PHYTOGENIC GENERATION OF COBALT OXIDE NANOPARTICLE USING *PHYLLANTHUS NIRURI* EXTRACT AND EVALUATION OF THEIR ANTIBACTERIAL AND ANTIOXIDANT PROPERTIES

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

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DECLARATION

We hereby declare that the project entitled **"PHYTOGENIC GENERATION OF COBALT OXIDE NANOPARTICLE USING *PHYLLANTHUS NIRURI* EXTRACT AND EVALUATION OF THEIR ANTIBACTERIAL AND ANTIOXIDANT PROPERTIES"** 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.

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CHAPTER-I

INTRODUCTION

Green nanoscience and technology have developed recently to a great extent due to their wide applications in catalysis, sensors, drug delivery, and biomedical purposes. There has been increasing research on the utilization of phytomolecules in the area of green synthesis [1,2]. Thus, several investigators have used various phytochemicals from different biological sources such as roots, fruits, barks, flowers, and leaves. Among them, leaves are a rich source of polyphenols, amides, and proteins, which are utilized in the synthesis of noble metal (Au, Ag, Pd, Pt, and Cu) and metal oxide (TiO2, NiO, ZnO, and CdO) nanoparticles (NPs) [3,4]. Among the metal oxide nanoparticles, NiO is a cheap, nontoxic to humans in short-term exposure, abundantly available, and photo-stable material. Moreover, NiO is a Biomolecules 2020, 10, 89; doi:10.3390/biom10010089 www.mdpi.com/journal/biomoleculesBiomolecules 2020, 10, 89 2 of 12 P-type semiconductor with a wide bandgap of 3.6 to 4.0 eV and has potential applications in gas sensors, catalysis, battery, supercapacitors, and fuel cell applications [4]. However, long-term inhalation of NiO is damaging to the lungs, causing lesions and, in some cases, cancer. The calculated half-life of dissolution of NiO in blood is more than 90 days [5–7]. NiO-NPs have been synthesized by using different methods, including chemical precipitation, electrodeposition, hydrothermal, solvothermal, thermal decomposition, microemulsion technique, coprecipitation methods, and microwave irradiation [8–14]. Nevertheless, these processes have disadvantages owing to the involvement of high pressure, high temperature, and hazardous chemicals. The biosynthetic process is gaining interest since it avoids high costs, several synthesis steps, usage of toxic chemicals, and harsh atmospheric conditions for reduction and stabilization. NiO nanoparticles are prepared using different plant leaf extracts such as Azadiricta indica, Calotropis gigantea, Agathosma betulina, and Aegle marmelos [4,15–17]. The leaf extracts from natural sources of polysaccharides, flavonoids, terpenoids, polyphenols, glycosides, proteins, and vitamins act as reducing and capping agents in the preparation of nanoparticles [18]. Stevia rebaudiana Bertoni is a sweet herb belonging to the composite family and is native to South America. Its leaf extract is used as an alternative to table sugar and as a supplement in soft drinks, soy sauce, soju, yogurt, and other foods, in Korea, Brazil, and Japan. Stevia extract contains sugars, amino acids, lipids, chlorophylls, alkaloids, flavonoids, xanthophylls, hydroxycinnamic acids, and trace elements [19]. The leaf extract of stevia has been thought to provide health benefits such as anti-hypertensive, anti-hyperglycemic, and antihuman rotavirus activities [20,21]. It has been used extensively for the synthesis of silver, gold, and palladium NPs [22–24]. Terpenoids, polyphenols, proteins, and aldoses have been proposed to play a significant role in the formation (reducing and capping) of metal NPs.

Metal nanoparticles (MNPs) and metal oxide nanoparticles (MONPs) are used in numerous fields. The new nano-based entities are being strongly generated and incorporated into everyday personal care products, cosmetics, medicines, drug delivery, and clothing to impact industrial and manufacturing sectors, which means that nanomaterials commercialization and nanoassisted device will continuously grow. They can be prepared by many methods such as green synthesis and the conventional chemical synthesis methods. Green synthesis includes infinite accession to produce MNPs and MONPs with demanding properties. The structure– function relationships between nanomaterials and key information for life cycle evaluation lead to the production of high execution nanoscale materials that are gentle and environmentally friendly. Majority of plants have features as sustainable and renewable suppliers compared with microbes and enzymes, as they have the ability to pick up almost 75% of the light energy and transform it into chemical energy, contain chemicals like antioxidants and sugars, and play fundamental roles in the manufacture of nanoparticles. Plants considered the main factory for the green synthesis of MNPs and MONPs, and until now, different personification procedures, and production of functional nanodevices. Plant species have been used to study this, but the determined conditions should be taken into consideration to execute this preparation. In this study, we focus on the biosynthesis procedures to synthesize MNPs and MONPs, including comparison between green synthesis and the classical chemistry methods as well as the several new orientation of green synthesis of nanoparticles from different plant parts, especially plant leaf extracts. Plants with reducing compounds is the preferred choice for the synthesis of noble metals – metal ions can be reduced to the corresponding metals in the absence of any other chemicals under microwave irradiation conditions using benign solvent, water. Noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd) and other metals such as copper (Cu) and nickel (Ni), which are characterized by their optical, electronic, mechanical, magnetic, and chemical properties, leading to different technological applications. Plants with numerous reducing agents are suitable candidates for the manufacture of noble MNPs. The main purpose of this research is to give a background on green nanotechnology prospective evolution, pertinent concerns appeared related to the green synthesis of metal and metal oxide from plant extracts, nanoparticle formation mechanism, and the importance of flavonoids, vitamin B2, ascorbic acid (vitamin C), and phenolic compounds in the MNP and MONP production. The traditional sorghum beers are produced in many countries in Africa, but diversity in the production process may depend on the geographic localization. These beers are very rich in calories; B-group vitamins including thiamine, folic acid, riboflavin, and nicotinic acid; and essential amino acids such as lysine. However, the Western beers are more attractive than the traditional sorghum beers. The traditional sorghum beers have poor hygienic quality, organoleptic variations, and shorter shelf life compared with the Western beers. Many research studies on traditional sorghum beers have been carried out and documented in several African countries, especially the microbiological and biochemical properties, the technologies used in the manufacture processes, and synthetic characteristics of African traditional sorghum beers. The excellent resources for the production of greener biomaterials are plants and considerable advances have been achieved in many fields such as biotechnology and gene transfer. The manufactured biological nanomaterials have a great application in the pharmaceutical industry such as novel pharmaceuticals preparation, drug delivery.

Global research studies give a great interest to green nanotechnology, as green nanotechnology is a resultant field and nascent branch of nanotechnology. Green nanotechnology is the perfect solution to decrease the negative effects of the production and application of nanomaterials, lowering the nanotechnology riskiness. The generation of engineered nanomaterials represents an essential breakthrough in nanotechnology and materials science. The real world should be created by moving these products beyond the laboratory. More than thousands of such products are available in the market, of which a large majority are integrated in everyday personal care products, cosmetics, and clothing. Development of the modern products that consumers need are expected to affect positively almost every industrial and production sectors, involving medicine and drug delivery. The continuous growth of the nanomaterials marketing and nano-assisted device is very obvious. The commercialization of successful disruptive technologies is fundamental for numerous implementations to humans and global development, but critical interest is necessary for potential, health assessment and environmental effects of these materials. It is a clear reality that the health hazards due to nanoparticles exposure are slowly comprehended and need to be addressed rapidly and their manufacture and utilization are practically uncontrolled, particularly in the universe development. This is predominately discouraging when the new nano-based entities are being generated and incorporated into consumer products at an alarmingly quick rate, thus oversight mechanisms is an urgent need since the final existence of the majority of the nanotechnology innovations resulted from the research groups which considered simple startup work must based on instructions and recommendation from regulatory bodies and should not be oppositely affected by the boosted cost loads connected with such increased oversight. Health and safety regulations will have to carefully negotiate regulatory testing cost load, which will in turn have an essential role in giving priority to hazards associated with nanomaterials. The essential aspect of the green chemistry emerging sector is the utilization of a group of basics lowers or removes the hazardous substances utilization or generation concerning design or production and chemical products' application while designing new chemical processes visualizes small risk as the execution criteria. Green chemistry basics implementation in the new materials expansion and enforcements is all the more considerable in opinion of the principle that the technology is an early expansion phase and is foreseeable to be widely utilized and doled out around the world. The strong relation between chemical structure and function groups that connects specifically to nanomaterials and boosting understanding "key" information for life cycle evaluation of such methods could lead to new "design principles" for the production of high rendering nanoscale materials that are benign and environmentally friendly. The molecules, cells, and organs of the aforementioned plants have been bioengineered to provide new nanomaterials with demanding sustainable advantages. Green nanotechnology gives us the chance to prevent the negative effects. Green nanotechnology has an enterprising effect on the nanomaterials or the products design by removing or lowering pollution, which means that it remediates the existing environmental problems. The environmental friendly methods such as catalytic potential, electrical conductivity, optical sensitivity, magnetic behavior, or biological reactivity are used to characterize the chemical, physical, and biological properties of nanomaterials in addition to many factors such as size, shape, surface charge, chemical structure, surface area, and coagulation properties of nanoscale distinct materials. The organic solvents and chemical reagents are not used in the preparation of metal nanoparticles (MNPs). MNPs have unique properties with their nanostructures. The atoms ordered to the nano-scale differ from the bulk metallic materials, and the unique properties of MNPs and metal oxide nanoparticles (MONPs) are engendered from them. MNPs and MONPs have many applications such as catalysts; drug delivery systems; boosting contrast agents; active food packaging materials components pointing to nano-biosensor construction; gene transfer system; antibiotics, antiseptics, and disinfectants to control pathogens and pests; and nanoelectronic components.

To synthesize MNPs and MONPs, researchers used a strong base (reducing agent), e.g., sodium borohydride or sodium hydroxide, in metal ion reduction from salt solutions, followed by the addition of a capping agent or a stabilizer (stabilizing agent) . To dissolve the stabilizers, they used solvents and the reagents that act as reducing agents, which are toxic substances and have counteractive and harmful effects if the rest of these materials are left in the rear part of the nanosystem, as the bottom-up path to synthesize the nanoparticles often needs the offensive chemical reduction agents such as sodium borohydride and hydrazine and a capping agent and may also involve a volatile organic solvent such as toluene or chloroform. Although these procedures may effectively produce pure products, the manufacturing cost is very high, both materially and environmentally. This may provide new stand by accession achieving this synthesis and steer them to consider safety applications of MNPs and MONPs. The green synthesis of MNPs and MONPs is considered one of the alternatives that depends on the green chemistry principles by using the biological systems. The green synthesis of MNPs and MONPs is accomplished by using prokaryotic or eukaryotic organisms (involving microorganisms, plants, and animals) or their parts, and can take place intracellularly or extracellularly. The primary and secondary metabolites of plants are used to produce MNPs and MONPs by executing a target metal ion reduction. Formation of coating layer (stabilizing layer) on the surface of the MNPs and MONPs by reducing compounds or other besetment molecules lowering them to coagulate/ aggregate otherwise ordered in an upset way within their preparation. MNPs and MONPs preparation and their properties can be polished by setting different conditions such as temperature, pH, and reagent concentration. The scientists have utilized the organ/tissue extracts or the whole organisms of plants to execute the green synthesis of MNPs and MONPs. Various plant parts such as leaves, seeds, barks, roots, and fruits, is the factory for the nano-object production with different properties, but the researchers should consider the specific phytochemical profile of each plant part with different structures and concentrations according to the needs of each organ and the type of biotic or abiotic stress to which a plant may be exposed. Plants are the main factory for the green synthesis of MNPs and MONPs. The green synthesis of MNPs and MONPs may be done by using the living organisms, which symbolize the kingdom of the biology system. The living organisms are not only necessary for food and nutritional purposes but also used in green synthesis. Due to the biomass abundance of many plants, the scientists give priority to the plants to execute the green synthesis of MNPs and MONPs because of their molecular ammunition and biomass profusion. The resulted response to the stress factors (pathogens, herbivores, and climate changes) and survival agents (seasonal changes and reproductive manner) concerning plants are affected by the primary and secondary metabolites of the plants, and these strategies will make the plants the main bioreactors and molecule suppliers for green synthesis. Due to the presence of metallic counterparts and the stabilization of the surface of the MNPs and MONPs , the primary compounds of plants such as amino acids , citric acid, flavonoids, phenolic compounds, terpenoids, heterocyclic compounds, enzymes, peptides, polysaccharides, saponins , and tannis are responsible for the metal ion reduction. The whole organs/ tissues or the extracts of the organs/tissues and different parts (e.g., seeds, leaves, barks, roots, and fruits) of the plants are utilized for the green synthesis of MNPs and MONPs and may produce nano-objects with several properties [59,60], so we deal with each part of the plants discretely for their different concentrations and their unique phytochemical characterization, and this depends on the biotic or abiotic stress type to which a plant perhaps subjected and the needs of each organ.

The research studies on the green synthesis of MNPs and MONPs using plants can easily understanding the molecular mechanism, coordinating bioreduction, nucleation, growth, and stability. The first stage was utilization of the plant extracts selected from the endemic or global biological variation. The extract from different plant parts and species in the presence of metal salts results in the production nanoparticles of different sizes, shapes, compositions, and activities. Reduction of noble metals including gold (Au), silver (Ag), and platinum (Pt) and other metals such as copper (Cu) was studied in many research studies on the green synthesis of MNPs and MONPs.

Noble metal synthesis Noble metals are characterized by their optical, electronic, mechanical, magnetic, and chemical properties, which attract interest and lead to various applications in different technological applications. MNPs are synthesized by using extremely reactive reducing agents, e.g., sodium borohydride (NaBH4) and hydrazine, which are not ecofriendly. The use of toxic chemicals in these methods limits their use due to environmental precautions. The plants' ability to synthesize MNPs has conquered a new axis and spectacular approach toward the development of natural nano-factories. Majority of plants have features as sustainable and renewable resources compared with microbes and enzymes as they have the ability to pick up nearly 75% of the light energy from sun and convert it into chemical energy, which needs expensive production methods. Furthermore, plants contain chemicals like antioxidants and sugars and play essential roles in the manufacture of nanoparticles. Consequently, a pressing need to promote more cost effective and environmentally friendly alternatives to these existing procedures, the environmentally compatible solvent system choice, using an eco-friendly reducing agent for stabilizing the nanoparticles are three essential criteria for a “green” nanoparticle synthesis. The preferred choice is plants with reducing compounds for synthesis of noble metals. A schematic illustration of plants as a source for the green synthesis of nanoparticles and the properties and biomedical implementation of nanoparticles. Green synthesis of MNPs using the extracts obtained from the leaves of different plant species leading to the production of structures with different compositions, shapes, and sizes.

1.1.Synthesis of MNPs and MONPs by utilizing plant leaf extract

The bio variations of plants offers a plentiful biochemical property and introduces particular source to synthesize nanoparticles. The extract from the plant leaf can be obtained very simply to use and has numerous metabolites that act as reducing agents to synthesize nanoparticles. A solution containing metals such as nickel, cobalt, zinc, and copper is mixed with the extract of the plant leaf at room temperature. Different factors such as pH, temperature, contact time, metal salt concentration and phytochemical profile of the plant leaf particles affect the nanoparticles goodness, nanoparticle stabilization, quantity produced, and yield rate. The metal ion reduction in plants is faster than that in fungi and bacteria, as they need a long time for incubation because of the presence of water-soluble phytochemicals. The numerous phytochemicals present in the plant leaf extracts can be extracted facilely, so the plant leaf extracts are considered as a wonderful tool for MNPs and MONPs synthesis. The advantage of plant leaf extracts to act as stabilizing agents and reducing agents facilitates the nanoparticle synthesis. Biomedical reducing agents are present at different concentrations in different types of leaf extracts, so the leaf extract composition has a great effect on the nanoparticle synthesis. Terpenoids, flavones, ketones, amides, aldehydes, and carboxylic acids are the essential phytochemicals involved in the nanoparticle synthesis.

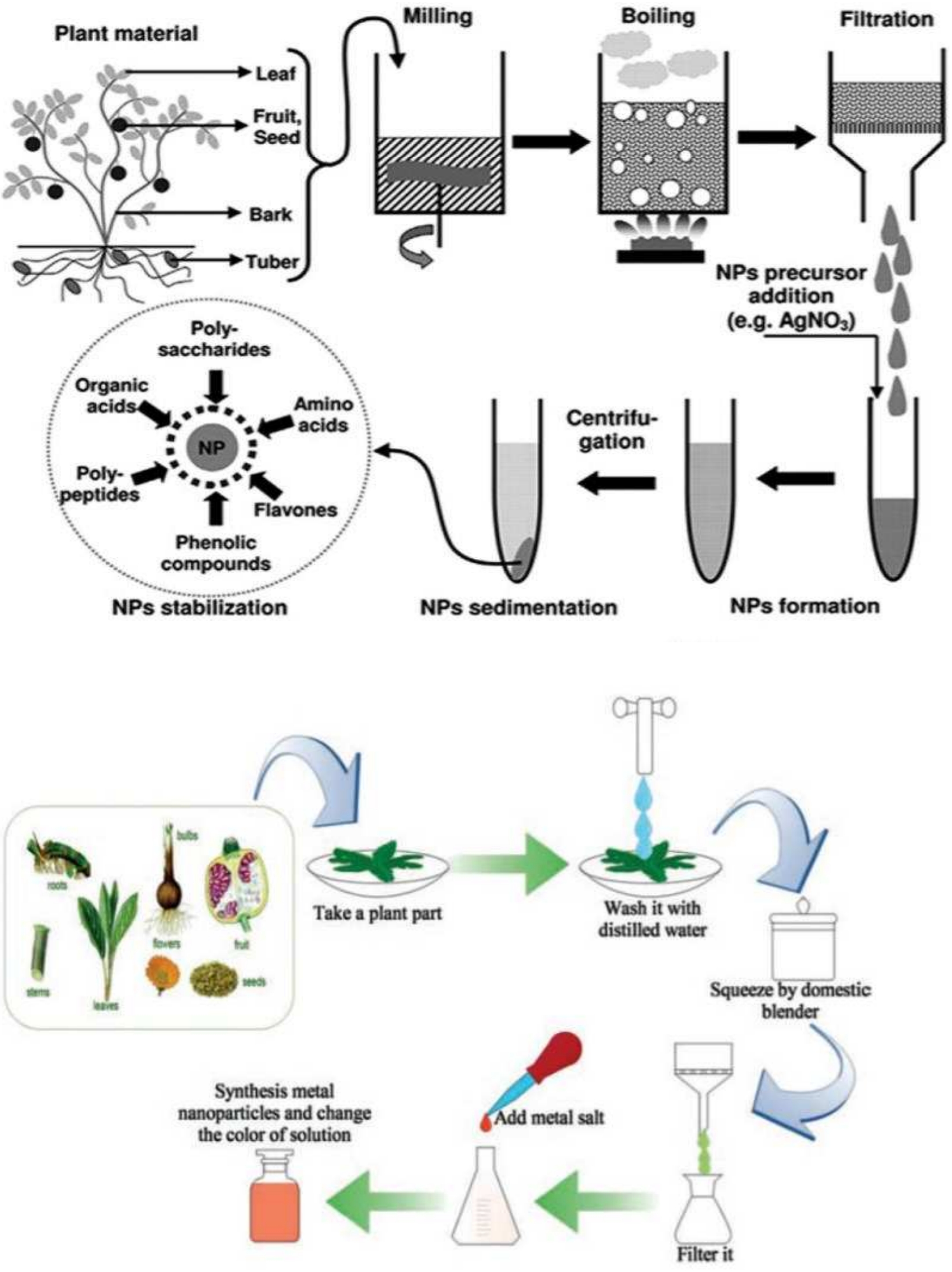


Fig.1. Two schematic features of MNP synthesis using plant extracts

Nanoparticles synthesis from plant leaf extracts mechanism Proteins and carbohydrates are important constituents of the plant extracts, which act as reducing agents and are responsible for the formation of MNPs and metal ion reduction. Functional amino groups and proteins in the plant extracts play an essential role in the metal ion reduction. Huang et al. discussed that the functional groups of alkaloids, flavones, and anthracenes, such as –C–O–C–, –C–O–, –C=C–, and –C=O–, assist the MNP synthesis. Kesharwani et al. proposed that the metal ion reduction may be carried out with the help of quinones and plastohydroquinone molecules present in the plant leaf extract, which indicate that the extracellular MNP synthesis can be done by biomolecules and heterocyclic compounds in plants. Despite the complete vision of MONP synthesis by using plants is not well understood until now, the phytochemicals of the plants led to the production of MONP, like MNP. First, the phytochemicals of the plant extract are responsible for the metal reduction. Oxygen produced from either atmosphere or degrading phytochemicals links the reduced metal ions. Electrostatic attraction will link metal oxide ions to each other and lead to the formation of nanoparticles. They are stabilized by phytochemicals that prevent agglomeration between them. The superoxide-driven Fenton reaction is the main provenance for reactive oxygen species (ROS) and is repressed by the phenolic compounds with carboxyl groups and hydroxyl groups of plants. Mukherjee et al. suggested the use of high- and low-weight phytochemicals, proteins, and starch mixtures present in the plant extracts. Newman et al. also explained the possibility of the production of MNPs and MONPs by proteins of plant extracts, which act as reducing and stabilizing agents. Markarov et al. proposed that metal atoms will be encapsulated as organic covering in three steps for their magnitude stabilization after reduction by plant extracts, as shown in Figure 8b. Metal ion reduction and nucleation of reduced metal atom will be in the activation phase, the nanoparticle stability increased through the growth phase, and the shape of the nanoparticles formed during the termination phase.

They could summarize the process by the following steps:

(1) The metals such as copper, silver, gold, zinc, titanium, iron, and nickel result in the formation of their metal oxides by phytochemicals.

(2) Using phytochemicals, metal ions will go through growth and stabilization phases.

(3) Oxygen is produced either by degradation of phytochemicals or by atmosphere, and before growth and stabilization phases, which explains the MONPs production mechanism may also be executed by different methods.

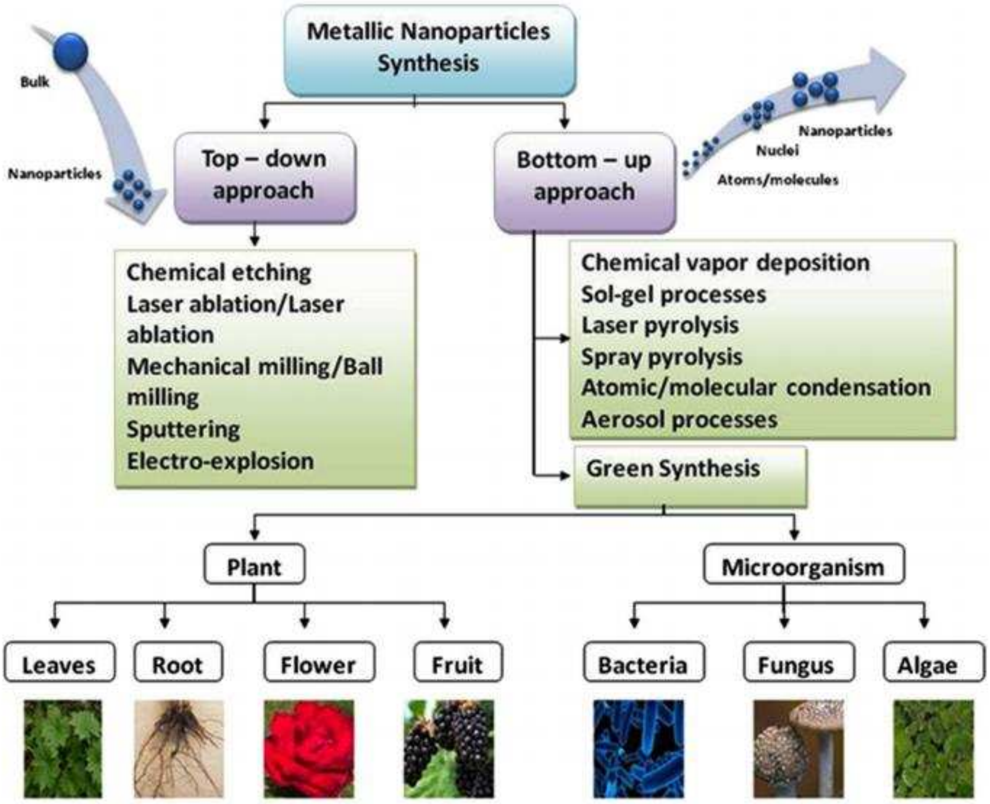


Fig.2. Different Synthesis routes of metal nanoparticles

Stabilization and functionalization by using biodegradable polymers and enzymes The high chemical activity with an improved surface of the engineered nanoparticles is mainly because of the unfavorable intense and predominantly irreversible operations like aggregation. Reduction of the specific surface area and the interfacial free energy can be achieved by aggregation, thereby minimizing the particle reactivity, so it is fundamental to boost the nanoparticle stability improvement during storage, transportation, and its overall life cycle. The majority of the stabilization methods involve Dispersant molecules such as surfactants or polyelectrolytes, which not only modify the chemistry and nanoparticle surface physics but also fabricate an enormous waste stream because they take up a worthy (more than 50%) of the nanoparticle mass fraction system. Hence, there is a necessity to find environmentally benign stabilization and functionalization passages as well as bioconvenient to obviate pollution and the following counteractive effects on the environment, i.e., non-immunogenic, nontoxic, and hydrophilic stabilizing agents. Different stabilizing agents are used to prevent the aggregation of the nanoparticles and to functionalize the particles for the desired implementation at the same time. However, the usual acute reaction conditions and the toxic chemicals may not be appropriate for the biological and biochemical implementation. Presently, there are numerous "green stabilizing agents" such as polyphenols, enzymes, citric acid, vitamins (B, C, D, and

K), biodegradable polymers, and silica, which has the ability to stabilize and functionalize MNPs without the unfavorable effects on the environment and biosynthesis.

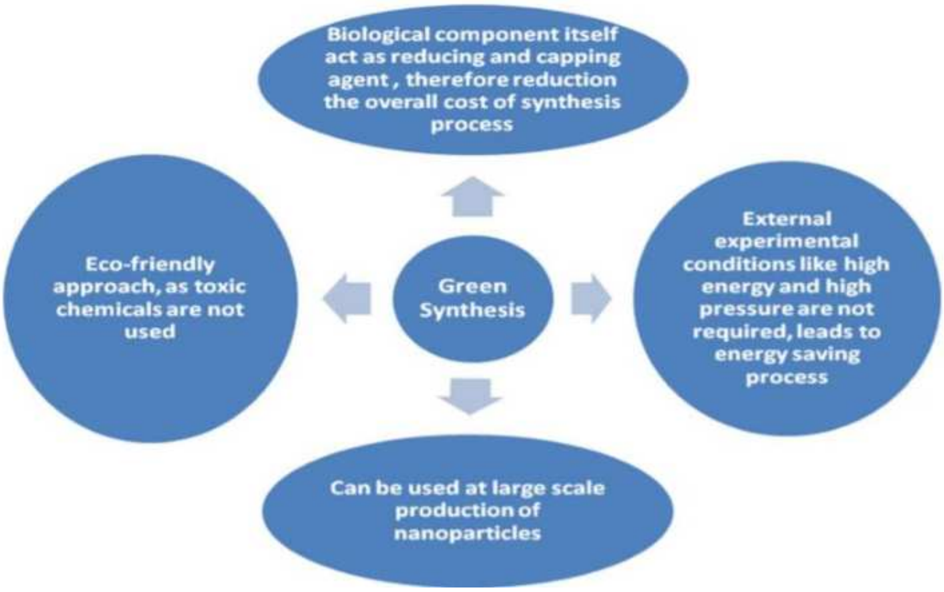


Fig.3. Significance of green synthesis

It is very substantial to functionalize and stabilize MNPs for varied implementation; however, simple and relatively low-cost recoverability and therefore nanoparticles' reuse is currently acquiring an increased attention among the scientific society. Nanoparticles have magnetic properties have been inclusively used in the metal ion and dye coat, drug delivery, enzyme immobilization, and protein and cell separation fields because the magnetic separation of these nanoparticles offers individual high competency and cost leverage and is fast in comparison with other nanoparticles, which are harmoniously emerging as heterogeneous supports (so called magnetic nano-cores) in numerous catalytic transformations, providing easy recoverability with easy magnet advantages, thereby eliminating solvent swelling exigency before or catalyst filtration after the reaction.

Biodegradable polymers perhaps produced from numerous renewable sources (corn, wood, cellulose, polylactides, thermoplastic starch, plant oils, gelatin, and chitosan), petroleum sources (aliphatic polyesters or aliphatic–aromatic copolyesters), small molecules in bacteria, or biomass and petroleum mixtures. debated the nanoparticles stabilized by surface active polymers, which are adsorbed strongly on the particle surface due to the van der Waals attractive forces between the surface of the particle and the monomer units in polymer chain, preventing the aggregation because of their large surface energy minimization in comparison with the native particles. Block copolymers are even stronger nanoparticle separation and show individual properties such as surface reactivity, flexibility, selectivity, and impedance. MNPs stabilization can be fulfilled by metals in a polymer gel simple enclosure, free radical polymerization with a radical initiator, thiol-supported polymer adsorption, or in situ MNPs formation during polymerization.

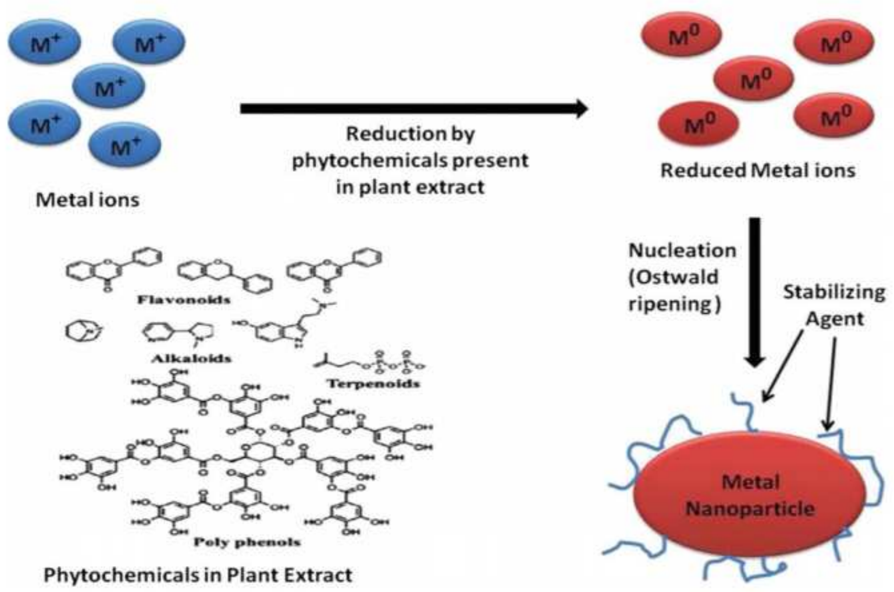


Fig.4. Mechanism of formation of metal nanoparticle

Over the last decade, novel synthesis approaches/methods for nanomaterials (such as metal nanoparticles, quantum dots (QDs), carbon nanotubes (CNTs), graphene, and their composites) have been an interesting area in nanoscience and technology. To obtain nanomaterials of desired sizes, shape, and functionalities, two different fundamental principles of synthesis (i.e., top down and bottom up methods) have been investigated in the existing literature. In the former, nanomaterials/nanoparticles are prepared through diverse range of synthesis approaches like lithographic techniques, ball milling, etching, and sputtering. The use of a bottom up approach (in which nanoparticles are grown from simpler molecules) also includes many methods like chemical vapor deposition, sol–gel processes, spray pyrolysis, laser pyrolysis, and atomic/molecular condensation. Interestingly, the morphological parameters of nanoparticles (e.g., size and shape) can be modulated by varying the concentrations of chemicals and reaction conditions (e.g., temperature and pH).

Nevertheless, if these synthesized nanomaterials are subject to the actual/ specifc applications, then they can sufer from the following limitation or challenges:

(i) stability in hostile environment,

(ii) lack of understanding in fundamental mechanism and modeling factors
(iii) bioaccumulation/ toxicity features,
(iv) expansive analysis requirements
(v) need for skilled operators,
(vi) problem in devices assembling and structures, and
(vii) recycle/reuse/regeneration.

1.2. Applications

There are two main classes of applications of metal oxide nanoparticles:

- high surface area materials
- materials taking advantage of the size-dependence of physical properties.

For example, materials for supercapacitors rely on the large surface area per weight or film thickness for their function. This is a geometrical consideration and is not related to unique size dependent physical properties. Catalysis applications are an example where both the high surface area and size-dependent properties play a role. The surface energy, and energy of surface sites is expected to depend on the particle size, and hence, the catalytic activity may be enhanced due to a change of the (surface) physical properties with size. Similar arguments hold for high surface area sensors, and more research is needed on the elucidation of mechanisms in such applications. In the fabrication of high surface area materials, the controlled synthesis of nanoparticles with a relatively small size distribution has several advantages including better control over film deposition and film properties. For example, thin, porous films of TiO2 nanoparticles are transparent to visible light, whereas the use of commercial nanopowders results in white, opaque films. A similar observation for ZnO films is being applied in the fabrication of sun block cream; using ZnO nanoparticles fabricated in a controlled way (although not quantum-sized), the cream is transparent instead of the white paste that results from using micron-sized ZnO particles. Similarly, it is expected that better control over the nanoparticle synthesis of a variety of materials will result in better electrochromic or smart windows, transparent conducting oxides, etc. An example includes dye-sensitized solar cells, which are based on porous, nanostructured metal oxide films sensitized with a dye, where high surface areas are needed to adsorb a large number of dye molecules. It has been found that the efficiency of these solar cells is significantly improved if TiO2 nanoparticles are synthesized in a controlled fashion. Applications of metal oxide nanoparticles based only on the size dependence of the physical properties have not been realized yet (as far as the author is aware). As research on the size dependence of the physical properties of metal oxide nanoparticles progresses, new applications will undoubtedly surface.

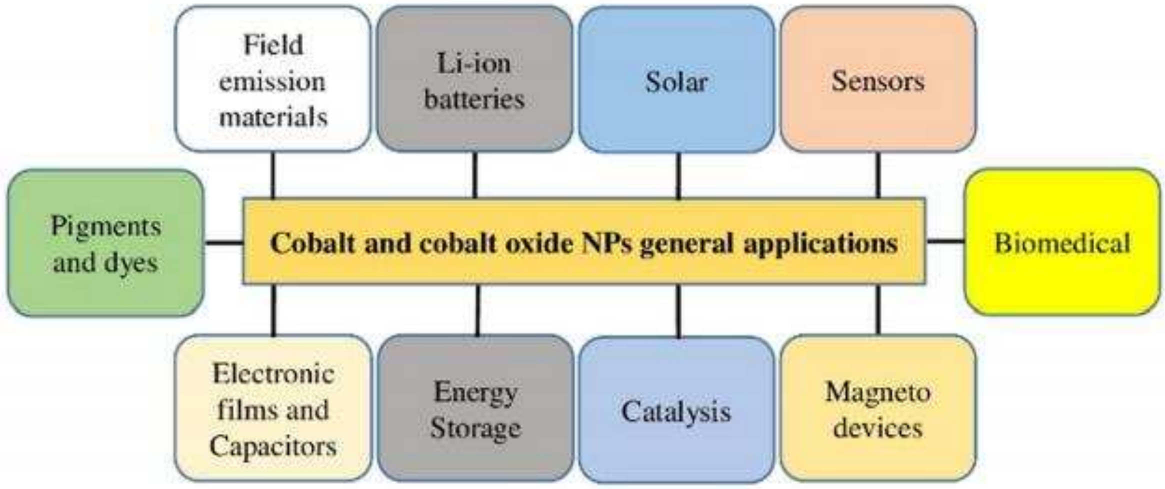


Fig.5. Applications of cobalt oxide nanoparticles

CHAPTER-II

LITERATURE SURVEY

Co_3O_4 NPs has attracted numerous research interests due to its low cost and good electroactivity. However, cobalt is a transition metal and is capable of exhibiting several possible oxidation states (Co^{2+}, Co^{3+}, and Co^{4+}). Therewithal, Co_3O_4 is a known multifunctional, antiferromagnetic p-type semiconductor with spinel crystal structure. The direct optical band gaps of Co_3O_4. NPs were about 1.48 and 2.19 eV and it can be used as photocatalyst to degrade several organic pollutants using visible light. Cobalt can be found in different spin states in its oxide forms such as low, high, and intermediate spin. These spin states make the physics of the Co3O4 attractive from a fundamental viewpoint and in spintronic applications. Hence, Co_3O_4NPs finds immense applications in areas such as field effect transistor, energy storage, catalysis, anode material in Li-ion rechargeable batteries, electrochromic sensors, solar cells and photocatalyst [25]. In addition, Co_3O_4 NPs have antibacterial, anticancer, antioxidant, antifungal, and enzyme inhibition properties due to their superior biomedical applications [26,27]. Also, there is a need to develop and utilize safer synthetic methods, which should be simple, nontoxic, clean, and efficient with low cost. Biological resources such as plants and microorganisms can be used in a swift, effective, simple, and economical way to produce the desired Co_3O_4NPs. Plant mediated biosynthesis of Co_3O_4NPs has been successfully done. Hence, biosynthesis of NPs is evolved into a significant offshoot of nanotechnology. Plant derived materials are used for the fabrication of NPs, and is credible alternatives to the physical and chemical methods [28]. The use of plant extract eliminates the laborious and complicated protocols of physicochemical methods [29]. The significance of the green synthesis (Figure 2) over chemical and physical methods is:

- ✓ one pot and clean synthesis,
- ✓ environmentally gracious,
- ✓ cost effective,
- ✓ swift, facile and easily scaled up for large scale syntheses of NPs,

Furthermore, there is no need to use high amount of temperature, energy, pressure and toxic chemicals [28,29]. Using plant material for synthesis of Co_3O_4NPs has received a great deal of attention due to its environmentally gracious, simple, rapid, non-toxic, and economical protocol which provides a single step technique for the green synthesis processes [30,31]. stabilizing the Co_3O_4 NPs by combination of biomolecules such as amino acids, saponins, enzymes, proteins, steroids, phenols, tannins, vitamins, sugar and flavonoids, which are already presented in the plant extracts having medicinal importance and are environmental benign [32,33]. Some plants are already reported to facilitate Co_3O_4 NPs and reported in Table 1. Various parts of plant such as leaf, latex, flower, root, seed, peel, and fruit can be used for synthesis of Co_3O_4 NPs with different morphologies and sizes by biological approaches. The water soluble chemical components are mainly accountable for generation and stabilization of NPs. Thereafter, the synthesized NPs need to be characterized using numerous techniques

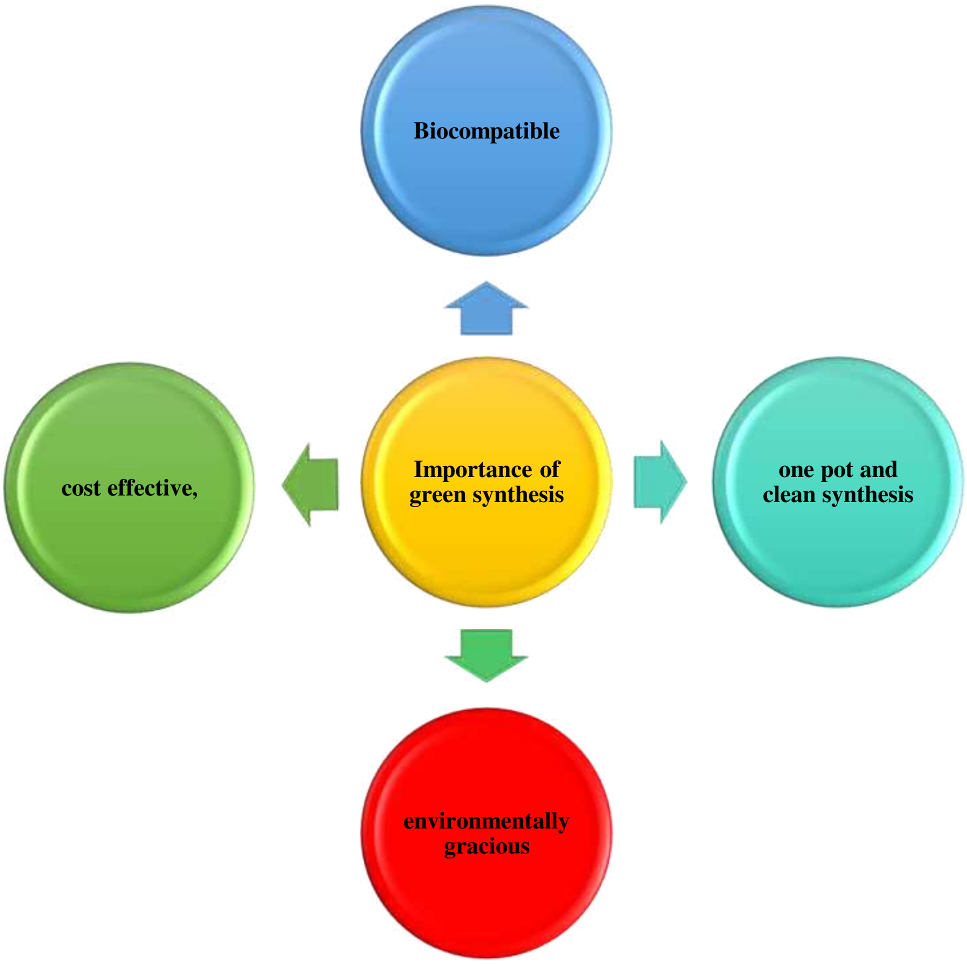
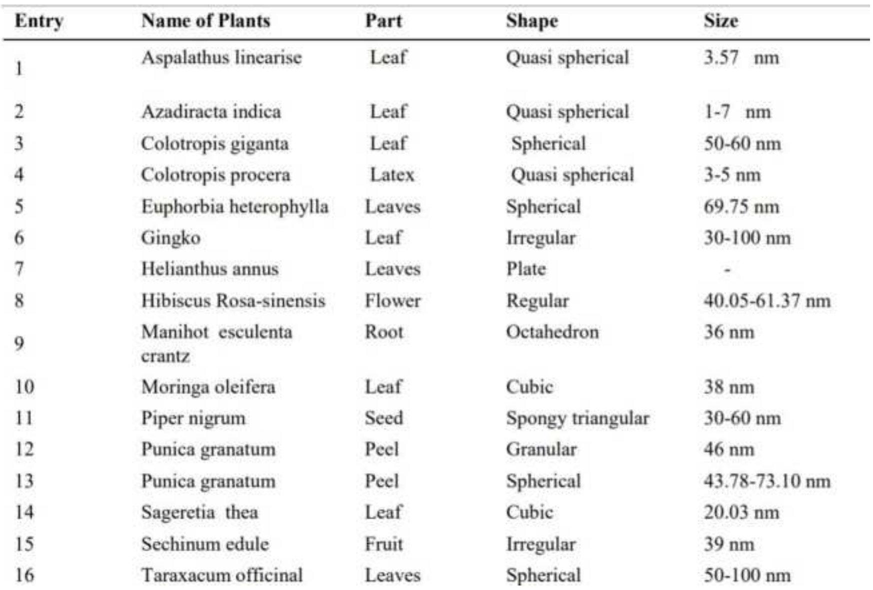


Fig.6. Overall importance of green synthesis



Entry	Name of Plants	Part	Shape	Size
1	Aspalathus linearise	Leaf	Quasi spherical	3.57 nm
2	Azadiracta indica	Leaf	Quasi spherical	1-7 nm
3	Colotropis giganta	Leaf	Spherical	50-60 nm
4	Colotropis procera	Latex	Quasi spherical	3-5 nm
5	Euphorbia heterophylla	Leaves	Spherical	69.75 nm
6	Gingko	Leaf	Irregular	30-100 nm
7	Helianthus annus	Leaves	Plate	-
8	Hibiscus Rosa-sinensis	Flower	Regular	40.05-61.37 nm
9	Manihot esculenta crantz	Root	Octahedron	36 nm
10	Moringa oleifera	Leaf	Cubic	38 nm
11	Piper nigrum	Seed	Spongy triangular	30-60 nm
12	Punica granatum	Peel	Granular	46 nm
13	Punica granatum	Peel	Spherical	43.78-73.10 nm
14	Sageretia thea	Leaf	Cubic	20.03 nm
15	Sechinum edule	Fruit	Irregular	39 nm
16	Taraxacum officinal	Leaves	Spherical	50-100 nm

Table 1. Green synthesis of cobalt oxide NPs using different plant source with morphology and size.

Phyllanthus niruri is a widespread tropical plant commonly found in coastal areas, known by the common names gale of the wind, stonebreaker or seed-under-leaf. It is a relative of the spurges, belonging to the genus *Phyllanthus* of the family Euphorbiaceae. It grows 50–70 cm (20–28 in) tall and bears ascending herbaceous branches. The bark is smooth and light green. It bears numerous pale green flowers which are often flushed with red. The fruits are tiny, smooth capsules containing seeds. *Phyllanthus niruri* has been used in traditional medicine for various illnesses, like jaundice, chronic dysentery, dyspepsia, cough, indigestion, diabetes, urinary tract diseases, skin diseases, ulcer, sores and swelling. Lignans, flavonoids, triterpenes, sterols, alkaloids, and essential oils are found in this plant.

The main objectives of the present investigation is

- To synthesize Co_3O_4 nanoparticle by phytogenic method using
- To characterize the formed nanoparticle by UV-Vis and FT-IR spectral studies.
- To study the antibacterial and antioxidant property of Co_3O_4 nanoparticle.

CHAPTER-III

EXPERIMENTAL DETAILS

3.1. Preparation of Phyllanthus niruri extract

Phyllanthus niruri leaves were collected freshly washed with distilled water to remove impurities. 10 g of Phyllanthus niruri leaves was grinded using mortor and pestle and homogenized with 150 mL distilled water. The solution was heated at 75°C along with continuous stirring, cooled down and filtered. The filtrate (light greenish yellow color) was collected and used for the synthesis of cobalt oxide NPs.

Fig.7. Phyllanthus niruri extract

3.2. Synthesis of Cobalt-Oxide nanoparticles

For the fabrication of cobalt oxide NPs, freshly prepared leaf extract (90 mL) was added to1 M solution of cobalt nitrate hexahydrate, heated at 70°C till precipitates appeared and then, temperature reduced to 60 °C and kept the solution at 60 °C for 90 min. The mixture was kept overnight at room temperature for 10 min. The colour of the solution changes to dark brown indicating the formation of cobalt oxide nanoparticles.

Fig.8. Co3 O4 nanoparticles prepared using *Phyllanthus niruri* extract

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 excited state. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb 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 colored (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 sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{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.

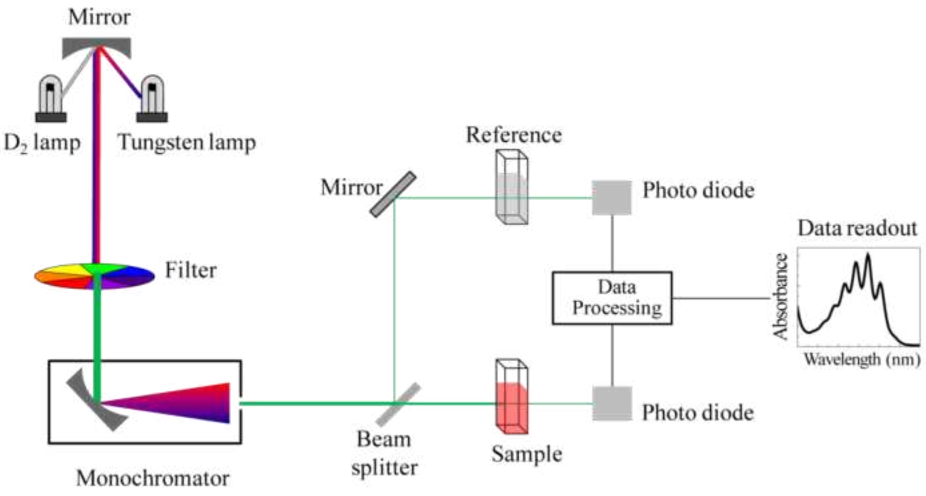
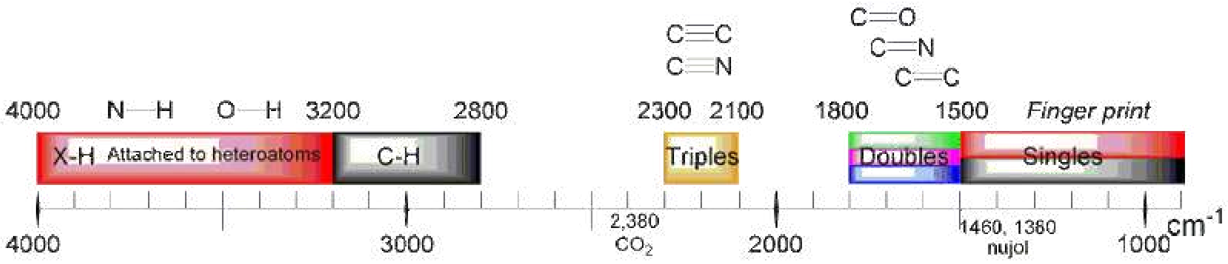


Fig.9. Schematic diagram of UV- visible spectrophotometer

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 neighborhood 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_2 concentrations in greenhouses and growth chambers by infrared gas analyzers.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:[8] 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.



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 [98]. 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 behavior. 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 flavor, texture, nutritional value, and safety of food. Different types of natural and synthetic antioxidants are available to limit the side effects of oxidation.

