and safety handled compounds to be used as corrosion inhibitors. The objectives of the research are

- In our present study, I have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution for harmful organic chemicals.
- The influence of flower of Mimusops elengi, leaves of Camellia sinensis, leaves of Nerium oleander extract as natural inhibitor for mild steel in 1M hydrochloric acid using weight loss measurements with different concentration and temperature have been investigated.
- > To investigate the effect of temperature on corrosion using the chemical methods.
- To determine the metal-inhibitor interaction mechanism using Langmuir, Tempkin and Freundlich adsorption isotherm.
- To evaluate the effects of flower of *Mimusops elengi*, leaves of *Camellia sinensis*, leaves of *Nerium oleander* extract on the corrosion of mild steel in 1M HCl through weight loss, polarization and electrochemical impedance spectroscopy measurements.

There is no report in literature on the use of these flower of *Mimusops elengi*, leaves of *Camellia sinensis*, leaves of *Nerium oleander* extract as corrosion inhibitors. Corrosion problem can be properly addressed only through education and it is therefore the aim of this present work to bring to the attention of as many people as possible the reasons for the occurrence of corrosion and the methods of it.

## **3. MATERIALS AND METHODS**

The experimental procedures adopted for the present work are quite conventional in nature which has worked well in corrosion inhibition studies. A brief outline of the procedure adopted in this project work has presented here.

## **3.1 COMPOSITION OF THE MILD STEEL SPECIMEN USED**

## **TABLE 3.1 COMPOSITION OF COMMERCIAL MILD STEEL**

Element	Percentage composition
Carbon	0.060
Manganese	0.308
Silicon	0.002
Sulphur	0.009
Phosphorous	0.001
Iron	99.620

For the current study, Mild steel 304 type was used for the inhibition studies.

#### **3.2 INHIBITOR USED**

The following inhibitor was selected for this present study. They are

- 1. Mimusops elengi
- 2. Camellia sinensis
- 3. Nerium oleander

### **3.3 COLLECTION OF FLOWERS**

The flowers and waste leaves were separated from the plant. The separated flowers were shade dried, without exposing the material to sunlight. After drying, it was powered in a mixer and fine powder was collected.

#### **3.4 EXTRACTION OF FLOWERS**

The flower sample was weighed and10 gram of the sample was added to the 250 ml beaker containing 100 ml of water. It was boiled in hot water bath at 100<sup>o</sup>C. The extract was obtained by filtering the sample. The filtered sample was used to prepare various concentrations of inhibitors by diluting 5, 10, 15, and 20 mL in 100 mL SMF.

## 3.4.1 Camellia Sinensis (Green tea leaves)



#### Classification

The plant classification details are

Kingdom	: Plantae
Division	: Magnoliophyta
Class	: Magnoliopsida
Sub-class	: Dillenidea
Order	: Theales
Family	: Theaceae
Genus	: Camellia L
Species	: Camellia Sinensis

## 3.4.2 Mimusops elengi (Spanish cherry)



## Classification

Kingdom	:Plantae
Class	:Dicotyledons
Order	:Ericales
Family	:Sapotaceae
Genus	:Mimusops
Species	: M. elengi

## 3.4.3 Nerium oleander (Arali leaves)



## Classification

Kingdom	: Plantae	
Order	: Gentianales	
Family	: Apocynaceae	
Subfamily	: Apocynoideae	
Tribe	: Nerieae	
Genus	: Nerium.L	
Species	: N. oleander	

#### **3.5 EXPERIMENTAL PROCEDURES**

#### **3.5.1 WEIGHT LOSS MEASUREMENTS**

Mild steel specimens of size 2.5 x 5 cm, with a small hole of about 1 cm diameter near its upper edge were used for weight loss studies. Before each experiment, the sample were abraded using emery papers of 1/0, 2/0, 3/0, 4/0 grade, washed with distilled water and acetone and finally dried at room temperature in order to obtain reproducible results.

The initial weight of each specimen was noted before immersion using an analytical balance. Then the specimens were immersed in 100 mL of distilled water solution without and with a known concentration of the inhibitor for a period of time. After that, the mild steel specimens were taken out and then washed under running tap water using a brush to remove corrosion products, rinsed with distilled water, dried and reweighed. The experiments were done in triplicate to ensure reproducibility. The mean values of weight loss were calculated.

Similar experiments were calculated under the same operating condition but with different concentrations of the inhibitor and corrosion rate was calculated from the following equation. From the weight loss measurements, the corrosion rate was calculated using the following relationship.

Corrosion rate (mmpy) =  $87.6 \times W/DAT$ 

Where,

Mmpy - millimeter per year

- W Weight loss in mg
- D Density in gm/cm3
- A Area of specimen cm2

T - Time in hours

The inhibition efficiency (%IE) and degree of surface coverage ( $\theta$ ) were calculated using equation below respectively.

$$\% IE = W1 - W2/W1x \ 100$$
$$\theta = W1 - W2/W1$$

W1, W2 are weight loss in the absence and presence of the inhibitor respectively.

#### 3.6 KINECTIC AND THERMODYNAMIC CONSIDERATION

From the weight loss measurements, various thermodynamic parameters were calculated and adsorption isotherms were established to provide important clue to the nature of the metal inhibitor interaction. The values of activation energy ( $E_a$ ) were calculated with the help of Arrhenius Equation.

 $Log CR2/CR1 = E_a/2.303R[1/T1-1/T2]$ 

The equilibrium constant Kads for the adsorption process from Langmuir adsorption isotherm is related to the standard free energy of adsorption by the expression.

$$K_{ads} = 1/55.5 \exp \left[-\Delta G^0_{ads}/RT\right]$$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the molar concentration of water in solution expressed in mol/lit. The standard free energy of adsorption,  $\Delta$ Gads, which can characterize the interaction of adsorption molecule and metal surface, was calculated by previous equation and K<sub>ads</sub> is given by the following expression.

#### $K_{ads} = (\theta/1 - \theta)x1/c$

Where  $\theta$  is the degree of surface coverage and C is the concentration of inhibitor. Enthalpy of activation,  $\Delta$ H0ads is another criterion from which the mode of adsorption can be probed.  $\Delta$ H0ads was obtained by applying the transition state equation.

 $CR = RT/Nh \exp[\Delta G^{0}_{ads}/R] \exp[\Delta H^{0}_{ads}/RT]$ 

Where CR is the corrosion rate, h is the plank's constant, N Avogadro number,  $\Delta S^{0}_{ads}$  is the entropy of activation, T is the absolute temperature and R is the universal gas constant. A plot of log (CR/T) against 1/T was made for the blank and various additives with a slope of ( $-\Delta H^{0}/R$ ) and an intercept of log (R/Nh) +  $\Delta S^{0}/R$  from the slope an intercept values, the  $\Delta H0$ ads and  $\Delta S0$ ads value were computed, respectively.  $\Delta G^{0}_{ads}$  and activation energy (E<sub>a</sub>) were calculated using the following equation.

 $Q_{ads} = 2.303R \left[ (\log \theta_2 / 1 - \theta_2) - (\log \theta_1 / 1 - \theta_1) \right] x \left[ T_2 T_1 / T_2 - T_1 \right]$ 

#### **3.7 ADSORPTION ISOTHERM**

Corrosion inhibition of mild steel in sea water solution by the chosen flavonoid compounds can be explained based on molecular adsorption. Basic information on the interaction between the inhibitors and the mild steel surface can be provided by the adsorption isotherm.

The degree of surface coverage ( $\theta$ ) for different inhibitor concentration was evaluated from weight loss data, using the equation given below.

 $\theta = CR_o - CR/CR_o$ 

Where  $CR_o$  and CR are the corrosion rates in solution in the absence and presence of inhibitor respectively. In order to find out the adsorption isotherm, attempts were made to fit various adsorption isotherm.

#### **3.8 POTENTIODYNAMIC POLARIZATION MEASUREMENTS**

After measuring the steady open circuit potential value, the mild steel electrode was polarized both cathodically and anodically and the potentiodynamic polarization curves were recorded at the potential range of  $3000\text{mV}\pm\text{OCP}$  with a scan rate of 10 mVs-1. The measurements were made with the aerated unstirred test solution without and with different concentration of inhibitors. The values of I<sub>corr</sub> and Ecorr
were obtained from the points of intersection of the extrapolated anodic and cathodic Tafel lines. Percentage inhibition efficiencies were calculated for various concentrations of the inhibitor from the Icorr values using the following formula

 $IE(\%) = I_{corr} - I'_{corr} / I_{corr} x 100$ 

Where Icorr and I'corr are the corrosion current values without and with inhibitor.

#### **3.9 ELECTROCHEMICAL IMPEDANCE MEASUREMENTS**

The same type of mild steel specimens and the cell steps used in the electrochemical polarization studies, were used for measuring the impedance parameters. The impedance were collected at the open circuit corrosion potential. The electrochemical impedance measurements are carried out using CHI electrochemical workstation.



FIG.3.1 ELECTROCHEMICAL WORKSTATION

Depending on the concentration of the additives, values of the steady state Ecorr were attained in 10-15 min. To ensure the stability of Ecorr, the working electrode was maintained at its corrosion potential for further 5 minutes in sea water solution.

The impedance diagrams are given by Tafel plot representation. The values of the charge transfer resistance (Rct) were obtained from Tafel plot by determining the difference in the values of impedance at low and high frequencies. The double layer capacitance (Cdl) values were computed from the Tafel plot and the Rct values the following equation.

#### $C_{dl} = 1/2\pi fmaxRct$

Where fmax is the frequency at which the imaginary component of the impedance (-Zmax) is maximal.

For Rct values, the (IE%) was calculated using the equation

 $IE(\%) = R'ct - Rct / R'ct \ge 100$ 

Where Rct and R'ct are charge transfer resistance values in the absence and presence of the inhibitors respectively.