RESULTS AND DISCUSSION

4.1.UV spectral behavior

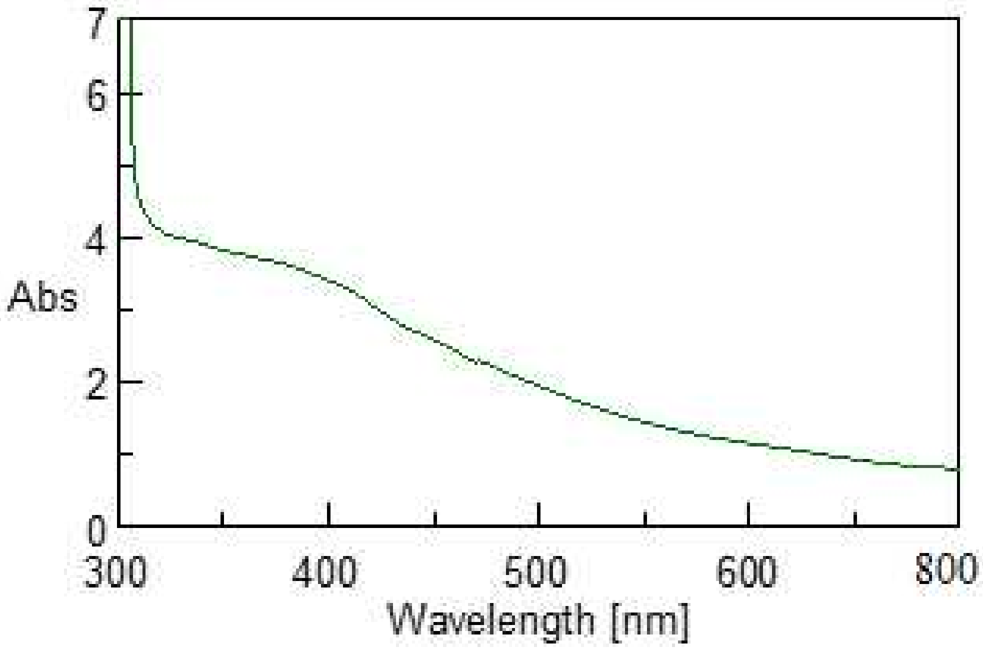


Fig. 10. UV-Visible spectral bahaviour of cobalt oxide nanoparticles

The UV-Visible of the samples were studied using JASCO V- 530 spectrophotometer using a 1 cm quartz cuvette filled with the samples. UV-vis absorption spectrum of synthesized cobalt oxide NPs shows absorption band at about 408 nm (Fig. 10). This absorption band can be attributed to the plasma resonance absorption of the cobalt oxide NPs. Origin of light absorption by metal nanoparticles is the consistent oscillation of the electrons in conduction band induced by the interaction of electro-magnetic field. The distinguishing feature of the CoONPs is to exhibit a surface plasmon absorption band in the regions of 350–550 nm [34]. The strong surface plasmon might be owing to the formation of nonoxidized cobalt nanoparticles. The leaf extracts of *Phyllanthus niruri* acts as a reducing-cum-surface capping agent that can be credited to the fabrication of nanoscale cobalt oxide [35]. Cobalt oxide NPs were formed from the reduction of cobalt(II) nitrate hexahydrate in the presence , leaf extracts of *Phyllanthus niruri* which act as a reducing, stabilizing and capping agent [36]. One-step in-situ green synthesis consists of the nucleation and growth processes through reduction of cobalt ions into neutral cobalt atoms and the particles are nucleated and finally stabilized with the bioactive compound in extracts [37].

4.2.FTIR Analysis

Functional group analysis was done by using perkin-Elmer 1650 FT-IR spectrophotometer using KBr technique.The results of FTIR study (Fig.11) showed that the peaks at 3278 cm^{-1} – 3376 cm^{-1} were due to stretching vibration of N-H groups in amines. C=O stretching in polyphenols and carboxyl was observed at 1471 cm^{-1} – 1684 cm^{-1}, bands at 1105 cm^{-1}, 1198 cm^{-1} were attributed to the C=C stretching in aromatic ring. C-O stretching in amino acids showed a band at 840 cm^{-1}. In addition to the absorption bands of these biomolecules, two peaks appear at 658 cm^{-1}, and 630 cm^{-1}, in the IR spectrum are the characteristic peaks of Co_3O_4 nanoparticle.

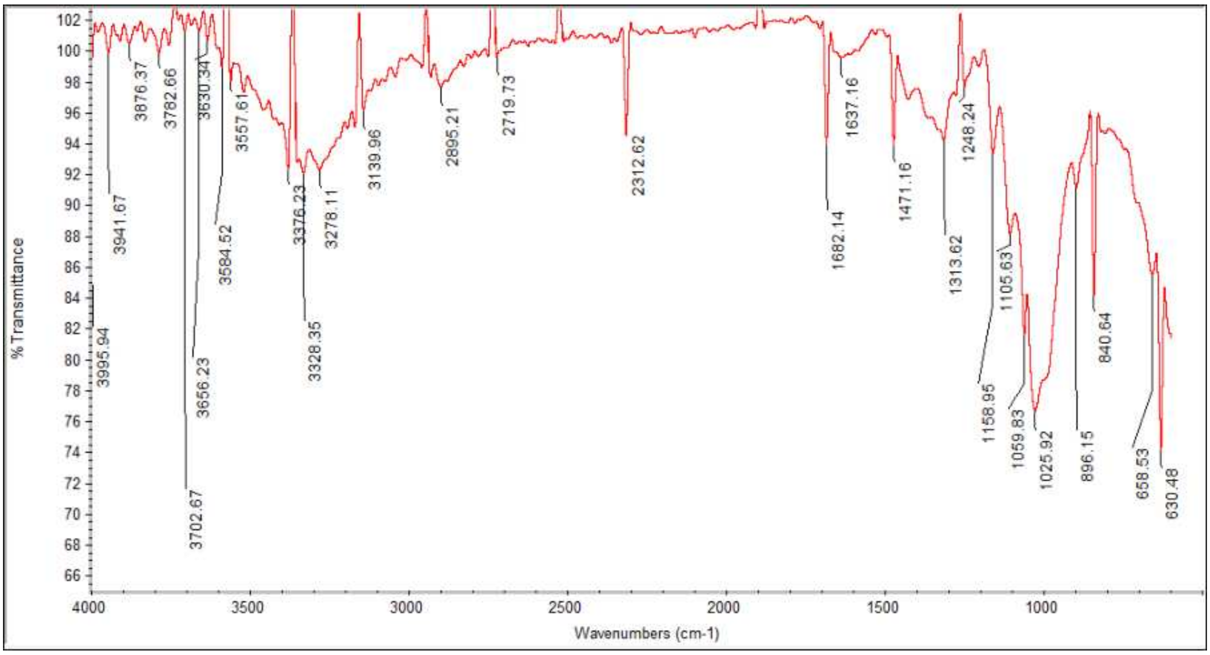


Fig.11 FTIR spectral behavior of Co_3O_4 nanoparticles

4.3 Antibacterial activity

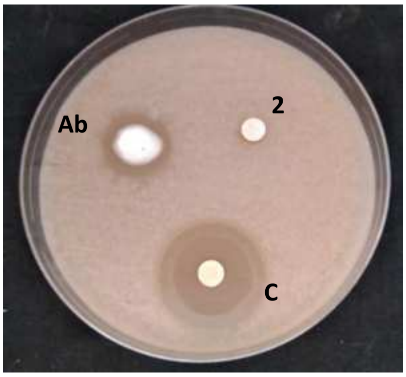
Results of Co_3O_4-NPs' antibacterial activities against I- *Escherichia coli,* II- *Staphylococcus aureus,* III- *Bacillus licheniformis,* IV- *Bacillus subtilis,* V- *Bacillus cereus* are presented in table 1 . Cobalt oxide nanoparticles produced good antibacterial activities against both gram positive and gram negative bacteria. The antibacterial activities of Co3O4-NPs were higher against gram positive bacteria as compared to gram negative bacteria. Antibacterial activity was studied by following the below procedure

- ✓ Muller hinton agar medium was prepared and autoclaved at 121ºC for 15 minutes
- ✓ The agar medium was transfered to petri plates under aseptic conditions in inoculation chamber and allowed to solidify
- ✓ bacterial liquid culture was swabed uniformly over the agar surface and the test sample loaded filter paper discs were placed. Ampicillin loaded discs was used as control
- ✓ Incubated at 37 ºC for 24 hours
- ✓ The zone of inhibition was measured and recorded.

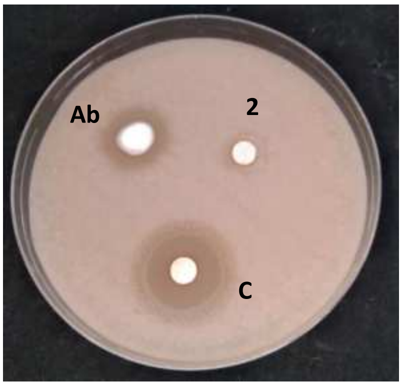
Bacteria	**Zone of inhibition in mm**		
	Ab-Antibiotic Ampicillin	**C-Cobalt oxide nanoparticles**	**2-extract**
Escherichia coli	15	35	-
Staphylococcus aureus	16	30	-
Bacillus licheniformis	12	32	-
Bacillus subtilis	14	33	-
Bacillus cereus	11	30	-

Table 2. Antibacterial activity of cobalt oxide nanoparticle

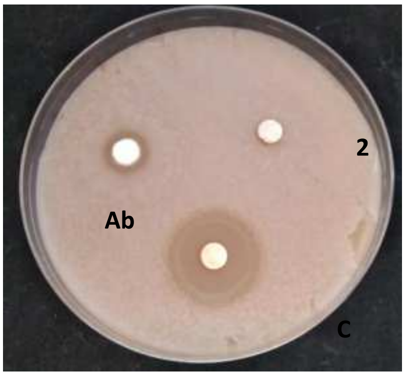
Escherichia coli



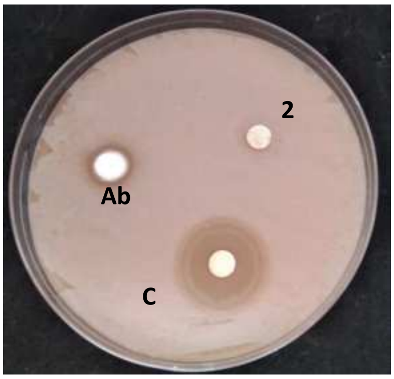
Staphylococcus aureus



Bacillus licheniformis



Bacillus subtilis



Bacillus cereus

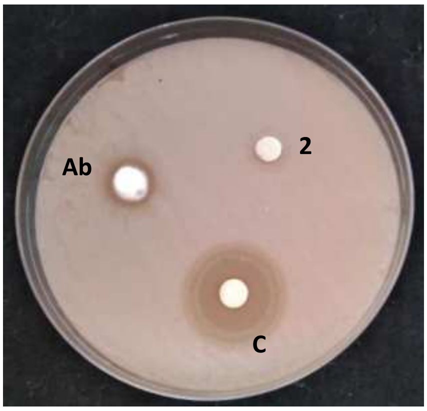


Fig.12. Antibacterial activity of cobalt oxide nanoparticles

4.4 Antioxidant activity

The total antioxidant activity was evaluated by phosphomolybdenum method described by Prieto et al. [38]. 1.0 ml of the extract was mixed with 1.0 ml of the standard reagent solution (0.6M sulphuric acid, 28mM sodium phosphate and 4 mM ammonium molybdate). The tubes were capped and incubated in a thermal block at 95°C for 90 min. After cooling to room temperature, the absorbance was measured at 695 nm against a reagent blank. The total antioxidant capacity was expressed as percentage. For cobalt oxide nanoparticle the antioxidant activity was found to be 88% with reference to the standard. Hence the prepared nanoparticle exhibits very good antioxidant property.

%Antioxidant activity = Absorbance Test/Absorbance Control * 100

Concentration1mg/ml	OD at 695 nm	%Antioxidant activity
Standard	1.250	100
Cobalt oxide nanoparticle	1.100	88

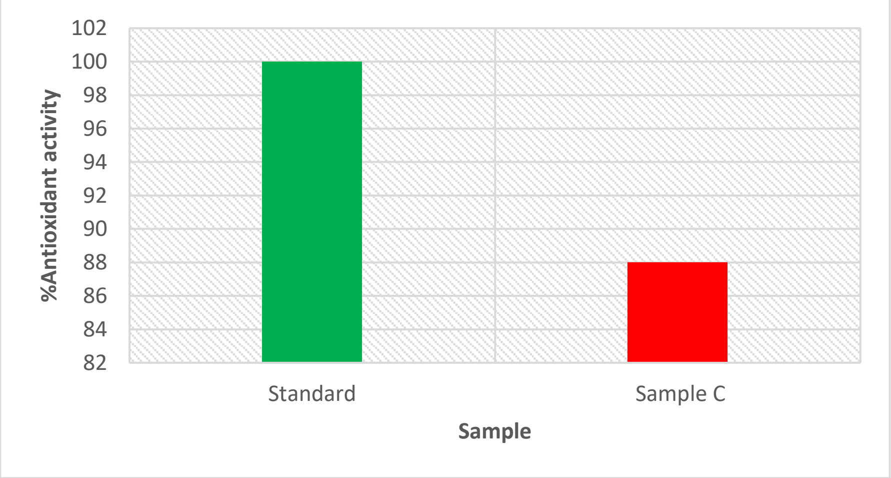


Table.3 Antioxidant activity of Co_3O_4 nanoparticle with reference to standard

Conclusions

Several conculsions have been made with synthesized cobalt oxide nanoparticles.

- ✓ Firstly, cobalt oxide nanoparticles were synthesized by cost effective and eco-friendly green method by using Phyllanthus niruri leaf extract and cobalt nitrate hexahydrate.
- ✓ The prepared nanoparticles, were analyzed by various techniques such as UV, FTIR spectral studies.
- ✓ These techniques revealed the successful synthesis of cobalt oxide nanoparticles.
- ✓ Antibacterial activities and antioxidant studies revealed that the synthesized cobalt oxide nanoparticles have very good inhibition against gram positive and gram negative bacteria and very exhibits good antioxidant property.

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Synthesis and characterization of poly(aniline co-ortho nitroaniline) – TiO_2 composites and its application in photo degradation of methylene blue

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

R. Annapackiam

M. Bala abirami

I. Esther angel

M. Josephin preethi

J. Maheswari

D. Sasirekha

St. Mary's College (Autonomous)

(Re-accredited with 'A+' Grade by NAAC)

Thoothukudi-628001.

2020-2021

DECLARATION

We hearby declare that the project entitled " **SYNTHESIS AND CHARACTERIZATION OF POLY(ANILINE CO-ORTHO NITROANILINE) – TiO_2 COMPOSITES AND ITS APPLICATION IN PHOTO DEGRADATION OF METHYLENE BLUE"** 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.

R. Anna packiam.
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D. Sasi Rekha
D. SASIREKHA

April 2021
Thoothukudi.

CERTIFICATE

This is to certify that project in chemistry entitled " **SYNTHESIS AND CHARACTERIZATION OF POLY(ANILINE CO-ORTHO NITROANILINE) – TiO_2 COMPOSITES AND ITS APPLICATION IN PHOTO DEGRADATION OF METHYLENE BLUE** " 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 2020-2021.

NAME	**REGISTER NUMBER**
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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 our secretary, **SR. FLORA MARY** for providing infra structural facilities.

We thank our principal **Rev. Dr. Sr. A.S.J.LUCIA ROSE** and our Head of the Department **Dr. J. MARTIN RATHI** for providing us necessary arrangements for the successful completion of our project.

We wish to express our heartfelt thanks to our guide **Dr. B. DIVYA** for her valuable suggestions, gentle guidance, enthusiastic ideas, to carryout and complete our work perfectly.

We also thank the department of biotechnology for providing us the facilities

under the STAR college scheme.

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

It's our pleasure to thank all **OUR FRIENDS** for their enthusiasm which helped us to complete this work.

We express our love and gratitude to **OUR FAMILY** for the encouragement given to us.

CONTENTS

Synthesis and characterization of poly(aniline co-ortho nitroaniline) – TiO_2 composites and its application in photo degradation of methylene blue

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.

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2020-2021

DECLARATION

We hearby declare that the project entitled **" SYNTHESIS AND CHARACTERIZATION OF POLY(ANILINE CO-ORTHO NITROANILINE) – TiO_2 COMPOSITES AND ITS APPLICATION IN PHOTO DEGRADATION OF METHYLENE BLUE"** 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.

R. ANNAPACKIAM

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April 2021
Thoothukudi.

CERTIFICATE

This is to certify that project in chemistry entitled **"COPOLYMERISATION OF "** 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 2020-2021.

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CONTENTS

INTRODUCTION

1.1 Polymers

The word Polymer is derived from the Greek word ‘poly’ means many and ‘mer’ means ‘unit’ meaning many units or parts. Polymers are long, repeating chains of molecules made when hundreds of monomers join together under different conditions. The small molecules combine with each other to form polymer molecules are termed monomers. The process in which the monomer molecules are linked together forming a big polymer molecule is called ‘Polymerization’ through various reaction mechanism.

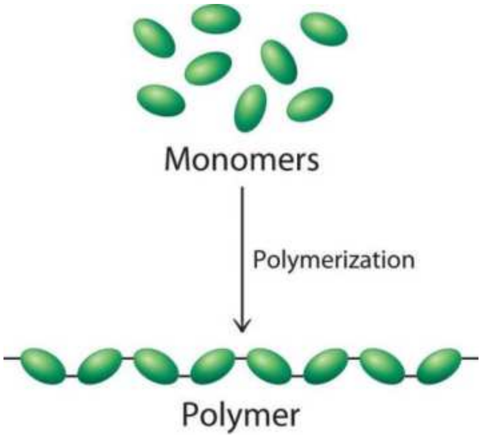


Fig. 1.1 Polymerization

Polymerization may be classified into two types known as

- Chain-Growth or Addition Polymerization
- Step- Growth or Condensation Polymerization.

Addition polymerization is the addition reaction of monomers which contains double or triple bonds repeatedly to form polymers. The molecular weight of the resultant polymers is a multiple of monomer's molecular weight since the process is an addition reaction.

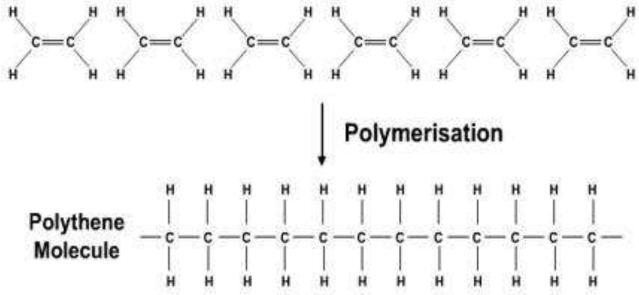


Fig. 1.2 Addition polymerization

Condensation polymerization is a process which involves condensation reactions between two different bi-functional or tri-functional monomers. The molecular weight of resultant polymer may be less than that of monomer since it forms with the elimination of byproducts.

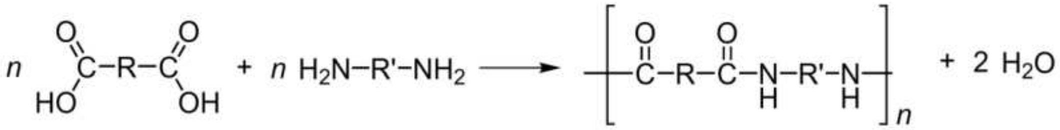


Fig. 1.3 Condensation polymerization

Polymers have unique properties, depending on the type of molecules being bonded and how they are bonded. Some polymers bend and stretch, like rubber. Others are hard and tough, like epoxies and glass [1].

1.2 Copolymers

A copolymer is a polymer which is formed when two or more different types of monomers are linked in the same polymer chain, which is different from a homopolymer where only one monomer is used [2]. Many commercially important polymers are copolymers. Some of the examples are polyethylene-vinyl acetate, nitrile rubber, and acrylonitrile butadiene styrene. The process in which a copolymer is formed from multiple species of monomers is known as copolymerization [3].

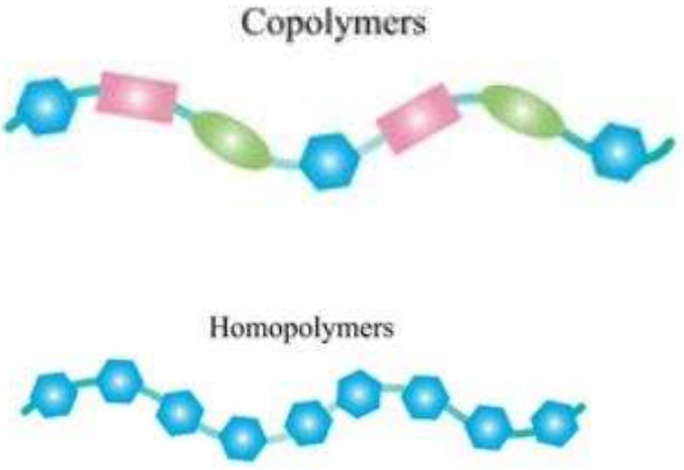


Fig. 1.4 Copolymer and Homopolymer

1.3 Classification of Copolymers

The copolymer generally consists of replicating units of two diverse monomers. Such copolymers are categorized based on their structures as linear and branched copolymer. Copolymer which is made of a single chain are known as Linear Copolymer and those with polymeric side chains are called Branched Copolymers.

Linear copolymers based on the arrangement of the monomers on the main chain may further classified as block copolymers, random copolymers, alternate copolymers, and periodic copolymers.

1. Block copolymers are the single chain polymers which are formed when more than one homopolymer unit is linked through an covalent bond. Acrylonitrile butadiene styrene is an example.

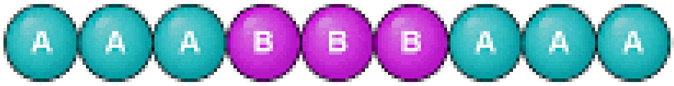


Fig. 1.5 Block copolymer

2. In random copolymers, repeating units are randomly positioned in the chain which follows some statistical rule and thus also known as statistical copolymer. These are generally formed from free radical polymerization method.

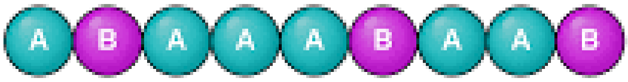


Fig. 1.6 Random copolymer

3. Alternate copolymers contains monomers arranged in an alternated position the polymer chain. The general formula of an alternating copolymer made up of monomers A and B is $(\text{-A-B-})_n$.

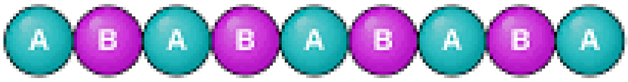


Fig. 1.7 Alternating copolymer

4. The periodic copolymer has a repeating sequence of chain arranged with monomers.

Branched copolymer is a polymer in which the monomers are linked to form a branched structure. Star, comb, grafted, and brush copolymers are the types of branched copolymers.

A star copolymer contains three or more than polymeric chains that are attached to the same central core.

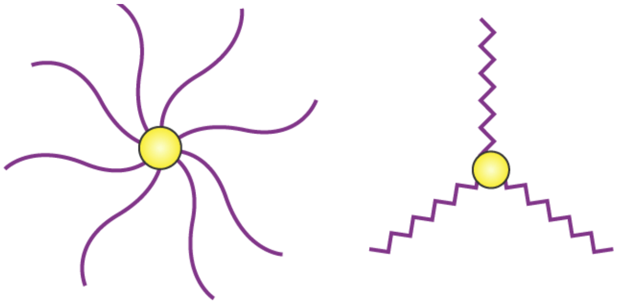


Fig. 1.8 Star copolymer

In graft copolymers, a linear backbone of one monomer is randomly distributed with branches of another monomer. The side chains are structurally different from the main chain of the polymer and may be homopolymer or copolymer [2].

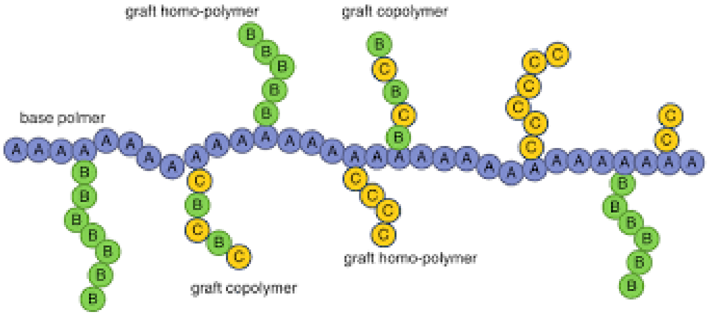


Fig. 1.9 Graft copolymer

1.4 Uses of Copolymers:

Based on the arrangement of repeating units in the polymer chain, different properties are observed that are beneficial for many applications. Copolymers offer benefits that are not usually observed in polymers created from single species of monomers. Diverse properties that are indigenous to individual class of monomers are combined to form a single polymer [2].

Synthetic fibres made from the homopolymer of acrylonitrile, for example, have excellent dimensional stability and resistance to weathering, chemicals, and microorganisms but poor affinity for dyes.

Copolymer**,** any of a diverse class of substances of high molecular weight prepared by chemical combination, usually into long chains, of molecules of two or more simple compounds (the monomers forming the polymer). The structural units derived from the different monomers may be present in regular alternation or in random order, or strings of several units of one kind may alternate with strings of another [4].

1.5 Conducting polymers

Conducting polymers are the polymers which conduct electricity. Polyacetylene was the first discovered conducting polymer. These polymers have a conjugated p- orbital system in which the electrons can freely move within the polymer chain. In conjugated polymers each carbon atom has one unpaired electron. It can freely move along the chain. This electron delocalization provides the way for charge mobility along the backbone of the polymer chain of the conducting polymers. The properties of these polymers may be change by doping. In the doped form, the backbone of a conducting polymer consists of a delocalized pi system. In the undoped state, the polymer may have a conjugated backbone which is retained in a modified form after doping [5]. polyaniline, polypyrroles, polythiophenes and polyphenylene vinylenes are some of the conducting polymers [6].

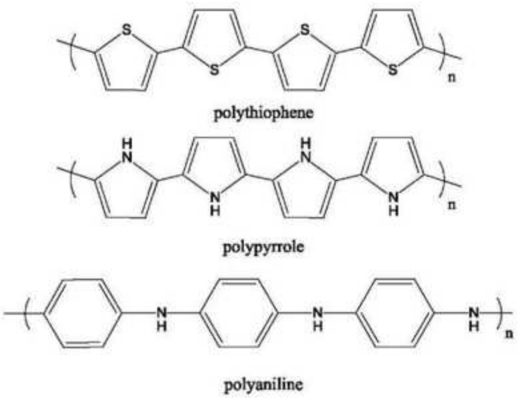


Fig. 1.10 Examples of conducting polymers

1.6 Polyaniline

Polyaniline is a conducting polymer of semi flexible rod polymer family. Although the compound itself discovered over 150 years ago, only since the early1980 has polyaniline capture the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity. Amongst the family of conducting polymers and organic semi conductor polyaniline has many attractive processing properties. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past 50 years. Space- filling model of the local structure of a polyaniline chain in the reduced leucoemeraldinebase oxidation state, based on the crystal structure of the tetramer [7].

Polyaniline has many different forms, fully reduced form is leucoemeraldine, fully oxidized form is pernigraniline, and partially oxidized form is emeraldine state which can be tuned by varying synthesis procedure as well as extent of doping. Leucoemeraldine and pernigraniline are nonconducting in nature and the partially doped state, emeraldine salt is conducting in nature [8].

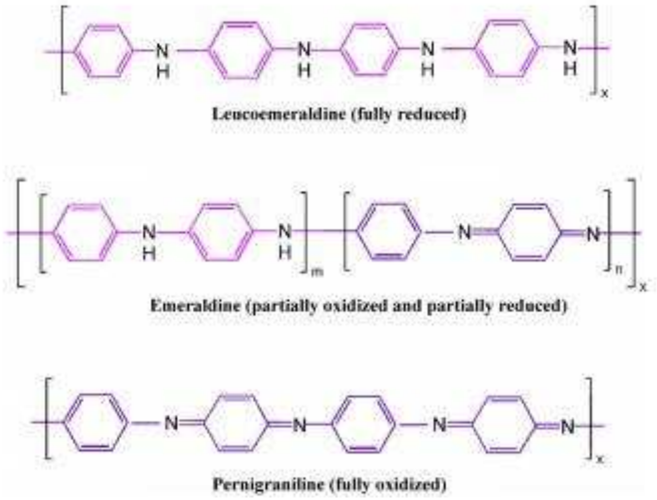


Fig. 1.11 Different forms of polyaniline [8]

1.7 Composites

Coming to the point of composites, it can be either natural or synthetic. Wood, a natural composite, is a combination of cellulose or wood fibers and a substance called lignin. The fibers give wood its strength; lignin is the matrix or natural glue that binds and stabilizes them. Other composites are synthetic. Plywood is a man-made composites that combines a natural and synthetic materials. Thin layers of wood veneer are bonded together with adhesive to from flat sheets of laminated wood that are stronger than natural wood [9]. The definition of a “composite” is two or more materials with markedly different physical or chemical properties categorized as “matrix” or “reinforcement” combined in a way to act in concert, yet remain separate and distinct at some level because they don’t fully merge or dissolve into one another[10].

1.8 Polyaniline composites

Polyaniline composites can be prepared easily by the polymerisation of aniline in the presence of reinforcing materials. The added materials will get embedded in the polymer matrix. Based on the blended materials and the methods of preparation, polyaniline composites exhibit different physical and chemical properties. Polyaniline composites have been used as gas sensors in various fields [11]. Polyaniline composites have good corrosion resistance and it is used as inhibitors for corrosion and also used in antistatic applications [12].

1.9 Methylene blue

A dye is a colored substance that chemically bonds to the substrate to which it is being applied. This distinguishes dyes from pigments which do not chemically bind to the material they color. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments are colored, because they absorb only some wavelengths of visible light. Dyes are usually soluble in water whereas pigments are insoluble. Some dyes can be rendered insoluble with the addition of salt to produce a lake pigment [13].

Methylene blue, commonly known as methylthioninium chloride, and called by other names such as urelene blue, provayblue, proveblue. Methylene blue is a formal derivative of phenothiazine. It is a dark green powder which gives a blue solution when dissolved in water. The hydrated form has 3 molecules of water per unit of methylene blue. Methylene blue has a pH of 6 in water (10g/l) at 25 °C. It is prepared by oxidation of dimethyl-4-phenylenediamine in the presence of sodium thiosulfate.

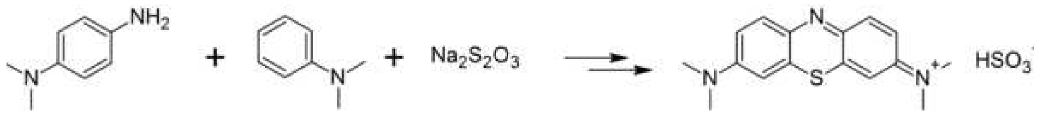


Fig. 1.12 Synthesis of methylene blue

It used as a medication as well as dye. As a medication, it is mainly used to treat methemoglobinemia. The maximum absorption of light is near 670 nm. The specifics of absorption depends on a number of factors, including protonation, adsorption to other materials, and metachromasy - the formation of dimers and higher-order aggregates depending on concentration and other interactions[14].

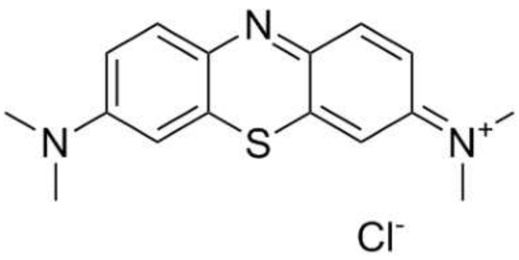


Fig. 1.13 Structure of methylene blue

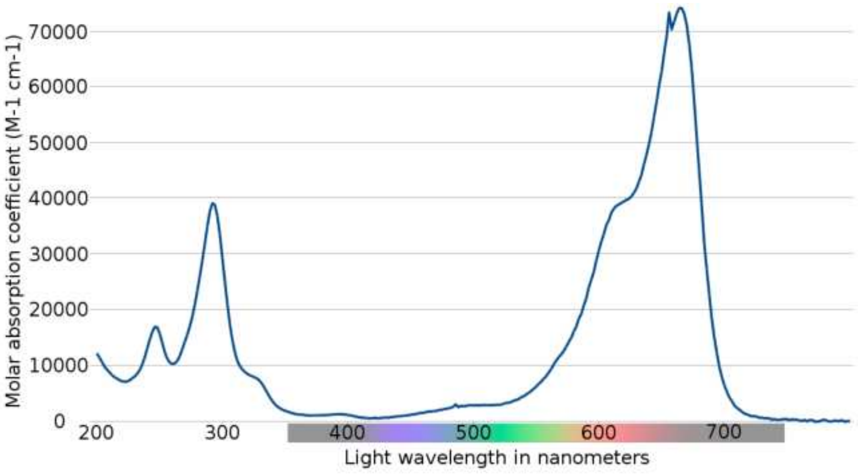


Fig. 1.14 UV-Visible spectrum of methylene blue [14].

1.10 Titanium dioxide

Titanium, the ninth most common element in the Earth's crust, is a metal commonly found in plants and animals. Titanium naturally interacts with oxygen to form titanium oxides, commonly found in ores, indigenous dusts, sands and soils. Pure titanium dioxide is a fine, white powder that provides a bright, white pigment. Titanium dioxide is of two forms –pigment grade and ultrafine grade [15].

Titanium dioxide, also known as titania, a white, opaque, naturally occurring mineral existing in three crystalline forms as rulite, anatase, and brooktie. It can be mined and used as a source for commercial titanium. TiO_2 has an extremely high melting point of 1,843℃ and boiling point of 2,972℃ and so occurs naturally as a solid. It is insoluble in water. TiO_2 is used as a bleaching and opacifying agent in porcelain enamels, making them more brighter, harder, and acid resistance. It is also used in cosmetics, such as in skin care products and sunscreen lotions, because of its property to absorb ultraviolet light.

The photocatalytic activity of TiO_2 helps to exhibit self-cleaning and disinfecting properties under exposure to ultraviolet radiation. Alloys are characterized by being lightweight, very high tensile strength (even at high temperatures), high corrosion resistance, and their thermostable propertities, thus used in aircraft, pipes in power plants, armour plating, naval ships, spacecraft, and missiles. Because of its unique properties, titanium dioxide is widely used in nanoscience and nanotechnology. Because of its bright whiteness, it is used in products such as paints, coatings, papers, toothpaste, face powder, and food colouring [16].

1.11 Colourimeter

A colourimeter is a light-sensitive device used for measuring the transmittance and absorbance of light passing through a liquid sample. The device measures the intensity or concentration of the colour that develops upon introducing a specific reagent into a solution. Colorimeter is also known as filter photometer. It generally refers to the device that measures the absorbance of a particular wavelength of light by a specific solution. Changeable colour filters are present in the colorimeter which is used to select the wavelength of light needed for the solution under study, in order to maximize accuracy. The usual wavelength range of colorimeter is from 400 to 700 nanometers. To use the colorimeter in the ultraviolet range (below 400 nm), some modifications in the colorimeter should be carried out. In modern colorimeters the filament lamp and filters are replaced by light-emitting diodes of different colours [17].

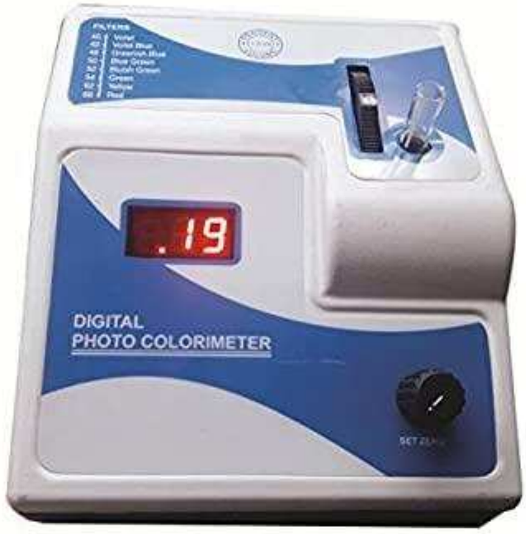


Fig. 1.15 Colourimeter

LITERATURE REVIEW

An infrared electrochromic film constructed by copolymer of aniline and o-nitroaniline has been successfully prepared by cyclic voltammetry. The effects of polymerization of aniline and o-nitroaniline on electrochromic properties and optical properties were investigated by cyclic voltammetry, scanning electron microscopy, FTIR spectrometer, and UV–Visible spectrophotometer. The results indicate that the film can exhibit three colors apple green, dark green, and dark blue at different voltages of −0.1, 0, and 0.8 V. A fast response time, a high coloration efficiency, a significant optical modulation and a large average emissivity range were achieved for the new film [18].

Polyaniline, a conducting polymer, was incorporated into sheets of paper forming a new composite material combining the universal properties of paper product with the chemical and electrically conducting properties of the conducting polymer. Paper conducting polymer composite have been prepared by polymerizing aniline directly onto the paper sheet using ammonium peroxydisulfate as an oxidant at different temperatures and characterized by FT-IR and SEM. The thermo-oxidative degradation was studied by thermo gravimetric analysis (TGA); electrical conductivities measurements of the composites were significantly increased over those of the precursor paper. [19].

Electrochemical-assisted photodegradation of methyl orange has been investigated using Titanium dioxide thin films which were prepared by sol-gel dip-coating method. Photoelectrochemical degradation was studied using different light sources ranging from ultraviolet to visible light and with different light intensity. The higher agitation speed improves slightly the rate of photodegradation. Investigation on the electrode after repeated usages show the electrode can be reused up to 20 times with percentage of deficiency less than 15%. The study on the effect of solution temperature indicated that the activation energy of the methyl orange degradation is 18.63 kJ mol^{-1}[20].

SCOPE

In this modern world, we are using different types of dyes for different purposes. But we never mind to dispose it properly. Wastes from dye industries are dumped into rivers, sea etc., without proper decomposition of dye.

Composites can be easily prepared and they are effective in many fields. Conducting polymer composites has been extensively studied recently. This is due to their easy preparation and processibility. In this context polyaniline composite have attracted many researches sue to its unique properties.

Titanium dioxide is a very good photocatalytic agent. Its efficiency greatly increases when it is embedded in any matrix. Literature shows that the band gap of titanium dioxide can be reduced when it is embedded in polyaniline matrix [21]. So a copolymer composite of titanium dioxide alone with aniline and o-nitroaniline was chosen for this photo degradation studies. The prepared composite is used to degrade the dye, methylene blue. It is an efficient method since sunlight is used to degrade the dye. Less toxic and cheaply available chemicals were employed by this method.

EXPERIMENTAL DETAILS

4.1 Chemicals

Aniline was bought from Spectrum reagents and chemicals which is of 99% purity. Ortho nitro aniline was bought from Loba chemie which is of 98% purity. Titanium dioxide was bought from Spectrum reagents and chemicals. Hydrochloric acid was bought from isochem laboratories. Potassium perdisulphite and Methylene blue were bought from Merck.

4.2 Preparation of the composite

A mixture of .01mol of aniline and 0.01mol of o-nitro aniline were taken in 200mL of 1M hydrochloric acid. The mixture was stirred in a magnetic stirrer equipped with Teflon coated paddle for 10 minutes for dispersion. Then titanium dioxide is added in 25 weight percentage of aniline and it is again stirred for another 10 minutes. Then the oxidizing agent, 0.015mol of Potassium perdisulphite is added to the mixture. Colour change to green was noted within five minutes. The mixture was then stirred for 4 hours. Green colour solution obtained was kept in the refrigerator for 48 hours and then it was filtered through filter paper and washed several times with water. After that it was dried at room temperature, green lumps obtained were grounded in a mortar.

4.3 Preparation of standard methylene blue solution

A 0.01 molar solution of methylene blue was prepared in a 100ml standard measuring flask. 1ml of this solution was then diluted to 100ml.

4.4 Photo degradation of methylene blue

10 ml of the diluted solution of methylene blue was taken in five 100mL beakers each with different concentrations of the composites as 0.01g, 0.02g, 0.03g, 0.04g and 0.05g. It was then kept in the sunlight for an hour. Then the solution was taken and filtered. Absorbance was noted for all the solutions in the colorimeter at 680nm.

4.5 UV- Visible Spectral analysis

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

4.6 FT-IR Spectral Analysis

FTIR spectra were recorded for the composite using Nicolet Si5 spectrometer using KBr pellets in the range of 4000 – 400 cm^{-1}

RESULTS AND DISCUSSION

The ratio of aniline and o-nitroaniline is chosen 1:1, since this ratio decides the nature of the polymer. If the concentration of o-nitro aniline is low in the co monomers feed, delocalization due to the presence of electron donating and withdrawing groups may not be very effective, so the resulting polymer will be of low conductivity [22].

5.1 UV- Visible spectral studies

The UV-Visible spectrum of of poly(Aniline-co-o-nitroaniline) - TiO_2 composite is given in fig 5.1 . Peaks are present at 226nm, 324nm, 402nm, 520 – 800nm

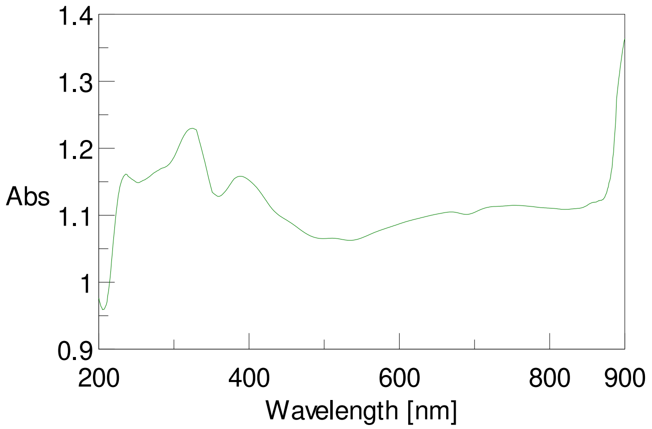
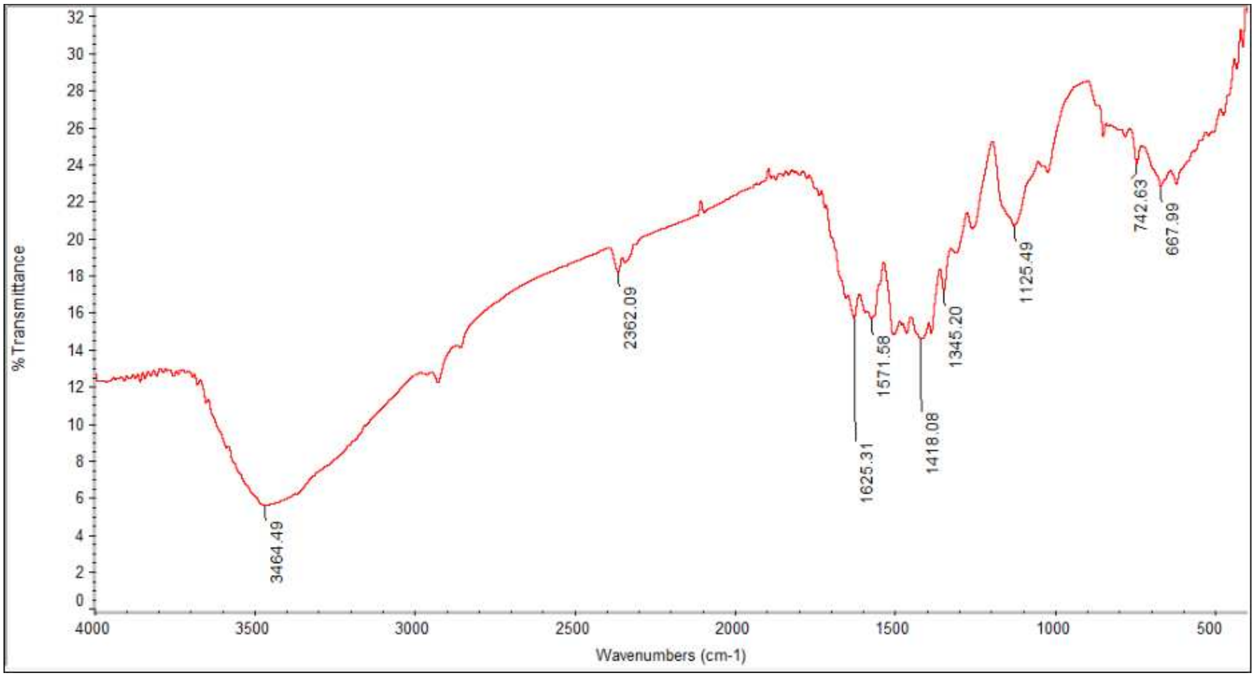


Fig. 5.1 UV – Visible spectrum of poly(Aniline-co-o-nitroaniline) –TiO_2 Composite

The first absorption band at 226 nm was due to the π to π* transition of the benzenoid ring present in the composite [22]. Peak at 324nm is due to Titanium dioxide [23]. The peak due to polaron to π* transition is found at 402nm [24]. This peak depends on the level of doping of the polymer composites. For poly(Anline- co-o –nitroaniline) copolymer, a broad peak in the range of 520 – 800nm is seen in the spectrum [22]. That is due to the charge transfer from the highest occupied molecular orbital of the benzenoid ring to the lowest unoccupied molecular orbital of the quinonoid ring of the metal composite. This band is very much broadened due to the presence of Titanium metal in the polymer matrix. This peak indicates the emeraldine form of polyaniline [23]. Normally titanium dioxide reflects more than 85% of the light in the visible region and polyaniline aniline composites reflect light to a very small extend. This is due to the immobilization of titanium dioxide in the polyaniline matrix [21].

5.2 FTIR studies of the composite

FTIR spectra of the composite is given in the figure 5.2. Peaks are present at 667cm^{-1}, 742cm^{-1}, 1125 cm^{-1}, 1345 cm^{-1}, 1418 cm^{-1}, 1572 cm^{-1}, 1625 cm^{-1}, 2362 cm^{-1}, 3464 cm^{-1}



The band at 3464cm^{-1} is due to –OH stretching [25]. C=C stretching of quinonoid ring is present at 1507 cm^{-1}. C=C stretching of benzenoid ring is present at 1418 cm^{-1} [26]. The band present at 1245cm^{-1} is assigned for N-H bending [25, 27]. The very small band present at 818cm^{-1} is due to the C–H out of plane bending vibration.

Normally in Infrared Spectroscopy, asymmetric and symmetric stretching bands of NO_2 groups are located at around 1535 and 1345 cm^{-1} [28]. In this composite a strong band at 1345 cm^{-1} is observed in the spectra of the composite and it is due to the N O stretching vibrations of the nitro groups present in the polymer. 1125 cm^{-1} is due to B–

(NH^+) =Q structure which is formed during the protonation process. In addition, the peak at 667cm^{-1} is attributed to $-NH_2$ wagging [27]. 1575 cm^{-1} is the C=N stretching of the quinoid ring [21]. The band at 742 cm^{-1} is due to the Ti-O bond [23].

5.3 Photo degradation of methylene blue

Methylene blue along with different weights of the composite is kept in the sunlight for an hour and the absorbance values are noted down using colourimeter with the filter set at 680nm. Absorbance values for the methylene blue and the mixture of methylene blue with different amount of the composites are given in the table 5.1.

Absorbance value for the dye is more than the dye with composite. With 0.01g of the composite the absorbance value decreases more. This is due to the photochemical degradation of the dye, since the composite contains titanium dioxide. Titanium dioxde plays a major role in the photochemical degradation of the dye. With 0.02g of the composite the absorbance values increases. Next with the increase in the concentration of the composite the absorbance values increases.

Even though photochemical degradation of the dye takes place, absorbance values increases. This is due to the nature of the composite. This composite polyaniline- co- o-nitro aniline – titanium dioxide composite is dark green in colour. This colour masks the colour of the dye. So the absorbance values increases. This shows that for photo degradation studies of such composites should be done at very low concentration of the composite.

Table 5.1 Absorbance values of methylene blue and the composite

Concentration	**Absorbance values**
Methylene blue	1.33
Methylene blue +0.01g of composite	0.95
Methylene blue +0.02g of composite	1.21
Methylene blue +0.03g of composite	1.23
Methylene blue +0.04g of composite	1.30
Methylene blue +0.05g of composite	1.63

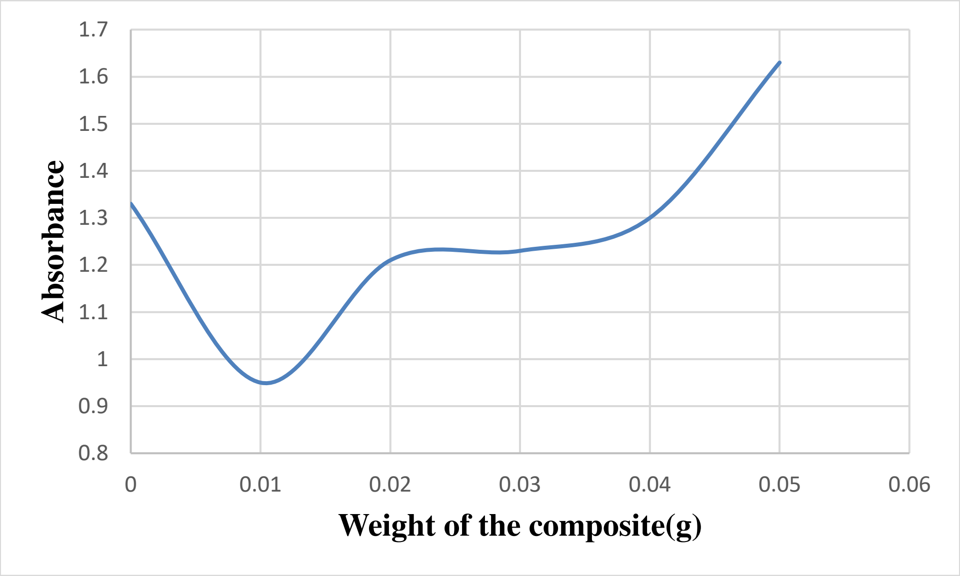


Fig. 5.3 Plot of weight of the composite and absorbance

CONCLUSIONS

A copolymer composite of polyaniline with o-nitroaniline with titanium dioxide was synthesized and characterized. Photocatalytic degradation of the dye methylene blue was studied and the results showed that the composite efficiently degrades the dye when kept in the sunlight. So this can be used to clean waste water containing this dye efficiently. Results suggests that colourimeter method of finding the concentration of the dye is efficient only when the concentration of the composite is low.