## 3.10 FOURIER TRANSFORM INFRARED SPECTROSCOPIC STUDIES (FT-IR)

The FT-IR is a characterization technique that will reveal the presence of the amorphous phases in the corrosion product. The mild steel coupons were immersed in 1M HCl along with the henna extract for a period of 24 hours. After 24 hours, the specimens were taken out and dried. The surface film was scrapped carefully and its FT-IR spectrum was recorded using FT-Infra Red Spectrophotometer.



#### FIG.3.2 INFRARED SPECTROSCOPY

#### 4. RESULTS AND DISCUSSION

In this chapter, the results and the analysis of the weight loss, electrochemical studies on the corrosion behavior of mild steel in hydrochloric acid medium and the effect of Spanish cherry extract as inhibitors in combating the corrosion have been presented.

#### **4.1 WEIGHT LOSS MEASUREMENTS:**

In these studies, the corrosion parameters such as weight loss, corrosion rate and inhibition parameters such as inhibition efficiency (%), surface coverage ( $\theta$ ) have been determined and discussed under the following headings.

- 1. Effect on changing the concentration of Acid
- 2. Effect of temperature

#### **4.1.1 The Effect on changing concentration of acid:**

The inhibition effect of various concentration of acid with different concentration of henna extract has been studied for a fixed period an immersion time (24 hours). The corrosion rate (mmpy), inhibition efficiency (%), surface coverage ( $\theta$ ) was listed out in table.

TABLE 4.1 CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUSCONCENTRATION OF Mimusops elengiEXTRACT WITH DIFFERENT ACIDCONCENTRATION

Concentration	Concentration	Weight loss	Corrosion	Inhibition	Surface
of acid	of Inhibitor	(g)	rate	Efficiency	<b>Coverage</b> (θ)
( <b>M</b> )	(ppm)		(mmpy)	(%)	
1.00	Blank	0.132	0.0122	-	-
	100	0.081	0.0150	38.63	0.0077
	200	0.080	0.0148	39.39 53.03	0.0074
	300	0.062	0.0150	55.05	0.0055
1.50	Blank	0.154	0.0143	-	-
	100	0.088	0.0150	42.10	0.0086
	200	0.073	0.0135	51.97	0.0065
	300	0.047	0.0087	69.07	0.0045
2.00	Blank	0.181	0.0168	-	-
	100	0.109	0.0202	39.77	0.0104
	200	0.107	0.0198	40.88	0.0100
	300	0.084	0.0155	53.59	0.0075

The plant extract is taking place by adsorption mechanism with the increase in concentration of the plant extract more constituents are being adsorbed on the surface, enhancing more uniform surface coverage, which decrease the corrosion. The constituent on the metal surface makes a barrier for mass and charge transfers and thus protects the metal surface from corrosion. The degree of protection increases with the increase in surface fraction occupied by the adsorbed molecules. The surface coverage parameter is calculated from the I.E. % values, which is used to represent the fraction of the surface occupied by the adsorbed molecules.

The results shows that extract reduce the corrosion of mild steel in 1M HCl.



### FIG.4.1 VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Mimusops elengi

#### EXTRACT ON MILD STEEL IN 1M HCI CONCENTRATION.



#### FIG.4.2 VARIATION OF INHIBITION EFFICIENCY WITH CONCENTRATION OF

#### Mimusops elengi EXTRACT ON MILD STEEL IN 1M HCL SOLUTION



### FIG.4.3 VARIATION OF CORROSION RATE WITH CONCENTRATION OF Mimusops elengi

#### EXTRACT ON MILD STEEL IN 1.5M HCI CONCENTRATION

TABLE 4.2. CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUSCONCENTRATION OF Camellia sinensisEXTRACT WITH DIFFERENT ACIDCONCENTRATION

Concentration	Concentration	Weight loss	Corrosion	Inhibition	Surface
of acid	of Inhibitor	(g)	rate	Efficiency	Coverage (0)
( <b>M</b> )	(ppm)		(mmpy)	(%)	
1.00	Blank	0.132	0.0122	-	-
	100	0.083	0.0015	37.12	0.0079
	200	0.082	0.0015	37.87 43.18	0.0076
	300	0.075	0.0013		0.0067
1.50	Blank	0.154	0.0143	-	-
	100	0.089	0.0016	40.90	0.0086
	200	0.085	0.0015	44.80	0.0076
	300	0.079	0.0014	40.70	0.0076
2.00	Blank	0.181	0.0168	-	-
	100	0.125	0.0023	30.93	0.0120
	200	0.122	0.0022	32.59	0.0114
	300	0.120	0.0022	33.70	0.0107



#### FIG.4.4 VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF

#### Camellia sinensis EXTRACT ON MILD STEEL IN 1M HCl SOLUTION



#### FIG.4.5 VARIATION OF INHIBITION EFFICIENCY WITH CONCENTRATION OF



#### Camellia sinensis EXTRACT ON MILD STEEL IN 1.5M HCI SOLUTION

#### FIG.4.6 VARIATION OF CORROSION RATE WITH CONCENTRATION OF

Camellia sinensis EXTRACT ON MILD STEEL IN 1.5M HCI CONCENTRATION

TABLE 4.3 CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUSCONCENTRATION OF Nerium oleander EXTRACT WITH DIFFERENT ACIDCONCENTRATION

Concentration	Concentration	Weight loss	Corrosion	Inhibition	Surface
of acid	of Inhibitor	(g)	rate	Efficiency	<b>Coverage</b> (θ)
( <b>M</b> )	(ppm)		(mmpy)	(%)	
1.00	Blank	0.132	0.0122	-	-
	100	0.069	0.0012	47.72	0.0066
	200	0.061	0.0011	53.78 62.12	0.0057
	300	0.050	0.0009		0.0044
1.50	Blank	0.154	0.0143	-	-
	100	0.070	0.0012	54.54	0.0068
	200	0.062	0.0011	59.74	0.0056
	300	0.052	0.0009	66.23	0.0050
2.00	Blank	0.181	0.0168	-	-
	100	0.099	0.0018	45.30 38.67	0.0095
	200	0.111	0.0020	34.25	0.0103
	300	0.119	0.0022		0.0106



## FIG.4.7 VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Nerium oleander



#### EXTRACT ON MILD STEEL IN 1M ACID SOLUTION

#### FIG.4.8 VARIATION OF WEIGHT LOSS WITH CONCENTRATION OF Nerium oleander

#### EXTRACT ON MILD STEEL IN 1M ACID SOLUTION



## FIG.4.9 VARIATION OF CORROSION RATE WITH CONCENTRATION OF *Nerium oleander* EXTRACT ON MILD STEEL IN 1.5M ACID SOLUTION

From the above data it was clear that corrosion inhibition of mild steel containing Minusops *elengi* extract with 1.5 M acid concentration shows good Inhibition efficiency about 69%

#### **4.1.2 EFFECT OF TEMPERATURE:**

Effect of Temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations of *Mimusops elengi*, Camellia Sinensis, Nerium oleander at 303K.

To again insight into the nature of inhibitor adsorption, the effect of temperature on the corrosion behavior and the inhibition efficiency of mild steel in 1M HCl in the presence of different concentration of *Mimusops elengi, Camellia Sinensis, Nerium oleander* were studied by weight loss method for a fixed immersion time at 24 hours.

The data revealed that on increasing the temperature from 273K to 303K, the corrosion rate increase while the I.E. (%) and surface coverage ( $\theta$ ) decrease. This suggests that some desorption of some of the adsorbed inhibitor from the metal surface at higher temperature. This gives a clue that the mechanism of adsorption of the inhibitor may be mainly due to physisorption, because the physisorption which is due to weak vander waal's force disappears at elevated temperature. Thus as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency.

# TABLE 4.4 CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUSCONCENTRATION OF Mimusops elengi (Spanish cherry)EXTRACT WITH HCI AT 303K

Temperature (K)	Concentration of Inhibitor (ppm)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
	100	0.225	0.0041	-70.45	0.0216
	200	0.194	0.0035	-46.96	0.0181
	300	0.258	0.0047	-95.45	0.0230
303	100	0.142	0.0026	7.792	0.0138
	200	0.135	0.0025	12.337	0.0122
	300	0.101	0.0018	34.415	0.0097
	100	0.177	0.0032	2.209	0.0170
	200	0.142	0.0026	21.546	0.0132
	300	0.205	0.0038	-13.259	0.0183

Table 4.4 - 4.6 shows the corrosion inhibition of mild steel at 303K. From the table we can come to a conclusion that the corrosion increases as the temperature increases.

# TABLE 4.5 CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUSCONCENTRATION OF Camelia Sinensis EXTRACT WITH HCI AT 303K

Temperature (K)	Concentration of Inhibitor (ppm)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
	100	0.225	0.0041	32.57	0.0216
	200	0.194	0.0035	21.21	0.0181
	300	0.258	0.0047	15.90	0.0230
303		5			
	100	0.142	0.0026	15.58	0.0138
	200	0.135	0.0025	5.197	0.0122
	300	0.101	0.0018	0.649	0.0097
	100	0.177	0.0032	9.392	0.0170
	200	0.142	0.0026	9.945	0.0132
	300	0.205	0.0038	38.121	0.0183

TABLE 4.6 CORROSION PARAMETERS OF MILD STEEL CONTAINING VARIOUS

CONCENTRATION OF Nerium oleander ( Arali leaves ) EXTRACT WITH HCl AT 303K

Temperature (K)	Concentration of Inhibitor (ppm)	Weight loss (g)	Corrosion rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
	100	0.094	0.0017	28.78	0.0090
260	200	0.081	0.0015	38.63	0.0075
	300	0.075	0.0013	43.18	0.0067
	100	0.142	0.0026	7.792	0.0138
300	200	0.107	0.0019	30.519	0.0096
	300	0.106	0.0019	31.168	0.0102
		5			
	100	0.184	0.0034	1.657	0.0176
335	200	0.129	0.0023	28.72	0.0120
	300	0.103	0.0019	43.093	0.0092

#### **4.2 ADSORPTION ISOTHERM**

The adsorption of an organic compound adsorbed and a metal surface is regarded as a substitution adsorption process between the organic molecule in the aqueous solution and water molecule adsorbed on the metallic surface.

$$Org_{(sol)} + XH2O_{(ads)} \rightarrow Org_{(ads)} + XH2O_{(sol)}$$

Where, X is the size ratio representing the number of water molecule replace by one molecule of organic compound adsorbed. The adsorption of organic compounds can be described by two main types of interaction. They are physisorption and chemisorption.