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“STRUCTURAL AND SURFACE MORPHOLOGICAL STUDY OF SYNTHESIZED POLY N,N- DIMETHYL ANILINE/ GRAPHITE 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

K.Bhuvaneshwari

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(Re-accredited with ‘A^{+}' Grade by NAAC)

Thoothukudi- 628001.

2020-2021

DECLARATION

We hereby declare that the project entitled **" STRUCTURAL AND SURFACE MORPHOLOGICAL STUDY OF SYNTHESIZED POLY N,N-DIMETHYL ANILINE/ GRAPHITE COMPOSITE"** submitted to St.Mary's college (Autonomous), Thoothukudi, affiliated to ManonmaniamSundaranar 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, 2021

Thoothukudi.

CERTIFICATE

This is to certify that project in Chemistry entitled **" STRUCTURAL AND SURFACE MORPHOLOGICAL STUDY OF SYNTHESIZED POLY N,N-DIMETHYL ANILINE/ GRAPHITE 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 2020-2021.

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CONTENTS

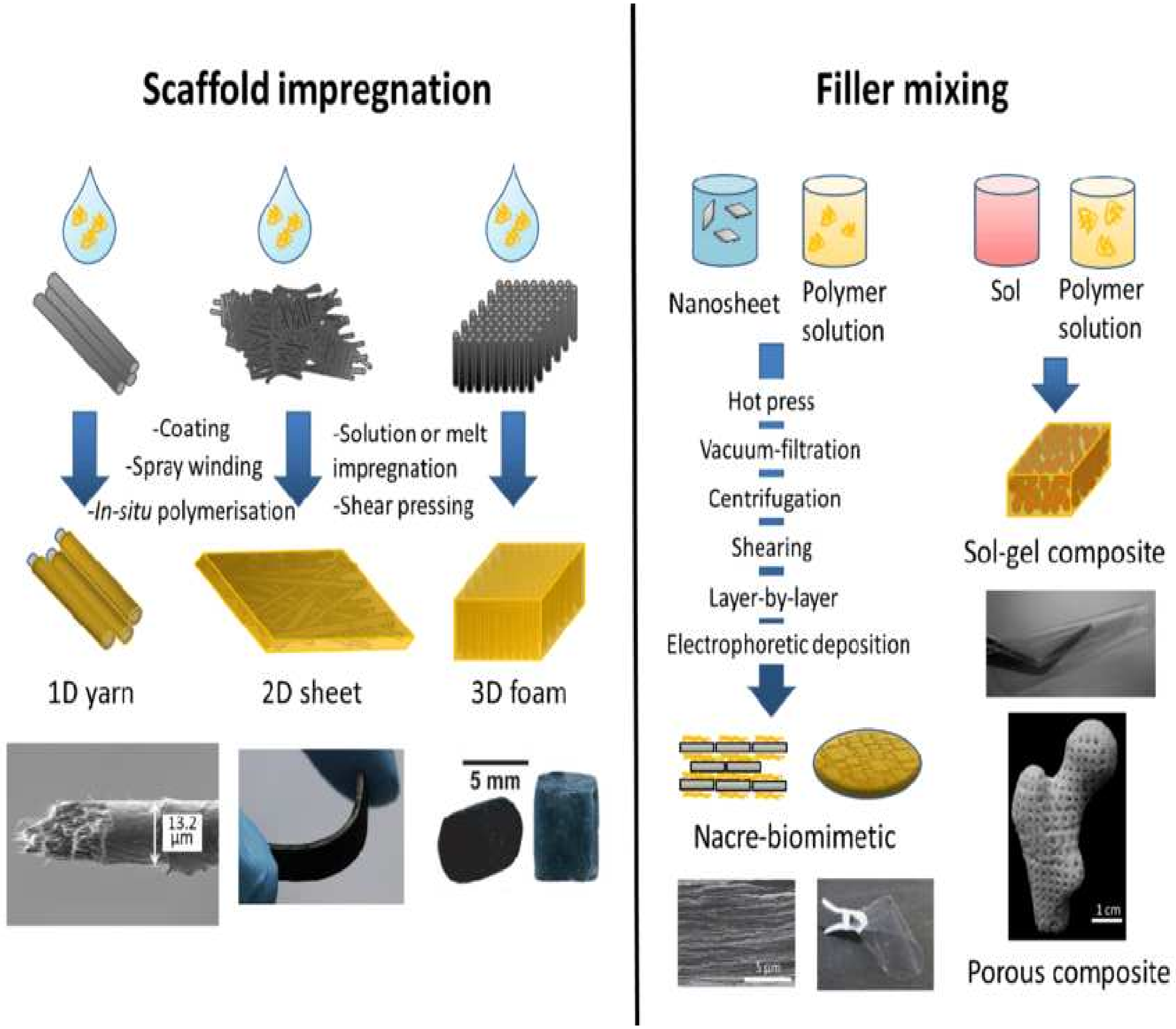
CHAPTER 1

INTRODUCTION

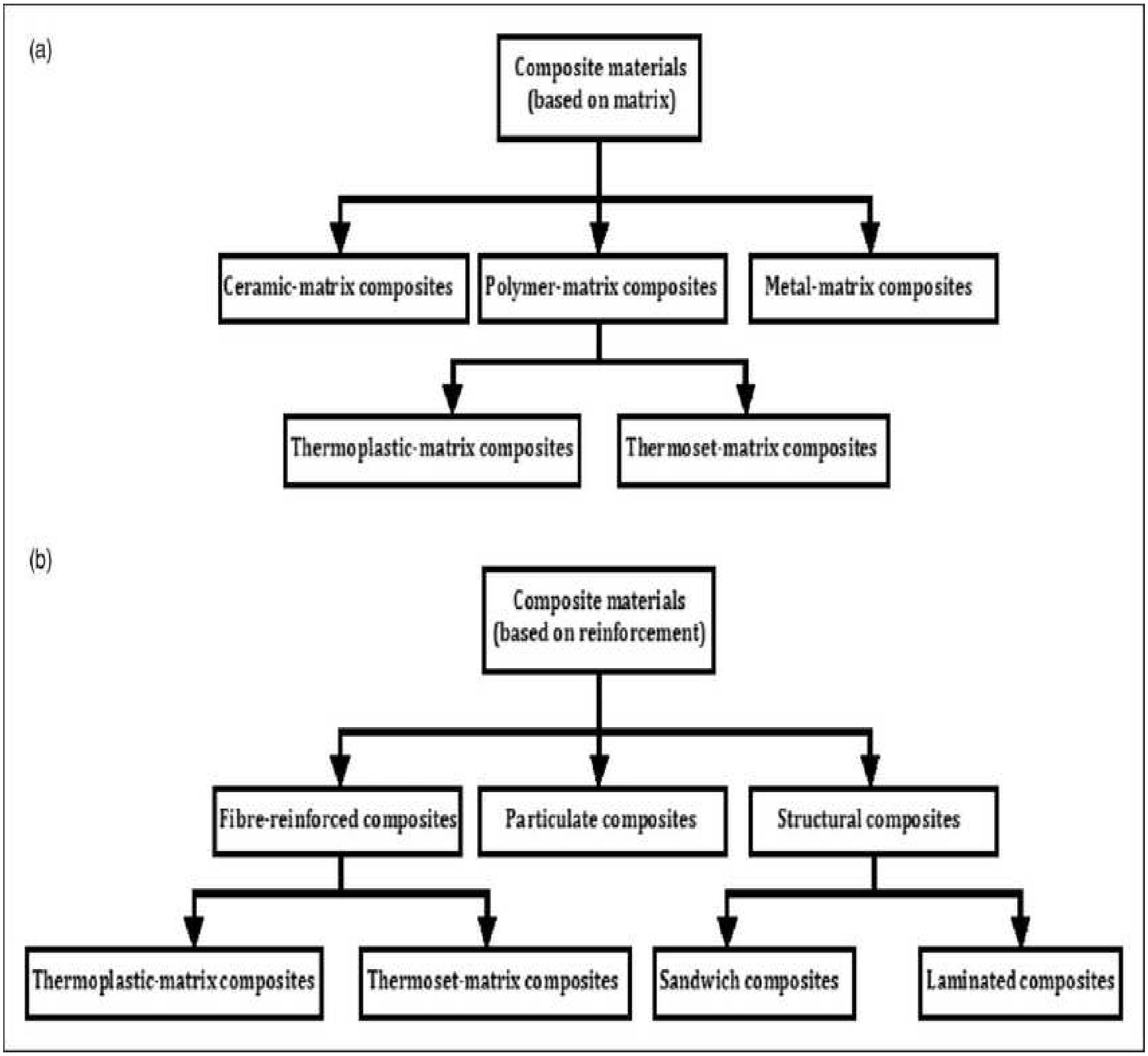
1. COMPOSITES

A composite material is a material which is produced from two or more constituent materials. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions. Modern technologies require materials with unusual combinations of properties that cannot be met by the conventional metal alloys, ceramics,and polymeric materials. Composites are a rather formidable combination and that are needed for aerospace, underwater, and transportation applications. For instance aircraft engineers are increasingly searching for structural materials that have low densities, are strong, stiff, abrasion and impact resistant and are not easily corroded. Frequently, strong materials are relatively dense also, increasing the strength or stiffness generally results in a decrease in impact strength. Material property combinations and ranges have been, and are yet being, extended by the development of composite materials. Generally, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is attained. According to this principle of combined action, better property combinations are fashioned by the judicious combination of two or more distinct materials.

Composites include multiphase metal alloys, ceramics, and polymers. There are also a number of composites that occur in nature. Most composites have been created to improve combinations of mechanical characteristics such as stiffness, toughness and high-temperature strength. Many composite materials are composed of just two phases; one is termed the matrix, which is continuous and surrounds the other phase, often called the dispersed phase. The properties of composites are a function of the properties of the constituent phases, their three main divisions are particle-reinforced, fiber-reinforced and structural composites. The dispersed phase for particle reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions) for fiber-reinforced composites, the dispersed phase has the geometry of a fiber (i.e., a large length-to-diameter ratio). Structural composites are combinations of composites and homogeneous materials. There are various reasons where new material can be favoured. Typical examples include materials which are less expensive, lighter or stronger when related to common materials. More recently researchers have also begun to actively include sensing, actuation, computation and communication into composites which are known as robotic materials. Composite materials are generally used for buildings, bridges and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.The most advanced examples perform routinely on spacecraft and aircraft in demanding environments.



One of the earliest uses of composite material was by the ancient Mesopotamians around 3400 B.C., when they glued wood strips at different angles to create plywood. The concept of "composite" building construction has existed since ancient times.



A polymer matrix composite (PMC) is a composite material composed of a variety of short or continuous fibers bound together by an organic polymer matrix. Some of the advantages with PMCs include their lightweight, high stiffness and their high strength along the direction of their reinforcements. Other advantages are good abrasion resistance and good corrosion resistance.The function of the matrix in PMCs is to bond the fibers together and transfer loads between them. PMCs matrices are typically either thermosets and thermoplastics. Thermosets are by far the predominant type in use today. Thermosets are subdivided into several resin systems including epoxies, phenolics, polyurethanes, and polyimides. Of these, epoxy systems currently dominate the advanced composite industry.Thermoset resins require addition of a curing agent or hardener and impregnation onto a reinforcing material, followed by a curing step to produce a cured or finished part. Once cured, the part cannot be changed or reformed, except for finishing. Some of the more common thermosets include epoxy, polyurethanes, phenolic and amino resins, bismaleimides (BMI,polyimides), polyamides. Thermoplastics currently represent a relatively small part of the PMC industry. They are typically supplied as nonreactive solids (no chemical reaction occurs during processing) and require only heat and pressure to form the finished part. Unlike the thermosets, the thermoplastics can usually be reheated and reformed into another shape, if desired. Graphite composites have exceptional mechanical properties. The material is strong, stiff, and lightweight. Graphite composite is the material of choice for applications where lightweight and superior performance is paramount, such as components for spacecrafts, fighter aircrafts, and racecars. Graphite fibers (sometimes called carbon fibers) are made from organic polymer such as polyacrylonitrile. The material is drawn into fibers and kept under tension while it is heated under high temperature (> 1000C). 2 dimensional carbon-carbon crystals (graphite) are formed when the hydrogen is driven out. The carbon-carbon chain has extremely strong molecular bonds (diamond is a 3 dimensional carbon-carbon crystal), and that is what gives the fibers its superior mechanical properties. Historically, graphite composites have been very expensive, which limited its use to only special applications. However, over the past fifteen years, as the volume of graphite fiber consumption has increased and the manufacturing processes have improved, the price of graphite composites has steadily declined. Today graphite composites are economically viable in many applications such as sporting goods, performance boats, performance vehicles, and high performance industrial machinery. Applications of

Graphite Composite Materials Composite materials are extremely versatile. The engineer can choose from a wide variety of fibers and resins to obtain the desired material properties. Also the material thickness and fiber orientations can be optimized for each application.

The three greatest advantages of graphite composites are:

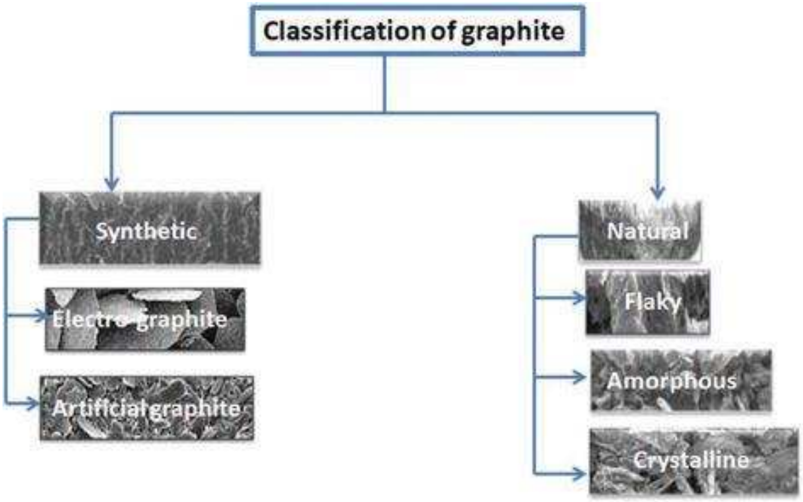
- High specific stiffness (stiffness divided by density)
- High specific strength (strength divided by density)
- Extremely low coefficient of thermal expansion (CTE)

2.Polymer/Graphite Composite

The polymer/graphite composites exhibit a high thermal conductivity and an electrical conductivity at a fairly low concentration. Polymer/graphite composites have been used in many applications including structural, aerospace and sporting goods. Most recently, researchers have focused their attention on the development of polymer/graphite composites for applications whereby thermal conductivity is needed . It is documented in the study that the significance of thermal conductivity and/or thermal diffusivity in polymer composites is related to the need for considerable levels of thermal conductivity in circuit boards and heat exchangers. According to the studies, conductive composites are frequently used in wide applications such as heating elements, temperature-dependent sensors, self-limiting electrical heaters, switching devices, antistatic materials for electromagnetic interferences and shielding of electronic devices.

Graphite is a carbon-based layered material whose structure is composed of successive layers of graphene sheets (carbon) and received much interest owing to its exceptional thermal, mechanical and electrical properties . It is thermodynamically stable and soft with the successive layers being parallel to the base plane. The layers are bonded together by van der Waals forces.

Graphite consists of carbons that are hexagonally bound to each other by covalent bonds with an interatomic separation of 0.142 nm and an interlayer separation of 0.335 nm. It is sp2-hybridized with three of four valence electrons of hexagonally attached carbons that are linked to the valence electrons of the neighbouring carbon by σ-bonding. Therefore, the fourth electron resonates freely within the graphene layer but it is no longer interacting with a specific carbon atom. Van der Waals forces acting between adjacent graphene layers result from the delocalization of π-electrons. Thus, the interatomic interaction within the single graphene layer is stronger, that is, 75 times when compared to the interaction between the adjacent layers . Hence, there has been much graphite modification that takes place in between the layers in order to improve its dispersion in different polymeric materials. Graphite can be classified into two types: natural and synthetic graphite as shown below.



2.1 Natural graphite

Naturally occurring abundant graphite is classified into three categories depending on the geological environment, that is, amorphous, flake and highly crystalline. Amorphous graphite has a content of graphite ranging from 25 to 85% depending on the geological conditions. It is usually derived from mesomorphic environment such as shale, slate and coal. Amorphous graphite is regarded as the less pure form of graphite with lack of considerable ordering and presence of microcrystalline structure. It has been applied in different applications where graphite is often utilized, however, its utilization depends on the degree of purity. Flake graphite is formed in either metamorphic or igneous geologic environments. It is obtained through froth floatation which results in 80–90% graphite. Flake graphite is less abundant as compared to amorphous graphite and has good electrical properties. It has been employed in various applications of graphite such as secondary steel manufacture, lubricants, pencils, powder metallurgy and coatings. Despite being found almost all over the world, crystalline (Vein/lump) graphite is commercially mined in Sri Lanka. It originates from crude oil deposits that through time, temperature and pressure were converted to graphite. As reflected by its name, it has a higher degree of crystallinity due to its direct deposition from a high-temperature fluid phase and its purity is more than 90%. Thus, it has good electrical and thermal conductivity. Vein graphite enjoyed its success in different applications such as batteries, lubricants, grinding wheels and powder metallurgy.

2.2. Synthetic graphite

Synthetic graphite is produced by treating carbonaceous precursors such as coal, petroleum and synthetic or natural organic chemicals in inert atmosphere to temperatures above 2400°C as well as thermal treatment of nongraphitic carbons, graphitization or chemical vapour deposition (CVD) from hydrocarbons under temperatures of 1883°C . High temperatures are often employed to facilitate solid-state phase transition effect in order to produce graphite crystals. The production method is the primary factor that influences the resulting graphite properties. Synthetic graphite can also be categorized into two, that is, electro-graphite and artificial graphite. Electro-graphite is a pure carbon-shaped graphite produced from coal tar pitch and calcined petroleum pitch in the electric furnace, while artificial graphite results from the thermal treatment of calcined petroleum pitch at 2800°C. In general, the synthetic graphite has a low density, a high electrical resistance and porosity. Synthetic graphite is employed in different applications such as energy storage, carbon brushes and aerospace.

2.3. Modification of graphite

Modification of graphite has been subject of research in order to afford interaction with large polymer molecules and to achieve a better graphite dispersion . There are three classic forms of modified graphite, that is, graphite-intercalate compounds (GICs), graphene oxide (graphite oxide (GO)) and expanded graphite (EG).

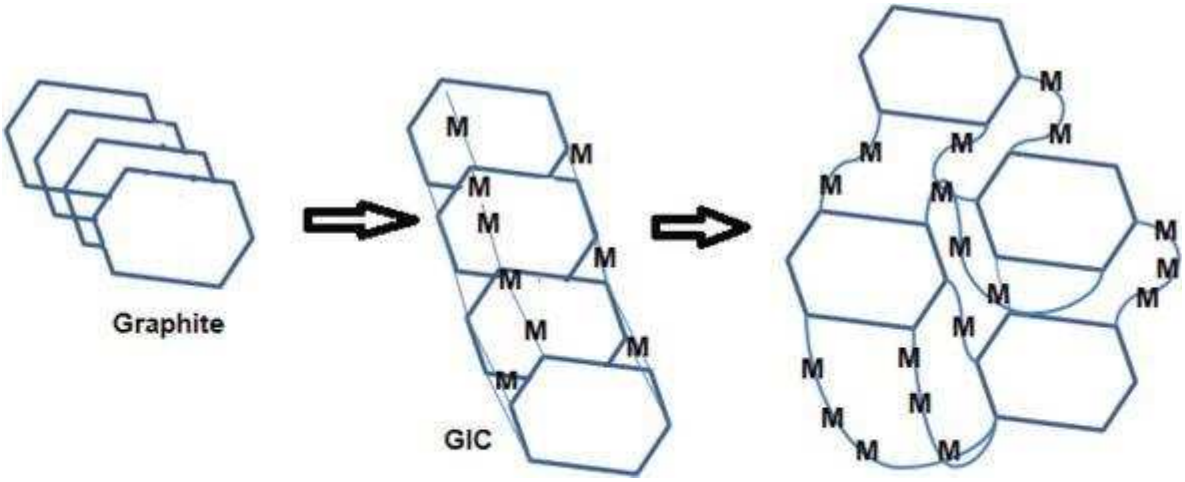
2.4 Graphite-intercalated compounds (GICs)

GICs result from the insertion of atomic or molecular layers of different chemical species called intercalant between graphene sheets of the host graphite material. GIC can be categorized into two depending on the character of their bonding, that is, covalent GICs and ionic GICs. Covalent GICs include graphite oxide (GO), carbon monofluoride and tetracarbonmonofluoride, whereas ionic GICs include graphite salts, graphite-alkali-metal compounds, graphite-halogen compounds and graphite-metal chloride compounds. Ionic GICs received much interest due to the capability of changing the electronic properties of graphite. The latter result in the presence of π-bonds in graphite that can accept/donate electrons from/to the intercalation. Further classification of ionic GICs depends on the staging of the GIC which is associated with the number of graphite layers between each intercalant layer.

2.5 Graphite oxide (GO)

GOs are known as pseudo-two dimensional solid materials with covalent between the layers. Graphite oxide is often prepared by heat treatment of graphite flakes with oxidizing agents such that polar groups are introduced on the graphite surface . This treatment also widens the interlayer spacing between the graphene sheets.

The exposure of intercalated graphite to thermal treatment beyond critical temperature or microwave radiation leads to a large expansion of graphite flakes along the c-axis than in-plane direction as shown below. The resulting material, which is known as expanded graphite (EG), has a vermicular or a worm-like structure with a low density, a high-temperature resistance and a high conductivity . A mixture of sulphuric acid and nitric acid is usually employed for graphite intercalation followed by heat or microwave treatment to produce expandedgraphite .



Schematic presentation of the preparation of expanded graphite (EG).

2.6 Graphene

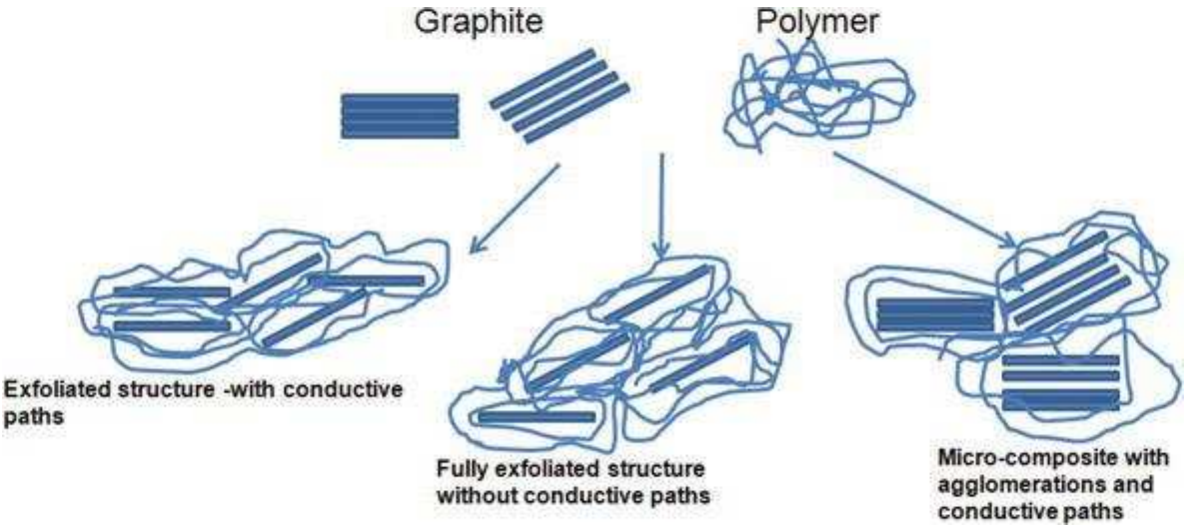
Graphene is a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice. It has been produced using different methods such as growth by chemical vapour deposition (both of discrete monolayers onto substrate and agglomerated powders), micro-mechanical exfoliation of graphite, and growth on crystalline silicon carbide . These methods afford defect-free material with excellent physical properties; however, the yield is not large enough for use as a composite filler. The thermal conductivity of graphene ranges between 600 and 5000 W m−1 K−1 with Young modulus of 1 TPa and a tensile strength of 130 GPa .

3. Graphite composites

In order to broaden the applications of polymers, the incorporation of a suitable filler with required functionality is the most cost-effective and reliable method . Some of the polymers fall short when it comes to electrical, thermal and mechanical as compared to ceramics and steel. However, the unique properties of polymers such as lightweight and mouldability into different shapes make them suitable candidates for various applications. Amongst other fillers, graphite features unique properties such as a high thermal and electrical conductivity, a low coefficient of thermal expansion, an exceptional thermal resistance, a high thermal shock resistance, improved stiffness and an increased strength. It is abundantly available and easily functionalized to afford various applications. The thermal conductivity of the graphite and/or its composites is of significant importance considering the demands as thermal conductance in heat exchangers, circuit boards, machinery, electronic appliances and many other applications as explained in Section 1.

3.1. Preparation of graphite composites

Beside the modification of graphite, the major contributor to the distribution of graphite in the polymeric matrix relies on the selected preparation method. Classic preparation methods for graphite/polymer composites are in situ polymerization, melt intercalation and solution-casting techniques. Complete dispersion of the graphite particles leads to poor thermal conductivity due to lack of conductive network path within the composite product.



3.1.1. In situ polymerization

In situ polymerization involves the polymerization of monomer (or/and oligomer) in the presence of the filler. This method is one of the most effective processes to facilitate the dispersion of the filler in the polymeric material. Moreover, it enhances strong interaction between the composite component, hence, the mechanical properties of the resulting composite are superior to the composite prepared by either solution casting or melt intercalation . This technique, however, is associated with some limitations such as polymer and filler selection and limited to laboratory scale. Moreover, it is environmentally unfriendly process which makes it not feasible for composite preparation.

3.1.2. Solution casting

In solution casting, the polymer is dissolved in suitable solvents and then the filler is added into the polymer solution . In order to improve the dispersion of the fillers, the sonication step is usually adopted . Some polymers are, however, not soluble in most available solvents which then limit the choice of a polymer for this technique. This process is not environmentally friendly due to the fact that the solvent has to be evaporated from the system which can be harmful except if the solvent is water.

3.1.3. Melt intercalation

Melt intercalation is the most favourable process with regard to industrial and environmental perspectives. Polymer and filler are mixed together in the melt-compounding technique which leads to exposure to high shear and heat. The mixture is heated to a temperature above the melting temperature of the polymer for certain period to allow homogeneity. Classic compounding techniques include a single-screw extruder, a twin-screw extruder and an internal mixer. All these techniques can be utilized alone or in combination to afford better dispersion of the fillers. Injection moulding and/or melt pressing are usually used to mould the composite for characterization. In general, the percolation threshold is little bit higher than the other processing techniques, that is, solution casting and in situ polymerization . Interestingly, the balance between the mechanical properties and other properties such as electrical conductivity can be achieved through this method which is of significance towards the commercialization of the resulting composite products. Its limitations involve the choice of polymer/filler, limited filler distribution and thermal degradation of the host polymer . The properties of the polymer such as molecular weight, viscosity and chain length play a major role on the properties of the resulting composite product, hence influencing conclusions reached by different authors.

5. Thermal conductivity

Numerous researchers studied the thermal conductivity of polymer composites with regard to their importance to reach appreciable levels of thermal conductance in circuit boards, heat exchangers, appliances and machinery. Amongst all thermal conductive fillers, graphite merits special interest not only due to its high thermal conductivity, that is, 25–470 W m−1 K−1, but high thermal stability, exceptional chemical resistance and mechanical properties [40].

The design of composites from graphite is inexpensive and available in abundance. This has initiated new ideas in the field of science for the development of a wide range of novel functional materials. Generally, the addition of graphite improved the thermal conductivity of the host polymer matrix irrespective of filler functionalization, the type of polymer and the method of preparation. Various processing techniques such as solvent casting melt blending and pan milling and masterbatch melt mixing have been used for the preparation of graphite composites. The type of mixing method seemed to have had an effect on the resultant thermal conductivity of the graphite/polymer composites. For instance, solution-casted composites had a high thermal conductivity as compared to melt-mixed system. It is understood that during solution casting, the EG particles will have a sufficient surface-to-volume ratio; as a result, they can contact easily and form conducting path networks at low EG contents. However, for melt mixing, one is of the idea that the EG particles' shape is changed during the melt-mixing process, resulting in a decrease of surface-to-volume ratio. Therefore, only a higher content of EG can contact and form conductive paths. Furthermore, the type of polymer had an influence on the thermal conductivity of the polymer/graphite composites, with the crystalline polymers having a higher thermal in the composites. It was further observed that the type of treatment on the graphite or its polymer composites also played a significant role in the improvement or non-improvement of the thermal conductivity of the polymer graphite composites. For example, the silane-treated graphite composites showed a higher thermal conductivity than the non-silane-treated graphite composites. In some cases, the treatment of the graphite with UV/O_3 did not have an influence on thermal conductivity of the resulting composite materials. Lately, the incorporation of the second filler with graphite can further enhance the thermal conductivity of the resulting composite products and widen the application of graphite composites.

CHAPTER 2

LITERATURE SURVEY

According to literature survey efficient and selective ortho-alkylation of N,N-dimethyl anilines via C–H addition to alkenes was achieved for the first time using a cationic half-sandwich yttrium catalyst in the year 2016 [1]. An extensive work on graphite and carbon powders for electrochemical applications was done in 2006 [2]. Intercalation and exfoliation routes to graphite nanoplatelets was carried in 2005 [3]. Also in 2005 Selective synthesis of N, N-dimethyl aniline derivatives using dimethyl carbonate as a methylating agent and onium salt as a catalyst was done [4]. Simultaneous electroanalysis of dopamine and ascorbic acid using poly (N, N-dimethylaniline)-modified electrodes was done in 2003 [5]. Preparation of polystyrene–graphite conducting nanocomposites via intercalation polymerization was done in 2001 [6]. A new 8-(*N*,*N*-dimethylaniline)guanosine derivative was prepared in 2000 [7]. In 1991 Femtosecond intermolecular electron transfer in diffusionless, weakly polar systems: nile blue in aniline and N, N-dimethylaniline, was carried out [8]. Lattice mode structure of graphite intercalation compounds was done in 1979 [9].

CHAPTER 3

OBJECTIVE AND SCOPE

Polymer composites are classified as multifunctional materials due to its excellent chemical properties [10,11] . The polymer composite materials take place in many industrial applications as it has wide range of properties and also low cost material. The polymer is progressively studied for foams [12] , thin film [13,14] coating [15] etc. Basically, polymeric materials either organic or inorganic are electrical insulators in their nature. Therefore this limits its potentials as smart material under electrical conducting application. Attemps to promotes from insulating to conductive polymer composites contribute the rising of nano-carbons filler like carbon nanotubes [16] carbon nanofibers [17,18] and grapheme [19,20]. Due to their excellent mechanical, thermal and electrical properties [21] in composites materials leads to new research area in polymer matrix composites (PMC). There are a lot of advantages by using conductive polymers composites compared to metallic conductors. For instance, they can be easily converted into low cost technologies, light weight, provide corrosion resistance and also offer a wide variety of electrical conductivities. Graphite, well known as graphene-based filler is naturally abundant and is reported as the best conductive filler for its excellent conductive properties and well dispersion in polymer matrix [22,23]. Recently, Shih, et al., found that graphite incorporated with polydimethylsiloxane (PDMS) shows highest temperature sensitivity and higher stability than the composites using carbon fillers as sensor [24]. In addition, polymer graphite composites also widely used as memory and energy storage [25], plastic chip electrode [26,27] etc.

In this work, conductive poly N,N -dimethylaniline graphite (PG) composite were prepared The morphological-structural properties are investigated by employing Atomic Force microscopy (AFM) UV-Visible spectroscopy and fourier transform infra-red spectroscopy (FTIR) in order to understand their structure–property relationships . Furthermore the conductivity of the polymer composite can be studied and its electrochemical behavior can be studied using electrochemical workstation.

CHAPTER 4

INSTRUMENTATION AND EXPERIMENTAL METHOD

For recording the UV-Vis absorption spectra, a computer controlled JascoV-500 spectrophotometer was used. The FT-IR spectra were recorded using a SHIMADZU instrument.

Atomic force microscopy

The AFM works much the same way a profilometer works only on a much, 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 urfeasy2scanBT02218is profilometer–a sharp cantilever tip interacts with the sample surface sensing the local forces between the molecules of the tip and sample surface.

EXPERIMENTAL METHOD

Chemical required:

- N,N-Dimethyl aniline – 6g
- Potassium perdisulphate – 13.5g
- Graphite – 0.5g
- Con. HCl – 5ml

Procedure

Poly (N,N- dimethyl aniline and graphite) was synthesized by chemical polymerization method using potassium per disulphate as the oxidising agent. For this 50mL of IN HCL was taken in a one litre beaker. To this 6g of N,N-dimethyl aniline was added and shaken uniformly using a magnetic stirrer , now 13.5g of potassium perdisulphate was added allowed to stirred for a while . Then 0.5g of graphite was added and the entire mixed was stirred

for 3 hrs. As the polymerisation was initiated the colour of the solution turned to dark brown. It was then kept overnight in the refrigerator.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 UV –Visible Studies:

UV-Visible spectra of N,N dimethyl aniline reported earlier shows a twin peak at 375nm and 400nm. The absorption around 400 nm is caused by the π → π* transition of benzenoid ring. In the polymer/graphite composite there is broad peak around 600nm due to polymerisation apart from the peak at 290nm.

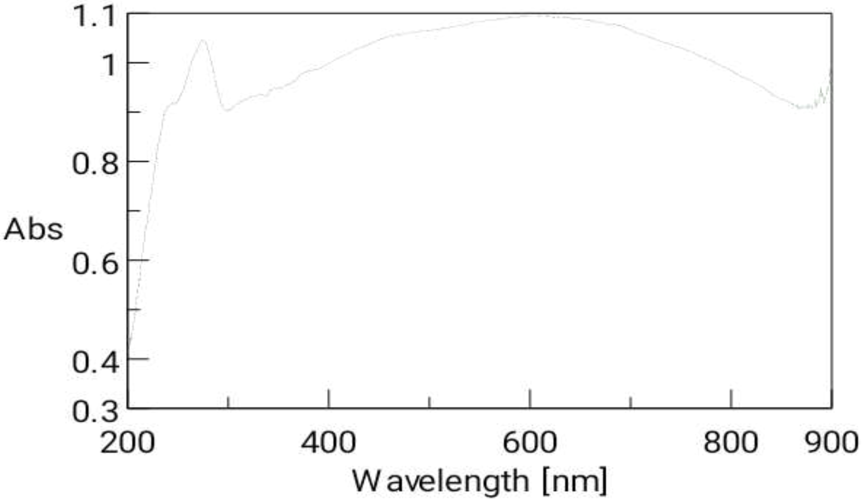


Fig 1. UV-Visible spectra of poly N,N-dimethyaniline-graphite composite

5.2 FTIR STUDIES

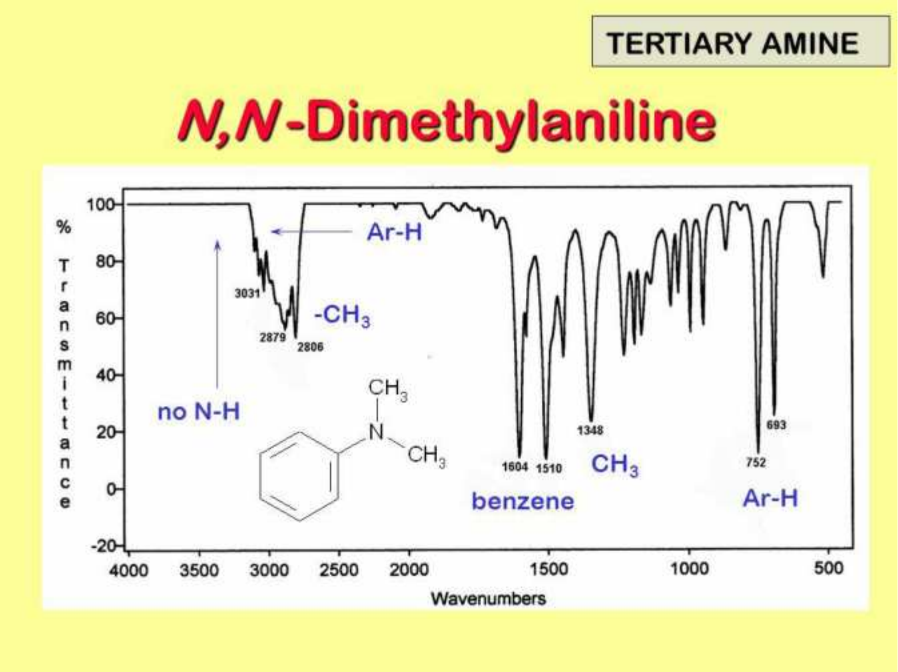


Fig 2. FTIR spectra of N,N-dimethyaniline

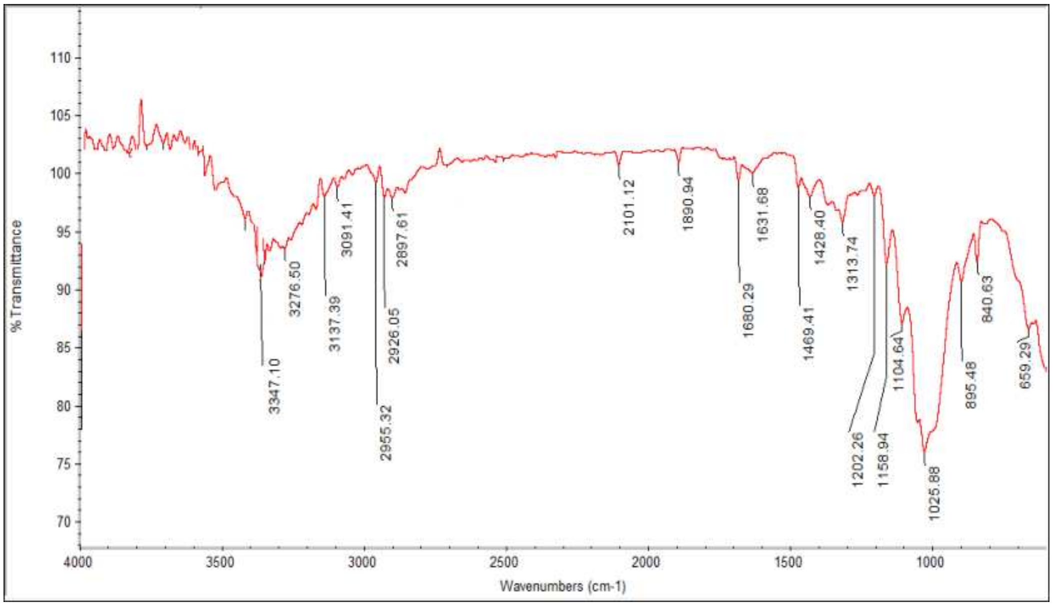


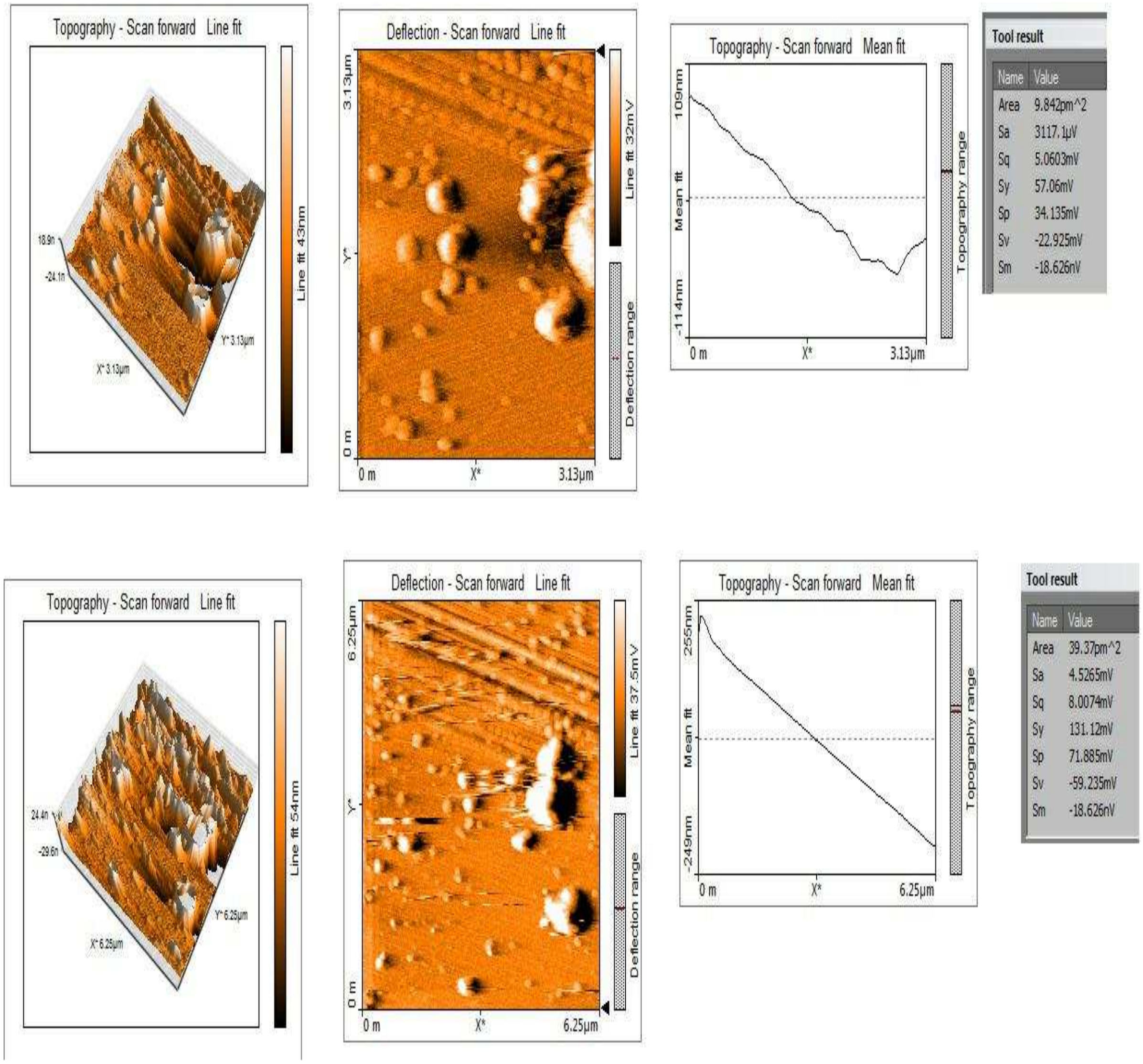
Fig 3. FTIR spectra of poly N,N-dimethyaniline-graphite composite

Comparing the FTIR of the monomer and the polymer/graphite composite the new band observed at 3347.10 cm^{-1} in the polymer /graphite composite is due to the incorporation of graphite in the polymer matrix. The polymer shows the absorption band at 1631.68 and 1469.41 cm^{-1} is an indicative of stretching vibration in quinoid rings and benzoid rings. Absorption band at 1313.74 cm^{-1} evidenced to the C-H stretching of CH_3 group. The polymer shows absorption band at 1158.94 cm^{-1} which confirms the C-N stretching of tertiary aromatic amine. The absorption band appeared at 840.63cm^{-1} and 659.29 cm^{-1} corresponds to the C-H (in-plane and out-plane).

5.3Atomic Force Microscopy(AFM)

AFM images show that the polymer matrix is smooth with spherical shaped graphite incorporated on the surface and in few areas the graphite is agglomerated.

IAS



Tool result

Name	Value
Area	9.842pm^2
Sa	3117.1µV
Sq	5.0603mV
Sy	57.06mV
Sp	34.135mV
Sv	-22.925mV
Sm	-18.626nV

Tool result

Name	Value
Area	39.37pm^2
Sa	4.5265mV
Sq	8.0074mV
Sy	131.12mV
Sp	71.885mV
Sv	-59.235mV
Sm	-18.626nV

Fig 4. AFM of poly N,N-dimethyaniline-graphite composite

CHAPTER 6

CONCLUSION

- ✓ By chemical polymerisation method Poly(N,N-dimethyl aniline)-graphite composite was prepared
- ✓ The polymer composite obtained was dark brown liquid and was subjected to UV-Visible, FTIR and AFM studies
- ✓ In the polymer/graphite composite there is broad peak around 600nm due to polymerisationapart from the peak at 290nm ($\pi \rightarrow \pi^*$ transition of benzenoid ring),
- ✓ Comparing the FTIR of the monomer and the polymer/graphite composite the new band observed at 3347.10 cm^{-1} in the polymer /graphite composite is due to the incorporation of graphite in the polymer matrix.
- ✓ AFM images show that the polymer matrix is smooth with spherical shaped graphite incorporated on the surface and in few areas the graphite is agglomerated.

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Brassica oleracea Var.botrytis STEM EXTRACT MEDIATED GREEN SYNTHESIS OF PLATINUM AND PLATINUM- SILVER NANOPARTICLES AND ITS ANTIBACTERIAL 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

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St.Mary's college (Autonomous)
(Re-accerdited with 'A+' Grade by NAAC)
Thoothukudi-628001
2020-2021

DECLARATION

We hereby declare that the project entitled **“*Brassica oleracea Var.botrytis* STEM EXTRACT MEDIATED GREEN SYNTHESIS OF PLATINUM AND PLATINUM-SILVER NANOPARTICLES AND ITS ANTIBACTERIAL 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.

C. Bhuvaneswari
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C. Santhiya devi
C.Santhiya Devi

April, 2021

Thoothukudi.

CERTIFICATE

This is to certify that the report of the project in chemistry entitled "*Brassica oleracea Var.botrytis* **STEM EXTRACT MEDIATED GREEN SYNTHESIS OF PLATINUM AND PLATINUM- SILVER NANOPARTICLES AND ITS ANTIBACTERIAL 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 2020-2021.

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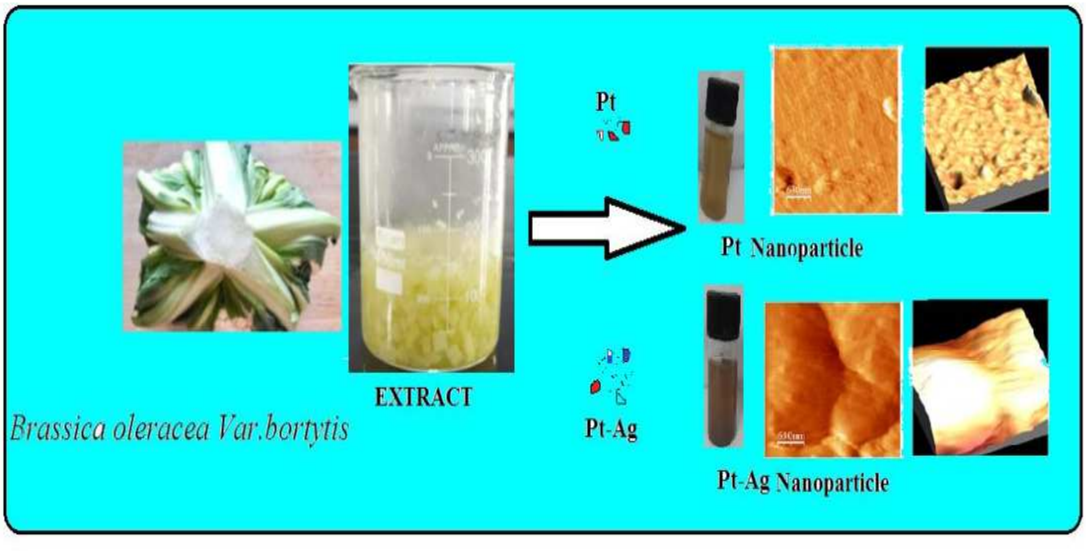
ABSTRACT

Eco-friendly synthesis of Platinum nanoparticles (Pt Nps) and Platinum-Silver nanoparticles (Pt-Ag Nps) using aqueous extracts from stem of *Brassica oleracea var.botrytis* was reported. The colour change and UV-Visible spectroscopy analysis confirmed the formation of Pt and bimetallic Pt-Ag Nanoparticles. Atomic Force Microscopy (AFM) analysis showed that the nanoparticles are of agglomerated rock like structure. Fourier Transform Infrared spectroscopy (FTIR) indicates the presence of reducing agents. Electrochemical studies also confirmed the reduction of metal nanoparticles. Also, the antimicrobial activity of the prepared Pt Nps and Pt-Ag Nps against the tested micro organism shows good inhibition efficiency.

Keywords: Nanoparticles, Green synthesis, Platinum and Silver.



CHAPTER I

INTRODUCTION

CHAPTER II

STATE OF THE ART & SCOPE OF THE WORK

CHAPTER III

MATERIALS & METHODS

CHAPTER IV

RESULTS & DISCUSSION

CHAPTER V

CONCLUSION

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CHAPTER 1

INTRODUCTION

1.1 NANO

A nanoparticle or ultrafine particle is usually defined as a particle of matter that is between 1 and 100 nanometers in diameter. Undetectable by human eye, nanoparticles can exhibit significantly different physical and chemical properties to their large materials counterparts.

Application of the nanoparticles in medicine depends on the ability to synthesis particles with different shape, monodispersity, chemical composition and size. Nanoparticles synthesis can be performed by various methods such as physical, chemical and biological approaches.

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 their 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 environment and air purification.

1.2APPLICATIONS OF NANOMATERIALS

In healthcare field, For example, utilises nanoparticles 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 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.Else where, 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 nanopartical such as titanium oxide are used in sunscreen due to the poor stability that conventional chemical UV protection offersin 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 wuth 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 ans mats used by the sports people in order to prevent illnesses caused by bacteria.

Nanoparticles have also been developed for the use in the millitary. 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 millitary 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 self-cleaning 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 witg 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, roots and flowers. These parts are rich source of reducing agents such as membrane proteins, phenols, flavonoids and other secondary metabolities [1]. In addition to this, plant extracts also contain capping agents such as extracellular tannic acids, peptides and enzymes [2]. Biowaste, in the form of vegetable or fruit waste, has become a major environmental concern due to its improper disposal.

1.3 Cauliflower (*Brassica oleracea var. bortytis*)

Among vegetables, India ranks second worldwide in cauliflower production, accounting for approximately 35% of total worldwide production [3]. Cauliflower(*Brassica oleracea var.bortytis*) forms an integral part of routine diet in India. As a habitual practice, cauliflower stem are cut off from the vegetable floret and discarded before cooking. The improper disposal leads to unwarranted growth of harmful microorganisms. In view of their ill effects, cauliflower and several other vegetable wastes are being extensively studied with an intention of finding their alternate applications as biofuels, compost etc [4].

Brassica oleracea has a compact flower head has numerous health benefits and contain essential nutrients such as vitamins, indole-3-carbinol, sulphoraphane etc., and these components prevent overweight and cervical cancers. Cauliflower has several anti-cancer ingredients such as sulphoraphane and plant sterols such as indole-3-carbinol. It contains good amounts of B-complex vitamins such as folates, pyridoxine (vitamin B_6), Pantothenic acid (vitamin B_5), thiamine (vitamin B_1), and niacin (vitamin B_3) as well as vitamin K.Vitamin C is also abundant in cauliflower, and it is a proven antioxidant that fights against harmful free radicals, boosts immunity, and prevents infections and cancers [5].

1.4 SILVER NANOPARTICLES

Silver nanoparticles (AgNPs) are increasingly used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical and chemical properties. These include optical, electrical, and thermal, high electrical conductivity and biological properties. Due to their peculiar properties, they have been used for several applications, including as antibacterial agents, in industrial, household and healthcare-related products, in consumer products, medical device coatings, optical sensors and cosmetics, in the pharmaceutical industry, the food industry, in diagnostics, orthopedics, drug delivery, as anticancer agents and have ultimately enhanced the tumor-killing effects of anticancer drugs. Recently, AgNPs have been frequently used in many textiles, keyboards, wound dressings and biomedical devices. Nanosized metallic particles are unique and can considerably change physical, chemical and biological properties due to their surface-to-volume ratio. Therefore, these nanoparticles have been exploited for various purposes. Inorder to fulfill the requirement of AgNPs, various methods have been adopted for synthesis. Generally, conventional physical and chemical methods seem to be very expensive. Interestingly, biologically-prepared AgNPs show high yield, solubility, and high stability. Among several synthetic methods for AgNPs, biological methods seem to be simple, rapid, non-toxic, dependable, and green approaches that can produce well-defined size and morphology.

1.5 PLATINUM NANOPARTICLES

Platinum nanoparticles are usually in the form of a suspension or colloid of nanoparticles of platinum in a fluid, usually water. A colloid is technically defined as a stable dispersion of particles in a fluid medium (liquid or gas). Spherical platinum nanoparticles can be made with sizes between about 2 and 100 nanometres (nm), depending on reaction conditions [1,2].

Platinum nanoparticles are suspended in the colloidal solution of brownish-red or black color. Nanoparticles come in wide variety of shapes including spheres, rods, cubes [3] and tetrahedral [4]. Platinum nanoparticles are the subject of substantial research, [5-7] with potential applications in a wide variety of areas. These include catalysis [7], medicine [5] and the synthesis of novel materials with unique properties [2,6, 7].

1.6 SCIENTIFIC CLASSIFICATION OF *Brassica oleracea var. bortytis*

NAME : Cauliflower

SCIENTIFIC NAME : *Brassica oleracea var. botrysis*

FAMILY : Brassicaceae

ORIGIN : Northeast Mediterranean

SPECIES : Brassica oleracea

RANK : cultiver

CULTIVAR GROUP : Botrytis Group

1.7 GREEN SYNTHESIS

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 [8, 9]. Alternatively, biological synthesis or ‘Green Synthesis’ of Nanoparticless 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 [9,12,18,19]. Biological method essentially makes use of plant extract or microorganisms for synthesizing AgNPs. However, from the viewpoint of industrial feasibility, plant mediated green synthesis of AgNPs is considered to be more economic and safer as compared to microbe-assisted synthesis since handling and maintaining microbial cultures is often tedious [12].

Colloidal silver particles have been reported to act as effective antimicrobial agents against bacteria and viruses [6-9]. They also possess promising catalytic activity which enable them to degrade harmful synthetic dyes such as methylene blue (MB), congo red, methyl orange and methyl red [6, 10 – 15]. Additionally, they have also been shown to act as efficient sensors for detecting heavy metals like mercury and copper ions [16, 17].

CHAPTER 2

STATE OF THE ART AND SCOPE OF WORK

2.1 LITERATURE SURVEY

Emerging use of Nanoparticles in diagnosis and treatment of breast cancer was reported by M.V.Yezhelyev et.al [20] and global cancer statistics was reported by Jamal A , et.al [21]. 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. [22].

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 [23].

Lara H.H, et.al reported the mode of antiviral action of silver nanoparticlels against HIV-1[24]. Silver nanoparticles fabricated in Hepes buffer exhibit cytoprotective activities toward HIV-1 infected cells, was illustrated by Sun R, et.al [25]. Nanostructure materials for applications in drug delivery and tissue engineering, was shown by Goldberg M, et, al [26].

Block Copolymer Mediated Synthesis of Dendritic Platinum Nanoparticles, written by Wang L, et. al [27]. 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. [28].

Malgras V, et,al. reported the Nanoarchitectures for Mesoporous Metal where the materials have been showcasing impressive enhancements of their electrochemical properties for further implementation, compared to their micro- and macroporous counterparts [29].

Yin and coworkers [30] 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 [31].

Biomimetic synthesis and patterning of silver nanoparticles was reported by NaikR,et.al [32]. Rapid synthesis of silver nanoparticles using dried medicinal plant of basil was reported by Ahmad N et.al [33]. Sivaraman S.K, et.al illustrated a green protocol for room temperature synthesis of silver nanoparticles in seconds [34].

A review on the biosynthesis of nanoparticles: technological concepts and future applications was written by Mohanpuria P, et.al [35]. Perumal-Samy R, et.al. did the Screening of 34 medicinal plants for antibacterial properties [36]. Studies on analgesic and anti-inflammatory activities of Vitexnegundo Linn, written by Telang R.S, et.al [37].

Larvicidal activity of few plant extracts against culexquinque-fasciatus and Anopheles stephensi, written by Pushpalatha E, et.al [38]. Investigation of the effect of pomengranate extract and monodisperse silver nanoparticles combination on MCF-7 cell line was reported by Sahin B, et.al.[39]. Green Synthesis, characterisation and application of nanoparticles was reported by Gaurav pal et al. [40].

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 [41].

The current generation is all about nanotechnology and nanoparticles. The field has captured applications from daily life technological applications to armories and space technology and from human cosmetics to medicine [42-44]. On the other hand, green-plant extraction method is a non-toxic and safe process [45-47]. Nowadays, these metal nanoparticals are used in shampoo,soap,cosmetics and toothpastes as well [48-50].

Henry G. Aritonang, Henry koleangan reported the synthesis of silver nanoparticles using aqueous extract of medicinal plant [51]. 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 [52].

Green synthesis of gold nanoparticles using plant extract as reducing agent was worked by paz elia and Raya czach. All GNPs prepared shows good bio compatibility and good stability for over three weeks was reported in this literature [53]. Synthesis of silver nanoparticles using buchu plant extract and their analgesic properties was confirmed by Herbert chiguvare et al.,[54].

Ratiram Gomaji et al reported the Ni NPs were obtained through a nickel salt with hydrazine hydrate at 80 C temperature by using ethylenediamine as protective [55]. 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., [56].

Shlomae et al reported the synthesis of copper nanoparticles using *Penicillium autantiogriseum*, *Penicillium citricum*, *Penicillium waksmanni* [57]. Biosynthesis of cadmium oxide nanoparticles using flowers extract of *Achillea wilhelmsii* as the reducing agents was reported by andeani et al [58]. Though there have been several studies reported on the biological synthesis of platinum nanoparticles using extracts from different plant species [59-64].

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 [65, 66]. Various techniques are available for the synthesis of nanofilms and nanowire [67-70]. Metal and metal oxide nanoparticles are used for antimicrobial activities drug delivery and cancer therapy [71-75]. Physical methods are expensive [76] and the by-products formed is useful in cosmetic and medical applications [77].

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 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 nanoparticles size. Hence for this investigation, Green method is chosen to synthesize nanoparticles.

Platinum and Silver was preferred to synthesize Nanoparticles. Even though Silver is rare, it is a basic natural element that makes up our planet. It was also slightly harder than gold and has excellent properties such as very ductile and malleable. Also, the pure silver has the highest electrical and thermal conductivity of all metals and has the lowest contact resistance.

Platinum is the most active metal. Platinum nanoparticles have potential applications in a wide variety of areas. Especially in catalysis, medicine and for the synthesis of novel materials with unique properties. This work especially deals with the platinum Nanoparticles and bimetallic Platinum- Silver Nanoparticles.

This work innovation gives importance particularly compensating as far as decreasing the poisonous quality. We cover this investigation to synthesize, characterize and applications of Platinum and its bimetallic combination with Silver. In the green strategies, plant extracts are the natural substances which are utilized to prepare the NPs for the pharmaceutical and other applications.

2.3 OBJECTIVES OF THE WORK

In view of the above scope, the main objectives of this investigation are

- To synthesise the nanoparticles through green method.
- To utilise plant waste part for synthesising nanoparticles.
- To synthesise bimetallic nanoparticle.
- To confirm the presence of nanoparticles through various characterisation techniques such as Potentiometric analysis, UV- Visible Spectrophotometric Analysis, FTIR Analysis, Voltammetric analysis, Differential Pulse voltammetry and Square wave Voltammetry.
- To study the surface morphology of the nanoparticles through Atomic Force Microscopic analysis.
- To study the applications of the synthesised nanoparticles.
- To study the anti-bacterial applications of synthesised nanoparticles against the different human pathogenic bacteria like E. coli, Bacillus sps.

CHAPTER 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

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

3.1 MATERIALS

Silver nitrate and potassium tetrachloropalatinate were purchased. Silver Nitrate with the purity of 99.8% was purchased from Isochem Laboratory Reagent, Kochi. Potassium Tetrachloroplatinate with the purity of 98% was purchased from Spectrochem Private Limited, Mumbai.

Fresh stem of *Brassica Oleracea Var.botrytis* were collected and thoroughly washed. Deionised-water was used throughout the experiments.

3.1.1 BOTANICAL DESCRIPTION

Fig 3.1 ***Brassica oleraceaVar.botrytis*** **BELONGS TO THE FAMILY Brassicaceae**

[Mustard family]

Fig 3.2 STEM OF *Brassica oleracea var. botrytis*

3.2 PREPARATION OF STEM EXTRACT

Fresh stem of *Brassica oleracea var.botrytis* was collected .The stem was washed with water and it was cut in to very small pieces. In order to remove the dust particles washing was repeated for thrice to get clear stem.

Fig 3.3 SMALL PIECES OF THE STEM *Brassica oleracea var.botrytis*

The cleaned 50 gm of *Brassica oleracea var.botrytis* pieces was now packed using filter paper. The packed portion was now filled in the soxhlet extractor to get the clear extract of *Brassica oleracea var.botrytis.* After one hour it was cooled to room temperature. The extract was filtered using Whatman filter paper. The collected extract was used for the synthesis of platinum and bimetallic platinum –silver nanoparticles.

Fig 3.4 ***Brassica Oleracea var.botrytis*** **EXTRACTION USING SOXHLET EXTRACTOR**

3.3 PREPARATION OF NANO PARTICLES

3.3.1 PREPARATION OF PLATINUM NANAOPARTICLES

50ml of 1Mm potassium tetrachloropalatinate solution was prepared. It was then added to 10 ml of *Brassica oleracea var.botrytis* extract. It was then stirred at a hot bath for 60 minutes. It was then centrifuged. The sample was then placed in a muffle furnace at 900°C for one hour.

3.3.2 PREPARATION OF PLATINUM-SILVER NANOPARTICLES

50ml of 1mM Silver nitrate 1mM potassium tetrachloroplatinate solution was prepared. 10ml of *Brassica oleracea var.botrytis* extract was then added to the solution. The solution was stirred at 85˚C for 60 minutes. The nanoparticles obtained were centrifuged and washed several times to remove any unreacted salts and extracts.

The obtained sample was then placed in an muffle furnace at temperature of 900˚C to get dried powder.

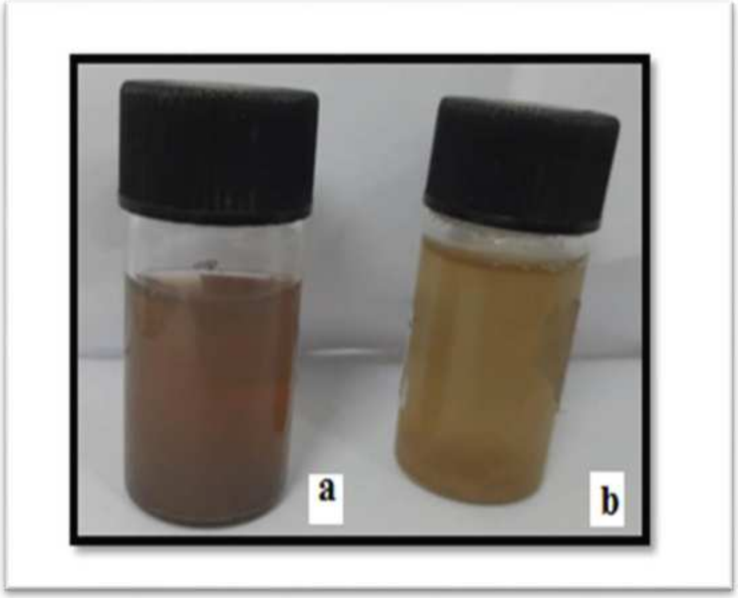

Fig 3.5 NANOPARTICLES OF a) Platinum (Pt) b) Platinum – Silver (Pt -Ag)

3.4 CHARACTERISATION OF NANOPARTICLES

Green synthesized nanoparticles were visually seen by the change of colour from green to brown. UV/visible spectroscopy was taken in the range JASCO, V-600 Diffuse Reflectance Spectrophotometer. FTIR analysis of the nanoparticles was carried out using Thermo Scientific Nicolet Is5 FITR Spectrometer.

AFM Microscopy was carried out using Nano Surf easy scan BT2218 profilometer. Electrochemical studies were carried out using CHI650C Electrochemical work Station.

3.5. INSTRUMENTS USED

3.5.1 POTENTIOMETER

Fig 3.6 POTENTIOMETER

A potentiometer is essentially a voltage divider used for measuring electric potential (volt); the component is on implementation of the same principle. It contains two electrodes namely working electrode and reference electrode. The electrodes are used to measure the electric potential. Platinum is the working electrode and calomel is the reference electrode used for measuring emf.

Potentiometer directly control significant amount of power. They can be used as position feedback devices in order to create closed loop control such as in a servo mechanism. Potentiometres are also very widely used as a part of displacement transducers because of the simplicity of construction.

3.5.2 COLORIMETER:

Fig 3.7 COLORIMETER

A Colorimeter is a device used in colorimetry that measures the absorbance of particular wavelength of light by a specific solution. It is commonly used to determine the concentration of a known solute in a given solution by the application of the Beer–Lambert law which states that the concentration of a solute is proportional to the absorbance.

During colour measurement, the change in the intensity of electromagnetic radiation in the visible wavelength region of the spectrum after transmitting or reflecting by an object or solution is measured. Such a measurement can help to find the concentration of substances, since the amount and colour of the light absorbed or transmitted depends on the properties of the solution, including the concentration of particles in it.

A colorimeter is an instrument that compares the amount of light getting through a solution with the amount that can get through a sample of pure solvent.

A colorimeter contains a photocell which is able to detect the amount of light passing through the solution under investigation. The current produced by the photocell depends on the quantity of light hitting it after passing through the coloured solution.

The higher the concentration of the colorant in the solution, the higher is the absorption of light; less light passing through the solution means less current created by the photocell. A colorimeter takes three wideband readings along the visible spectrum to obtain a rough estimate of a colour sample.

3.5.3 FOURIER TRANSFORM INFRARED SPECTROMETER (FTIR)

Fig 3.8 FOURIER TRANSFORM INFRARED SPECTROMETER (FTIR)

Fourier-transform infrared spectroscopy (FTIR) Spectroscopy or technique is used to find an infrared spectrum of absorption or emission of a solid, liquid or gas. It used to identify organic, polymeric, and inorganic materials and observe their chemical properties.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate.

FTIR measurements of samples prepared as KBr disks were performed on a Thermo Scientific Nicolet iS5 FTIR spectrometer.

3.5.4 UV-VIS SPECTROMETER (UV-VIS)

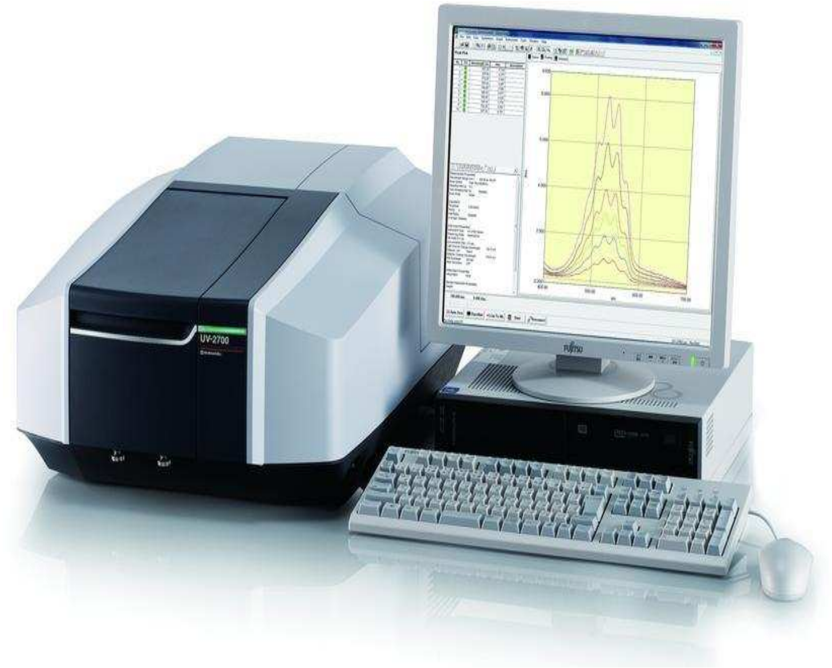

Fig 3.9 UV-VIS SPECTROMETER (UV-VIS)

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 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. There are four possible types of transitions (π–π*, n–π*, σ–σ*, and n–σ*), and they can be ordered as follows: σ–σ* > n–σ* > π–π* > n–π*.UV–Visspectralanalysiswas performedonaJASCO, V-600 Diffuse Reflectance spectrophotometer.

3.5.5 ATOMIC FORCE MICROSCOPY (AFM)

Fig 3.10 ATOMIC FORCE MICROSCOPY (AFM)

The AFM works much the same way a profilometer works only on a much, 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 easy2 scanBT02218 is profilometer.

3.5.6. ELECTROCHEMICAL WORKSTATION

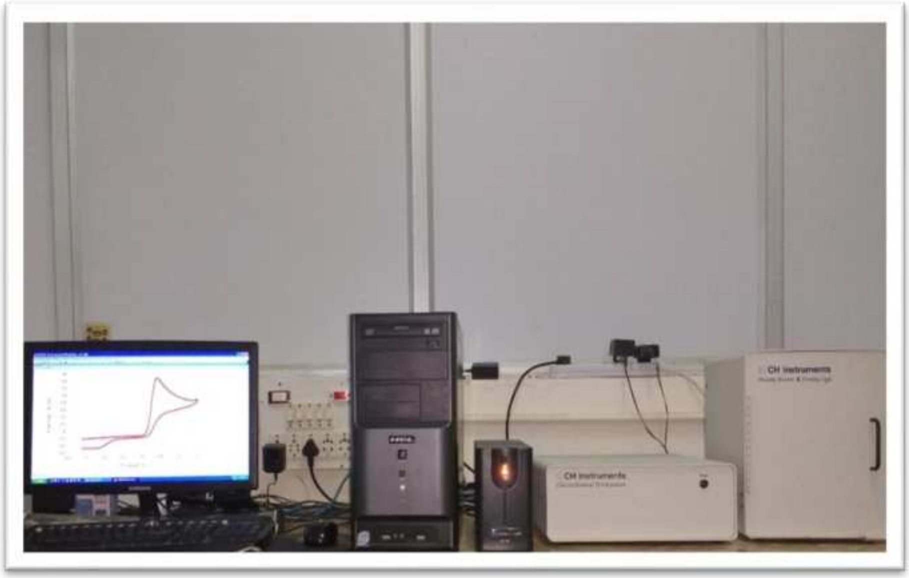

Fig 3.11 ELECTROCHEMICAL WORKSTATION

Electrochemical workstation offers several techniques (Cyclic Voltammetry, Differential Pulse Voltammetry, Square Wave Voltammetry, Impedance Spectroscopy, etc. Windows-based software, integrated digital CV simulator, impedance simulation and fitting program. These features provide powerful tools for the understanding of reaction kinetics, trace level analysis, fundamental research, corrosion, energy conversion and storage studies.

3.6 ANTI BACTERIAL STUDIES

Antibacterial activity of the prepared nanoparticles was determined using agar-well diffusion method.

3.6.1 AGAR DILUTION METHOD

Agar dilution involved an incorporation of different concentration of the antimicrobial agent in to nutrient agar medium followed by swabbing of the standardized number of microbial cells with the sterile cotton swab on to the surface of the agar plate [78-81]. The plates were incubated for 18-24 hrs at 35-37˚C and examined for the growth of inhibited zones the MIC is expressed as the highest dilution which inhibited growth by measuring the zone of inhibition.

Agar dilution is most often prepared in Petri dishes and has advantage to test several organisms on each plate.The dilutions are made in a small volume of water and cooled to agar which has been melted and cooled to not more than 60^0C .Blood may be added and if chocolate agar is required , the medium must be heated before the antibiotic is added.

The pH of the agar must be between 7.2 and 7.4 at room temperature. Supplemental cations must not be added to the sugar. It may be supplemented with 5% defibrinated sheep blood or lysed horse blood. The reproducibility of the results and satisfactory growth of most nonfastidious organisms can be expected advantages from agar dilution method. However, its disadvantages include the labor required to prepare the agar dilution plates and their relatively short-shell life.

CHAPTER 4

RESULTS & DISCUSSION

4. GREEN SYNTHESIS AND CHARACTERISATION OF PLATINUM (Pt) AND PLATINUM- SILVER (Pt-Ag) NANOPARTICLES

Platinum nanoparticles were synthesized using fresh stem of *Brassica oleracea var. botrytis* extract using green route method. The synthesized nanoparticles were characterized by FTIR and UV Visible Spectroscopy to assess their nature. Atomic force microscopy was used to assess their morphology. Electrochemical characterization was carried out using Electrochemical workstation. Anti-microbial studies were carried out using agar-well diffusion method.

4.1 POTENTIOMETRIC ANALYSIS

4.1.1 POTENTIOMETRIC ANALYSIS OF Pt NANOPARTICLES

40 ml of extract is taken in a beaker. The burette is filled with the prepared 0.001M Platinum Nps solution. The electrodes are dipped in the extract and the electric potential is measured for the pure extract. Then the platinum solution is added to the extract and the potential values are noted.

Similar readings are taken by increasing the volume of 0.001M K_2PtCl_4 solution by adding 1 ml to the extract till the reading becomes stable. The stable reading indicates the formation of nanoparticles. Table 4.1 represents the potentiometric data for the Platinum Nanoparticles. Fig 4.1 illustrates the plot of absorbance against the volume of Pt Nanoparticles.

Table 4.1 EMF VALUES OF Pt NANOPARTICLES

Volume of 0.001 M Pt solution added (mL)	EMF (Volt)
0.1	62
0.2	61
0.3	61
0.4	61
0.5	61
0.6	61
0.7	61
0.8	61
0.9	61
1.0	61

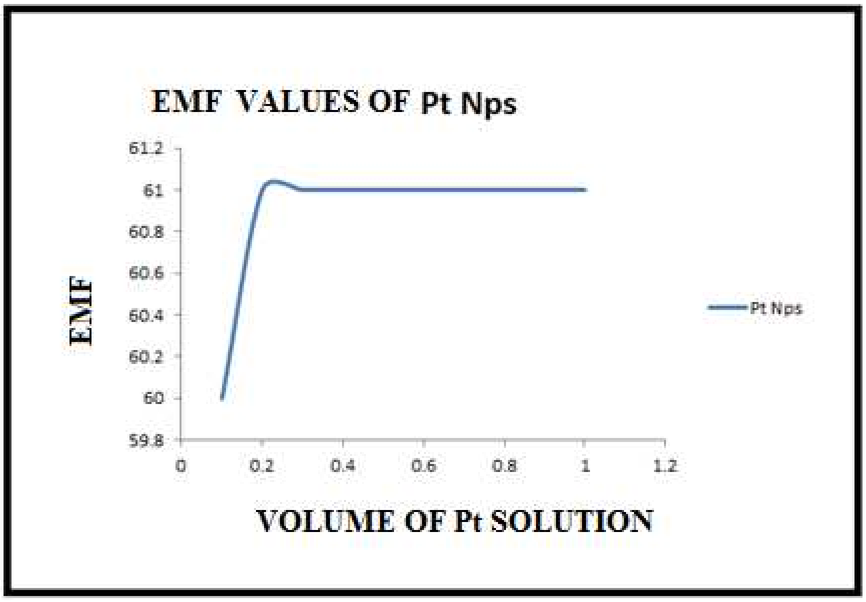

Fig 4.1 VOLUME OF PLATINUM NANOPARTICLES AGAINST EMF

4.1.2 POTENTIOMETRIC ANALYSIS OF BIMETALLIC Pt-Ag NANOPARTICLES

40 ml of extract is taken in a beaker. The burette is filled with the prepared bimetallic solution containing 0.001M K_2PtCl_4 and 0.001 M $AgNO_3$ solution. The electrodes are dipped in the extract and the electric potential is measured for the pure extract. Then the bimetallic solution is added to the extract and the potential values are noted. Similar readings are taken by increasing the volume of bimetallic solution by adding 1 ml to the extract till the reading becomes stable. The stable reading indicates the formation of nanoparticles. Table 4.2 represents the potentiometric data for the mixture containing Silver and Platinum solution. Fig 4.2 illustrates the plot of absorbance against the volume of Pt-Ag Nanoparticles.

TABLE 4.2 EMF VALUES OF PT - AG NANOPARTICLES

Volume of Pt - Ag solution added (ml)	Emf (volt)
0.1	41
0.2	46
0.3	48
0.4	48
0.5	48
0.6	48
0.7	49
0.8	49
0.9	50
1.0	50

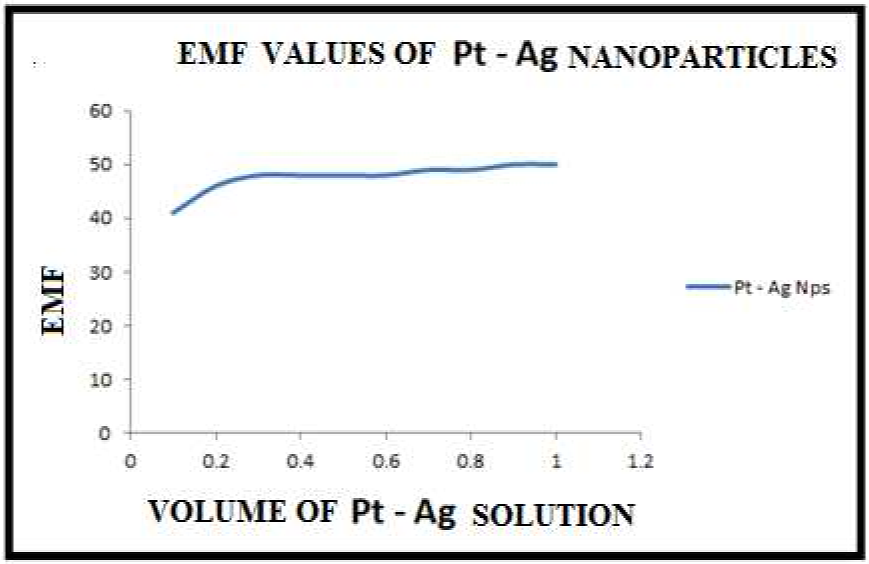

Fig 4.2 VOLUME OF PLATINUM- SILVER NANOPARTICLES AGAINST EMF

4.2 UV – VIS ANALYSIS

4.2.1 UV – VIS ANALYSIS OF Pt NANOPARTICLES

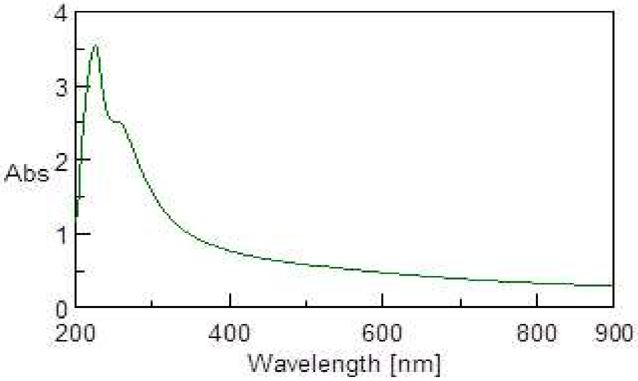

Fig 4.3 UV –VISIBLE DIFFUSE REFLECTANCE SPECTRA OF Pt NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

The optical absorbance properties of Pt Nanoparticle was investigated using stem extract of *Brassica oleraceaVar.botrytis* in the wavelength range 200-900nm at ambient temperature. Fig 4.3 shows the different absorption spectra. There is a strong absorption peak at 236 nm in figure 1which confirms the formation of Pt nanoparticles

4.2.2 UV – VIS DRS ANALYSIS OF Pt-Ag NANOPARTICLES

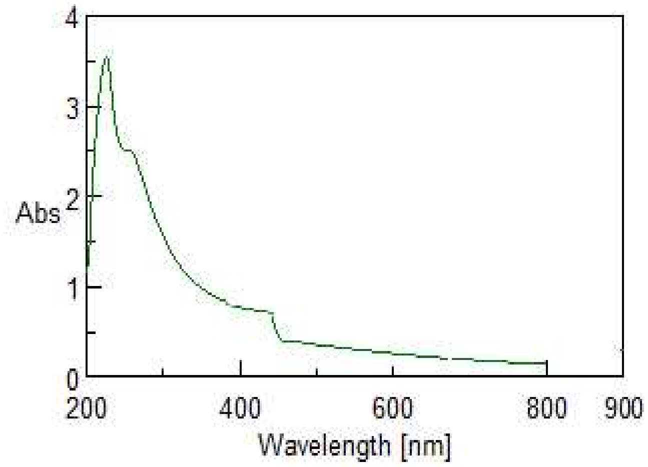

Fig 4.4 UV –VISIBLE DIFFUSE REFLECTANCE SPECTRA OF Pt-Ag NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

Also, the optical absorbance properties of bimetallic Pt-Ag Nanoparticles were investigated using stem extract of *Brassica Oleracea Var.botrytis* in the wavelength range 200-900 nm at ambient temperature. Fig 4.4 indicates the UV –Visible diffuse reflectance spectra of Pt-Ag Nanoparticles using stem extract of *Brassica Oleracea Var.botrytis.* There is a strong absorption peak at 236 nm and 450nm which confirms the presence of Pt- Ag nanoparticles.

4.3 COLORIMETRIC ANALYSIS

4.3.1 COLORIMETRIC ANALYSIS OF Pt NANOPARTICLES

Take 5 ml of the extract in a 100 ml beaker. Pipette out 1, 2, 3, 4 and 5 mL of Pt Nps solution into a separate 100ml beaker and label it as B1, B2, B3, B4 and B5. Stir well with a glass rod. Keep the solution at room temperature for 10 minutes. Switch on the instrument and keep the blank solution.

Measure the optical density of each solution by fixing the wavelength at 260 nm. The absorbance values are noted for B1, B2, B3, B4 and B5. Now, draw the graph between concentration (x-axis) and optical density (y-axis). Table 4.3 represents the colorimetric data of the synthesized Platinum nanoparticles. Fig 4.5 shows the plot of absorbance against the volume of Pt solution added.

TABLE 4.3 ABSORBANCE VALUE OF Pt NPS USING COLORIMETER

Volume of Pt solution (ml)	ABSORBANCE (nm)
1	0.3
2	0.32
3	0.54
4	0.58
5	0.59

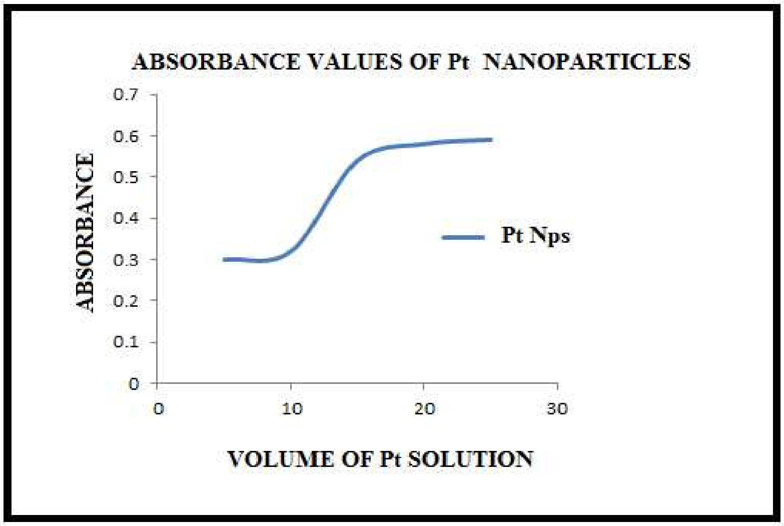

Fig 4.5 COLORIMETRIC ANALYSIS OF Pt NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

From the graph, it was clear that on increasing the concentration of the prepared Nanoparticles, the absorbance value also increased.

4.3.2 COLORIMETRIC ANALYSIS OF Pt - Ag NANOPARTICLES

The colorimetric analysis waS carried out for bimetallic Pt-Ag solution. 5 ml of Pt Nps and 5mL of Ag Nps solution was mixed in equal proportions. To the 5mL of the extract taken in five different beakers 1, 2, 3, 4 and 5 mL of the Pt- Ag Nanoparticles were added. The mixture is stirred well. After 10 minutes, the absorbance values are noted for the bimetallic solution using colorimeter. Table 4.4 shows the Volume of Bimetallic solution used and its absorbance values. Fig 4.6 represents the Colorimetric Analysis of Pt – Ag Nanoparticles using stem extract of *Brassica OleraceaVar.botrytis.* From the analysis, it was clear that on increasing the concentration, absorbance value also gets increased.

TABLE 4.4 ABSORBANCE VALUE OF Pt –Ag NPS

Volume of Pt –Ag solution (ml)	**ABSORBANCE**
5	0.45
10	0.47
15	0.53
20	0.67
25	0.78

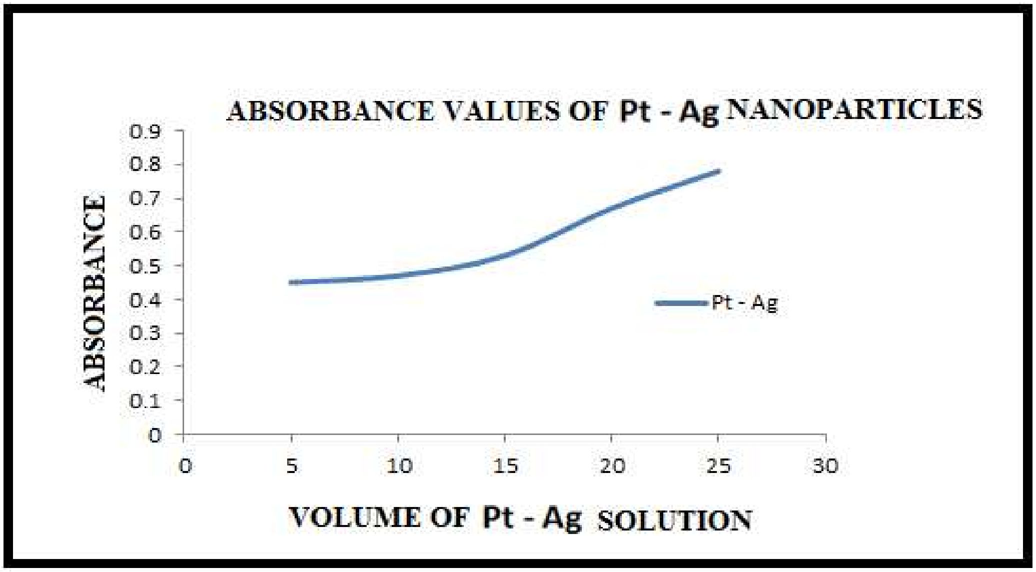

Fig 4.6 COLORIMETRIC ANALYSIS OF Pt –Ag NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

4.4 FOURIER TRANSFORM INFRAREDSPECTROSCOPIC ANALYSIS

4.4.1 FTIR ANALYSIS OF Pt NANOPARTICLES

FTIR analysis was carried out using KBr pellet and the spectrum of Pt nanoparticles is shown in figure 4.7.

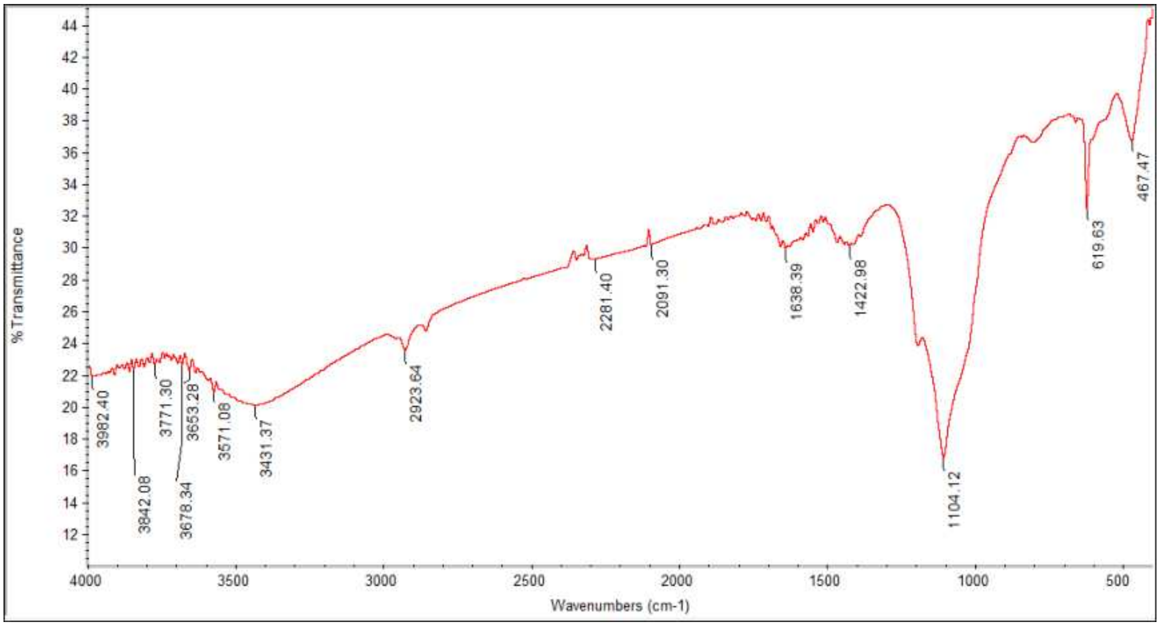

Fig 4.7 FT - IR SPECTRA OF Pt NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

In general FTIR bands for Pt stretching and bending occur in the fingerprint region, 400-850 cm^{-1}. The peak around 467 cm^{-1}corresponds to Pt–O stretching vibration. The phytochemicals responsible for formation of nanoparticles may be more in the leaves and aid in the formation of nanoparticles. The band at 1104 cm^{-1} corresponds to C-N stretching, 1422 cm^{-1} is associated with C=O stretching vibration. The band at 1638 is due to C=C stretching. The band at 2091, 2281 cm^{-1} 2923 cm^{-1} are C-C stretch, C-N Stretch C-H vibrations. The presence of O-H stretching and N-H stretching is observed peaks around 3000 cm^{-1}.

4.4.2 FTIR ANALYSIS OF Pt-Ag NANOPARTICLES

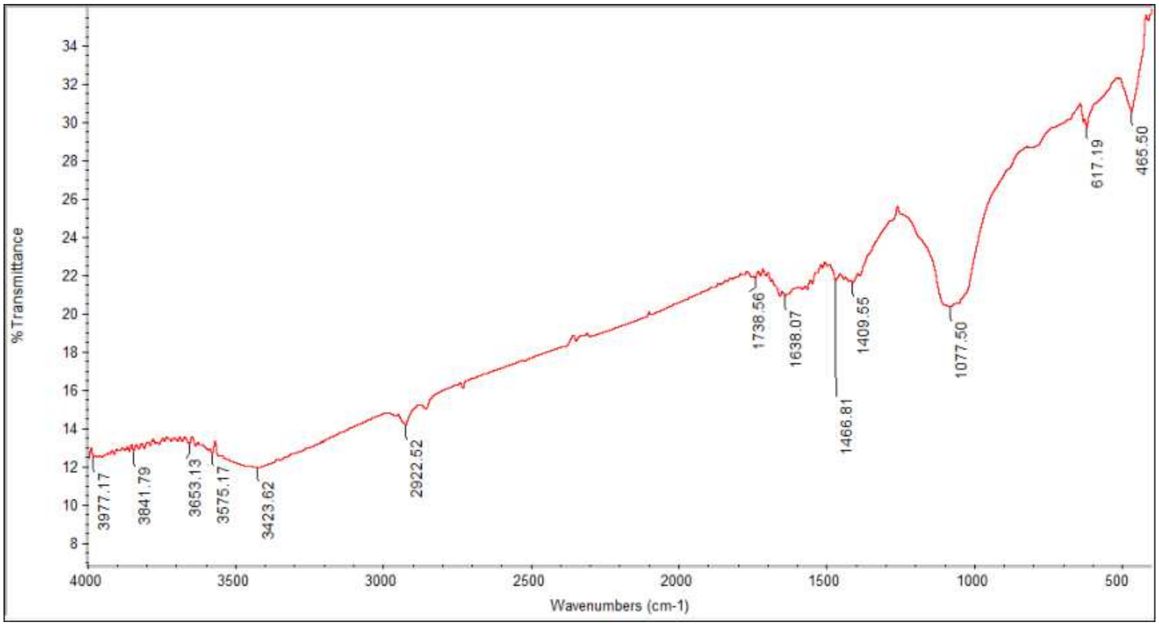

Fig 4.8 FT- IR SPECTRA OF Pt - Ag NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

FTIR analysis was carried out using KBr pellet and the spectrum of Pt-Ag nanoparticles is shown in figure 4.8. A peak around the finger print region confirms the Pt-Ag Nanoparticles. A peak at 1077 cm^{-1} indicates C-N stretching vibration. 1409 band indicates the C-C aromatic stretching. N-H bending is observed at 1638 cm^{-1} and C= O stretching at 1738 cm^{-1}. The band at 2922 cm^{-1}indicates C-H stretching. The bands around 3600 indicate the presence of hydroxyl group.

4.5 ATOMIC FORCE MICROSCOPY

4.5.1 AFM ANALYSIS OF Pt NANOPARTICLES

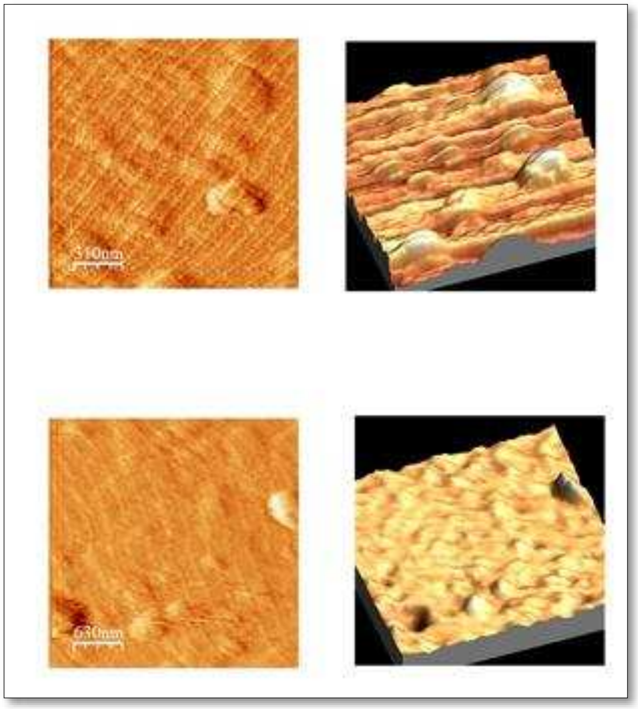

Fig 4.9 AFM IMAGES OF Pt NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

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 object.

An AFM topographical image of platinum nanoparticles is shown in figure 4.9 which shows the agglomerated rock like structure. The average length of the rock structure is 310 to 630nm. It may be due to the Metal bindings. Table 4.5 represents the Roughness and surface analysis of Pt NPs by AFM.

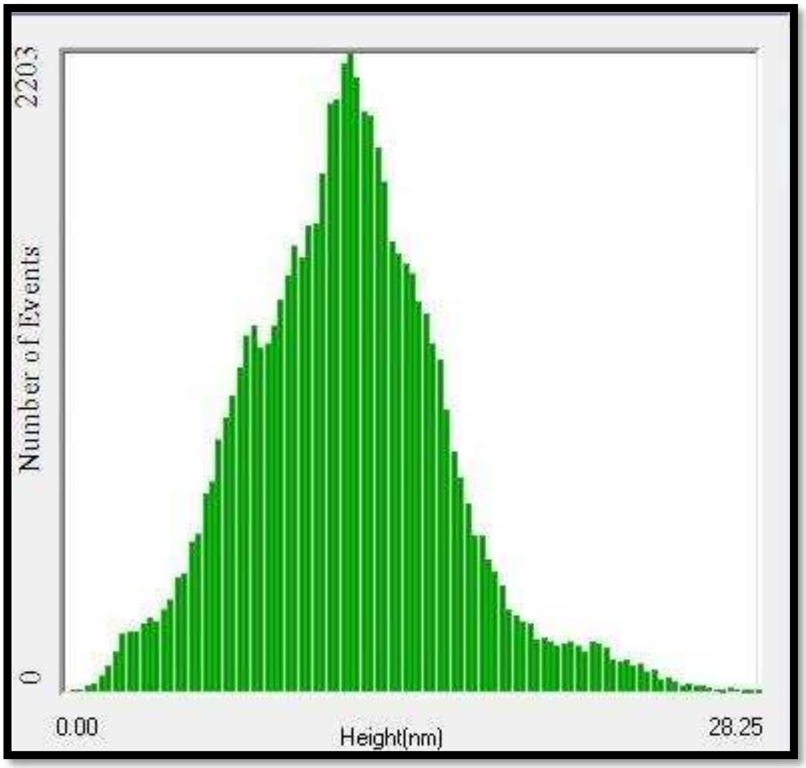

Fig 4.10 AFM HISTOGRAM OF Pt NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

AFM histogram is used to assess the accurate size distribution of synthesized nano particles. Synthesized platinum nanoparticles using stem extract of Brassica Oleracea var.botrytis were unimodel and symmetrical. Surface skewness is the scale to measure symmetry, if skewness is zero or near to zero, the particles have more symmetry. From the figure it can be seen that platinum NPs have more equal symmetry. Surface kurtosis is the scale to measure tails. This kurtosis classified as tailed, light tailed and heavy-tailed were normal distribution, double exponential distribution, Cauchy distribution respectively. From this, synthesized materials were double exponential symmetric distribution. If compared to normal symmetry it has a strong peak, more rapid and heavier tails and the values in-between 3 to 10. Platinum nanoparticles have the highest peak value (43.3308), highest average Roughness (3.1874), height (22.1613), and surface skewness (0.3145). This suggests that nanoparticles synthesized by stem extract is more symmetric, uniformly shaped and used for further applications.