These are influenced by the nature and charge of the metal, the chemical structure of the inhibitor and the type of electrolyte. The interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm. The dependence of  $C/\theta$  on C was to obtain the best fitting adsorption isotherm where  $\theta$  is the surface coverage which represents the part of the metal surface covered by inhibitor molecules. The values of  $\theta$  where evaluated from the corrosion rate using equation,

$$C/\theta = 1/k \ge C$$

Where k is binding constant of adsorption reaction and can be calculated from the reciprocal of the intercept. The relation between binding constant k and the standard free energy change of adsorption  $\Delta G_{ads}$  is the given the following equation.

$$\Delta G_{ads} = -2.303 \text{ RT} \log (55.5 \text{K})$$

The negative  $\Delta G0$  ads values indicated spontaneity of adsorption process of inhibitor molecules on the mild steel surface and strong interaction between inhibitor molecule and metal surface.

Figure 4.10-4.18 represents the Langmuir and Tempkin adsorption isotherm for the inhibitors used.



FIG.4.10 LANGMUIR ISOTHERM FOR Mimusops elengi (SPANISH CHERRY) AT 1M HCl AT

#### **ROOM TEMPERATURE**



FIG. 4.11 LANGMUIR ISOTHERM FOR Mimusops elengi (SPANISH CHERRY) IN 1.5M HCl

#### AT ROOM TEMPERATURE





FIG.4.13 LANGMUIR ISOTHERM FOR Nerium oleander (ARALI LEAVES) LEAVES IN 1M

HCI AT ROOM TEMPERATURE





#### **ROOM TEMPERATURE**



FIG.4.15 LANGMUIR ISOTHERM FOR *Nerium oleander* (Arali leaves) IN 2M HCL AT ROOM TEMPERATURE



#### FIG.4.16 LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (Camellia sinensis) IN

#### **1M HCL AT ROOM TEMPERATURE**



#### FIG.4.17 LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (Camellia sinensis) AT

#### **1.5M HCL AT ROOM TEMPERATURE**



# FIG.4.18 LANGMUIR ISOTHERM FOR WASTE GREEN TEA LEAVES (*Camellia sinensis*) IN 2M HCL AT ROOM TEMPERATURE

Many researchers have explained the Langmuir adsorption isotherm with an interaction of adsorbed species on the metallic surfaces. The Langmuir adsorption isotherm was drawn by plotting C Vs  $C/\theta$ . The straight line obtained in the graph clearly shows that the chosen inhibitor obeys the Langmuir adsorption isotherm. From this, it can be concluded that the inhibitor can act as a good inhibitor against corrosive materials.

#### 4.3. ELECTROCHEMICAL MEASUREMENTS:

#### 4.3.1 Polarization measurements:

The effects of inhibitors such as *Camellia sinensis, Nerium oleander, Mimusops elengi* concentration on the anodic and cathodic polarization behaviour of mild steel in 1M HCl solution has been studied by polarization measurements and the recorded Tafel plots for various inhibitors are shown in Fig.4.20. The respective electrochemical parameters derived from the plots including corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ , respectively), polarization resistance ( $R_p$ ) and inhibition efficiency (I.E. %) are given in Table 4.7. Figure 4.19 shows the Tafel curves for mild steel corrosion in 1M HCl. Figure 4.20-4.23 represents the Tafel curves for mild steel corrosion in 1M HCl with the inhibitor.

Anodic metal dissolution of iron and cathodic hydrogen evolution reaction was inhibited after the addition of extract to 1M HCl solution. The inhibition of these reactions was more pronounced on increasing concentration of the extract. The compound inhibits both anodic and cathodic reactions and is adsorbed on the surface, thereby blocking the corrosion reaction. In the presence of extract, the corrosion potential  $E_{corr}$  of mild steel shifted to the range (-0.42 to -0.39, -0.385,-0.405) mV/SCE, compared to the blank. This confirms that extract acts as positive inhibitor.



#### FIG.4.19 TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCl



#### FIG.4.20 TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH THE

#### **INHIBITOR** Camellia sinensis





#### **INHIBITOR** Nerium oleander



FIG.4.22 TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH THE

#### **INHIBITOR** Mimuspos elengi



# FIG.4.23 TAFEL CURVES FOR MILD STEEL CORROSION IN 1M HCL WITH VARIOUS INHIBITORS

(Bare – HCl, X-Camellia sinensis, Y-Nerium oleander, Z-Mimusops elengi.)