TABLE 4.5 ROUGHNESS AND SURFACE ANALYSIS OF Pt NPS BY AFM

Parameters	**Pt Nps**
Minimum value	0
Maximum value	43.3308
Peak to peak	43.3308
Roughness average	1.5369
Average height	22.1613
Surface skewness	0.3145
Surface kurtosis	14.6479
Plane offset	0.34260
Ironed surface	-1.0000

4.5.2 AFM ANALYSIS OF Pt –Ag NANOPARTICLES

An AFM topographical image of Pt-Ag nanoparticles is shown in figure 4.10 which shows the jack fruit like structure. The average length of the rock structure is 630nm. It may be due to the Platinum Silver bindings. Platinum - Silver nanoparticles have the highest peak value (345.230), highest average Roughness (27.08), height (148.694), and surface skewness (0.2424). This suggests that Pt-Ag nanoparticle synthesized by stem extract is more uniformly shaped. Table 4.6 shows the Roughness and surface analysis of Pt-Ag NPs by AFM.

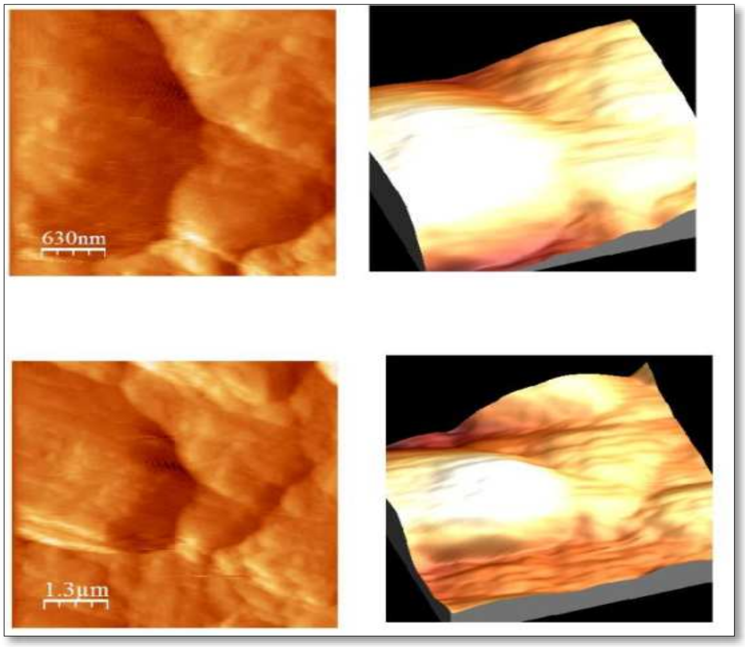

Fig 4.10 AFM IMAGES OF Pt-Ag NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var.botrytis*

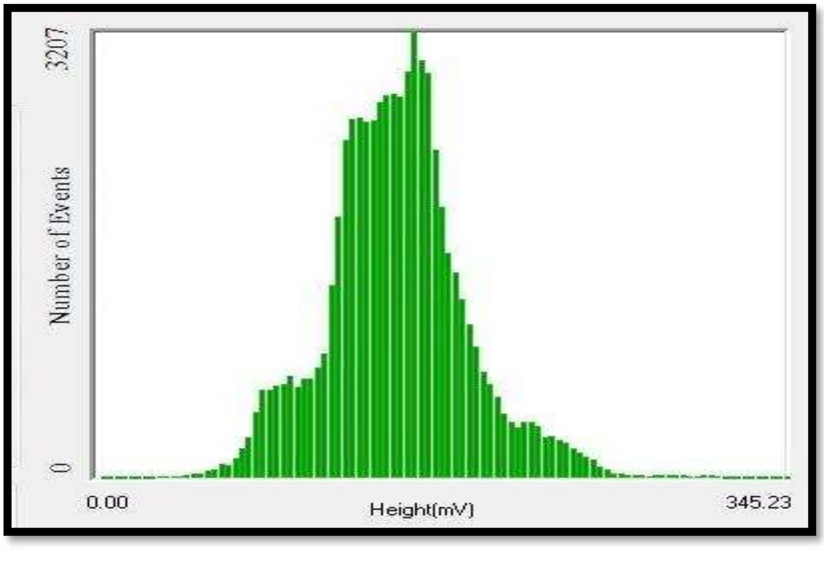

Fig 4.11 AFM HISTOGRAM OF Pt-Ag NANOPARTICLES USING STEM EXTRACT OF *Brassica oleracea var. botrytis*

TABLE 4.6 ROUGHNESS AND SURFACE ANALYSIS OF Pt-Ag NPS BY AFM

Parameters	**Pt Nps**
Minimum value	0
Maximum value	345.230
Peak to peak	345.230
Roughness average	27.08
Average height	148.694
Surface skewness	0.4103
Surface kurtosis	4.3321
Plane offset	0.37608
Ironed surface	-1.0000

4.6 ELECTROCHEMICAL ANALYSIS

4.6.1. CYCLIC VOLTAMMETRIC STUDIES

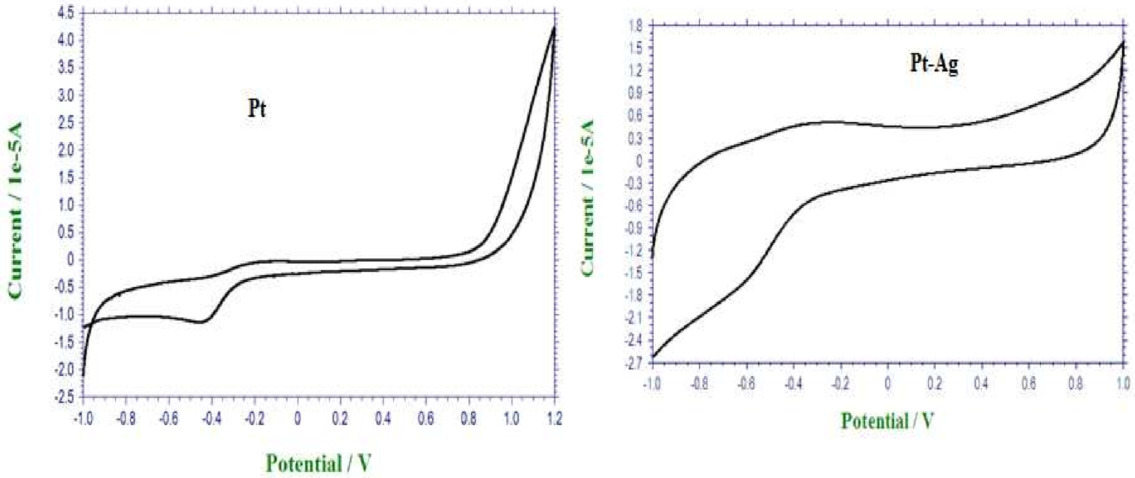

Fig 4.12 CYCLIC VOLTAMATTERIC BEHAVIOUR OF Pt AND BIMETALLIC Pt-Ag NANOPARTICLES

Cyclic Voltammograms of Pt and Pt- Ag nanoparticles are recorded in the potential range from -1.0 to 1.2 V at 100 mV/s . Platinum coated on glassy carbon electrode (GCE), Ag/AgCl and platinum wire electrode were used as working electrode, reference electrode and counter electrode respectively.

Figure 4.12 shows cyclic voltammetric behaviour of Pt and Pt-Ag Nanoparticles. The voltammogram shows one oxidation peak at -0.2673 mV and reduction peak at -0.4377 mV respectively. The good reversible redox behaviour confirms presence of Platinum .The peak was brodenend for Pt-Ag Nanoparticles.

4.6.2 DIFFERENTIAL PULSE VOLTAMMETRY

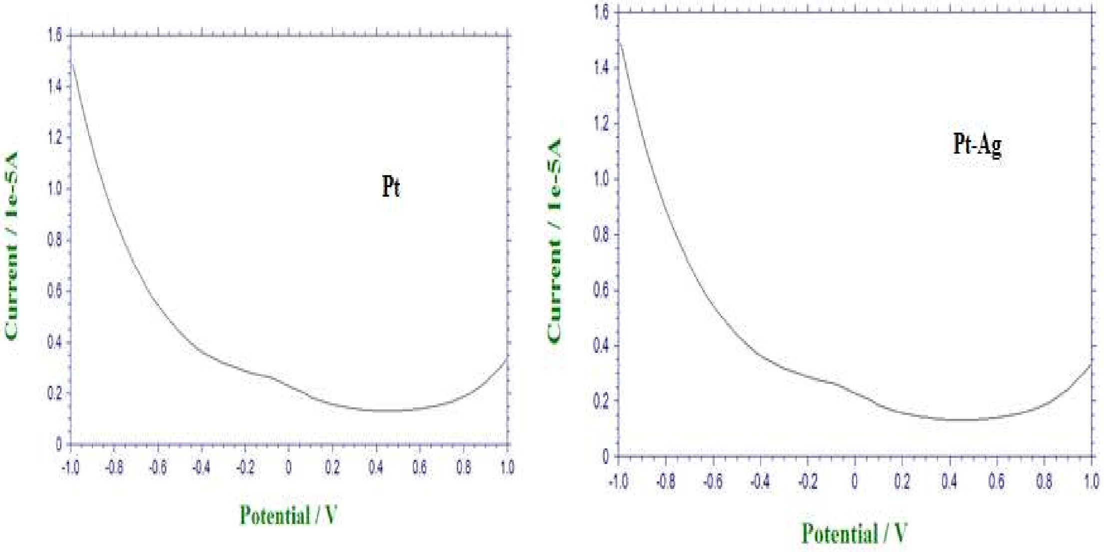

Fig 4.13 DIFFRENTIAL PULSE VOLTAMATTERY BEHAVIOUR OF Pt AND Pt- Ag NANOPARTICLES

DPV analysis carried out for the prepared nanoparticles was shown in Figure 4.13. The above result shows an oxidation peak around 0.2555V which confirms the presence of nanoparticles.

4.6.3 SQUARE WAVE VOLTAMMETRY

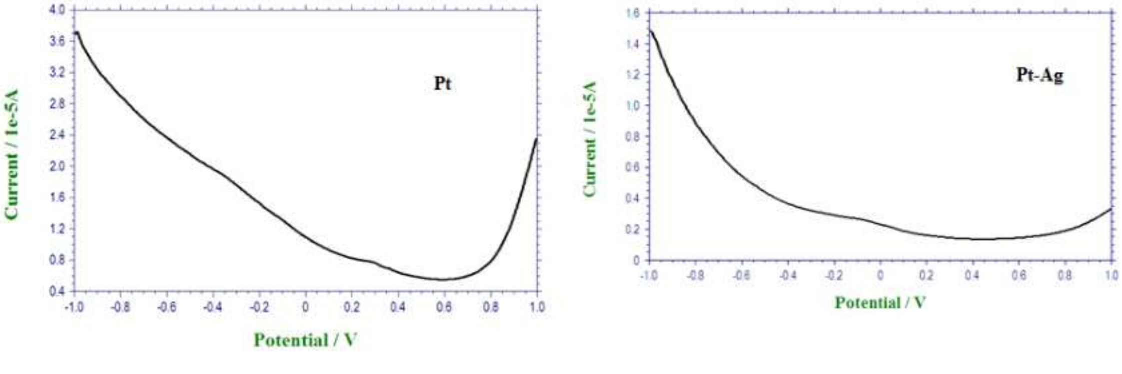

Fig 4.14 SQUARE WAVE VOLTAMATTERY OF Pt AND Pt- Ag NANOPARTICLES

Fig 4.14 represents the square wave voltamattery of Pt and Pt- Ag Nanoparticles which showed that the peak observed for Pt around 0.7mV. The peak was broadenend for the bimetallic Nanoparticles.

4.7 ANTI- MICROBIAL APPLICATIONS OF NANOPARTICLES

The prepared Nanoparticles were analysed for Anti-microbial activities. The inhibitory effect of prepared Nanoparticles against human pathogen *E.coli* and *Bacillus sps* was carried out using Agar well diffusion test.

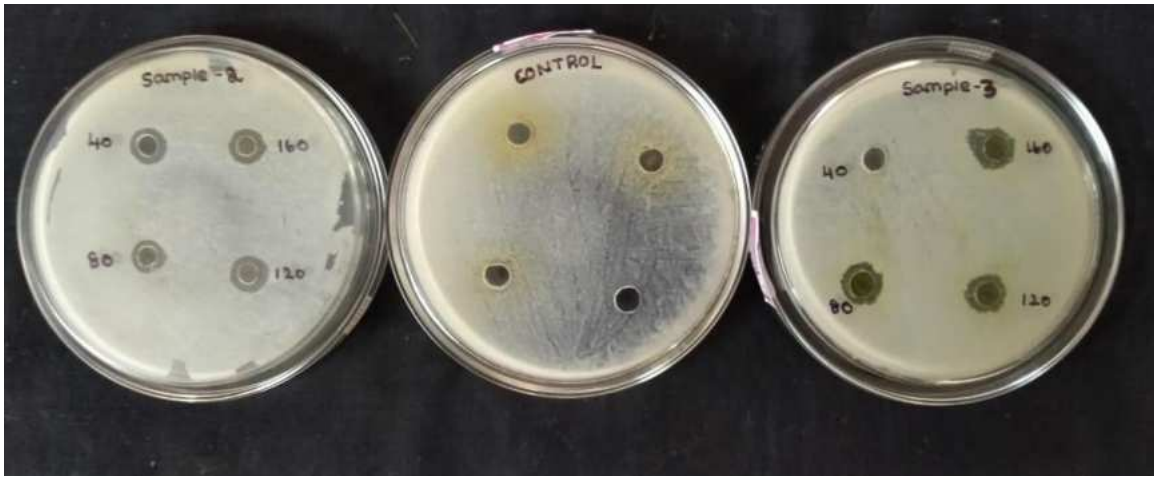

FIG 4.15 ANTI- MICROBIAL APPLICATIONS OF Pt AND Pt- Ag NANOPARTICLES

The antibacterial activities result showed that the Pt-Ag Nanoparticles shows good Inhibition efficiency against *E.coli and Bacillus sps* than Pt Nanoparticles. The results showed that the bimetallic Nanoparticles can be used for further applications. Fig 4.15 illustrates the Anti- Microbial Applications of Pt and Pt- Ag Nanoparticles. Table 4.7 and 4.8 represents the Inhibitory Effect of the extract, Platinum Nanoparticles and Bimetallic Platinum- Silver Nanoparticles against human pathogen *E.coli* and *Bacillus sps* using Agar well diffusion test.

TABLE 4.7 INHIBITORY EFFECT OF STEM EXTRACT, Pt NPS AND Pt-Ag NPS AGAINST HUMAN PATHOGEN *E.coli* USING AGAR WELL DIFFUSION TEST

S.No	**Samples used**	**Organism tested**	**Volume of the sample used (µl)**	**Zone of inhibition (mm)**
1	Extract	*E.coli*	40	0
2	Pt-Ag	*E.coli*	40	8
3	Pt	*E.coli*	40	4
4	Extract	*E.coli*	80	0
5	Pt-Ag	*E.coli*	80	11
6	Pt	*E.coli*	80	7
7	Extract	*E.coli*	120	0
8	Pt-Ag	*E.coli*	120	15
9	Pt	*E.coli*	120	10
10	Extract	*E.coli*	160	0
11	Pt-Ag	*E.coli*	160	19
12	Pt	*E.coli*	160	13

TABLE 4.8 INHIBITORY EFFECT OF PLANT EXTRACT, Pt NPS AND Pt-Ag NPS AGAINST HUMAN PATHOGEN *Bacillus Sps* USING AGAR WELL DIFFUSION TEST

S.No	**Samples used**	**Organism tested**	**Volume of the sample used (µl)**	**Zone of inhibition (mm)**
1	Extract	*Bacillus*	40	0
2	Pt-Ag	*Bacillus*	40	5.7
3	Pt	*Bacillus*	40	2
4	Extract	*Bacillus*	80	0
5	Pt-Ag	*Bacillus*	80	9
6	Pt	*Bacillus*	80	3.5
7	Extract	*Bacillus*	120	0
8	Pt-Ag	*Bacillus*	120	11.4
9	Pt	*Bacillus*	120	7.6
10	Extract	*Bacillus*	160	0
11	Pt-Ag	*Bacillus*	160	14.4
12	Pt	*Bacillus*	160	9..6

CHAPTER 5

CONCLUSION

Researchers 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.

Nanoparticles have been successfully prepared and it was employed in different fields such as water treatment, electronics, catalysis and medicine. Among noble metal based nanoparticles, Pt and Ag have diverse applications. Biogenic synthesis, characterisation and application of Pt NPs and bimetallic Pt-Ag NPs have been discussed in our project report. The plant extracts contain flavonoids, polyphenolics, cannabiniods, terpenes, glycosides, sugars, amine, carbonyl, proteins, aldehyde, amide and alcohols which reduce cap and stabilise the metal ions in the solutions.

In view of promising hope and eco-benign nature, the stem extract of Brassica oleracea var.botrytis were successfully used for the fabrication of Pt NPs and bimetallic Pt-Ag nanoparticles. The nanoparticles synthesised was characterised by Potentiometer, Colorimeter, UV-Vis, FTIR, AFM and Electrochemical workstation techniques. The Pt NPs shows good absorbance at 236 nm and Ag around 450 nm. The existence of different structures and morphologies of Pt NPs and bimetallic Pt-Ag NPs was due to the presence of different bioactive agents in the extract were confirmed from FTIR studies.

The surface morphology of the Pt and bimetallic Pt-Ag NPs were analysed using AFM technique. It was found that the nanoparticles are found to be agglomerated rock like structure and Jack fruit shape. Electrochemical studies were characterised using Cyclic voltammetry, Differential Pulse Voltammetry and Square wave Voltammetry. Antimicrobial activities of the nanoparticles reported from the agar well diffusion test showed that bimetallic Pt-Ag nanoparticles exhibit high inhibition activity than Pt Nanoparticle.

From the technological point of view these obtained silver nanoparticles have potential applications in the biomedical field and this simple procedure has several advantages such as cost-effectiveness, compatibility for medical and pharmaceutical applications as well as large scale commercial production.

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“A study on synthesis methods of silver nanoparticles and its bioapplication.”

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

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ACCREDITED WITH “A+” GRADE BY NAAC

THOOTHUKUDI – 628001

2020 – 2021

DECLARATION

We hereby declare that the project entitled **"A study on synthesis methods of silver nanoparticles and its bioapplication."** 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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CERTIFICATE

This is to certify that project in chemistry entitled **"A study on synthesis methods of silver nanoparticles and its bioapplication."** 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 2020-2021.

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CONTENTS

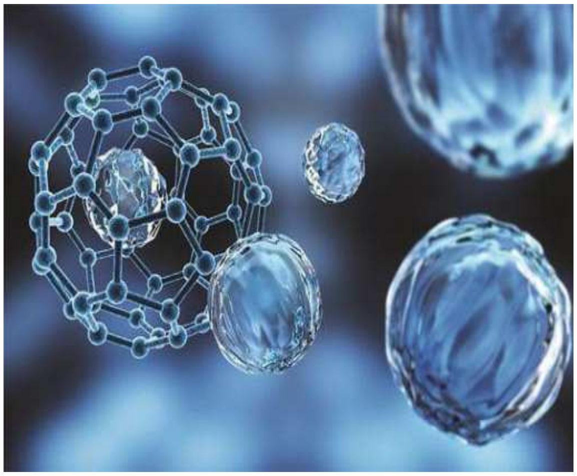
“A study on synthesis methods of silver nanoparticles and its bioapplication.”

Abstract

"A study on synthesis methods of silver nanoparticles and its bioapplications."

In the present study, silver nanoparticles were rapidly synthesized at room temperature by treating silver ions with some vegetables extract. The effect of various process parameters like the reductant concentration, mixing ratio of the reactants and the concentration of silver nitrate were studied. Silver nanoparticles are prepared using the extract of some vegetables like tomato, potato, carrot, beetroot and beans. About 10^{-3} M solution of silver nitrate is prepared as a stock solution. Vegetables were collected from the local markets of Tuticorin. The vegetables were washed, peeled and crushed in a domestic blender to extract the juice. The extracts were centrifuged for 2 minutes at 10,000rpm to get a clear solution and to remove any undesired impurities from it. At first step, to fix the concentration of the vegetable extracts, the extract are measured in the ratio of 0.5ml, 1ml, 1.5 ml, 2 ml, 2.5ml taken in a clean and a dry test tube. About 1ml of silver nitrate solution were added in all the respective test tubes and mixed to get an uniform distribution. Time has been noted from 0 minutes and observation has been done then and there. The exact concentration has been fixed by the appearance of yellowish brown colour. The yellowish brown colour is observed at various concentration for the extracts. After fixing the concentration the time taken for the formation of silver nanoparticles are determined using potentiometric method, from this the exact time at which the nanoparticle synthesised is determined for all the samples. The formation of silver nanoparticles was confirmed by UV-Visible spectra and IR spectra. The silver nanoparticles prepared using the extract are taken and mixed with the soil and the bean seed has been allowed to grow to find the efficacy of the nanoparticles. Hence, we conclude that silver nanoparticles synthesised using vegetable extract can be used as biofertilizer.

INTRODUCTION



A nanoparticle or ultrafine particle is usually defined as a particle of matter that is between 1 to 100 nanometers in diameter. At the lowest range metal particles smaller than 1nm are usually called atom clusters instead. Nanoparticles are usually distinguished from microparticles (1-1000), fine particles (size between 100 to 10,000nm) because their smaller size drives very differ physical or chemical properties, like colloidal properties and optical or electric properties.The properties of nanoparticles often different marketing from those of larger particles of the same substance. Since the typical diameter of an atom is between 0.15 and 0.6nm a large fraction of the nanoparticles material lies within a few atomic diameters from its surface. Therefore, the properties of that surface lays may dominate over those of the bulk material. This effect is particularly strong for nanoparticles dispersed in a medium of different composition since the interaction between the two material at their interface also becomes significant.

Nanoparticle occurs widely in nature and are object of study in many science such as chemistry, physics, geology and biology. Being at the transition between bulk materials and atomic or molecular structure. They often exhibit phenomena that are not observed at either scale. They are important component of atmospheric pollution and key ingredients in many industrialize products such as plastics, metals, ceramics, and magnetic articles. The production of nanoparticles with specific properties is an important branch of nanotechnology.

Importance of nanoparticles

Everyday material:

Nanoscale additives or surface treatments of fabrics can provide lightweight ballistic energy deflection in personal body armour, or can help the resist wrinkling, staining and bacterial growth. Clear nanoscale films on eyeglasses computer and camera displays, windows, and other surfaces can make them water and residue-repellent, anti-reflective, self-cleaning, resistant to ultraviolet or infrared light, anti fog, antimicrobial, starch-resistant, or electrically conductive. Nanoscale materials are beginning to enable washable durable **“smart fabrics”** equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture, and energy harvesting through movement. Light weighting of cars, trucks, airplanes, boats, and space craft could lead to significant fuel savings. Nanoscale additives in polymer composite materials are being used in baseball boats, tennis, rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housing, making them lightweight, stiff, durable and resilient. Carbon nanotube sheets are now being produced for use in next-generation air vehicles.

Environmental importance

Nanotechnology could help to meet the need for affordable, clean drinking water through rapid, low-cost detection and treatment of impurities in water. Engineers have developed a thin film membrane with nanopores for energy-efficient desalination. The molybdenum disulphide (MoS_2) membrane filtered two to five times more water than current conventional filters.

Nanoparticles are being developed to clean industrial water pollutants in ground water through chemical reactions that render the pollutants harmless. This process would cost less than methods that required pumping the water out of the ground.

Synthesis of nanoparticles by green synthesis

Green nanotechnology has two goals producing nanomaterials and products without harming the environment or human health and producing nano-products that provide solutions to environmental problems. It uses existing principles of green chemistry and green engineering to make nanomaterials and nanoproducts without toxic ingredients, at low temperatures using less energy and renewable inputs wherever possible, and using life cycle inputs whenever possible, and using life cycle thinking in all design and engineering stages.

In addition to making nanomaterials and product with less impact to the environment, green nanotechnology also means using nanotechnology to make current manufacturing processes for nano materials and products which are more environmentally friendly. For example, nanoscale membranes can help separate desired chemical reaction products from waste materials from paints. Nanoscale catalysts can make chemical reactions more efficient and less wasteful. Sensors more at the nanoscale can form a part of process control systems, working with nano-enabled information systems. Using alternative energy systems, made possible by nanotechnology, is another way to “**green**” manufacturing processes.

The second goal of green nanotechnology involves developing products that benefit the environment either directly or indirectly. Nanomaterials or products directly can clean hazardous waste sites, desalinate wastes, treat pollutants, or sense and monitors environmental pollutants. Indirectly, lightweight nanocomposites for automobiles and other means of transportation could sauce fuel and reduce materials used for production. Nanotechnology—enabled fuel-cells and light emitting diodes could reduce pollution from energy generation and help lower fossil fuels. Self cleaning nanoscale surface coatings could reduce or eliminate many cleaning chemicals used in regular maintenance routines and enhanced battery life could lead to less material use and less waste. Green nanotechnology takes a broad systems view of nanomaterials and products, ensuring that unforeseen consequences are minimized and that impacts are antedated throughout the fuel lifecycle. Nanoparticles used instead of larger particle, Materials made up of nanoparticle have a relative larger surface area when compared to the same volume of material made upof bigger particles. Therefore, materials made of nanoparticles have a much greater surface area per unit volume ratio compared with the material made up of bigger particles.

Green Synthesis of copper nanoparticles using *Piper retrofractum vahl* extract by Suci Amaliyah *et al*.,.The reaction was assisted by sonication stirring. The morphology and structure of synthesized CUNPS were characterized by UV-Vis, FT-TR, SEM-EDS, TEM and XRD. (1) Gold Nanoparticles were prepared using four different plant extracts as reducing and stabilizing agents by Paz Elia *et al*.,. The extracts were obtained from *Salvia officinalis, Lippia citriodora, pelargonium graveolens and punica granatum*. (2) Green Synthesis of silver nanoparticles using seed extract of *Alpinia Katsumadai* by Yangquing He *et al*.,. The results confirmed that *Alpinia Katsumadaibis* a potential biomaterial for synthesizing AgNPs with applications in antibacterial and antioxidant agents.(3) Green Synthesis of silver nanoparticles using leaf extracts of *Clitoria ternatea and Solanum nigrum* by Narayanaswamy krithiga *et al*.,. The purpose of the study is to synthesize and characterize the plant mediated silver nanoparticles and to investigate the shape and size of nanoparticle by X –ray diffraction and scanning electron microscope studies. (4) Green Synthesis of silver nanoparticles using *Azadirachta indica* aqueous leaf extract by Shakeel Ahmed *et al*.,. Techniques used to characterize synthesized nanoparticles are DLS, photoluminescences TEM and UV-Visible Spectrophotometer.(5)Biogenic synthesis of multi applicative silver nanoparticles by using *Ziziphus jujuba* leaf extract by NL Garade *et al*.,. The synthesised AgNPs were characterised by means of UV-Vis, XRD, FT-IR, TEM, DLS and zeta potential. Zeta potential indicates these particles are high stable in colloidal structure. (6) Synthesis of eco-friendly silver nanoparticle from plant latex used as an important taxonomic tool for phylogenetic interrelationship advances in biosearch by Amal Kumal Mondal *et al*.,. Nanoparticles synthesis proved under UV-Vis absorption spectroscopy. The nanoparticle solutions are kept under light proof condition. (7) Plant extract mediated synthesis of silver and gold nanoparticles and antibacterial activity against clinically isolated pathogens by D.Mubaraka *et al*.,.The nanoparticles were characterized by FTIR, SEM, equipped with EDS. (8) Green Synthesis of metallic nanoparticles via biological entities by Monaliben Shah *et al*.,. Nanoparticles production without the use of harsh, toxic and expensive chemicals. Commonly used in physical and chemical process. (9) Bio-fabrication of silver nanoparticles using the leaf extract of an ancient herbal medicine dandelion, evalution of their antioxidant, anticancer by Rijuta G. Saratate *et al*.,. HR-TEM size of AgNPs ranging between 5 and 30nm. (10) Plants emerging as nanofactories towards facile route in synthesis of nanoparticles by Syed Barker *et al*.,. Plant mediated nanoparticles synthesis has led to a remarkable progress via unfolding a green synthesis protocol towards nanoparticles synthesis. (11) Completely green synthesis and stabilization of metal nanoparticles by Poovathintodiyil Raveendrah *et al*.,. By gentle heating of an aqueous starch solution containing silver nitrate and glucose produce monodisperse, starched silver nanoparticles.(12) Synthesis of silver nanoparticles using *Acalypha indica* leaf extracts and its antibacterial activity against war borne pathogens by C. Krishnaraj *et al*.,. From high-resolution transmission electron microscopy analysis, the size of the silver nanoparticles was measured 20-30 nm. (13) Bio reduction of chloroaurate ions by geranium leaves and its endophytic fungus yields gold nanoparticles of different shapes by S. Shiv Shankar *et al*.,. In the case of gold nanoparticles synthesized using geranium leaves, the reducing and capping agents appear to be terpenoids. (14) Stress responses of aquatic plants to silver nanoparticles by Lin Yuan *et al*.,. Study of the phytotoxicity of AgNPs to aquatic plants by measuring physiologic and enzymatic responses to AgNP exposure. (15) Synthesis of silver nanoparticles in photo synthetic plants by Ram Prasad *et al*.,. The synthesis of nanoparticles with special emphasis on the use of plant parts. (16) Plant mediated biogenic synthesis of AgNPs and their antimicrobial activity by L.J.Frewer *et al*.,. The various plant parts extract mediated synthesis of AgNPs and their applications as antimicrobial. (17) Applications of silver nanoparticles in plant protection by Nomita Gupta *et al*.,. Synthesis of silver nanoparticle by physical and chemical methods. (18) Biosynthesized silver nanoparticles as a nanoweapon against phytopathogens exploring their scope and potential in agriculture by Sandhya Mishra *et al*.,. Potential application of AgNPs for plant disease management. (19) In vitro biosynthesis and genotoxicity bioassay of silver nanoparticles using plants by Kamal K Panda *et al*.,. Colloidal AgCl was identified to be the least cytotoxic and genotoxic. (20)

WASTAGE OF VEGETABLES DURING TRANSPORTATION

This section discusses the transportation related causes of the losses and wastage in the logistics and supply chain of perishable fresh food produce. It has been observed that, losses in transportation are one of the highest and major operational causes of wastage in Perishable food supply chain (Murthy *et al*., 2009) followed by inventory management (Shukla & Jharkharia, 2013). Rehman *et al*. (2007) found in his study that the losses mainly occurred during the transportation of the fresh produce to the market. Poor and inadequate transportation facilities contribute more to this problem (Gauraha & Thakur, 2008; Sharma & Singh, 2011; Kader, 2005). Singh *et al*., (2008) attempts to assess the extent and magnitude of post-harvest losses in Uttar Pradesh and found transportation and distribution of agricultural commodities as the factor responsible for such losses. Author found transit loss contributing around 24 % of the total loss. In transportation, time being a critical factor to deliver the fresh produce in a timely manner and in a proper quality. At farm level also there are various losses due to the ignorance of time factor. Verma & Singh (2004) found delays in moving the harvested fresh produce to the market as the reason of losses at the farm level. There are inherent difficulty of collecting and transporting small quantities of fresh produce from the numerous small farms results to high post-harvest losses. Rehman *et al*., (2007) observed during the survey that most of the farmer picked their crops in the morning, packed in wooden crates and using pickup/truck as a mode of transportation to transport their produce to the outside market. Loss at Market level is mainly due to the transportation practices followed in marketing channels (Verma & Singh, 2004). Mathi (2007) studied the supply chain management of Guava in Allahabad, Uttar Pradesh and found ordinary transportation, irresponsible driving and rough roads as one of the reasons for postharvest losses. Some crops required special facilities like controlled temperature transportation and unavailability of such is the reason for the marketing loss (Ozcan, 2007). Products are handled roughly and transported in open trucks. It takes twenty four hours or more to the fresh produce to arrives at the retailer, typically an open market vendor or a pushcart after harvesting. As it is piled into large cane baskets or on to truck beds without cushioning or packaging, that leaves it exposed to the sun in temperature and deteriorates the quality of the fresh produce (Jain, 2007). Faulty system of transport and delayed delivery of fresh produce causes wastage in the retail market (CEAGESP, 2002). It reaches the store shelf too late and with a short remaining shelf life which causes wastage in the perishable food supply chain at the retailer level (Mena *et al*., 2011) and additionally results to the penalty (Shukla & Jharkharia, 2013). The bulkiness in the transportation of the fresh produce makesthe handling and transportation a difficult task, leading to huge wastage of around Rs. 23,000 crore or nearly 35 percent of the total production (CII, 1997). Transportation related challenges are very high in the India because of unavailability of well transportation mode, high cost of transportation, lack of temperature controlled vehicle for the movement of goods etc. (Negi & Anand, 2015) (21).Adoption of improved transportation method, which strengthen the need for specialized transportation vehicles like reefer trucks for perishable commodities which can maintain the quality of fresh products and enhance the shelf life and will also results in reducing the transit losses (Murthy *et al*., 2007) .

Objectives

The present investigation was carried out with the following objectives:

- To study the synthesise of the silver nanoparticles using extracts of some vegetables by various methods like Potentiometric, Calorimetric methods.
- To characterize the synthesized silver nanoparticles by UV,IR methods.
- To study the applications of the synthesized nanoparticles.

Experimental Part

Vegetables chosen for experiment

Tomato

Kingdom: Planto

Clade: Tracheophytes

Order: Solanales

Family: Solanaceae

Genus: solanum

Species: S.lycopersicum

Binomial name: Solanumlycopersicum

Tomatoes are the major dietary source of the antioxidant cycopene, which has been linked to many health benefits, including reduced risk of heart diseases and cancer. They are a great source of potassium, folate, vitamin C and vitamin K. Consumption of tomatoes and tomato based products has been linked to improved skin health and a lower risk of heart disease and cancer.

Potato

Scientific name: Solanum tuberosum

Rank: Species

Genus: Solanum

Clade: Tracheophytes, Angiosperms, Eudicots, Asterids

Species: *S.tuberosum*

Family: *Solanaceae*

Kingdom: Plantae

Potatoes are rich in vitamins, minerals and antioxidants, which make them very healthy. Potatoes are used to improve blood sugar control, reduce heart disease risk and high immunity. Carbs are the main dietary component of potatoes. Those cooled down after boiling may provide some resistant starch, which can improve gut health. Potatoes also contain small amounts of high-quality protein. Potatoes are a good source of several vitamins and minerals, including potassium, folate, and vitamins C and B6.

Carrot

Botanical name: Daucuscarota

Family: Apiaceae

Kingdom: Plantae

Clade: Tracheophytes, Angiosperms, Eudicots, Asterids

Order: Apiales

Carrots are an excellent source of vitamin A and specifically beta carotene which is responsible for their orange colour. Carrots also offer potassium, calcium, magnesium, phosphorus, folate, vitamin E and vitamin K. Carrots are a particularly good source of beta carotene, fiber, vitamin K1 and antioxidants. They also have a number of health benefits. They are a weight-loss-friendly food and have been linked to lower cholesterol levels and improved eye health. Carrots are about 10% carbs, consisting of starch, fiber, and simple sugars. They are extremely low in fat and protein.

Beetroot

Scientific name: Beta vulgaric subsp. Vilgarisconditiva group

Cultivar group: contiva group

Rank: Cultivar group

Species: Beta vulgaris

Origin: Beta vulgaris subsp.maritima

Beetroot is of exceptional nutritional value especially the greens, which are rich in calcium, iron, and vitamins A and C. Beetroots are an excellent source of fibre, manganese and potassium. Beetroot provides a wide range of possible health benefits, such as reducing blood pressure, improving digestion, and lowering the risk of diabetes. Beetroots are high in several beneficial plant compounds, especially betanin, vulgaxanthin, and inorganic nitrates. In particular, inorganic nitrates are associated with reduced blood pressure. Beetroots can reduce risk of heart disease and other ailments. This root veggie can also improve oxygen use, stamina, and exercise performance.

Beans

Kingdom: Plantae

Family: Fabaceae

Order: Fabales

Clade: Trachephytes, Angiosperms, Eudicots, Rosids

Genus: Phaseolus

Species: P.vulgaris

Binomial name: Phaseolus vulgaris

A bean is the seed of one of several genera of flowering plant family Fabaceae, which are used as vegetables for human or animal food. They can be cooked in many different ways including boiling, frying, and baking, and are used in many traditional dishes throughout the world. They are excellent sources of dietary fibre, protein, vitamin B and many other vitamins and minerals. They can be help to reduce blood sugar, improve cholesterol levels and help maintain a healthy guts.

Preparation of the vegetable extract for synthesis of Ag Nanoparticles

About 17 mg of the silver nitrate Himedia, Mumbai, India, was dissolved in 100 ml of distilled water (1×10^{-3} M). The extracts for study is isolated from the vegetables like tomato, potato, carrot, beetroot and beans by crushing it in the form of juice using domestic blende. The stock solution of extract of about 0.05% was prepared. The silver nanoparticles are synthesized by adding about 1ml, 1.5ml, 2ml, 2.5ml, 3ml, 3.5ml etc., of the vegetable extract to each of 5 ml silver nitrate solution.

By visual method the formation of brownish yellow colour shows the formation of silver nanoparticles. This is due to the reduction of Ag^+ ions present in the solution. The formation of silver nanoparticle was confirmed by measuring the absorbance around 420nm in the UV-Visible spectrophotometer. Further the silvernanoparticles were characterized by IR studies. The time taken for synthesizing the silver nanoparticles was studied by potentiometric method.

POTENTIOMETERIC METHOD:

The vegetables such as tomato, potato, carrot, beetroot and beans are crushed in pestle and mortar. About 20ml of the extract is taken in a beaker and it is diluted with water to 40ml. . The Calomel electrode and Silver electrode are connected to the respective terminals of the potentiometer and are dipped in the extract taken in the beaker and titrated against silver nitrate solution taken in the burette. $AgNO_3$ solution taken in the burette is added interms of 0.5ml to the extract and stirred well. The emf values are noted respectively and the timing is also noted for each reading. The reading is noted until a constant value of emf is obtained. From this method we can fix the concentration at which the silver nanoparticle is synthesised and we can know the time taken for the synthesis of silver nanoparticles A graph is plotted by taking the emf value and time taken for synthesis in the x-axis and the volume of AgNO3 in the y-axis.

COLORIMETERIC METHOD:

The samples of the vegetable extract of about 5ml is pipette out in a provided test tubes and about 0.5ml, 1ml,1.5ml, 2ml, 2.5ml of $AgNO_3$ solution is added to it. The solution is allowed to stand for few minutes for uniform distribution. The optical density is measured in the colorimeter by keeping the nm range at 420. The absorbance values are noted. A graph is drawn between the concentration along x-axis and the optical density along y-axis.

Characterization of synthesised silver nanoparticles

UV- Visible spectral analysis

Synthesis of AgNPs solution with the vegetable samples was observed by UV-Visible spectroscopy. The absorption spectra of synthesized AgNPs were measured using JASCO V-600 Diffuse reflectance spectrophotometer with samples in Quartz cuvette operated at a resolution of 1 nm. Naturally synthesized Ag NP's gave sharp peaks around 420nm in the visible region of the electromagnetic spectrum.

Fourier Transform- Infrared spectroscopy (FT-IR) analysis

FT-IR spectra of samples were measured using a Thermo Scientific Nicolet iS5 FT-IR spectrometer. The FT-IR spectrum of AgNPs after synthesis was analyzed and the possible functional groups for the formation of silver nanoparticles were recorded.

Application of Synthesised Silver nanoparticle:

The synthesised silver nanoparticles were utilised as a manure for growth of the plants. The synthesised silver nanoparticles are mixed with the soil collected from Thoothukudi area and some seeds are germinated for growth. Nearly equal volumes of soil is collected in separate cups and 10ml of vegetable samples under study were taken and mixed to it. During soaking the silver nanoparticles got impregnated within the soil and they aided for the enhancement of growing the seed. Then seeds of same variety is allowed to grow in the soil and the growth of the plant is monitored by measuring the length of the plant grown.

Results and Discussion

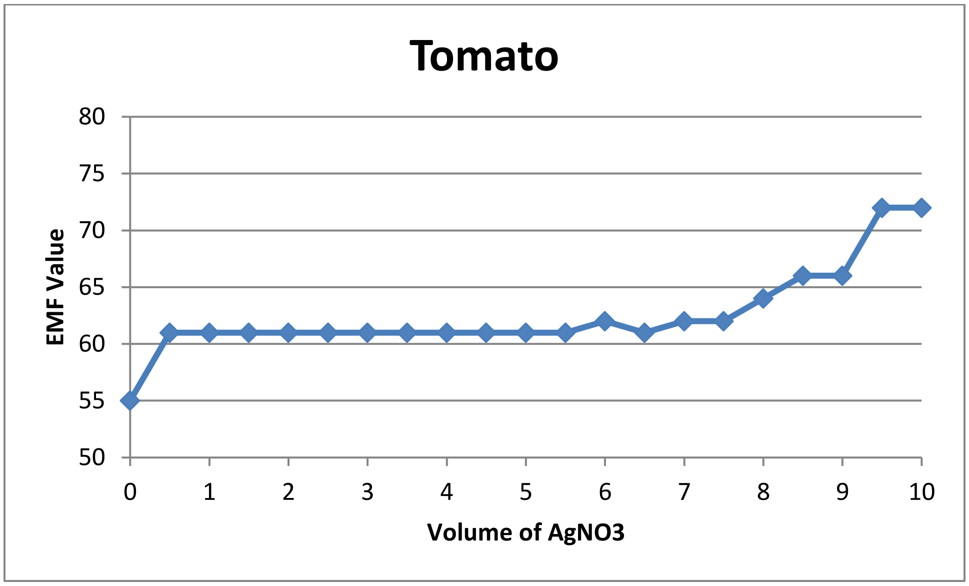
Visual method

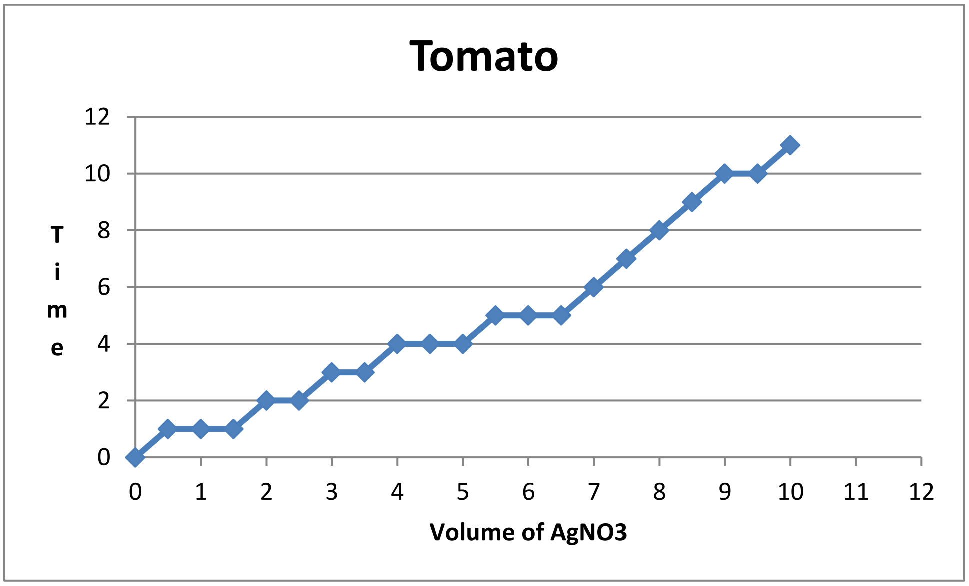
During synthesis of silver nanoparticles the colour of the solution turned from colourless to yellowish brown showing the formation of silver nanoparticles.

Potentiometric Mehod

Tomato:

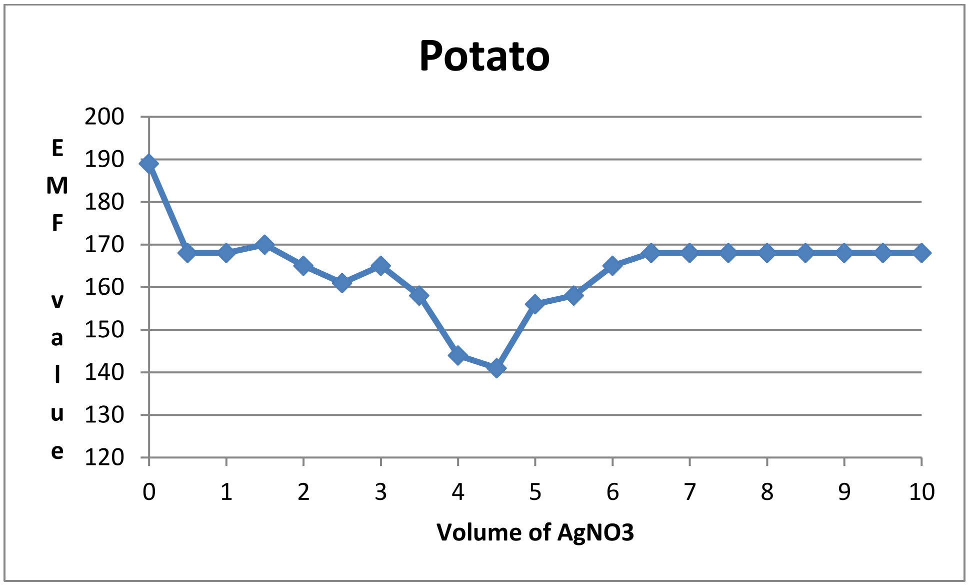
S.No	Volume of $AgNO_3$ (ml)	EMF Value	Time (min)
1.	0	55	0
2.	0.5	61	1
3.	1.0	61	1
4.	1.5	61	1
5.	2.0	61	2
6.	2.5	61	2
7.	3.0	61	3
8.	3.5	61	3
9.	4.0	61	4
10.	4.5	61	4
11.	5.0	61	4
12.	5.5	61	5
13.	6.0	62	5
14.	6.5	61	5
15.	7.0	62	6
16.	7.5	62	7
17.	8.0	64	8
18.	8.5	66	9
19.	9.0	66	10
20.	9.5	72	10
21.	10.0	72	11

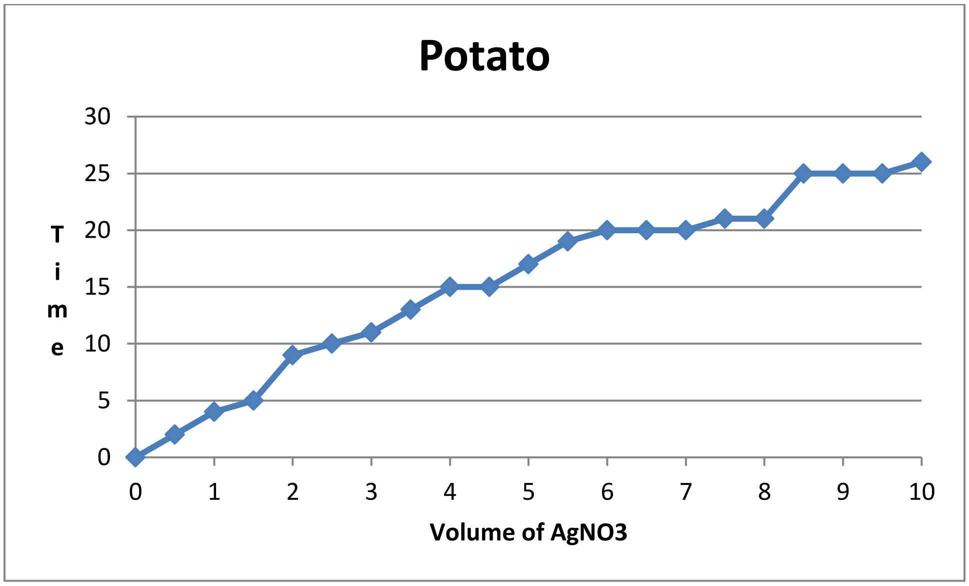

Tomato
EMF Value
80
75
70
65
60
55
50
0
1
2
3
4
5
6
7
8
9
10
Volume of AgNO3


Tomato
Time
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Volume of AgNO3

Potato:

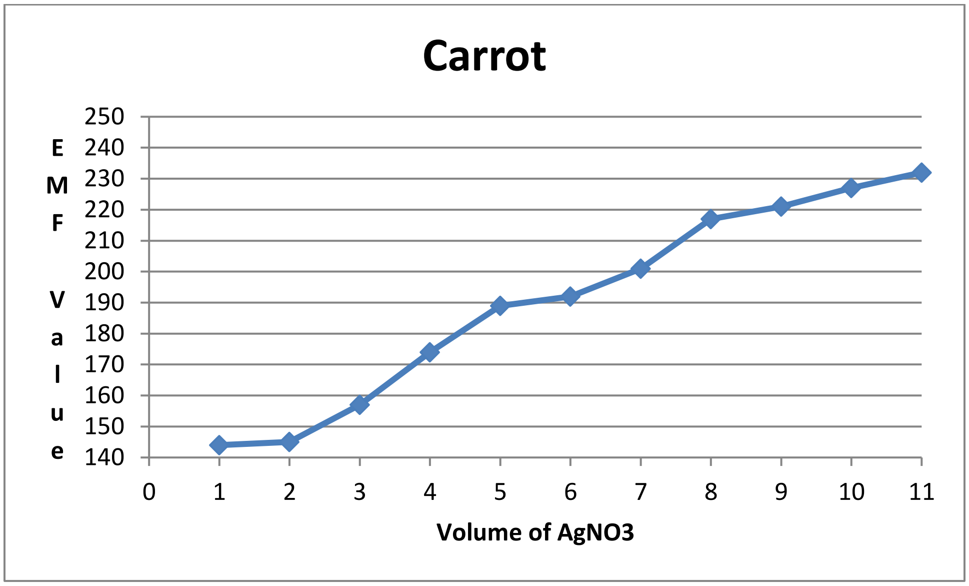
S.No	Volume of $AgNO_3$(ml)	EMF Value	Time (min)
1.	0	189	0
2.	0.5	168	2
3.	1.0	168	4
4.	1.5	170	5
5.	2.0	165	9
6.	2.5	161	10
7.	3.0	165	11
8.	3.5	158	13
9.	4.0	144	15
10.	4.5	141	15
11.	5.0	156	17
12.	5.5	158	19
13.	6.0	165	20
14.	6.5	168	20
15.	7.0	168	20
16.	7.5	168	21
17.	8.0	168	21
18.	8.5	168	25
19.	9.0	168	25
20.	9.5	168	25
21.	10.0	168	26

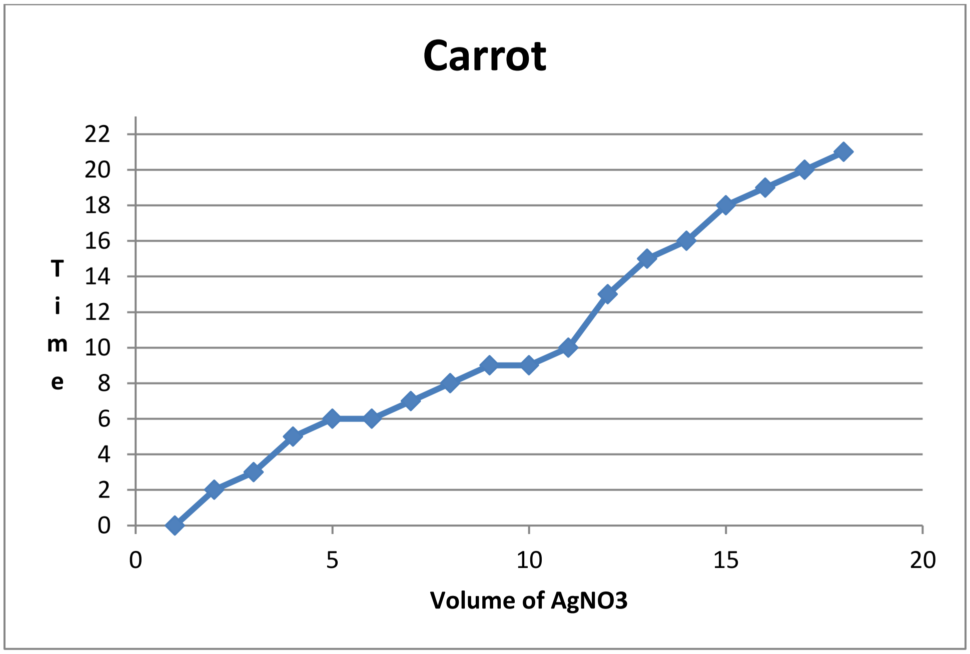

Potato
EMF value
200
190
180
170
160
150
140
130
120
0
1
2
3
4
5
6
7
8
9
10
Volume of AgNO3


Potato
Time
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
9
10
Volume of AgNO3

Carrot:

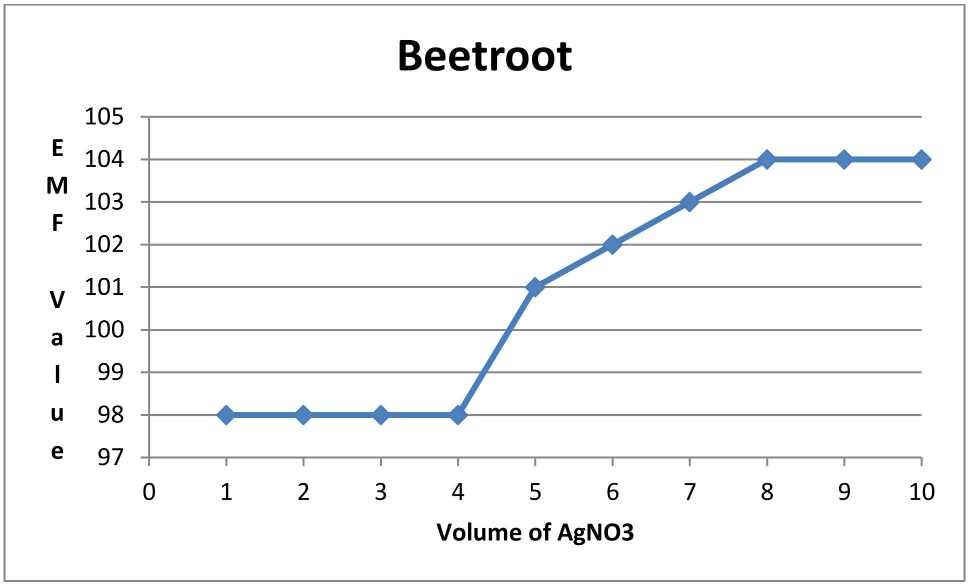
S.No	Volume of $AgNO_3$ (ml)	EMF Value	Time (min)
1.	0	144	0
2.	0.5	145	2
3.	1.0	157	3
4.	1.5	174	5
5.	2.0	189	6
6.	2.5	192	6
7.	3.0	201	7
8.	3.5	217	8
9.	4.0	221	9
10.	4.5	227	9
11.	5.0	232	10
12.	5.5	229	13
13.	6.0	227	15
14.	6.5	227	16
15.	7.0	227	18
16.	7.5	227	19
17.	8.0	227	20
18.	8.5	227	21
19.	9.0	227	21
20.	9.5	227	21
21.	10.0	227	21

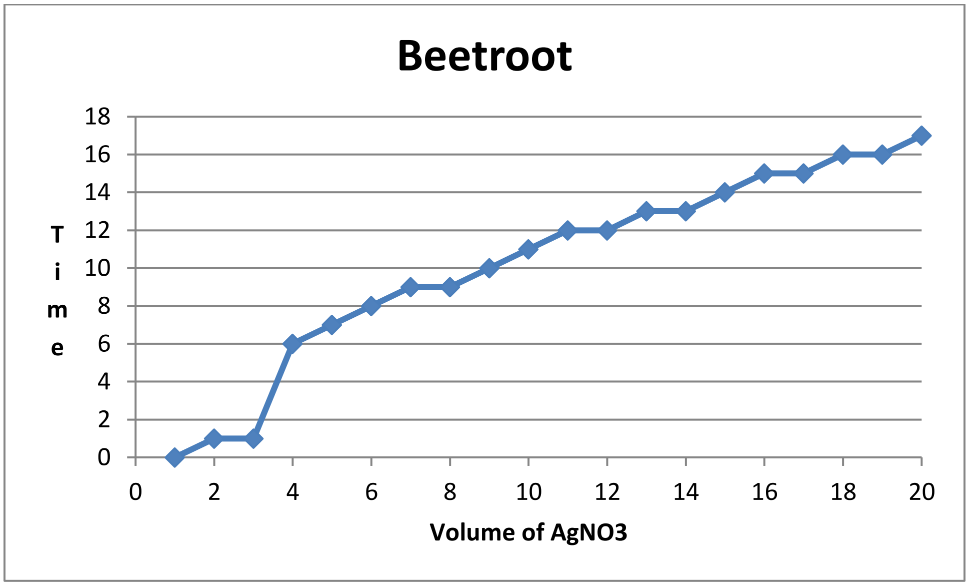

Carrot
EMF Value
250
240
230
220
210
200
190
180
170
160
150
140
0
1
2
3
4
5
6
7
8
9
10
11
Volume of AgNO3


Carrot
Time
22
20
18
16
14
12
10
8
6
4
2
0
0
5
10
15
20
Volume of AgNO3

Beetroot:

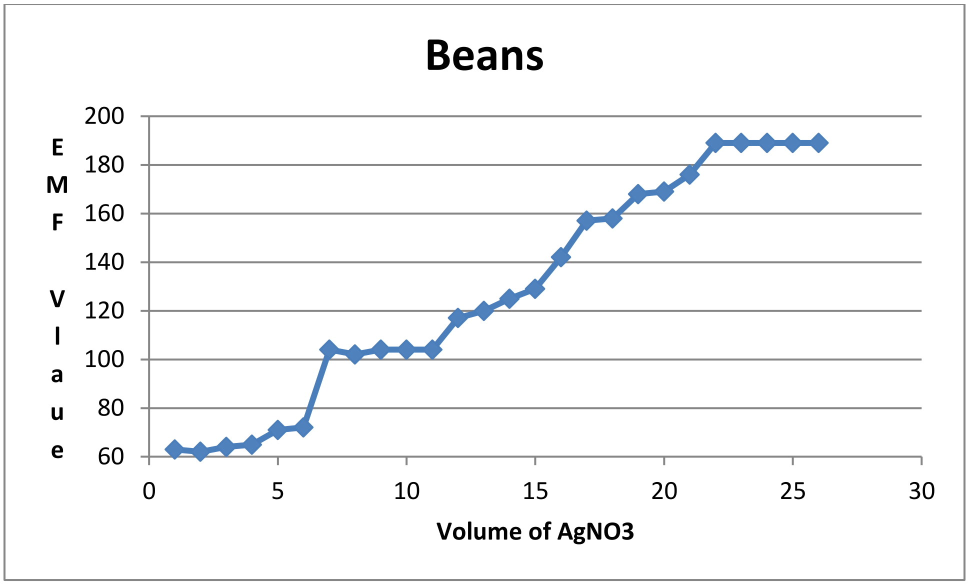
S.No	Volume of $AgNO_3$ (ml)	EMF Value	Time (min)
1.	0	98	0
2.	0.5	98	1
3.	1.0	98	1
4.	1.5	98	6
5.	2.0	101	7
6.	2.5	102	8
7.	3.0	103	9
8.	3.5	104	9
9.	4.0	104	10
10.	4.5	104	11
11.	5.0	104	12
12.	5.5	104	12
13.	6.0	104	13
14.	6.5	104	13
15.	7.0	104	14
16.	7.5	104	15
17.	8.0	104	15
18.	8.5	104	16
19.	9.0	104	16
20.	9.5	104	17
21.	10.0	104	17

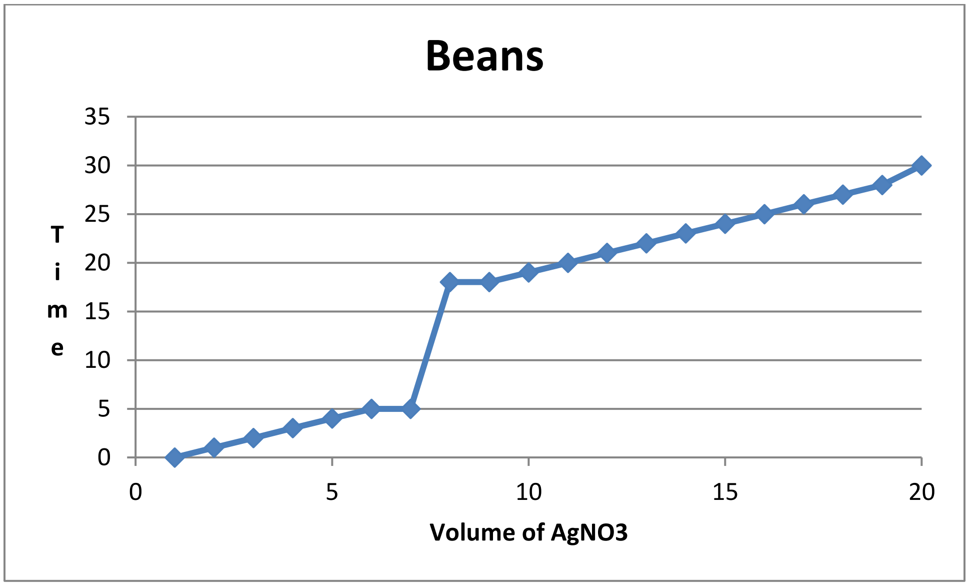

Beetroot
EMF Value
105
104
103
102
101
100
99
98
97
0
1
2
3
4
5
6
7
8
9
10
Volume of AgNO3


Beetroot
Time
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
Volume of AgNO3

Beans:

S.No	Volume of $AgNO_3$ (ml)	EMF Value	Time (min)
1.	0	63	0
2.	0.5	62	1
3.	1.0	64	2
4.	1.5	65	3
5.	2.0	71	4
6.	2.5	72	5
7.	3.0	104	5
8.	3.5	102	18
9.	4.0	104	18
10.	4.5	104	19
11.	5.0	104	20
12.	5.5	117	21
13.	6.0	120	22
14.	6.5	125	23
15.	7.0	129	24
16.	7.5	142	25
17.	8.0	157	26
18.	8.5	158	27
19.	9.0	168	28
20.	9.5	169	30
21.	10.0	176	30
22.	10.5	189	31
23.	11.0	189	31
24.	11.5	189	31
25.	12.0	189	31


Beans
EMF Vlaue
200
180
160
140
120
100
80
60
0
5
10
15
20
25
30
Volume of AgNO3

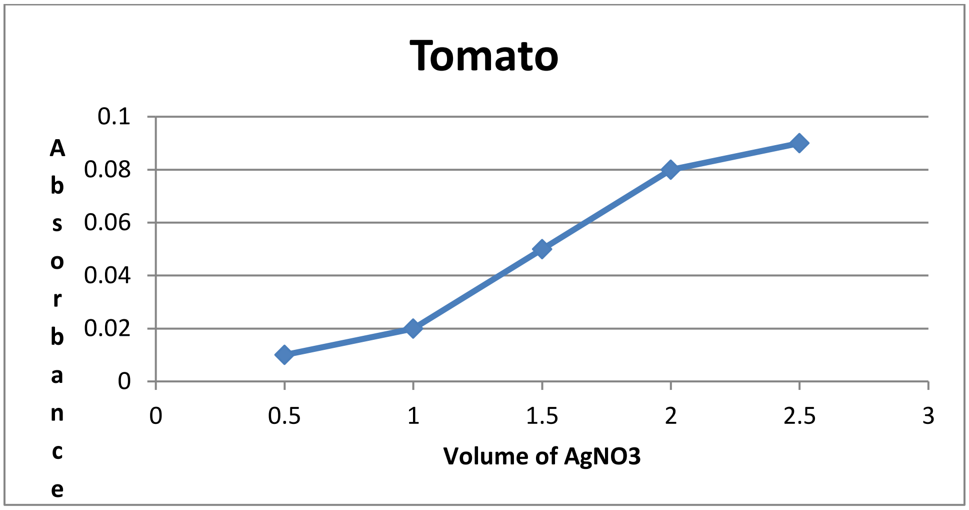

Beans
Time
35
30
25
20
15
10
5
0
0
5
10
15
20
Volume of AgNO3

From the above reading the formation of the silver nanoparticles is noted by the constant emf value and the time is recorded for the formation of the nanoparticles and in addition the exact volume of Silver nitrate needed for formation is also noted. From the above reading the formation of synthesis of silver nanoparticle for tomato the volume of silver nitrate required is around 0.5ml and it is formed around 1 minute with the constant emf value of 61;for potato the volume of silver nitrate required is around 6.5 ml and it is formed around 20 minutes with the constant emf value of 168; for carrot the volume of silver nitrate required is around 6ml and it is formed around 15 minutes with the constant emf value of 227; for beetroot the volume of silver nitrate required is around 3.5ml and it is formed around 9 minutes with the constant emf value of 104; for beans the volume of silver nitrate required is around 10.5ml and it is formed around 31 minutes with the constant emf value of 189.

Calorimetric Analysis

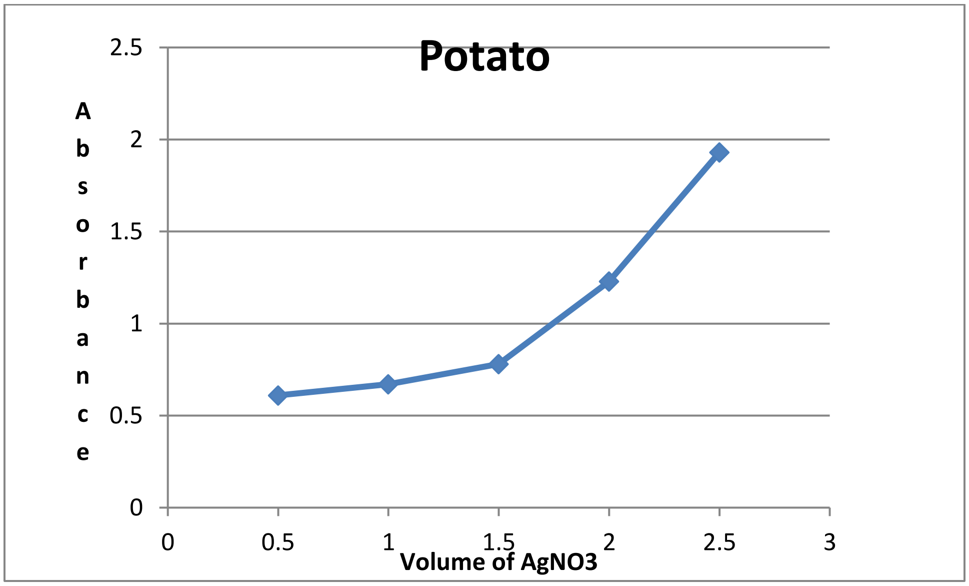
Tomato

S.No	Volume of $AgNO_3$	Colorimeter Reading (Abs)
1	0.5	0.01
2	1	0.02
3	1.5	0.05
4	2	0.08
5	2.5	0.09



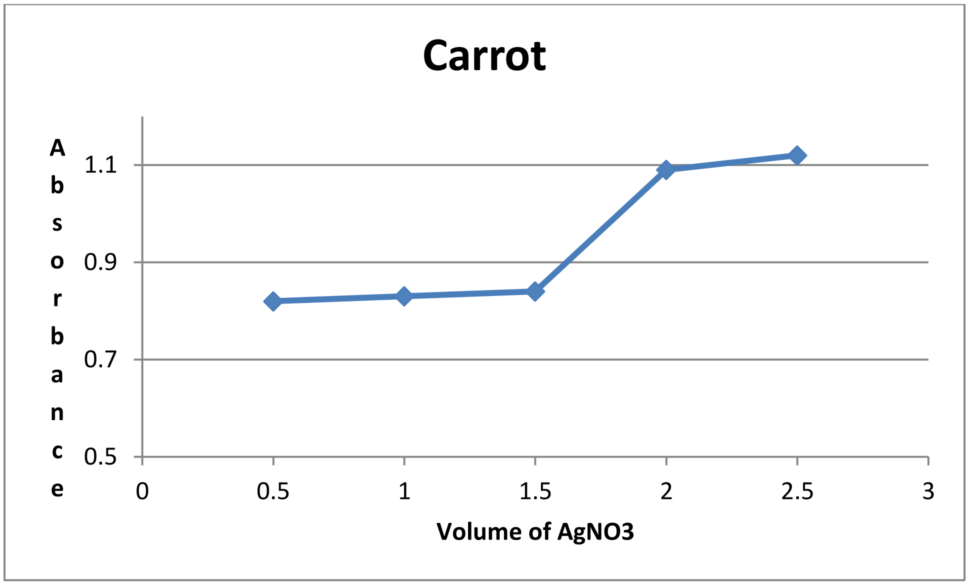
Potato:

S.No	Volume of $AgNO_3$	Colorimeter Reading (Abs)
1	0.5	0.61
2	1	0.67
3	1.5	0.78
4	2	1.23
5	2.5	1.93



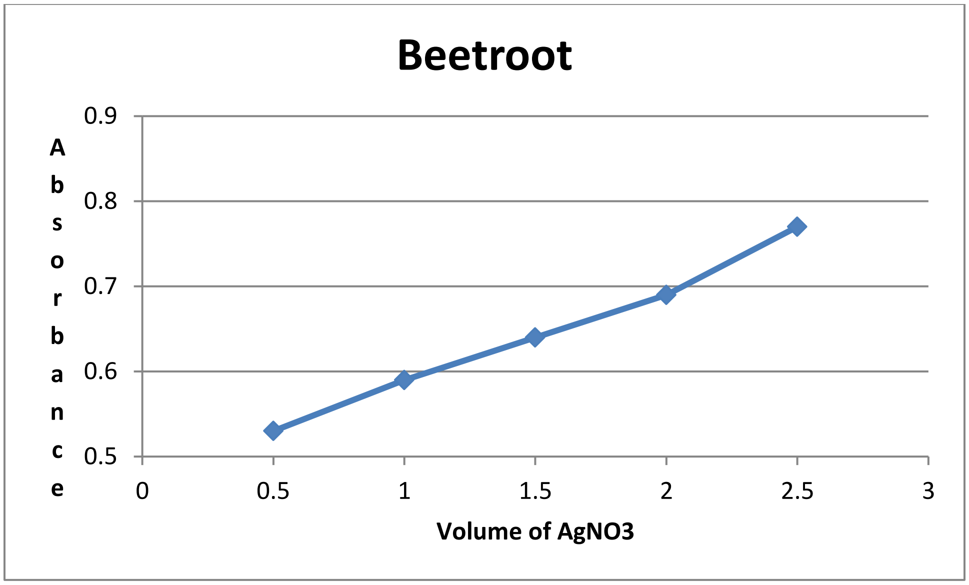
Carrot

S.No	Volume of AgNO$_3$	Colorimeter Reading (Abs)
1	0.5	0.82
2	1	0.83
3	1.5	0.84
4	2	1.09
5	2.5	1.12



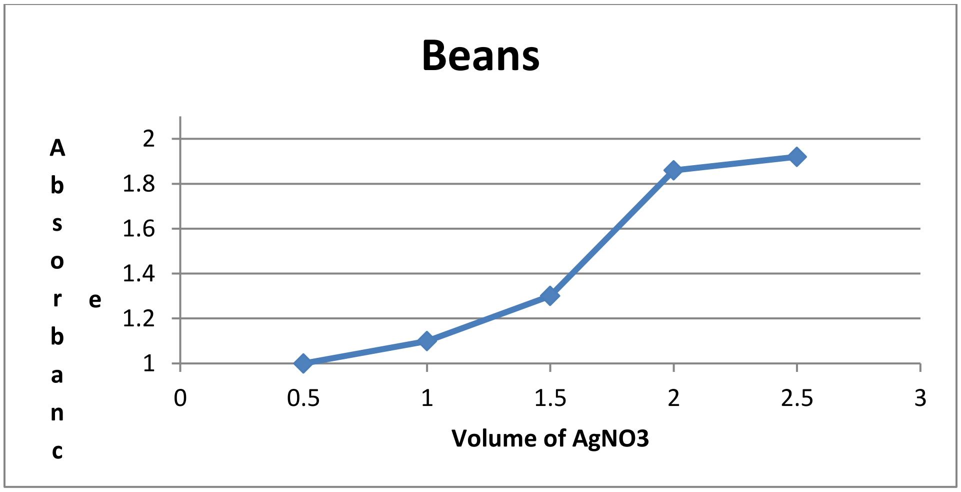
Beetroot

S.No	Volume of AgNO$_3$	Colorimeter Reading (Abs)
1.	0.5	0.53
2.	1.0	0.59
3.	1.5	0.64
4.	2.0	0.69
5.	2.5	0.77



Beans:

S.No	Volume of AgNO$_3$	Colorimeter Reading (Abs)
1	0.5	1
2	1	1.1
3	1.5	1.3
4	2	1.86
5	2.5	1.92

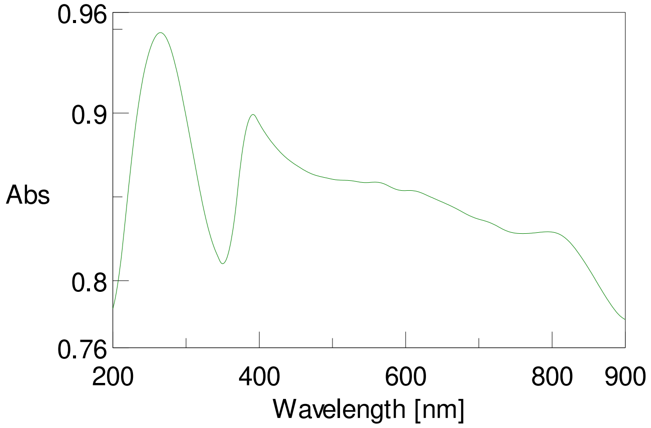


From the above reading it is observed that as the concentration increases the absorbance increases.From the graph it was clear that on increasing the concentration of the prepared nanoparticles the absorbance values also increases.

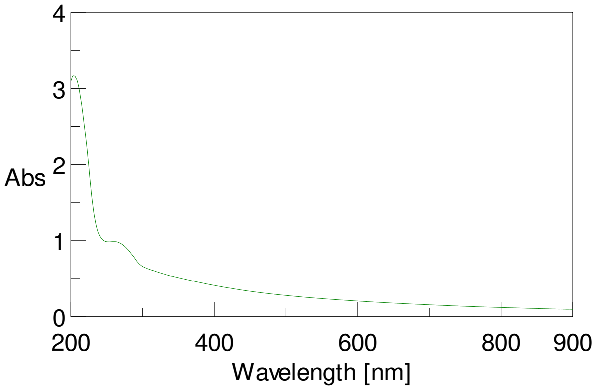
UV-Visible Spectroscopic analysis

The formation of nanoparticles was easily detected and characterized by UV-Visible spectroscopy owing to the Surface Plasmon resonance (SPR) in the interaction of electromagnetic radiation and the electrons in the conduction band around the nanoparticles.In the wavelength range of 200-900nm, an optical absorption band λ max value of around 420 nm indicated the presence of AgNPs in the solution.

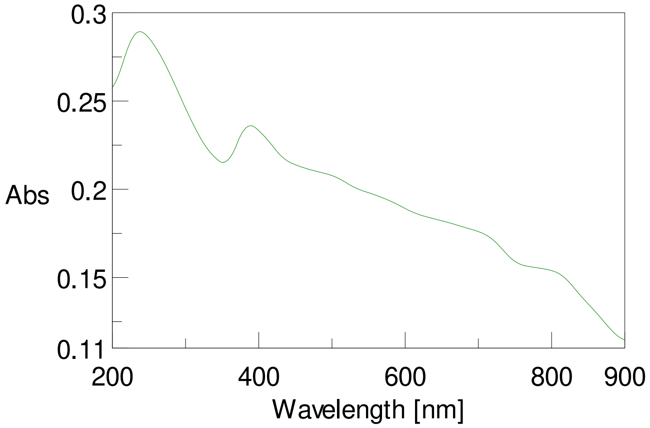
Tomato



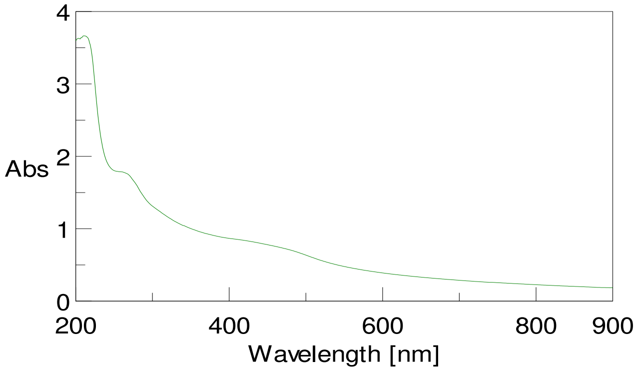
Potato



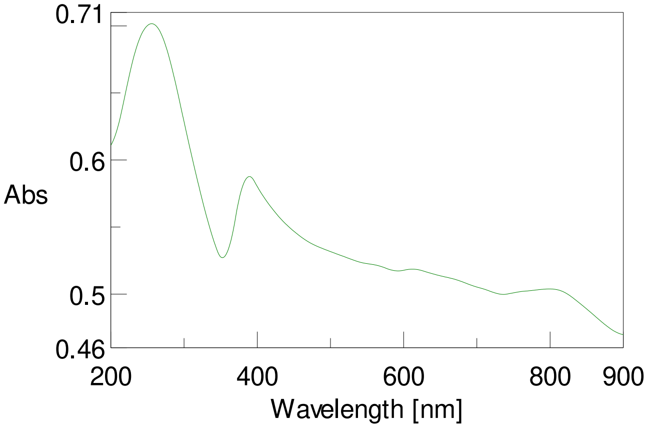
Carrot



Beetroot



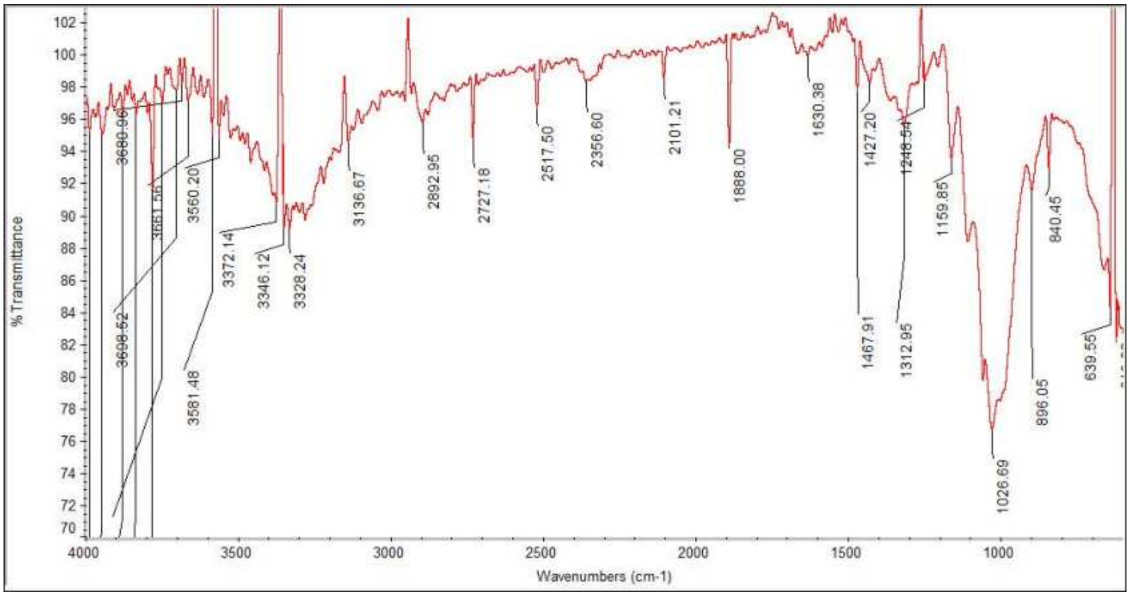
Beans



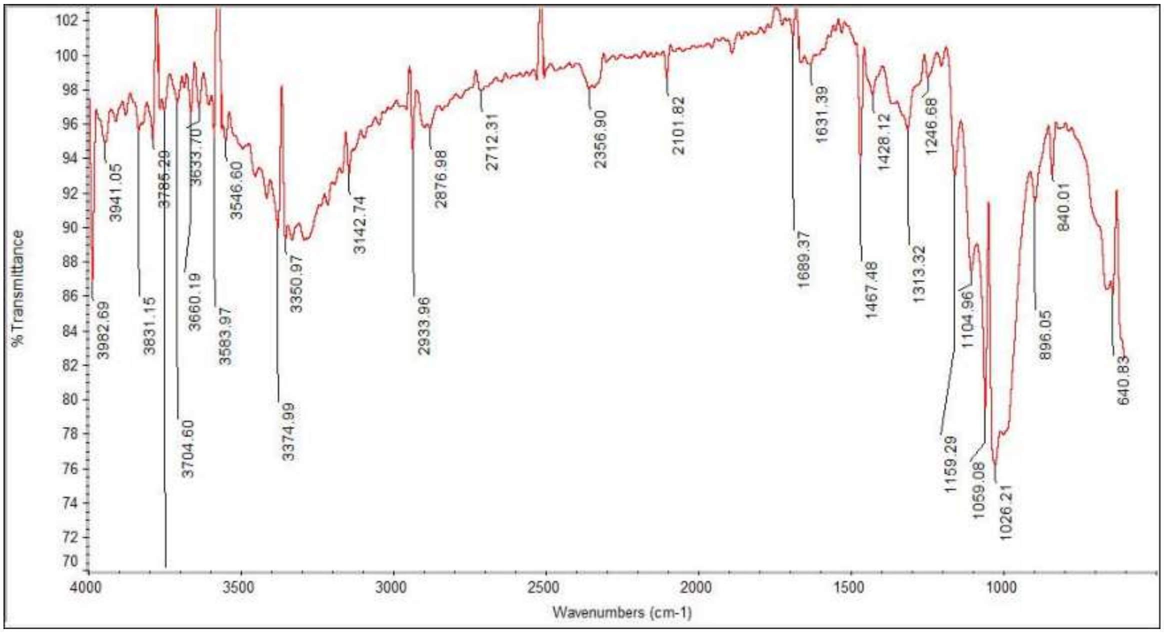
From the above UV data the absorption peak around 420nm is obsereved in all the synthesised nanoparticles which confirms the formation of silver nanoparticles.

FT-IR (Fourier Transform Infra Red Spectroscopy)

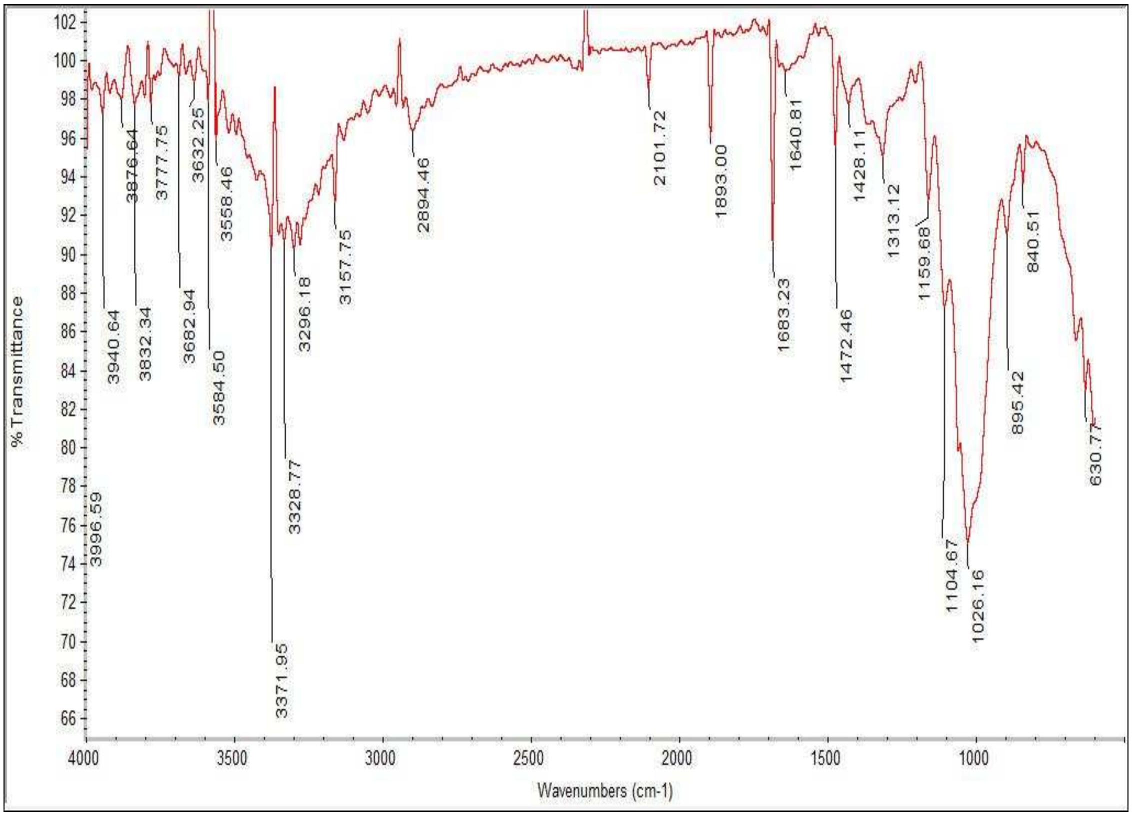
Tomato



Potato



Carrot



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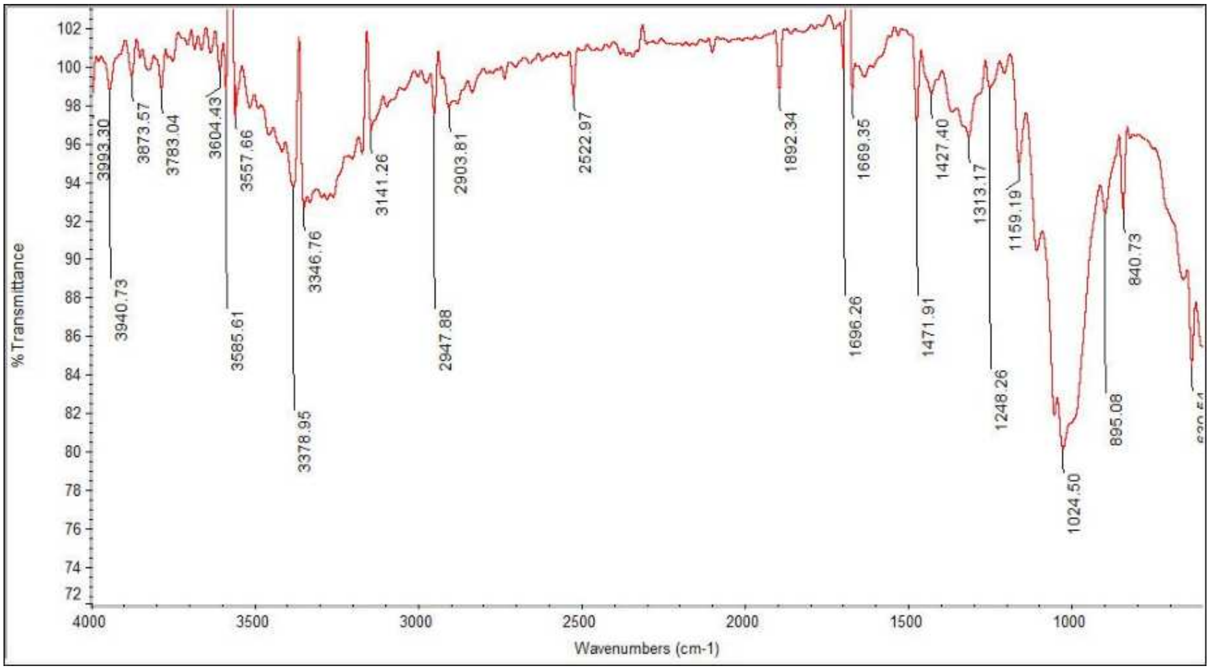

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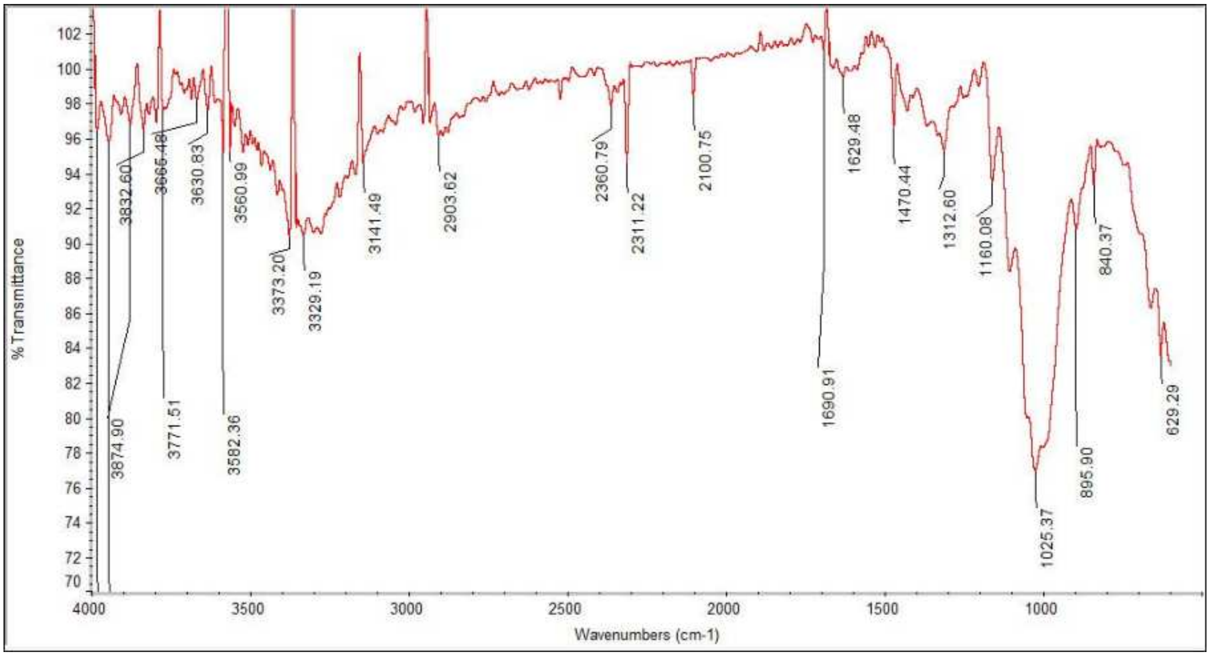

From the IR spectra data of the samples, prominent peaks are exhibited around 2927, 1631 and 1383 cm-1 which corresponds to the presence of silver nanoparticles.

Application of Silver nanoparticles

Nearly equal volumes of soil is collected in separate cups and 10ml of vegetable samples under study were taken and mixed to it and the seed is allowed to dry, the length of the seed grown is measured in centimetres.

Plant without adding nanoparticles

Tomato

Potato

Carrot

Beetroot

Beans

From the measurement of the length of the plant it was observed that the length of plant without mixing nanoparticle is around 11cm whereas the soil mixed with tomato sample is around 12.5cm, potato sample is around 14.5cm, carrot is around 12.5cm, beetroot is around 15cm, beams is around 15cm. From the above measurement it is observed that the soil mixed with the synthesised nanoparticles has enhanced the growth of the seed.so from this study we conclude the vegetables that are wasted due to crushing during transportation, lack of freshness can be utilised for manure purpose.

Conclusion

In the present study, silver nanoparticles were rapidly synthesized at room temperature by treating silver ions with some vegetables extract. Silver nanoparticles were synthesised using the extract of some vegetables like tomato, potato, beans, carrot and beetroot. About 10^{-3}M solution of silver nitrate is prepared as a stock solution. The yellowish brown colour is observed at various concentration of the extracts. After fixing the concentration the time taken for the formation of silver nanoparticles are determined using potentiometric method, from this the exact time at which the nanoparticle synthesised is determined for all the samples. The formation of silver nanoparticles was confirmed by UV-Visible spectra and IR spectra. Synthesised Silver nanoparticles are used as biofertilizer. Hence the silver nanoparticles prepared using the extract are taken and mixed with the soil and the bean seed has been allowed to grow to find the efficacy of the nanoparticles. Hence, we conclude that silver nanoparticles synthesised using vegetable extract can be used as biofertilizer.

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“Synthesis and Characterisation of p-aminobenzoic acid-co-p-anisidine”

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

M. Agnes Mary
M. Ancy
P. Jemima
K. Kantha Lakshmi
D. Karthika Lakshmi
S. Pon Selvi

St. Mary’s College (Autonomous)

(Re-accredited with ‘A^{+}' Grade by NAAC)

Thoothukudi- 628001.

2020-2021

DECLARATION

We hearby declare that the project entitled **"Synthesis and Characterisation of p-aminobenzoic acid-co-p-anisidine"** 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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M. AGNES MARY

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D. KARTHIKA LAKSHMI

S. Ponselvi
S. PON SELVI

April, 2021

Thoothukudi.

CERTIFICATE

This is to certify that the project in chemistry entitled **"Synthesis and Characterisation of p-aminobenzoic acid-co-p-anisidine "** 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 2020-2021.

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CONTENTS

CHAPTER 1

INTRODUCTION

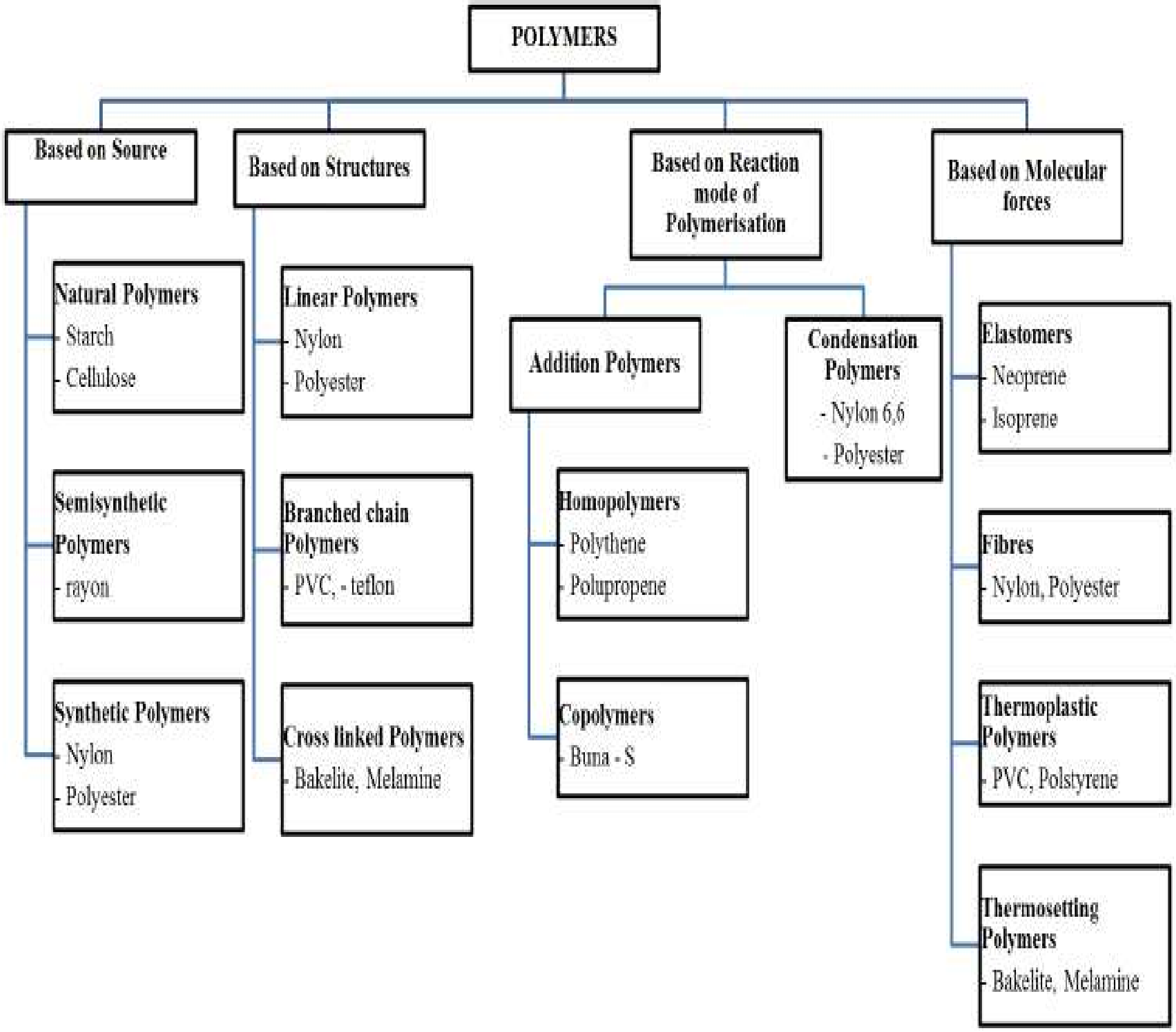
1.Polymerization

Polymerization is a process in which relatively small molecules called monomers combine chemically to produce a very large chainlike or network molecule called a polymer. The monomer molecules may be all alike, or they may represent two, three, or more different compounds. Usually at least 100 monomer molecules must be combined to make a product that has certain unique physical properties such as elasticity, high tensile strength, or the ability to form fibres that differentiate polymers from substances composed of smaller and simpler molecules. Often many thousands of monomer units are incorporated in a single molecule of a polymer. The formation of stable covalent chemical bonds between the monomers sets polymerization apart from other processes such as crystallization in which large numbers of molecules aggregate under the influence of weak intermolecular forces.

Polymers form a very important class of material without which the life seems very difficult. They are all in everyday use such as in rubber, plastic ,resin and in adhesives and adhesives tapes. The word polymer is derived from a greek word poly-many and mers-parts or units of high molecular mass each molecule of which consist of very large number of single structural units joined together in a regular manner. In other words polymers are giant molecules of high molecular weight called macromolecules. The polymerization is a chemical reaction in which two or more substance combine together with or without evolution of anything like water, heat or any other solvents to form a molecule of high molecular weight.

1.1 Classification of polymers

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless form and numbers because of very large number and type of atoms present in their molecule. Polymer can have different chemical structure, physical properties, mechanical behavior, thermal characteristics, etc., and on the basis of these properties polymers are classified in different ways.