TABLE 4.7 POLARIZATION MEASUREMENTS FOR MILD STEEL CORROSION IN 1M

Inhibitor (ppm)	Ecorr	Icorr	I.E.%	βa	βc	Rp
				(mV/dec)	(mV/dec)	(ohm)
Blank	-0.42	6.353	-	11.125	9.336	33
Camellia sinensis	-0.39	5.297	16	9.584	5.235	55
Nerium oleander	-0.385	5.934	6.5	9.254	4.143	55
Mimusposelengi	-0.405	2.613	58	12.369	5.850	91

HCI IN THE ABSENCE AND PRESENCE OF INHIBITOR

From the Table.4.7 it was clear that the inhibitor moves to the positive potential values.

#### **4.3.2 EIS MEASUREMENTS:**

The corrosion behavior of mild steel in 1M HCl in the absence and presence of various extract was investigated by EIS at open circuit potential after 24 hours of immersion. The Nyquist plot in the absence is shown in Fig.4.24. Figure 4.25 -4.28 shows the Nyquist plot in the presence of inhibitor.

Impedance results shows a semicircle indicating that a charge transfer process at the mild steel is the rate determining step. The charge-transfer resistance ( $R_{ct}$ ) values are calculated from the difference in impedance at lower and higher frequencies. The double layer capacitance ( $C_{dl}$ ) was computed using the equation

 $C_{dl} = 1$ 

 $2\pi f_{max}$ . R<sub>ct</sub>

where

 $f_{max}$  is the frequency at which the imaginary component of the impedance (- $Z_{max}$ ) is maximal.

Table.4.8 shows the impedance parameters. The values of charge transfer resistance ( $R_{ct}$ ) were increased in the presence of inhibitor compared with those in the blank. This phenomenon is associated with decrease in the double layer capacitance ( $C_{dl}$ ) values in the presence of inhibitors. The decrease in the  $C_{dl}$  values in the presence of inhibitors could be attributed to the adsorption of the phytochemicals present in inhibitors over the mild steel surface as organic compounds adsorption process on the metal surface is characterized by a decrease in  $C_{dl}$  value. The maximum inhibition efficiency (I.E. %) was fond to be good for the inhibitor *Nerium oleander* with 89%



FIG.4.24 NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HC1



FIG.4.25 NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE

#### **INHIBITOR** Camellia sinensis



#### FIG.4.26 NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE

#### **INHIBITOR** Nerium oleander



#### FIG .4.27 NYQUIST PLOT FOR MILD STEEL CORROSION IN 1M HCL WITH THE

#### **INHIBITOR** Mimusops elengi





(Bare – HCl, X- Camellia sinensis, Y- Nerium oleander, Z-Mimusops elengi.)

 Table. 4.8 Electrochemical Impedance data for mild steel corrosion in 1M HCl in the absence and

 presence of inhibitor (ppm)

INHIBITOR	Rct	C <sub>dl</sub>	I.E.	Surface
	$(\Omega \ cm^2)$	(mF)	%`	coverage
				(θ)
BLANK	49.9	0.1387	-	-
Camellia sinensis	104.9	0.0276	1.39	2.76
Nerium oleander	399.9	0.0019	89	0.19
Mimusops elengi	149.9	0.0118	74	1.18

#### 4.4 Fourier Transform Infrared Spectral Results:

The nature of inhibitor used for the mild steel corrosion were further confirmed by FT-IR spectra .

#### 4.4.1 FTIR STUDIES OF Camellia sinensis



Fig.4.29 FTIR ANANLYSIS OF Camellia sinensis

Fig.4.29 shows the FT-IR spectrum of inhibitor *Camellia Sinensis*. The phenolic –OH stretching appeared at 3441 cm<sup>-1</sup>. The peaks at 2925 cm<sup>-1</sup> can be assigned to aliphatic C-H. The aromatic C-C stretching frequency appeared at 1462 cm<sup>-1</sup>. The C-O stretching frequency appeared at 1653 cm<sup>-1</sup>

#### 4.4.2 FTIR STUDIES OF Nerium oleander



Fig.4.30 FTIR ANANLYSIS OF Nerium oleander

Fig.4.30 shows the FT-IR spectrum of inhibitor *Nerium oleander*. The peak at 1744 cm<sup>-1</sup> is due to the presence of C=O group. The phenolic –OH stretching appeared at 3140 cm<sup>-1</sup>. The peaks at 2924 cm<sup>-1</sup> can be assigned to aliphatic C-H and the peak at 2851 cm<sup>-1</sup> is due to C-H alkane group. The aromatic C-C stretching frequency appeared at 1400 cm<sup>-1</sup>. The C-O stretching frequency appeared at 1653 cm<sup>-1</sup>

#### 4.4.3 FTIR STUDIES OF Mimuspos elengi



Fig.4.31 FTIR ANANLYSIS OF Mimusops elengi

Fig.4.31 shows the FT-IR spectrum of inhibitor *Mimusops elengi*. The peak at 1736 cm<sup>-1</sup> is due to the presence of C=O group. The phenolic –OH stretching appeared at 3136 cm<sup>-1</sup>. The peaks at 2925 can be assigned to aliphatic C-H and the peak at 2853 is due to C-H alkane group. The aromatic C-C stretching frequency appeared at 1400 cm<sup>-1</sup>. The C-O stretching frequency appeared at 1653 cm<sup>-1</sup> The phenol group of would donate electron to the metal to achieve its noble state of orbit, while the metal would receive the electron to become more stable. This indirectly retard further redox reaction and could resist metal from corrosion attack.

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.



In the anodic reaction, oxidation of iron leads to  $Fe^{2+}$ . In the cathodic reaction, proton gets reduced to generate hydrogen gas. On adding inhibitor, they start to become protonated and these protonated molecules get adsorbed on the surface via electrostatic interaction with Cl<sup>-</sup>. Hence the process of physical adsorption takes place.

In acidic solution, the oxygen atom of the inhibitor can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species. The adsorption can occur via electrostatic interaction between positively charged inhibitor molecules and negatively charged metal surface leading to physisorption of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared electron pairs of unprotonated oxygen atom of the inhibitor and vacant d-orbitals of metal surface atoms.

### CONCLUSION

- Camellia sinensis (Green tea leaves), Mimusops elengi (Spanish cherry), Nerium oleander (Arali leaves) extract act as an efficient inhibitor for the corrosion of Mild steel 304 in 1M HCl solution.
- > Inhibition efficiency increases with increase in the concentration of inhibitor.
- > As the temperature increases, the inhibition efficiency decreases.
- > The adsorption of inhibition of mild steel follows the Langmuir adsorption isotherm.
- The results obtained from polarization measurements and electrochemical impedance spectroscopy measurement revealed that the extract acts as efficient inhibitor

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## SILVER NANOPARTICLES LOADED ON SEA SHELL

## **USING** Alkanna tinctoria **BARK EXTRACT**

### AND ITS APPLICATIONS

#### **Project in Chemistry**

Submitted to St.Mary's College (Autonomous) in partial Fulfillment for the award of the Degree of Bachelor of Science in Chemistry

Project done by

#### PON SHANTHINI . R

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Thoothukudi-628001

2022-2023

### DECLARATION

We hereby declare that the project entitled "SILVER NANOPARTICLES LOADED ON SEASHELL USING Alkanna tinctoriaBARK EXTRACT AND ITS APPLICATIONS" submitted to St. Mary's College (Automonous), Thoothukudi affiliated to Manonmaniam Sundarnar University for the Degree of Bachelor of science is our original work and that it has not previously formed the basis for the award of any degree, Diploma or Similar title.

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April, 2023

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### CERTIFICATE

This is to certify that the report of the project in chemistry entitled "SILVER NANOPARTICLES LOADED ON SEA SHELL SURFACE USING Alkanna tinctoria BARK EXTRACT AND ITS APPLICATIONS" is submitted to St. Mary's College (Autonomous), in partial fulfillment for the award of the Degree of Bachelor of Science in Chemistry and is a record of the work done by the following students during the year 202-2023.

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#### CONTENTS

CHAPTER NO.	TITLE	PAGE NO
CHAPTER I	INTRODUCTION	
1.1	ADVANTAGES OF NANOPARTICLES.	2
1.2	GREEN SYNTHESIS OF AgNPS	4
1.3	Alkanna TinctoriaBARK	5
1.4	Marmorofusus nicobaricus	6
1.5	ANTIBACTERIAL ACTION OF AgNPS	7
1.6	ANTIFUNGAL ACTION OF AgNPS	8
1.7	DPPH	8
1.8	HYDROGEN PEROXIDE	9
CHAPTER II	STATE THE ART & SCOPE OF WORK	
2.1	LITERATURE SURVEY	10
2.2	SCOPE OF THE WORK	17
2.3	OBJECTIVES OF THE WORK	18

CHAPTER III	MATERIALS AND METHODS	
3.1	MATERIALS REQUIRED FOR SYNTHESIS	19
3.2	INSTRUMENTATION	19
3.3	PROCEDURE	20
3.4	METHODS	23
3.4.1	UV SPECTROSCOPY	23
3.4.2	INFRARED SPECTROSCOPY	24
3.4.3	ATOMIC FORCE SPECTROSCOPY	25
3.4.4	X-RAY DIFFRACTOMETER	26
3.4.5	ANTIBACTERIAL ACTIVITY	27
3.4.6	ANTIFUNGAL ACTIVITY	28
3.4.7	HYDROGRNPEROXIDESCAVENGINGASSAYNANOPARTICLESWITHAlkanna tinctoriaLOADEDWITHMarmorofususnicobaricus	29
3.4.8	DPPH RADIAL SCAVENGING ACTIVITY	30
CHAPTER IV	RESULTS AND DISCUSSIONS	
4.1	CHARACTERISTICS OF SILVER NANOPARTICLES	33
4.1.1	ULTRA VIOLET SPECTROSCOPY	33
4.2	INFRARED SPECTROSCOPY	36
4.3	ATOMIC FORCE MICROSCOPY	39
4.4	X-RAY DIFFRACTION STUDIES	41
4.5	APPLICATIONS	44