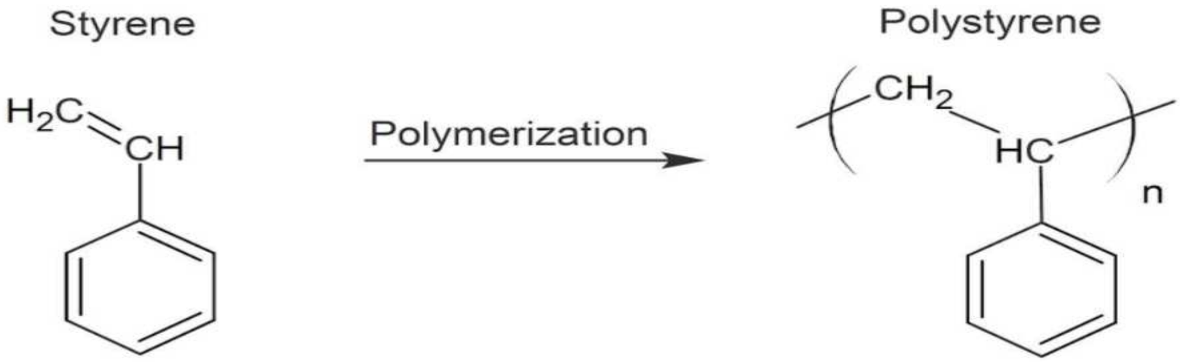


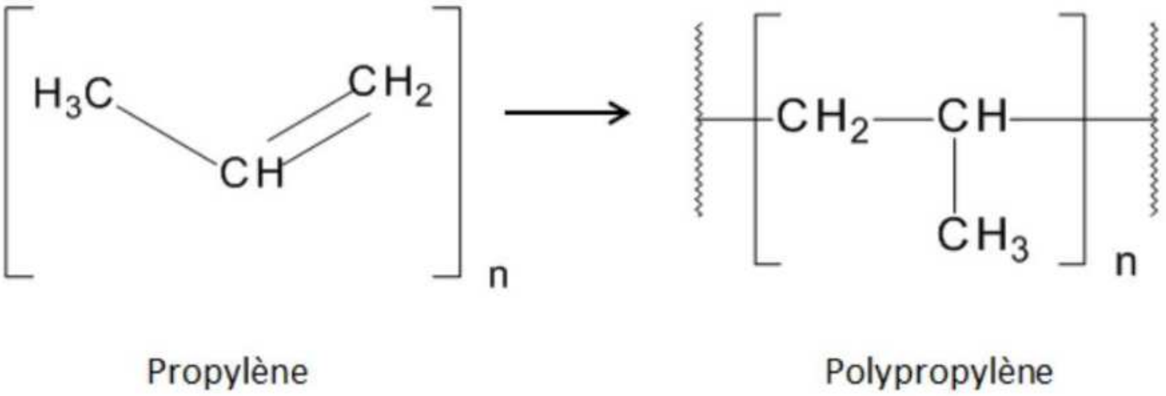
1.2 **Types of polymerization:**

- Chain -Growth or Addition polymerization.
- Step-Growth or Condensation polymerization.
- Copolymerisation.
- Conducting polymerization.

I. Addition Polymerization:

As the name suggests addition polymers form when an addition reaction occurs. The repeating monomers form a linear or branch structure depending on the type of monomer. During addition polymerization, the monomers rearrange themselves to form a new structure. But there is no loss of an atom or a molecule. Addition polymers include polystyrene, polyethylene, polyacrylates, and methacrylates.Again there are four types of addition polymers they are,





1. **Free Radical Polymerization:** Here the addition polymer forms by addition of atoms with a free electron in its valence shells. These are known as free radicals. They join in a successive chain during free radical polymerization.

2. **Cationic polymerization:** A polymerization where a cation is formed causing a chain reaction. It results in forming a long chain of repeating monomers

3. **Anionic Vinyl Polymerization:** Involves the polymerization of particularly vinyl polymers with a strong electronegative group to form a chain reaction.

4. **Coordination Polymerization:** This method was invented by two scientists Ziegler and Natta who won a Nobel Prize for their work. They developed a catalyst which let us control the free radical polymerization. It produces a polymer which has more density and strength.

Condensation polymers are formed by the reaction of bi- or polyfunctional molecules, with the elimination of some small molecule (such as water) as a by-product. Examples include polyester, polyamide, polyurethane, and polysiloxane.

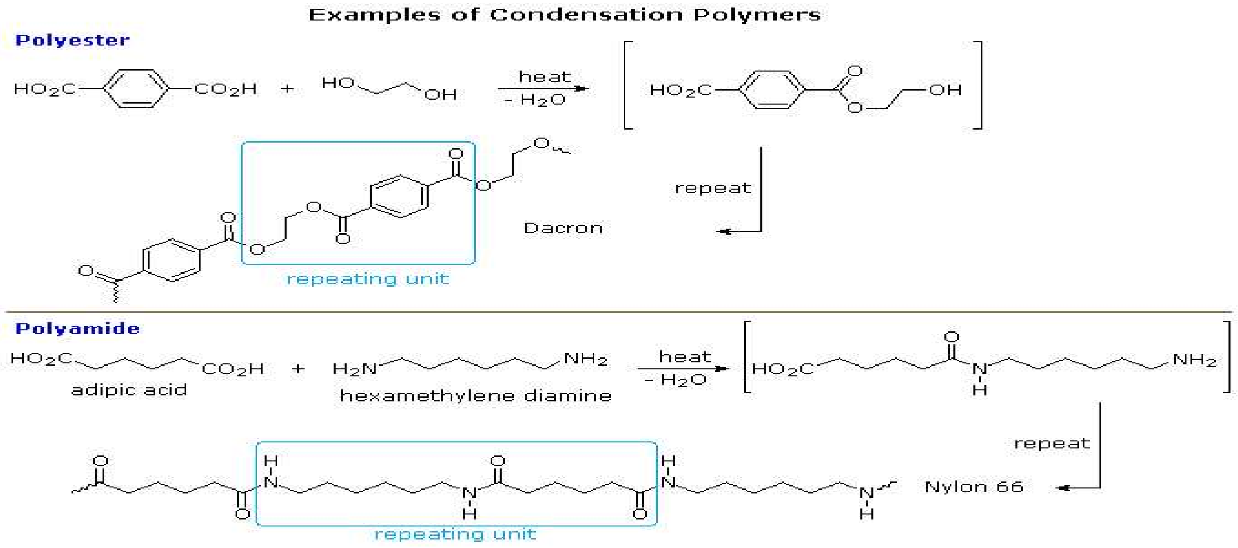
II. Condensation Polymerization:

Condensation polymers form from the step growth polymerization. Here when molecules of monomers react to form a bond they replace certain molecules. These molecules are the by-product of the reaction. In most cases, this by-product is a water molecule.

The type of polymers that result from a condensation polymerization depends on the monomers. If the monomer has only one reactive group, the polymers that form have low molecular weight. When monomers have two reactive end groups produce linear polymers and monomers with higher than two reactive groups results in a polymer with a three-dimensional network.

Polyester and nylon are two common condensation polymers. Even proteins and carbohydrates are a result of condensation polymerization. A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often occur with loss of a small byproduct, such as water, and generally combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66 are two examples of synthetic condensation polymers also known as step-growth polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbonheteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly (β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria.



3. Copolymerization

A **copolymer** is a polymer derived from more than one species of monomer. The polymerization of monomers into copolymers is called copolymerization. Copolymers obtained by copolymerization of two monomer species are sometimes called bipolymers. Those obtained from three and four monomers are called terpolymers and quaterpolymers respectively.

Copolymers can be classified based on how these units are arranged along the chain. Copolymers consists of linear and branched polymers. Linear copolymers consist of a single main chain and include alternating copolymers, statistical copolymers and block copolymers.

Branched copolymers consist of a single main chain with one or more polymeric side chains, and can be grafted, star shaped or have other architectures

If the polymer consist of different repeating units then the polymer is called copolymers.Depending on the arrangement of the types of monomers in the polymer chain ,it is classified into

- **Random polymers**:In random copolymers two or more repeating units are distributed randomly.
- **Alternating copolymers**:Alternating copolymers are made of alternating sequence of different monomers.
- **Block copolymers**:In block copolymers long sequences of monomer are followed by long sequence of another monomer.
- **Graft copolymers**:Graft copolymers consist of a chain made from one type of monomers with branches of another type.

Commercial copolymers include acrylonitrile butadiene styrene (ABS), styrene/butadiene co-polymer (SBR), nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS) and ethylene-vinyl acetate, all formed by chain-growth polymerization. Another production mechanism is step-growth polymerization, used to produce the nylon-12/6/66 copolymer of nylon 12, nylon 6 and nylon 66, as well as the copolyester family.

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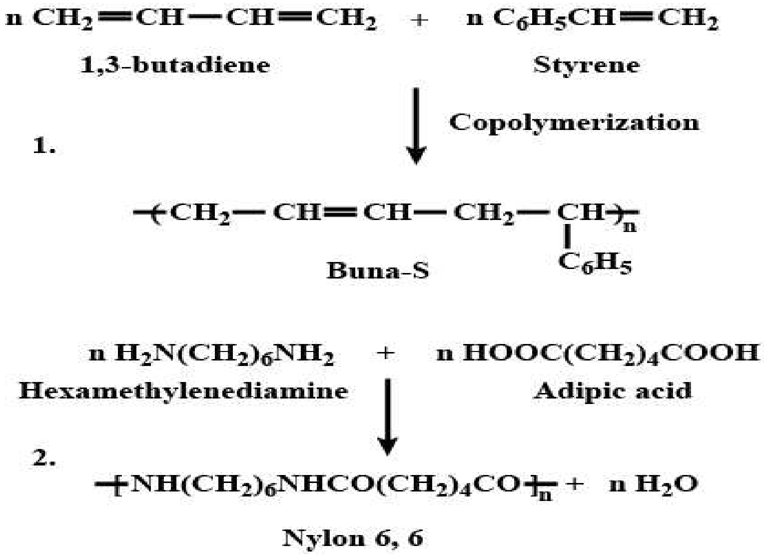


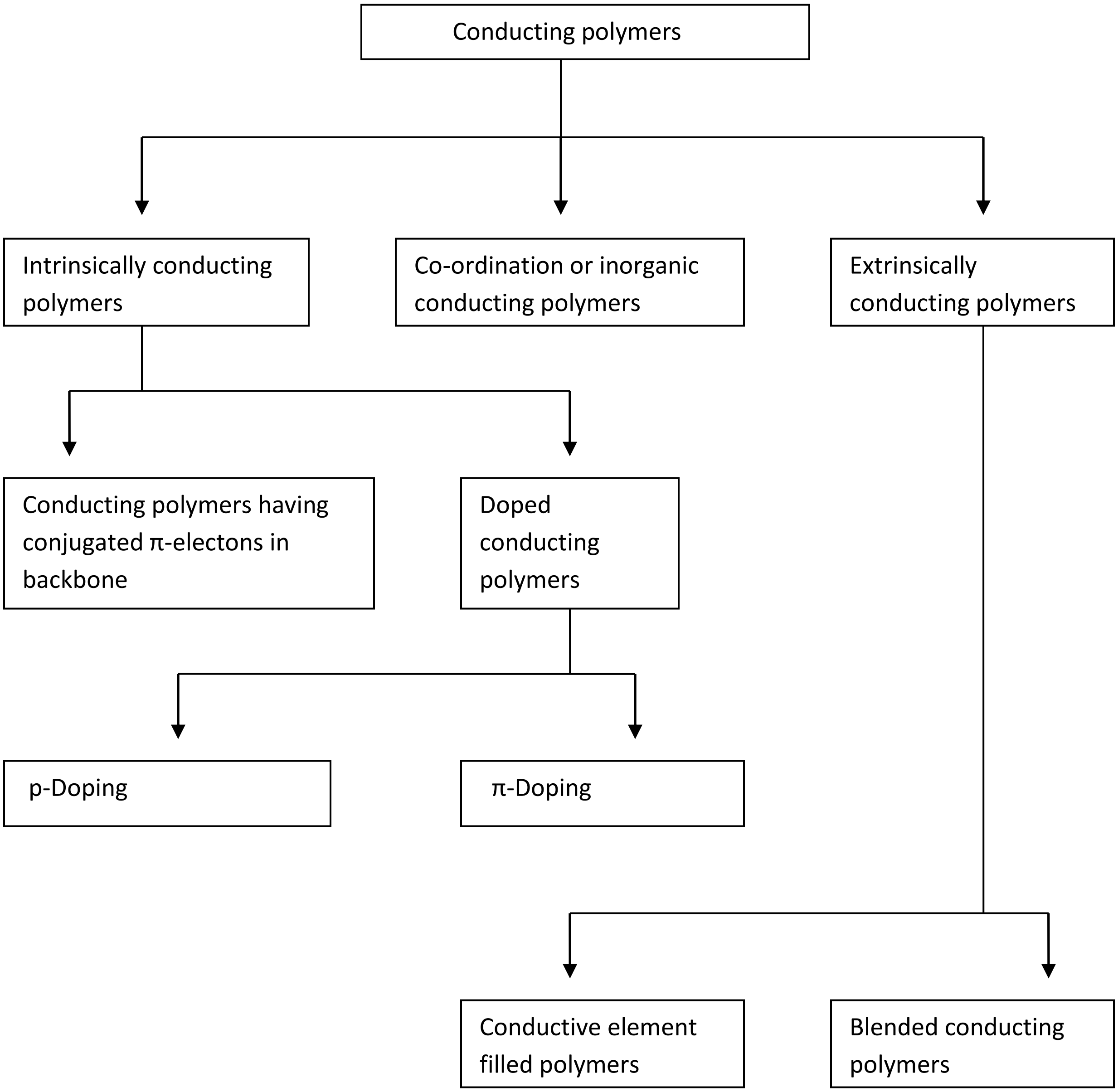
$$n\,CH_2{=}CH{-}CH{=}CH_2 + n\,C_6H_5CH{=}CH_2 \xrightarrow{\text{Copolymerization}} {-}\!\!\left(CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{CH}\right)_{\!n}$$

$$n\,H_2N(CH_2)_6NH_2 + n\,HOOC(CH_2)_4COOH \longrightarrow {-}\!\!\left[NH(CH_2)_6NHCO(CH_2)_4CO\right]_n + n\,H_2O$$

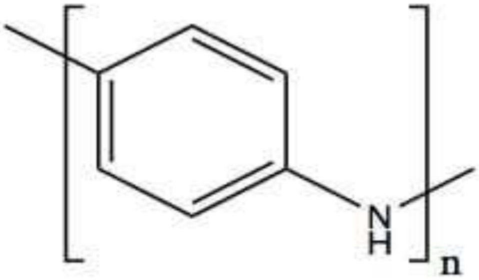
4. Conducting Polymers:

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Classification of Conducting Polymers:

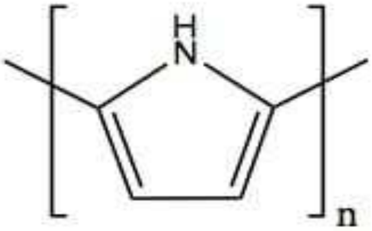


Some examples of the conducting polymers are polyacetylene, poly(phenyl vinylene), polypyrrole,polyaniline,polythiophene. .

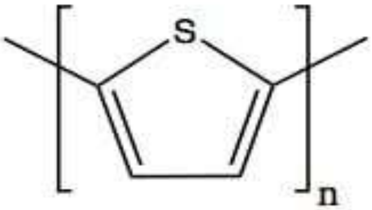


Polyaniline

Polyacetylene



Polypyrrole



Polythiophene

Poly(p-phenylene)

4.1 Requirements for Conducting Polymer Systems

The outermost shell of electrons in a material contains the valence electrons and these can be placed in the valence band that defines their lowest energy states. In order to conduct, an electron must obtain sufficient energy to promote it to the conduction band. It is generally recognized that for an organic polymer to support electronic conduction, the polymer must contain an overlapping set of molecular orbitals to provide reasonable carrier mobility along the polymer chain. Conducting polymers are usually polyconjugated structures, which are insulators in the pure state but when treated with an oxidizing or a reducing agent can be converted into polymer salts with electrical conductivities comparable to metals. The essential structural characteristic of all conjugated polymers is their quasi-infinite π system extending over a large number of recurring monomer units. This feature results in materials with directional conductivity. The extended π system of conjugated polymer are highly susceptible to chemical or electrical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to systematically control the electrical and optical properties with a great deal of precision

Conjugated polymers in their non-doped state are in fact intrinsic semiconductors whose band gap depends not only on the chemical constitution of the conjugated backbone but also on the nature of the substituent's attached to the main chain. Thus optical and electronic properties of the conjugated polymers can be varied to a very large extent by appropriate functionalization. Most extensively studied area of the application of undoped conjugated polymers is the fabrication of the polymeric light-emitting diodes, i.e. electronic devices which exploit the phenomenon of electroluminescence. Electroluminescence of conjugated polymers and more precisely poly(p-phenylene vinylene) was first reported by Burroughes et al. in 1990. These undoped conjugated polymers can also be used in the fabrication of a large variety of other devices like organic field-effect transistors. Polymer LEDs show attractive characteristics, including efficient light generation, with great potential for commercialisation. Again the polymer interests in polymers is in their potential use for rapid, low-cost processing using film-forming polymer solutions. Like the conductive polymers, the semi-conductive polymers obtain their properties from their conduction-molecular orbitals and valence molecular orbitals, i.e., bonding π and antibonding π^* orbitals, respectively. In electro-chemical light emitting cells, the semi-conductive polymer could be surrounded asymmetrically with a hole-injection electrode on one side, and a low work function, electron injecting metal contact like aluminum, magnesium, calcium etc. on the other side. The emission of light is then the result of radiative charge carrier recombination in the polymer as electrons from one side and holes from the other recombine. Conducting polymers are conjugated polymers, namely organic compounds that have an extended p-orbital system, through which electrons can move from one end of the polymer to the other. In conjugated polymers, the bonding leads to one unpaired electron (the π-electron) per carbon atom. Moreover, π-bonding, in which the carbon orbitals are in the $sp^2 p_z$ configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the “highway” for charge mobility along the backbone of the polymer chain. Electronically conducting polymers are extensively conjugated molecules, and it is believed that they possess a spatially delocalized band-like electronic structure. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors

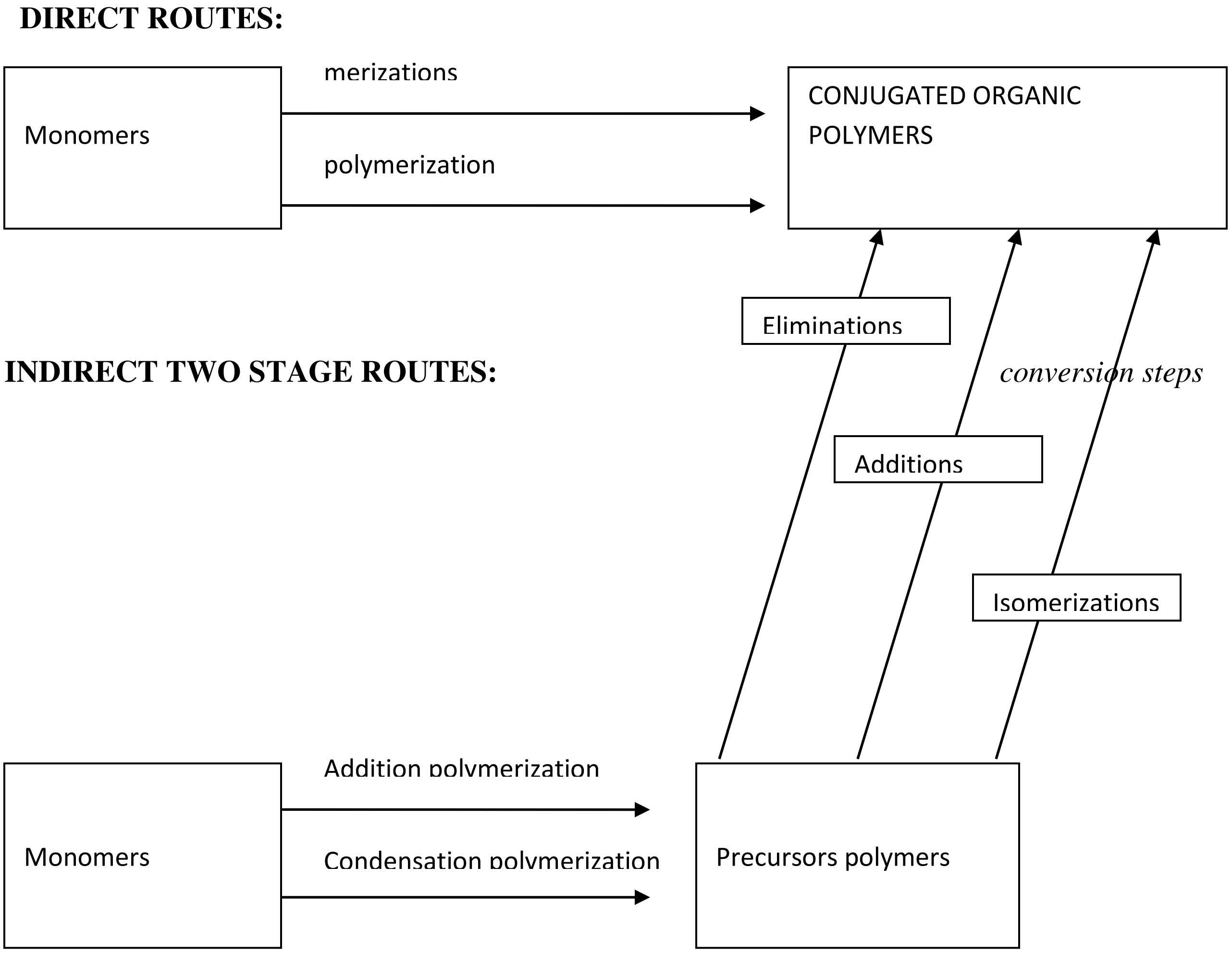
4.2 Doping

The concept of doping is the unique, central, underlying, and unifying theme which distinguishes conducting polymers from all other types of polymers. During the doping process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range

10−10 to 101 S/cm, is converted to a polymer which is in the ‘metallic’ conducting regime (−1 to 104 S/cm). The controlled addition of known, usually small (≤ 10 per cent) nonstoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone. Both doping and un-doping processes, involving dopant counter-ions which stabilize the doped state, may be carried out chemically or electrochemically. By controllably adjusting the doping level, a conductivity anywhere between that of the non-doped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator), whose conductivity can be adjusted by varying the relative proportions of each polymer, can be made. This permits the optimization of the best properties of each type of polymer. Trans-(CH)X and the emeraldine base form of polyaniline are used to illustrate the increases in electrical conductivity of many orders of magnitude which can be obtained by doping. In the“doped” state, the backbone of a conducting polymer consists of a delocalized pi system. In the undoped state, the polymer may have a conjugated backbone such as in trans-(CH)X which is retained in a modified form after doping, or it may have a non-conjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes truly conjugated only after p-doping, or a non-conjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping

4.3 Synthesis of Conducting Polymers

Polyacetylene and polyphenylene are the simplest models and can be regarded as sequence of either vinylene or phenylene units. However, even these very simple systems can be put together in quite a variety of ways to create a number of structurally different materials, so the task of those engaged in the synthesis of conjugated organic polymers ought to be to provide as wide a variety of well-characterized materials as possible for the detailed investigations of their electrical properties. In synthesis, there are mainly two main lines of approach the first could reasonably be called the direct route and second approach is designated the indirect approach. The direct route represents the classical approach to polymer synthesis in which an appropriate monomer is converted directly into a conjugated polymers via either an addition or a condensation process. One of the disadvantages of the direct approach stems from the experimental observation that some of structurally simplest conjugated polymers, for example, like polyacetylene and poly-para-phenylene, are essentially insoluble and intractable materials and this observation brings several practical difficulties. The main advantage of the indirect route is an increased flexibility in the design of synthesis. Thus, the precursor polymers may be formed by addition or condensation polymerization procedures, but the second stage may be accomplished by a variety of different reactions



Outline of possible routes to conjugated organic polymers

CHAPTER 2

LITERATURE SURVEY

Synthesis and properties of polyaniline, poly(*o*-anisidine), and poly[aniline-co-(*o*-anisidine)] using potassium iodate oxidizing agent was performed in 2016 [1], Synthesis, Characterization, and Electrochemical properties of a novel conducting copolymer obtained by p-anisidine and aniline with titanium (IV) oxide nanoparticles was done in 2015 [2], Copolymer of p-aminobenzoic acid with aniline was studied in 2014 [3], Synthesis and characterization of Poly(aniline- co-m-aminobenzoic acid) deposited on poly(vinyl alcohol) was done in 2013 [4], Synthesis and Visible Photocatalytic Activities of Poly(aminobenzoic acid)/TiO_2 Nanocomposite was carried out in 2013[5], Direct condensation polymerization of N-alkylated p-aminobenzoic acid and packing of rigid-rod main chains with flexible side chains was done in 2010 [6], Comparison of poly(o-anisidine) and poly(o-anisidine-co-aniline) copolymer synthesized by chemical oxidative method [7] Chain-growth condensation polymerization of 4-aminobenzoic acid esters bearing tri(ethylene glycol) side chain with lithium amide base was done in [8], Synthesis, characterization, and properties of Poly(2,3-aminobenzoic acids) and their copolymers with aniline was done in 2003[9], Influence of copolymer composition on the transport properties of conducting copolymers: poly(aniline-co-o-anisidine) [10], Synthesis and characterization of pyrrole and anisidine copolymers [11].

CHAPTER 3

OBJECTIVE AND SCOPE

Anisidine is an aromatic amine (methoxyaniline) and exists in three isomeric forms i.e., ortho, meta, and p-anisidine. The p-anisidine is widely used as an intermediate in the production of numerous azo and triphenylmethane dyes, and pigments. It is also used in the production of pharmaceuticals including the guaiacol expectorant, as an antioxidant for polymercaptan resins, and as a corrosion inhibitor for steel. By considering the importance of p-anisidine as an intermediate for the production of various dyes, pharmaceuticals and several other organic products, it is advantageous to find out an alternate approach that can enhance the physicochemical and thermal properties of p-anisidine in the useful way. Recently, healing therapy or therapeutic touch is used as an alternative treatment approach in several fields, and known as the biofield energy treatment.

Electropolymerized molecularly imprinted polymer (MIP) of para-aminobenzoic acid (pABA) on glassy carbon electrode was reported as novel and simple sensor poly(para-aminobenzoic acid) deposited for melamine detection[Electrochemical sensor based on a poly(para-aminobenzoic acid) film modified glassy carbon electrode for the determination of melamine in milk. With these senors it is feasible to use the molecular imprinting methodology when preparing sensing devices for analytes that are electrochemically inactive.

Here an attempt is made to prepare a modified copolymer of para-aminobenzoic acid (pABA) and p-anisidine by chemical oxidation method. The copolymer prepared was then characterized using the following techniques

- UV-Visible Spectrophotometer

- Fourier Transform Infra Red Spectroscopy (FTIR)
- Atomic Force Microscopy (AFM).

The project work can be extended further by coating the polymer on stainless steel or mild steel and study its electrochemical behavior and anti corrosion property using electrochemical workstation.

CHAPTER 4

INSTRUMENTATION AND EXPERIMENTAL METHOD

For recording the UV-Vis absorption spectra, a computer controlled JascoV-500 spectrophotometer was used. The FT-IR spectra were recorded using a SHIMADZU instrument.

Atomic Force Microscopy

The AFM works much the same way a profilometer works only on a much, 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 urfeasy2scanBT02218is profilometer–a sharp cantilever tip interacts with the sample surface sensing the local forces between the molecules of the tip and sample surface.

EXPERIMENTAL METHOD

CHEMICALS USED:

- p-amino benzoic acid
- Hydro chloric acid
- p-anisidine
- Potassium perdisulphate

PROCEDURE:

Poly(p-aminobenzoic acid-co-p-anisidine) was synthesized by chemical oxidative polymerization method in hydrochloric acid medium and potassium perdisulphate as an oxidant. About 500ml of 1M HCl was taken in a 500ml beaker, to this about 6.8g of p-amino benzoic acid and 6.16g of p-anisidine were added. The resulting mixture was stirred uniformly using an electromagnetic stirrer. Then about 13.5g of potassiumperdisulphate was added into the above solution. The stirring was continued for 3hrs complete the reaction, then kept in refrigerator overnight.Then the precipitate obtained was filtered and dried.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 UV Visible Studies:

UV-VIS spectra of the monomer p-amino benzoic acid and p-anisidine as reported earlier is shown in Fig.1. In the case of p-amino benzoic acid a broad hump is observed around 290-320nm, whereas for p- anisidine it is still more broad ,in the case of the copolymer there is a broad peak at 250nm which is attributed to the л-л* transition for the benzenoid ring.

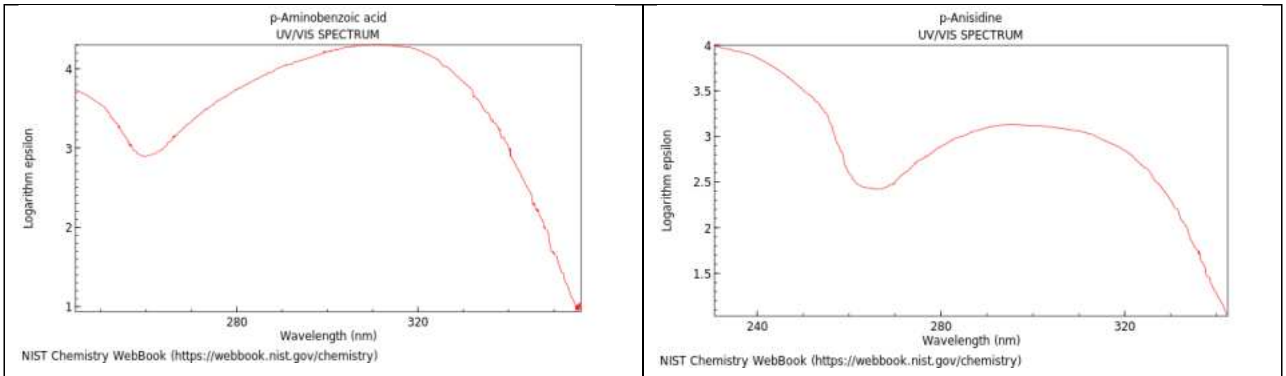


Fig.1:UV-Vis spectrum of p-aminobenzoic acid and p-anisidine

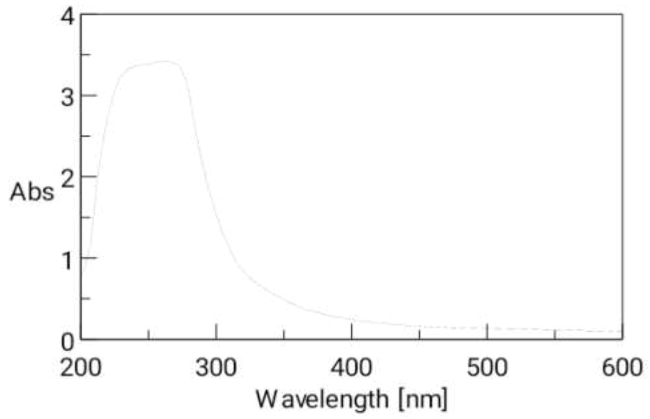
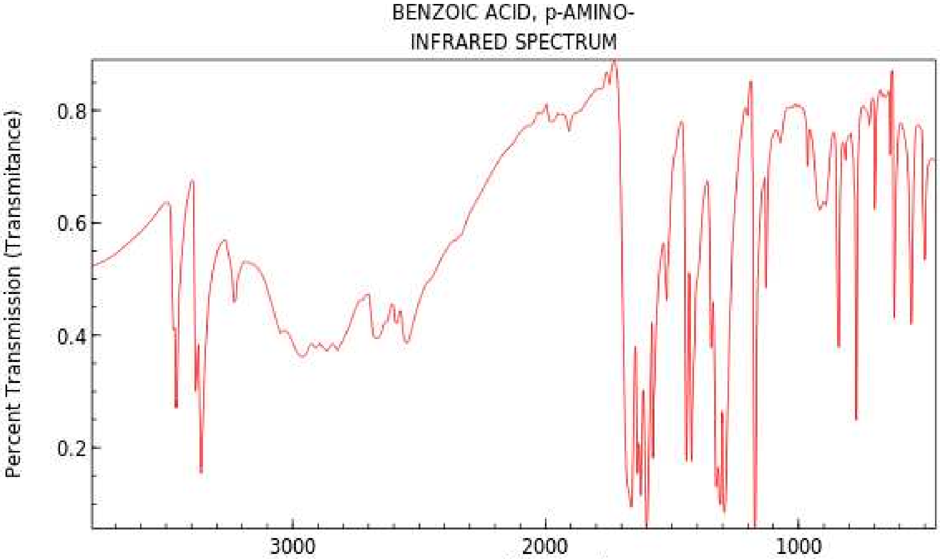


Fig.2.UV-Vis Spectra of p-aminobenzoicacid-co-p-anisidine

5.2 FTIR Studies

The FTIR spectra of p- amino benzoic acid and p-anisidine shows the following bands namely a sharp band at around 3350cm^{-1} (N-H stretching), 3000cm^{-1}(O-H stretching),1691 cm^{-1} (C=O),1400 cm^{-1} (quinoid C=C stretching), 1500cm^{-1} (benzenoid C=C stretching),1450 cm^{-1} (stretching of aromatic ring), 1200 cm^{-1} (C-H stretching),1150 cm^{-1} (N=Q=N stretching Q= quinoid ring) , 900 cm^{-1} and 950 cm^{-1} (aromatic C-H in plane bending) , 850 cm^{-1} and 800 cm^{-1} (C-H out of plane bending and confirms 1,4 disubstituted benzene ring). The C-H stretching (methyl) in p-anisidine was attributed to peaks at around 2800-2900 cm^{-1} .The peaks are sharp in the monomers due to free –OH as well as inter and intra molecular hydrogen bonding, whereas in the case of the polymer the peaks are rather broad due to polymerization.



NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

Fig.3 FTIR spectra of p-aminobenzoic acid

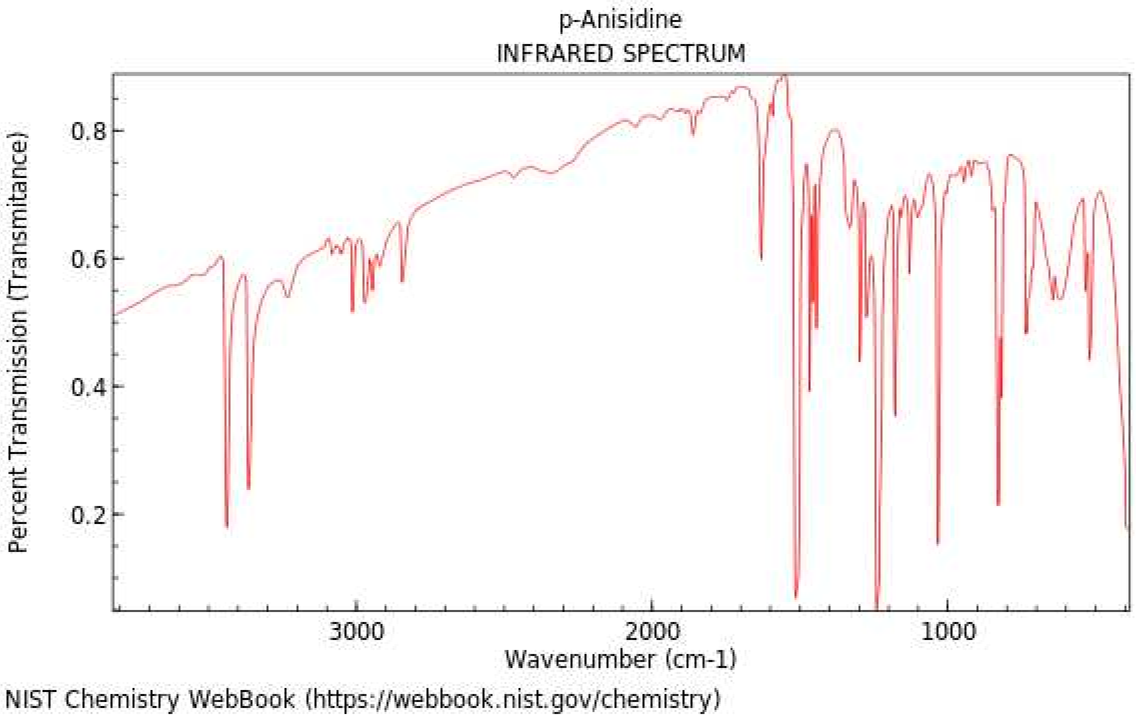


Fig.4 FTIR spectra of p-anisidine

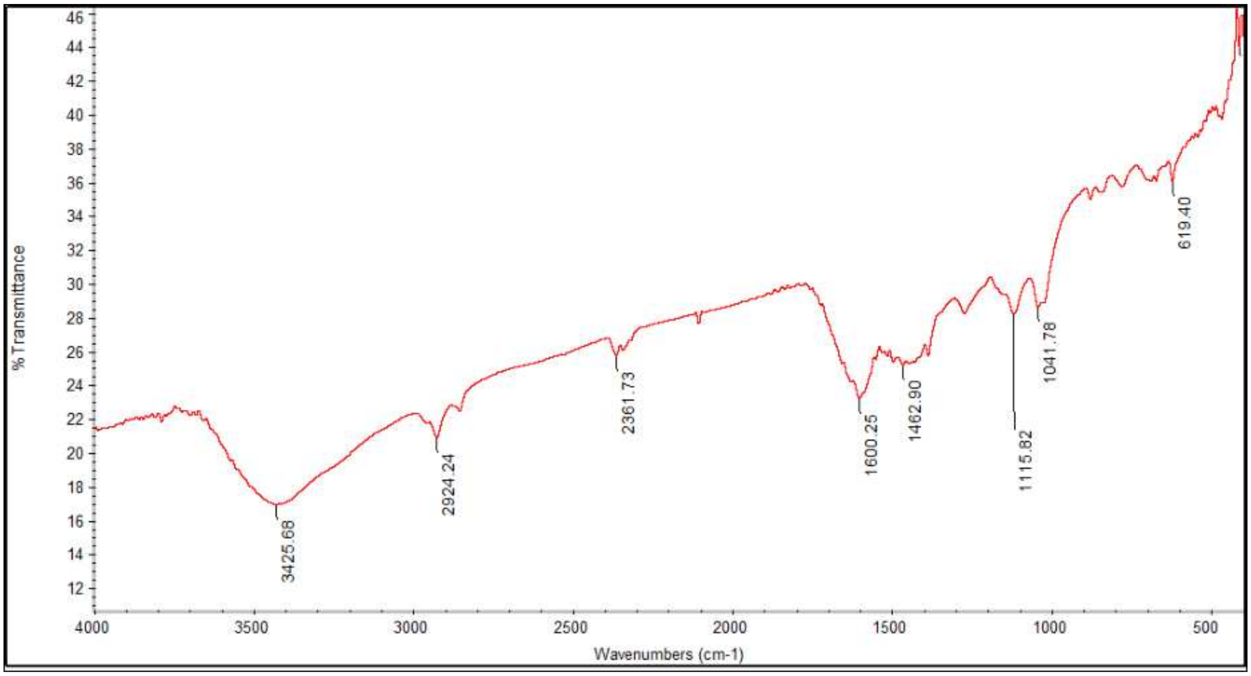
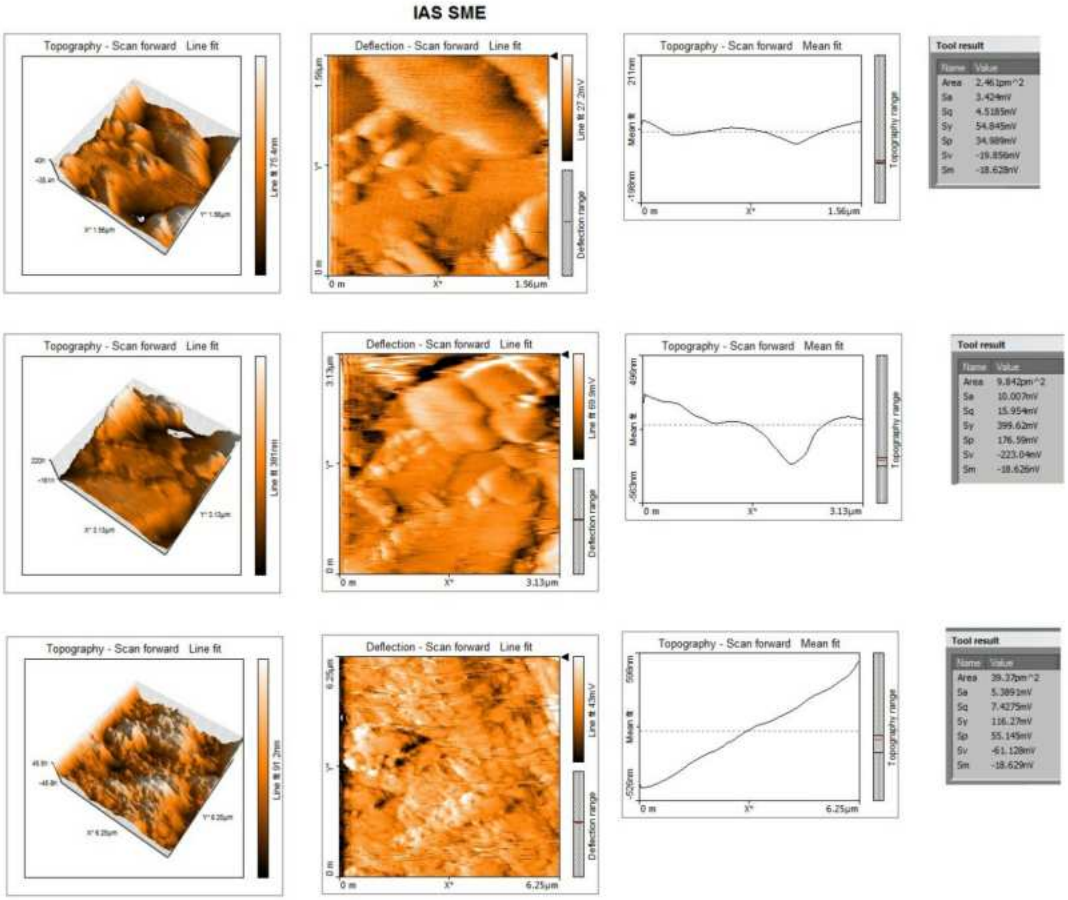


Fig.5 FTIR spectra of p-aminobenzoicacid-co-p-anisidine

5.3 ATOMIC FORCE MICROSCOPY STUDIES

Surface morphology was studied using atomic force microscopy. The images scanned reveal a combination of smooth and rough surface and is expected to have conductivity and catalytic property.



Tool result

Name	Value
Area	2.461pm^2
Sa	3.424mV
Sq	4.5185mV
Sy	54.845mV
Sp	34.989mV
Sv	-19.856mV
Sm	-18.628mV

Tool result

Name	Value
Area	9.842pm^2
Sa	10.007mV
Sq	15.954mV
Sy	399.62mV
Sp	176.59mV
Sv	-223.04mV
Sm	-18.626mV

Tool result

Name	Value
Area	39.37pm^2
Sa	5.3891mV
Sq	7.4275mV
Sy	116.27mV
Sp	55.145mV
Sv	-61.128mV
Sm	-18.629mV

CHAPTER 6

CONCLUSION

- The copolymer p-aminobenzoicacid-co-p-anisidine was prepared by chemical oxidation method using potassium per disulphate.
- The dark brown solid copolymer was then characterized by UV-Visible studies, FTIR and AFM
- UV-Visible studies reveal the presence of a broad peak at 250nm attributed to the л-л* transition for the benzenoid ring
- FTIR studies reveal the presence of polymeric linkage by the presence of broad peaks in the copolymer and sharp intense peaks in the monomer.
- AFM studies reveal rather a rough surface and is expected to have catalytic property

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A STUDY ON COLOR REMOVAL EFFICIENCY OF ACID ORANGE 52 SOLUTION BY ELECTROCOAGULATION

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

T.ANTO THERESINAL

V.KRISHNAVENI

T.MUNIESWARI

M.RIZWANA FATHIMA

C.SUBBULAKSHMI

S.SUPRIYA

ST.MARY’S COLLEGE(AUTONOMOUS)

RE-ACCREDITED WITH “A^{+}” GRADE BY NAAC

THOOTHUKUDI-628001

2020-2021

DECLARATION

We hereby declare that the project entitled "**A STUDY ON COLOR REMOVAL EFFICIENCY OF ACID ORANGE 52 SOLUTION BY ELECTROCOAGULATION**" 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.

T. Anto Theresinal
T.ANTO THERESINAL
V. Krishnaveni
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T. Munieshwari
T.MUNIESHWARI
M. Rizwana fathima
M.RIZWANA FATHIMA
C. Subbu lakshmi
C.SUBBULAKSHMI
S. Supriya
S.SUPRIYA

APRIL 2021
THOOTHUKUDI

CERTIFICATE

This is certify that project in chemistry **"A STUDY ON COLOR REMOVAL EFFICIENCY OF ACID ORANGE 52 SOLUTION BY ELECTROCOAGULATION"** 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 2020-2021.

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

CHAPTER-I

INTRODUCTION

The electrocoagulation (EC) process is an electrochemical means of introducing coagulants and removing suspended solids, colloidal material, and metals, as well as other dissolved solids from water and wastewaters. The EC process has been successfully employed in removing pollutants, pesticides, and radionuclides. This process also removes harmful microorganisms. More often during EC operation, direct current is applied and electrode plates are sacrificed (dissolved into solution). The dissolution causes an increased metal concentration in the solution that finally precipitates as oxide precipitates. Due to improved process design and material of construction, the EC process is being widely accepted over other physicochemical processes. One of the major challenges facing mankind today is to provide clean water to a vast majority of the population around the world. The need for clean water is particularly critical in Third-World Countries. Rivers, canals, estuaries and other water-bodies are being constantly polluted due to indiscriminate discharge of industrial effluents as well as other anthropogenic activities and natural processes. The reuse of wastewater has become an absolute necessity. There is, therefore, an urgent need to develop innovative, more effective and inexpensive techniques for treatment of wastewater. A wide range of wastewater treatment techniques are known which includes biological processes as well as a range of physico-chemical processes that require chemical additions. A host of very promising techniques based on electrochemical technology are being developed that do not require chemical additions. These include electro coagulation, electro-flotation and electro-oxidation. Electro coagulation, has reached profitable commercialization. This process has the potential to extensively eliminate the disadvantages of the classical treatment techniques [1]. In addition, this process has been applied to treat water containing Foodstuff wastes, oil wastes, dyes, suspended particles, chemical and mechanical polishing waste, and organic matter from landfill leachates, defluorination of water, synthetic detergent effluents, mine wastes and heavy metal-containing solution. Dyeing and finishing are the two important processes generally applied in most of the textile manufacturing industries. These two processes generate considerable amount of wastewater, which may contain strong colour, suspended particles, high pH and high chemical oxygen demand (COD) concentration. [2]. It is estimated that 1-15% of the dye is lost during dyeing and finishing processes and is released into wastewaters. As a result, a high amount of these dyes can exist in effluents of dyeing processes. Most kinds of synthetic dyes are toxic substances to human and aquatic life, which [3, 4] can be removed by adsorption, precipitation, chemical degradation, photo-degradation, biodegradation, [5] chemical coagulation and electro-coagulation. [6, 7, 8] The objective of these Studies is Removal of Dyes from wastewater using electro-coagulation process at different pH, dyes concentration, electrode material, conductivity, current density, residence time and effects of A.C. and D.C. current.

As per the world health organization (W.H.O) use of colored water even approved hygienically, is not acceptable and colored water is generally not preferred by consumers. Color in water is due to aromatic compounds produced from decay of natural herbal substances. Existence of Color is the major reason for the undesirable taste, odor and disinfections. The quality of water is decided according to color of water and its appearance. Colored water is not preferred by the people. If the people have given the choice, they will select the clean water without any color. Apart from consumer's, different industries like paper industry, beverage productions, dairy, textile industry, plastic production, and cloth washing demands colorless water as the colored water is not preferable in those industries, this is the reason the color in water is considered to have an adverse effect. Chemical particles present in the water affects the color of water which cannot be separated by the simple process of filtration is called the true color. Suspended and colloidal partials present in the water also affect the water which is called as the manifest color which can be easily removed by filtration process. The color of raw water affects the hardness and density of raw water and ultimately scale and sludge will get deposited in inner side of container. Color water increases the environmental load factor. As per green chemistry is concern, environmental load factor should be lower. So it is essential to sustain environmental load factor to minimize the pollution by using fruitful catalysis. Color in water is the because of dissolution express from metals in soil and stone, from organic matter in soil and plants, and occasionally from industrial by-products. When color is present due to metals, it is ordinary due to iron, copper, or manganese ions in the water. Leaf and humate may add very complex phenolic substance, strophanthin, and their byproducts to the water, resulting in a yellow or brown tinge. Industries can add a variety of chemicals with different colours. Suspended and dissolved particles in water influence color. Suspended material in water bodies may be a result of natural causes and/or human activity. Clean water with a low collection of dissolved materials appears blue and point out less yield. Dissolved organic matter, such as humus, peat or decaying plant matter, can produce a yellow or brown color. Some algae or dinoflagellates produce reddish or deep yellow waters. Water rich in flora fauna and other algae usually appears green. Soil runoff produces a variety of yellow, red, brown and gray colors weathered rocks and soils, the land-use activity and the type of trees and plants growing within the watershed will influence the types and amount of dissolved and suspended material found in a lake or stream. Color may also be affected by the concentration of natural dissolved organic acids such as tannins and lignin's, which give water a tea color. These are formed when plant material is slowly broken down by organisms into very small particles that are dissolved into water. Tannins that are yellow to black in color are the most abundant kind found in lakes and streams and can have a great influence on water colour. Lakes that are surrounded by coniferous forests (evergreens such as pine, spruce, hemlock and fir trees) are generally brown in color because pine needles that fall to the ground are very slow to degrade. This is also true of lakes surrounded by wetlands, where plants decompose very slowly. Naturally occurring organic compounds such as tannins and lignins, derived from the decomposition of plant and animal matter, can give surface water and groundwater a tea-like yellow brown hue, as well as a musty smell, is known for its "root beer" color.