4.5.1	ANTIBACTERIAL ACTIVITY	44
4.5.2	ANTIFUNGAL ACTIVITY	48
4.5.3	HYDROGEN PEROXIDE SCAVVENGING ASSAY FOR Ag NPs	50
4.5.4	HYDROGEN PEROXIDE SCAVVENGING ASSAY FOR AgNPs LOADED ON Marmorofususnicobaricus	54
4.5.5	DPPH RADICAL SCAVENGING ACTIVITY	58
CHAPTER V	CONCLUSIONS AND REFERENCES	
5.1	CONCLUSIONS	60
5.2	REFERENCES	61

### LIST OF TABLES

TABLE NO	CONTENTS	PAGE NO
110		110
4.1	Particle size of Silver Nanoparticles	41
4.2	Particle size of Silver Nanoparticles loaded on Marmorofusus nicobaricus	43
4.3	$SD \pm$ Means of zone of inhibition obtained against <i>Staphylococuss aurens</i> and <i>Pseudomonasaeruigunosa</i>	47
4.4	SD± Means of zone of inhibition obtained by Asperigillus niger	49
4.5	Absorbance of Silver nano particles at various concentration	50
4.6	Percentage of inhibitions of synthesised the silver nano particles	51
4.7	IC50 Value of tested sample:63.09 /ml	52
4.8	Absorbance of silver nano particles at various concentration	54
4.9	Percentage of inhibition of synthesised	55
	Silver nano particles	
4.10	IC50 Value of tested sample:69:39 /ml	56
4.11	Absorbance of ag nanoparticles at various concentration by DPPH scavenging effect	58
4.12	Absorbance of Ag nanoparticle loaded on Marmorofusus nicobaricus at various concentration by DPPH scavenging effect	58

### LIST OF FIGURES

Figure	Contents	Page no.
number		1.01
1.1	Marmorofusus nicobaricus	6
3.1	Bark extract	20
3.2	Residue from Alkanna tinctoria	21
3.3	Residue from Alkanna tinctoria and Marmorofusus nicobaricus	22
3.4	UV spectrometer	23
3.5	IR spectrometer	24
3.6	Atomic Force Microscopy	25
3.7	X-Ray Diffractrometer	26
4.1	UV visible Spectra of Alkanna tinctoria Bark	33
4.2	UV visible spectra image of silver nanoparticles using Alkanna tinctoria	34
4.3	UV visible Spectra image of silver nano particles using Alkanna tinctoria loaded on Marmorofusus nicobaricus	35
4.4	Infrared spectroscopy of Alkanna tinctoria bark	36
4.5	Infrared spectra image of s of silver nano particles using <i>Alkanna tinctoria</i> bark	37
4.6	IR Spectra image of silver nanoparticles using Alkannatinctoria loaded on Marmorofusus nicobaricus	38
4.7	Atomic Force Microscopy of silver nano particles using Alkanna tinctoria	39
4.8	Atomic Force Microscopy images of Silver Nanoparticles using <i>Alkanna tinctoria</i> loaded on	40

	Marmorofusus nicobaricus Sea shell	
4.9	X-Ray Diffraction Pattern of silver nanoparticles	41
4.10	X-Ray Diffraction Pattern of silver nanoparticles loaded on <i>Marmorofusus nicobaricus</i>	42
4.11	Effect Ag nanoparticles loaded on Marmorofusus nicobaricus against Pseudomonas aeruginosa	44
4.12	Effect of Ag nanoparticles loaded on Marmorofusus nicobaricus against Staphylococcus aurens	45
4.13	Effect of Ag nanoparticles against <i>Pseudomonasaurens</i>	46
4.14	Effect of Ag nanoparticles against Staphylococcusaurens	47
4.15	Effect of Ag nanoparticles against Aspergillus niger	48
4.16	Effect of Ag nanoparticles loaded on Marmorofususnicobaricus against Aspergillus niger	49
4.17	Concentration versus OD 230nm	51
4.18	Concentration versus percentage of inhibition	52
4.19	Hydrogen Peroxide Scavenging Assay for Aspergillus niger	53
4.20	Concentration versus OD 230nm	55
4.21	Concentration versus Percentage inhibition	56
4.22	Hydogen Peroxide scavenging assay of Ag Nanopaticles overload on <i>Marmorofusus</i> <i>nicobaricus</i>	57
4.23	DPPH scavenging effect of Ag nanoparticles	59
4.24	DPPH scavenging effect of Ag nanoparticles loaded on <i>Marmorofusus nicobaricus</i>	59

# **CHAPTER I**

# INTRODUCTION

# **CHAPTER II**

# **STATE OF THE ART & SCOPE OF THE WORK**

# **CHAPTER III**

# **MATERIALS AND METHODS**

# **CHAPTER IV**

# **RESULTS AND DISCUSSION**