1.1.THEORIES OF ELECTRO-COAGULATION

1.1.1. Electro-coagulation mechanism:

As shown in Fig, 1, Electro-coagulation technology offers an alternative to conventional coagulation process, where the metal salts are added to break the stable suspensions of the colloidal particles.

EC process involves three successive stages:

(a) formation of coagulants by electrolytic oxidation of the ’sacrificial electrode’;

(b) destabilization of the contaminants, particulate suspension, and breaking of emulsions;

(c) aggregation of the destabilized phases to form flocs.

In electro-coagulation, coagulants are produced in situ within the reactor without direct addition of any chemicals. Coagulants are produced by electrolytic oxidation of appropriate anode materials, such as stainless steel, Aluminium, carbon, graphite, iron etc. Which result in formation of highly charged polymeric metal hydroxyl species. These species neutralize the electrostatic charges on the suspended solids and facilitate agglomeration resulting in separation from the aqueous phase. The technology removes metals, colloids particles and soluble organic pollutants from aqueous media by introducing highly charged polymeric hydroxide species. The treatment prompts the precipitation of certain metals and salts.

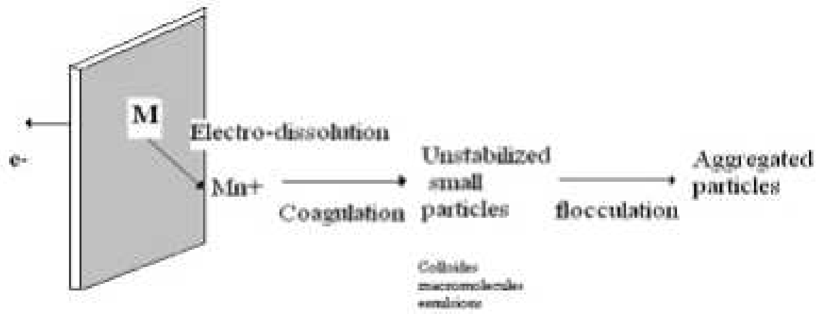

Fig.1. Electrocoagulation step wise process

An electrochemical reactor when connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. But, for wastewater treatment, due to metal dissolution, the use of electrodes with large surface area is required. This has been achieved by using cells with monopolarelectrodes either in parallel or series connections. It essentially consists of pairs of conductive metal plates placed between two parallel electrodes and a DC power source. The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity; pH, particle size, and chemical constituent concentrations.

1.1.2. Principles of Electrocoagulation

Electrolysis is a process in which oxidation and reduction reactions take place when electric current is applied to an electrolytic solution. Electrocoagulation is based on dissolution of the electrode material used as an anode. This so called “sacrificial anode” produces metal ions which act as coagulant agents in the aqueous solution *in situ*. At its simplest, an electrocoagulation system consists of an anode and a cathode made of metal plates, both sub-merged in the aqueous solution being treated. The electrodes are usually made of aluminum, iron, or stainless steel (SS), because these metals are cheap, readily available, proven effective, and non-toxic.

During EC, the following main reactions take place at the electrodes.

Anodic reactions:

$$Al(s) \longrightarrow Al^{3+} + 3e^{-} \qquad E^{o} = +1.66\ V$$

$$2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^{+} + 4e^{-} \qquad E^{o} = -1.23\ V$$

Cathodic reaction:

$$2H_2O + 2e^{-} \longrightarrow H_2\ (g) + 2OH^{-} \qquad E^{o} = -0.83V$$

Additionally, when chloride is present and the anode potential is sufficiently high, the following reactions may take place in the EC cell

$$2Cl^{-} \longrightarrow Cl_2 + 2e^{-} \qquad E^{o} = -1.36V$$

$$Cl_2 + H_2O \longrightarrow HClO + H^{+}\ Cl^{-} \qquad E^{o} = -0.93V$$

$$HClO \longrightarrow H^{+} + OCl^{-}$$

The formation of active chlorine species (Cl_2, $HClO$, OCl^{-}) enhances the performance of the EC reactor through oxidation reactions.

Electrocoagulation process involves oxidation and reduction reaction in which destabilization of contaminants (suspended, emulsified, or dissolved) happens because of application of electric current to the electrolytic solution. EC unit consists of an electrolytic cell and metal (Al or Fe) electrodes which are connected to an external power supply. The conductive metal plates are well known as ‗sacrificial electrodes which are made up of same or completely different materials as anode or cathode. In the EC process, anodic dissolution generates in situ coagulants along with hydroxyl ions and hydrogen gas at the cathode. These in situ coagulants cause the formation of flocs within the sort of metal (Al or Fe) hydroxides and/or poly hydroxides. The hydrogen gas generated at the cathode brings flocs at the water surface by providing further buoyancy. The benefits and drawbacks of EC process are given below.

1.3. Benefits of Electrocoagulation Process

- EC involves artless equipment and is easy to work.
- EC requires low investment, maintenance, energy, and treatment costs.
- EC treated wastewater furnish pleasant, odorless, clear and colorless water.
- EC is a low sludge producing process. EC generated Sludge is mainly composed of metallic oxides/hydroxides.
- There are no additional chemicals required in EC process.
- Flocs formed by EC are similar to chemical floc. EC flocs are much larger in size, enclose less bound water and are acid-resistant and more firm.
- The reuse of EC produced effluent contributes to a lesser water recovery cost because it contains a lesser amount of total dissolved solids (TDS) as related with chemical treatments.
- The gas bubbles generated at the time of electrolysis can proceeds the pollutants to the top of solution from where it can be separated without difficulty.
- EC provides greater efficient pH range and pH neutralization result and can be suitably used with other renewable sources of energy.

1.4. Disadvantages of Electrocoagulation Process

- The sacrificial anodes are dissolved into solution due to oxidation, and need to be replaced at regular interval.
- Conductivity of the wastewater suspension must be high.
- Viscous hydroxide may be likely to solubilize in some cases.
- The electricity may be not easily available and expensive in some area.
- The efficiency of the electro coagulation unit decreases due to an impervious oxide film shaped on the cathode.

1.5. Applications

- ✓ Ground Water Cleanup
- ✓ Surface Water Cleanup
- ✓ Process Rinse Water And Wash Water
- ✓ Sewage Treatment
- ✓ Cooling Towers
- ✓ Water Pretreatment

GROUND WATER CLEANUP

Electrocoagulation is extremely effective in the removal of naturally occurring salts in well water, as well as the separation of iron, magnesium, calcium, metals, nitrates and sulfur. Ec is also well suited for the reclamation of ground water that has been contaminated with heavy metals, high molecular weight hydrocarbons and halogenated hydrocarbons

SURFACE WATER CLEANUP

Electrocoagulation Process rinse water and wash water Electrocoagulation routinely treats process and rinse water from the electroplating, computer board manufactures, textile industry, paint rinse water, steel production, mining industry, automotive industry, equipment repair industry, stack wash water, and pulp and paper. In most cases, the treated water can be recycled and reused.

SEWAGE TREATMENT

Electrocoagulation has proven effective in treating sewage water, sewage sludge concentrations, and sewage sludge metal fixation sufficiently to enable land application.

COOLING TOWERS

Electrocoagulation is used to pre-treat water entering towers as well as blow down water to remove algae, suspended solids, calcium, and magnesium buildup, thereby eliminating costly replacement water.

WATER PRETREATMENT

Water pretreatment with Electrocoagulation has proven effective in removing bacteria, silica and tss prior to subsequent polishing with reverse osmosis, ultra-filtration, nanofiltration, and photocatalytics.

CHAPTER-II
LITERATURE SURVEY

Electrocoagulation (EC) is an emerging technology that combines the functions and advantages of conventional coagulation, flotation, and electrochemistry in water and wastewater treatment. It has been successfully applied for treatment of soluble or colloidal pollutants in various industrial effluents including, effluent issues from food industries, tanneries, mechanical workshop (soluble oil) polymerization manufacture, and wastewater textile industries that containing heavy metals, suspensions solids, emulsified organics and many other contaminants. Electrocoagulation has the advantage of removing the smallest colloidal particles compared with traditional flocculation–coagulation, such charged particles have a greater probability of being coagulated and destabilized because of the electric field that sets them in motion. In addition, electrocoagulation-flotation is capable of reducing waste production from wastewater treatment and also reduces the time necessary for treatment. Manica et al.,[9] evaluated the effects of the electrocoagulation on membrane fouling and treatment performance in a membrane bioreactor operated with prolonged solids retention time and found that the integration of electrocoagulation with the membrane bioreactor technology proved to be an interesting alternative to improve the treatment performance and attenuate the fouling process, even operating the reactor without sludge discharge. Sakthi sharmila et al reported the removal of triazine dye using aluminium electrodes by electrochemical treatment [10]. S. Kongjao et al., employed electrocoagulation technique to treat waste water from tannery plant. They have reported that the treatment is more efficient when the electrodes are connected monopolar and in parallel modes [11]. More polluted tannery water was treated by using EF method (Electro-Fenton process - the addition of H_2O_2 to an electrocoagulation process to bring about oxidation reactions) [12]. Textile industries are among the most polluting industries regarding the volume and the complexity of treatment of its effluents discharge. For decolorizing synthetic azo-dye-containing industrial wastewater, a batch EC system with Al electrodes was proposed. By adopting this method decolorization rate was 98% in optimum conditions [13]. Many electrocoagulation systems were developed for the decolourisation of dyes such as Direct Red 23,Reactive Blue 140, azo-based Disperse Red 1[14,15], crystal violet (CV) [16], Acid Green dye 50 [17], Acid Brown 14 [18], Acid Red 14 [19], azo-based Orange II dye [20], azo-based Reactive Black 5 [21], Acid Blue 74 [22], basic red 18 [23] and reported. Similar to textile industry, the black liquor discharged from the pulp and paper industry contributes significantly to environmental pollution. Electrocoagulation method was adopted to treat the paper mill effluents from a modern bleached kraft mill. From the results it was found that this method is an effective alternative in paper mill effluent treatment [24]. By using the Al electrodes in batch mode this method becomes very effective [25]. Amita Deokate developed a textile waste water treatment reactor by solar powered electro-coagulation technique [26]. Effluents released from surface finishing and plating industry contains metals such as cadmium, lead, mercury, chromium, nickel, copper, zinc and cobalt which are harmful to human health even in very low concentrations. These heavy metals were successfully removed by electrocoagulation [27,28]. Deepak carried out experiments in an electro coagulation reactor with aluminum as sacrificial electrodes for treating pulp and paper effluents [29].

Modern dyes have a multiple variety and they are often intended to be produced to resist the breakdown of long-term exposure to sunlight, water, and other atrocious conditions, thus making the treatment of dye wastewater more difficult. The effluents from textile plants contain portions of dyes, which are important water pollution sources. The dyes are deeply colored, multicomponent, and consume dissolved oxygen, and destroy aquatic life. Moreover, some dyes and

their degradation products may be carcinogens and toxic, Therefore, it is necessary to treat the dyes before disposal. Many dyes are difficult to decolourise due to their complex structure and synthetic origin. A wide range of methods has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment. Electrocoagulation is an effective electrochemical approach for the treatment of dye effluent

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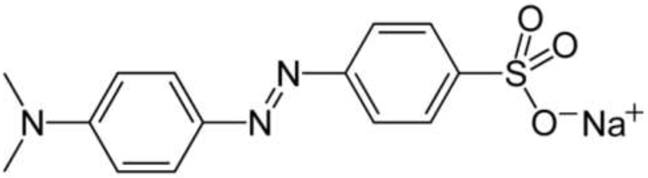
synthetic origin. A wide range of methods has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment. Electrocoagulation is an effective electrochemical approach for the treatment of dye effluent

The commercially available dye Acid orange 52 was selected for the present study. The dye purchased were of high purity, commercially available AR grade. The properties of the selected dye was given in Table 1 and their structures are shown in Fig.



Structure of Acid orange 52

Dyes	**Molecular formula**	**Molecular weight, g/mol**	**Wavelength λmax (nm)**	**C.I. No.**	
Acid orange 52	$C_{14}H_{14}N_3NaO_3S$	327.33	460	13025	

Table 1. Properties of Acid Orange 52

CHAPTER-III

EXPERIMENTAL DETAILS

2.1 Equipment Setup

The electrochemical reactor system is as shown in Fig. 2. The ECF unit mainly consists of aluminum sheet as cathode and anode and a DC power supply. Working volume of the electrochemical reactor was around 0.25 L, inter electrode distance was 1 cm and the effective electrodes area was approximately 18 cm^2. A digital DC source (PICO, 0-30V 0-5A CVCC MODE) was used to supply the power to the ECF system. A magnetic stirrer was used to provide thorough mixing to the solution.

Fig.2. Electrocoagulation setup

2.2. Choice of Electrode Material

Aluminum (Al) is one of metals which widely used in various industries such as construction, transportation, electrical component and packaging. Several thousand tons of Al is used every year, and in the meantime, a lot of Al scrap is also generated. The Al scrap can be reused as secondary Al in industrial sectors after melting. Thus, aluminum is used as electrodes for this electrocoagulation process.

2.3 Experimental Method

The acid orange dye solution of 0.25 L and concentration of 100 ppm was added separately to the electrocoagulation reactor system. Then the operating factors of current density (10-30 mA/cm2), electrolysis time (5-20 minutes), pH of the medium (1 to 13), stirring speed (150-350 rpm), inter electrode distance (0.8 to 2 cm) and NaCl concentration (1.5-5.0 g/L) were varied. The temperature was maintained at 25 °C. At the end of experiments, the solution was centrifuged to remove the sludge. The solution was centrifuged and the absorbance was measured by UV-Visible spectrophotometer (Deep Vision UV-VIS Single Beam spectrophotometer) at 460 nm respectively for Acid orange 52. The efficiency of dry removal was calculated using Eqs.(1),

Efficiency (%) = 1- (final absorbance / initial absorbance) x100 ------(1)

CHAPTER-IV

RESULTS AND DISCUSSION

4.1. Electrocoagulation

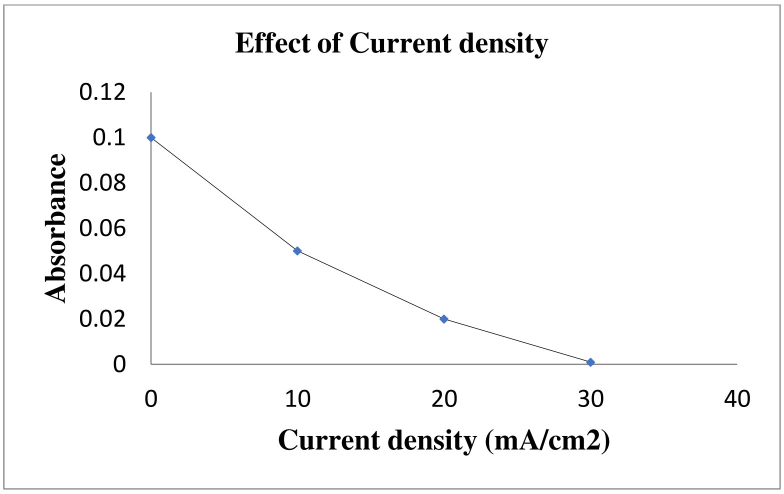
The Acid orange 52 dye solution of 0.25 L and concentration of 100 ppm was added to the Electrocoagulation reactor system. Then the operating factors of current density (10-30 mA/cm^2), electrolysis time (5-20 minutes) pH of the medium (2 to 10) and stirring speed (150-350 rpm), inter electrode distance (0.8 to 2cm) NaCl concentration (1.5-5.0g/L) were varied. The temperature was maintained 25 °C. At the end of experiments, the solution was centrifuged to remove the sludge. The solution was centrifuged and the absorbance was measured by UV-Visible spectrophotometer (Deep Vision UV-VIS Single Beam spectrophotometer) at 460 nm. The efficiency of dry removal was calculated using equation (1).

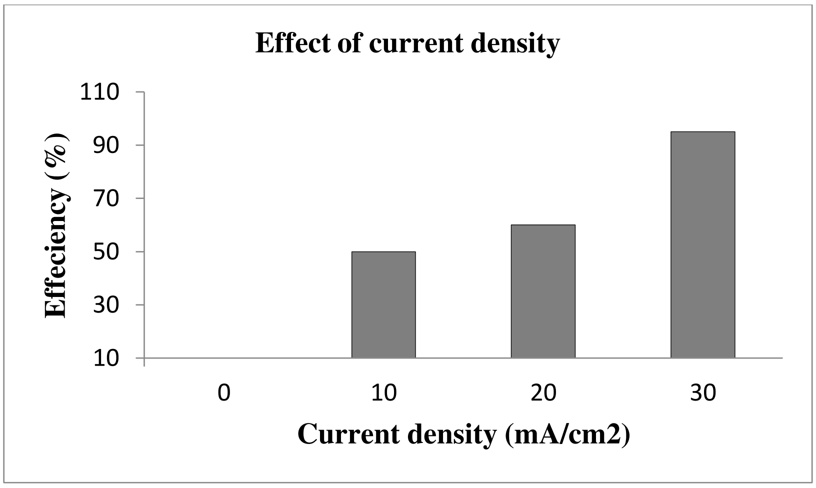
Efficiency (%) = 1- (final absorbance at 460nm / initial absorbance at 460nm) x100 ------(1)

4.4. Effect of Current Density

The initial absorbance spectra of Acid orange 52 solutions presented the highest peak at 460 nm, (Fig.2) thus the reduction of the highest peak was referred the dye removal efficiency. After treatment by EC the absorbance was measured at 460nm using a UV-VIS spectrophotometer. The peak at 460 nm decreased from 0.1 Abs at the initial to 0.05 Abs at the current density of 10 mA/cm2, and further decreased to 0.02 and 0.001 Abs at the higher current densities. The dye removal efficiency was increased by increasing current densities as linear relation. The efficiency was 50% at 10 mA/cm2 and increased to 60% at 20 mA/cm2 and reached the maximum of 95% at 30 mA/cm2. This is because a large amount of aluminium hydroxide particles (i.e., $Al(OH)_3$) are generated at the higher current densities. The aluminium hydroxide particles act as coagulant to destabilize the colloid particles of dye, and remove the destabilized dye from the water

Current density (mA/cm^2)	**Absorbance**	**Effeciency (%)**
0	0.1	0
10	0.05	50
20	0.02	60
30	0.001	95

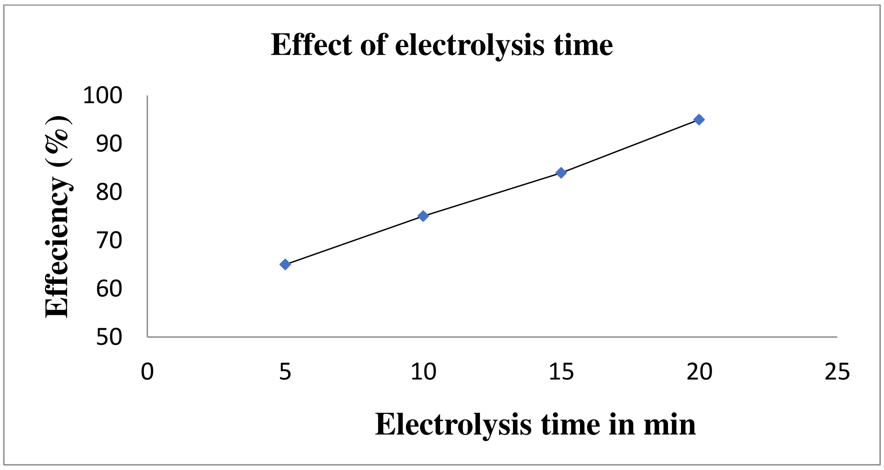




4.5. Effect of Electrolysis Time

At various electrolysis times, the dye removal efficiency was increased by increasing electrolysis times as exponential relation. The efficiency was sharply increased to 65% at 5 minutes, and continuously increased at the longer electrolysis times. The efficiency reached 75% at 10 minutes, then slightly increased to 84% at 15 minutes and reached its maximum of 95% at 20 minutes. The longer electrolysis times causes high sludge formation and prevents the chemical interaction during coagulation process and increase the energy consumption.

Electrolysis Time	Effeciency (%)
5	65
10	75
15	84
20	95



4.6. Effect of pH

To study the effect of initial pH of the solution on the removal by the EC process, the pH was varied from 2 to 10. It has been observed that pH has not much significance in the color removal efficiency. At pH 2.0 colour removal efficiency was 90% which was decreased to 70%

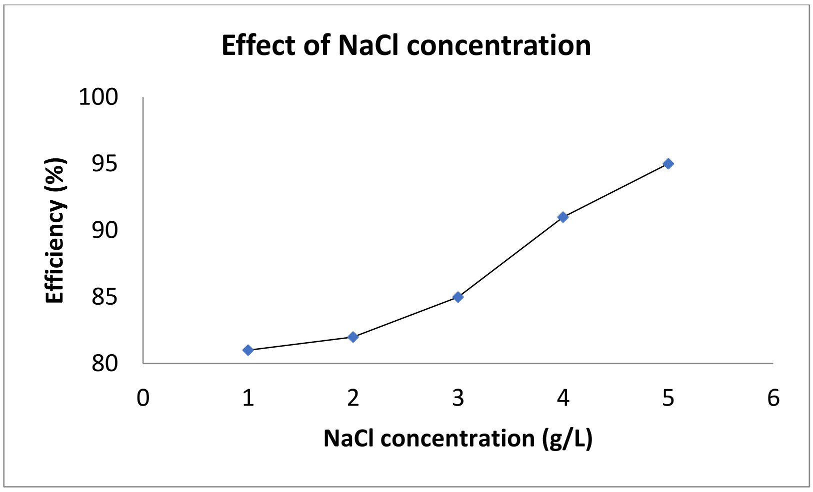
at pH4.0 and lowered to 35 at pH 10. Therefore, optimum pH value was considered as 2. Table shows the percentage removal of color by varying initial pH of the solution.

pH	Efficiency (%)
2	90
4	70
7	50
10	35

4.7. Effect of NaCl Concentration

NaCl played a role as conductive solution, and without NaCl addition the chemical reaction does not takes place in the EC system. Concentration of NaCl was varied from 1 to 5 g/L, the dye removal efficiency was in the range between 80-92%. Efficiency increases slightly when the concentration of NaCl increases. At the end of experiments, the surface of Al electrodes was decayed to produce the aluminium ions and form the coagulant as aluminium hydroxide. Further, the sludge of aluminium hydroxide particles and dye were observed at the water surface. The water became clear and colourless after sludge removal.

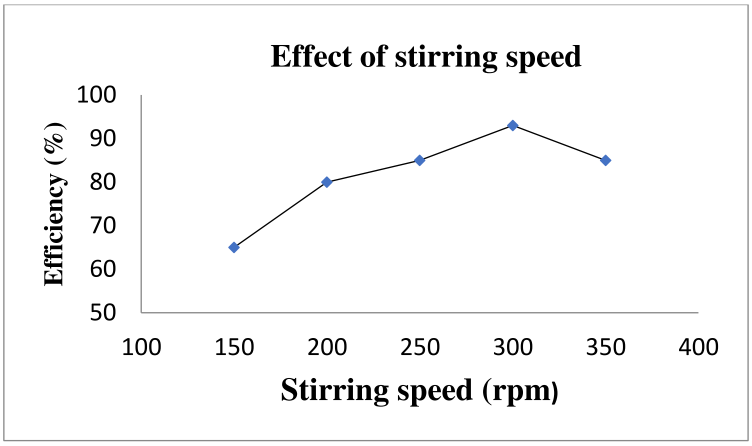
NaCl concentration (g/L)	Efficiency (%)
1	81
2	82
3	85
4	91
5	95



4.8. Effect of stirring speed

Influence of stirring speed on colour removal efficiency of acid orange 52 was studied by varying the stirring speed from 150 to 350 rpm. Efficiency increases slightly when the stirring speed increases and attains its maximum at 300rpm, above which the efficiency was decreased because, the flocculation process allows the aggregation of colloidal particles into flocs which could hinder the removal process and has negative effect on colour removal. The main function of stirring is to ensure a good homogenization of the mixture dispersing the coagulant species in the reactor, thus causing efficient contact between the neutralized molecules and destabilized colloids and the cationic metallic species.

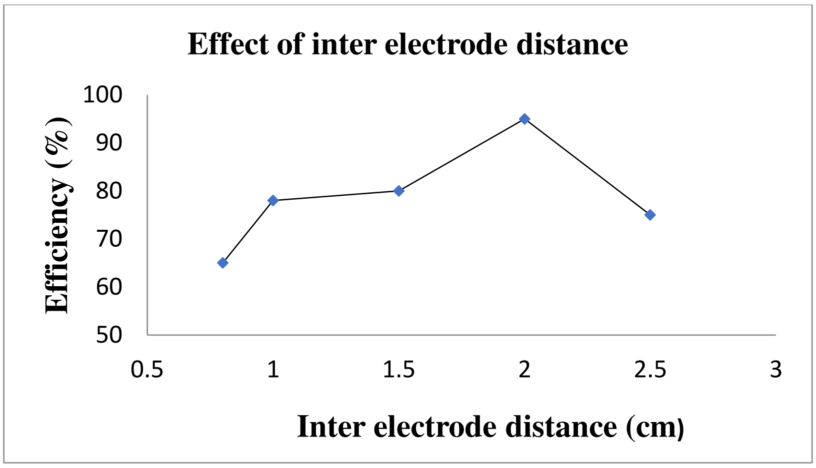
Stirring speed (rpm)	**Efficiency (%)**
150	65
200	80
250	85
300	93
350	85



4.9. Effect of inter electrode distance

The distance between the electrodes is an important parameter implicated in the design of the electrochemical cell. Optimizing the inter electrode distance contributes to the regulation of the electrocoagulation process. To study the influence of electrode distance on colour removal efficiency, the distance between the electrodes was varied between 0.8 and 2.5 cm. The results obtained with the EC treatment shown in the table. The removal efficiency is relatively low when the electrode distance was small and obtained its optimum at 2 cm.

Inter electrode distance (cm)	**Efficiency (%)**
0.8	65
1.0	78
1.5	80
2.0	95
2.5	75



At the end of experiment, the surface of Al electrodes was slightly decayed to produce the aluminium ions and form the coagulant as aluminium hydroxide. Further, the sludge of aluminium hydroxide particles and dye were observed at the bottom, as shown in figure. However, the water became clear and colourless after sludge removal.

Fig.5. Sludge formed after electrocoagulation

The sludge formed mainly contains aluminium hydroxide which was removed by centrifugation and dehydrated using water-miscible non-aqueous solvent like ethanol and formed into amorphous powder as shown in the figure. This powder can be used in the preparation of

- Fire retardant powders
- Zeolites
- Activated alumina
- calcined aluminas

Fig.6. Powdered form of sludge

4.2. UV-Visible behavior

The UV-Visible of the samples before and after coagulation is shown in Fig.3. UV spectral studies were studied using JASCO V- 530 spectrophotometer using a 1 cm quartz cuvette filled with the samples. The peak around 347 corresponds to the n-π* (N=N) in dye molecules. The peaks present around 220-264 nm is due to π*←π transition of the benzenoid rings present in the dye molecule. Colored compounds are colored because of the absorption of visible radiation. Since the synthetic dye sample solution was coloured there will be interaction of radiation from the visible part (λ= 380-720 nm) of the electromagnetic spectrum with a chemical species in a dye molecule. The intensity of the band in visible region was found to be decreased after coagulation.

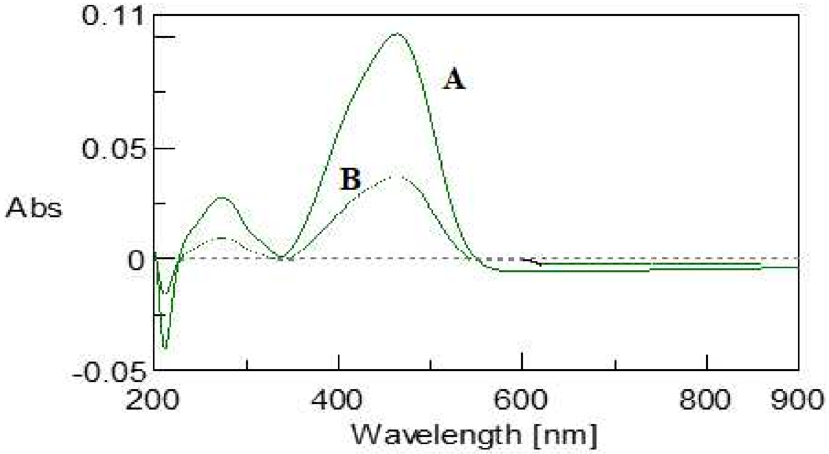


Fig.3. UV-Vis spectral behavior of Acid orange 52before A)and after coagulation (B)

4.3. FT-IR spectral behavior

The significant bands in the sample is due to the azo chromophore (-N=N-), C-N stretching and aromatic ring present in them (Fig.4). The bands due to the aromatic region in the range of 1400-1600 cm^{-1}are also significant as azo bond stretching appears between the bands of the aromatic region. The stretching of aromatic region is prominent and strong . The absorption band of the azo chromophore is clearly distinct from the C=C absorption bands which are quite evident in their spectrum. The azo absorption bands were sited between 1500 cm^{-1}and1700 cm^{-1}. Due to aromatic region, the higher energy bands appeared from 1590 cm^{-1}to 1619 cm^{-1}. The broad band around 3100 cm^{-1} can be referred to the N–H stretching vibration. The intensity of the bands was found to be decreased after coagulation.

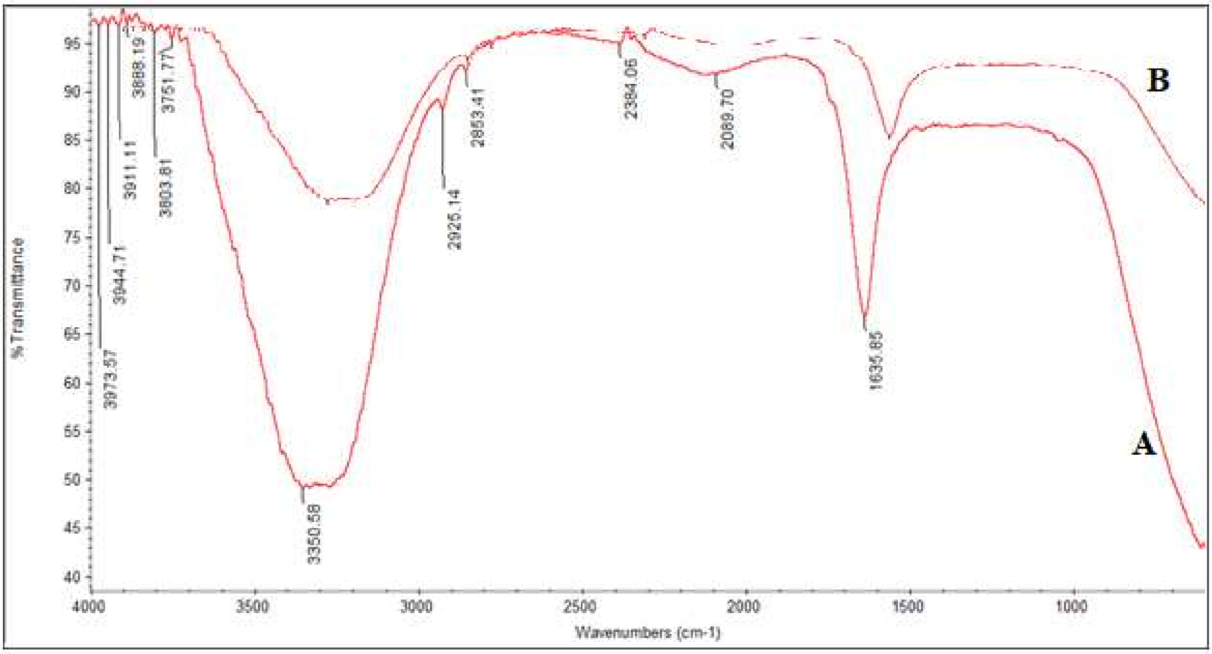


Fig.4. FTIR spectrum of Acid orange 52 before (A) and after coagulation (B)

Conclusion

- ✓ From the outcome it has been concluded that the electrocoagulation reaction (ECR) was effectively used for the removal of dyes acid orange 52
- ✓ Undeniably, the optimum operating circumstances was determined and shown below.

Working Parameters	**Optimum**
current density	30 mA/cm^2
electrolysis time	20 minutes
pH	2
stirring speed	300 rpm
inter electrode distance	2 cm
NaCl concentration	5.0 g/L

- ✓ From UV and FTIR spectral behavior its clear that the concentration of dye is decreased before and after coagulation process.

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Synthesis and characterization of poly(aniline-co-ortho nitroaniline)-$FeCl_3$ composites and its application in electrocoagulation of Malachite green

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

S. Jeslin Jenitha
A. Joy Julie Anslin
M. Muthu Usha
S. Ramalakshmi
H. Sherlin Blessey
G. Stella Angelin

St. Mary's College (Autonomous)
(Re-accredited by 'A+' Grade by NAAC)
Thoothukudi- 628001.
2020-2021

DECLARATION

We hearby declare that the project entitled **"SYNTHESIS AND CHARACTERIZATION OF POLY(ANILINE-CO-ORTHO NITROANILINE)-$FeCl_3$ COMPOSITES AND ITS APPLICATION IN ELECTROCOAGULATION OF MALACHITE GREEN"** submitted to St.Mary's college (Autonomous), Thoothukudi, affiliated of 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.

S. Jesline Jenitha
S. Jesline Jenitha

A. Joy Julie Anslin
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H. Sherlin Blessey.
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G. Stella Angelin.
G. Stella Angelin

April 2021

Thoothukudi

CERTIFICATE

This is to certify that project in chemistry entitled **“~~green~~ Synthesis and characterization of poly(aniline-co-ortho nitroaniline)-$FeCl_3$ composites and its application in electrocoagulation of Malachite** green” 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 2020-.2021

NAME	**REGISTER NUMBER**
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GUIDE

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I. A. Sophia

EXAMINERS

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PRINCIPAL

St. Mary's College (Autonomous)
Thoothukudi - 628 001.

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 Sr. FLORA MARY** for providing infra structural facilities.

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CONTENTS

Synthesis and characterization of poly(aniline-co-ortho nitroaniline)-$FeCl_3$ composites and its application in electrocoagulation of Malachite green

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Thoothukudi- 628001.

2020-2021

DECLARATION

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H. Sherlin Blessey

G. Stella Angelin

March, 2021

Thoothukudi.

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This is to certify that project in chemistry entitled **"COPOLYMERISATION OF "** 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 2020-2021.

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GUIDE HEAD OF THE DEPARTMENT

EXAMINERS PRINCIPAL

1.

2.

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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 **THE SECRETARY**,for providing infra structural facilities.

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CONTENTS

Introduction

Polymers are long chains of molecules formed from small molecules linked together. A hundred to million monomers may be present in a single polymer molecule. The word "polymer" can be splitted as poly and mers, poly means many in Greek and mer means unit. The properties of the polymer materials are unique depending on the type of molecules being bonded .Some polymers bend and stretch, like rubber. Polymers are made up of many materials in living organisms such as protein, cellulose and nucleic acids. The first polymer made independent of the products of organisms in 1907 by Leo Baekeland. Based on the structure, the polymers are divided into linear, branched and cross-linked polymers.

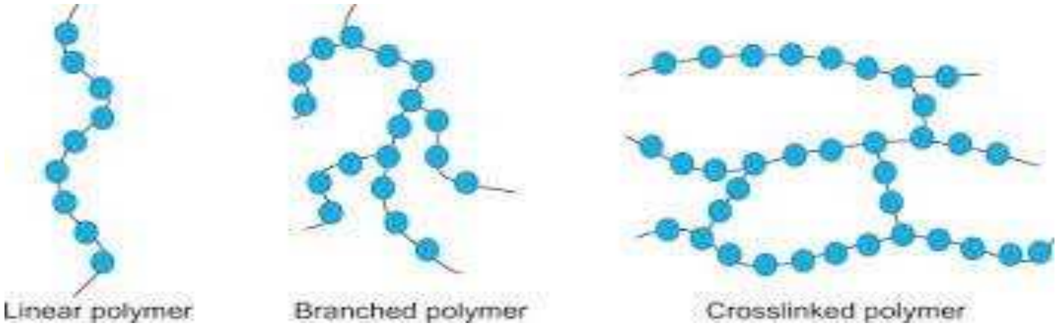

Fig. 1.1 Types of polymer

Based on the source polymers are divided into natural and synthesis polymers. The chemical reaction in which high molecular mass molecules are formed from monomers is known as polymerization [1].

Applications

- Electronic and photonic.
- Packaging and containers: films, bottles, food packaging, barrels.
- Insulation: electrical and thermal insulation, spray foams.
- Car parts: tires, bumpers, windshields, windscreen wipers, fuel tanks, car seats.
- Medical applications.

Popular polymers for manufacturing include polyethylene and polypropylene molecules can consist of 10,000 to 200,000 monomers [2].

1.1 Conducting polymers

In the mid of 1970s, polyacetylene was accidently prepared by Shirakawa, the first polymer which is capable of conducting electricity. The next discovery was by Heeger and Macdiarmid that polyacetylene would show an increase in conductivity of several orders of magnitude by doping with different compounds. This created an interest in among others to search for new polymers which will conduct electricity [3]. Soon after many different conducting polymers were discovered by various scientists.

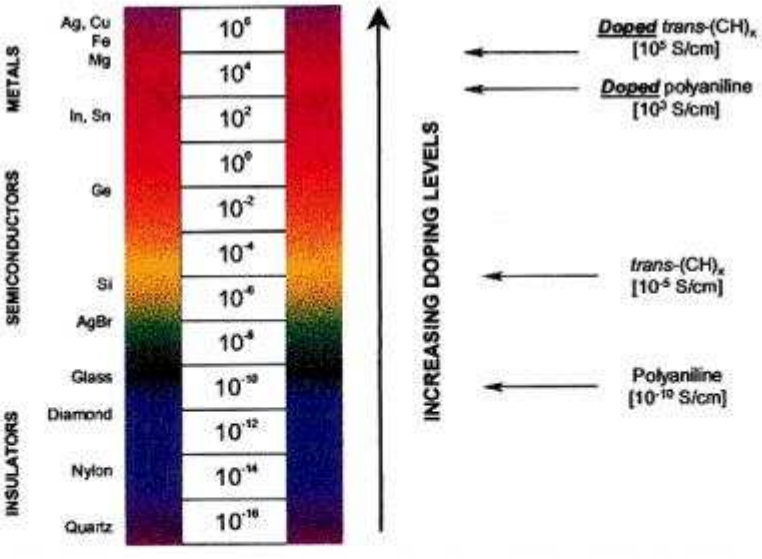

Fig. 1.2 Conductivity of insulators, semiconductors and metals [3]

Polypropylene, polyacetylene and polyaniline are some of the examples of conducting polymers. They can be prepared either by oxidative or electrochemical polymerization. Some of these polymers can be easily prepared by chemical oxidation method and they can also be directly deposited on electrode surfaces. Conducting polymers has a wide range of application and used in light-weight batteries, electrochromic displays, light emitting diodes, biosensors, etc. [4]

1.2 Copolymer

A copolymer is a polymer derived from more than one species of monomer. The polymerization of monomers into copolymer is called copolymerization. Copolymers obtained from three or four monomers are called terpolymers and quarter polymers respectively. Examples for commercial copolymer are acrylonitrile- butadiene, styrene-butadiene, styrene-acrylonitrile, styrene-isoprene-styrene, ethylene-vinyl acetate[5].

1.3 Types of copolymers

Random copolymer

In random copolymer two or more different repeating units are distributed randomly.

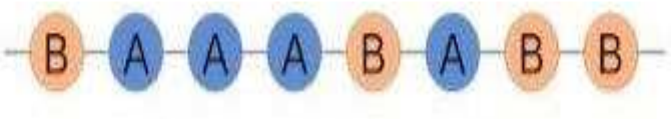

Fig. 1.3 Random copolymer

Alternating copolymer

Alternating copolymer are made of alternating sequence of the different monomers.

Fig. 1.4Alternating copolymer

Block copolymer

In block copolymers long sequences of monomers are followed by long sequences of other monomers.

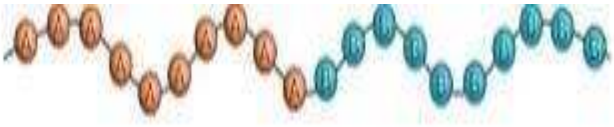

Fig. 1.5 Block copolymer

Graft copolymer

Graft copolymer consists of a chain made from one type of monomers with branches of another type [6].

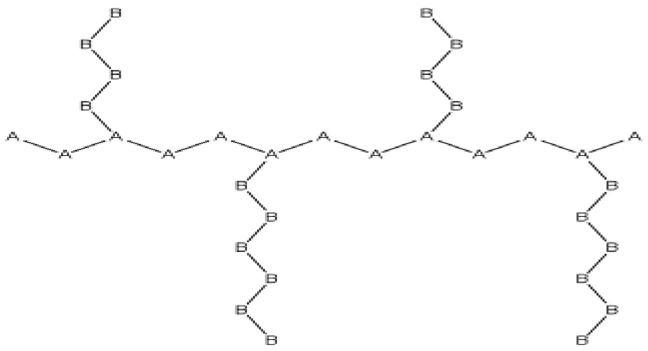

Fig. 1.6Graft copolymer

Copolymer consists of two structural units. They are linear and branched copolymer.

Linear copolymer

Linear copolymer consists of single main chain. It also include alternating copolymer, statistical copolymer and block copolymer.

Branched copolymer

It consists of single main chains with one or more polymeric side chains. It can be grafted, star shaped or it can have other architectures.

Periodic copolymer

Periodic copolymer consists of more than two species of monomer units in regular sequence.

Statistical copolymer

Statistical copolymer consists of monomer residues arranged according to the statistical rule [5].

1.4 Synthesis of copolymer

Copolymers are synthesized by chain growth method. Copolymers can also be by step growth condensation polymerization [7].

Uses of copolymer

Copolymerization is used to modify the properties of manufactured plastics.

- It is used to reduce crystallinity.
- It is used to modify glass transition temperature.
- It is used to control wetting properties.
- It is used to improve solubility [5].

1.5 Polyaniline

Polyaniline is an intrinsically conducting polymer with a variety of applications. Chemical synthesis with oxidizing agents and electrochemical polymerization are the common method used in the synthesis of polyaniline. Some uncommon methods employed are photochemical polymerisation and enzyme catalysed polymerization in the preparation of polyaniline [8]. Polyaniline can be synthesized in many forms like powder, nanotubes, nanowires, nanoflower and microspheres. Polyaniline can also be prepared as thin films and colloidal suspension also [9].

Normally polyaniline is synthesized by stirring aniline in hydrochloric acid medium is at room temperature. Oxidizing agent is then added slowly to the solution and continuously stirred for four to five hours. Emeraldine base of polyaniline is formed. The formed precipitate is washed with water and alcohol, and then it is stirred with ammonium hydroxide for several hours to convert emeraldine base form of polyaniline to emeraldine salt [10].

Polyaniline can also be synthesized electrochemically by electrolyzing aniline in acidic media using electrodes. Typically a three electrode system is used. Pharhad

Hussain et.al. used stainless steel as working electrode and saturated calomel electrode as reference electrode for the electrochemical synthesis of polyaniline[11].

Polyaniline exists in many different forms like Leucoemeraldine base, Proto-emeraldine base, Emeraldine base, Nigraniline base and Pernigraniline base. The fully reduced form of polyaniline is leucoemeraldine base and pernigraniline is the fully oxidized form. Other forms like proto-emeraldine, emeraldine and nigraniline bases are the intermediates between leuco-emeraldine base and pernigraniline base [12].

1.6 Composites

A composite material can be defined as a combination of two or more materials that results in better properties than those of the individual components used alone. In contrast to metallic alloys, each material retains its separate chemical, physical, and mechanical properties. The two constituents are a reinforcement and a matrix. The main advantages of composite materials are their high strength and stiffness, combined with low density, when compared with bulk materials, allowing for a weight reduction in the finished part. The reinforcing phase provides the strength and stiffness. In most cases, the reinforcement is harder, stronger, and stiffer than the matrix. The reinforcement is usually a fiber or a particulate [13].

1.7 Polyaniline composites

Polyaniline is a conducting organic polymer with a single and double bonds and hence are called conjugated polymers. Polyaniline is air-stable but unprocessable conducting polymer. To improve its processability it is blended with other polymers or any dopants. This will increase its conductivity and also its applications [14]. Polypropylene, polyethylene, ultra-high molecular weight polyethylene, polystyrene, polyamides are the polymers which are used for fabrication of electrically conducting polymer composites. To introduce conductivity, these polymers are filled with conductive polymers like polyaniline. Polyaniline composites is considered as one of the most useful conducting polymer composites due to its high environmental and thermal stability, low resistivity and ease of manufacturing. These composites are widely used in many applications e.g. solar energy conversion devices, rechargeable batteries, electrochemical sensors, super capacitors and corrosion protection [15].

1.8 Electro coagulation

Electro coagulation also known as radio frequency diathermy or short wave electrolysis. It is fast becoming popular as an alternative method for the treatment of water and waste water. It is a broad spectrum treatment technology that removes total suspended solids, heavy metals, emulsified oils, bacteria and other containments from water.

Benefits of Electrocoagulation

- Low operating costs
- Low power requirements
- Minimal chemical additions
- Low maintenance
- Sludge minimization

Applications of electro coagulation

- Ground water cleanup
- Surface water cleanup
- Process rinse water and wash water
- Cooling towers
- Water pretreatment

Advantages

It is easily operated due to its simplicity of its equipment hence, complete automation of the process is possible. It produces much is less sludge volume than other methods and sludge formed is more stable and non-toxic. Even the smallest colloidal particles are removed by elecrocoagulation since the applied electric current makes collision faster and facilitates coagulation. Waste water treated by electrocoagulation gives clear, colourless and odorless water. No chemicals are needed, so there is no chance of secondary pollution.

Disadvantages

- Regular replacement of sacrificial anode is necessary since the anode dissolves to the solution.
- Cathode passivation can occur which decreases the efficiency of the process.
- In some areas where electricity isn't abundant, the operating cost can be expensive [16].

1.9 MALACHITE GREEN

Malachite green is an organic compound that is used as a dyestuff and controversially as an antimicrobial in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Despite its name the dye is not prepared from the mineral malachite, and the name just comes from the similarity of color [17]. Malachite green has the chemical name 4-(p-(dimethyl amino)-α-phenylbenzylidene)-2, 5-cyclohexadien1-ylidene dimethyl ammonium chloride [18].

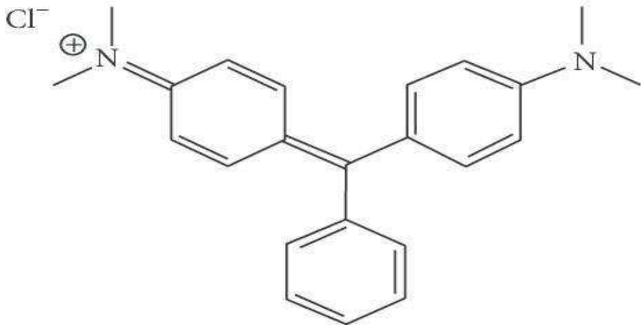

Fig.1.7 Structure of Malachite Green

Uses of Malachite Green

- Malachite green is traditionally used as a dye.
- It is used as an antibacterial
- It is used as endospore straining.
- It protects against harmful rays from technology [19].

An aniline/o-nitro aniline copolymer was prepared by Ruiruizaho et. al. simply by grafting electron-withdrawing o-nitro aniline groups onto polyaniline chains through a chemical oxidative polymerization and tested as a high voltage cathode material for Na-ion batteries. The results revealed that these composites can be used as a high capacity cathode for Na-ion batteries [20].

Electrochemical copolymerization of aniline with o-aminobenzonitrile by Masakisato et al. in an aqueous acid solution gave a copolymer film with a polyaniline-like structure in which some of the phenyl rings had a cyanide group. In copolymerization, the applied potential was cycled between −0.2 and 0.9 V vs. saturated calomel electrode at the rate of 50 mV s^{-1} [21].

Ayman S. Al Hussaini et al. gave a new method of cheap Synthesis of a new Copolymer (o-Nitro aniline-co-o-Phenylenediamine) composites with Hydrophilic bentonite by 1:1 molar ratios of the respective monomers with different percentages of Nano clay via modified in situ chemical co-polymerization and studied their antibacterial Efficacy. Results revealed that these composites showed a very good antibacterial activity [22].

Ku, Wang, Pattarachaiyakoop and Trada et. Al. reviewed on the tensile behaviour of natural fibre reinforced polymer composites and investigated on natural fibre as an alternative source of reinforcing materials in manufacturing of composites. Good availability, ease in processing and low cost is the main advantage for the use of reinforced material for the development of composites. Halpin -T Sai equation was used to predict the Young’s modulus of composite materials made of different types of natural fibers [23].

Smrutisikha et.al. worked on CNT's reinforced epoxy based composites. Fabrication of sample completed at room temperature. Flexural moduli, electrical conductivity, and glass transition temperature of epoxy resin and nanocomposite samples had been determined. SEM used to distribution behaviour of carbon nanotubes in the epoxy matrix. The increase in glass transition temperature represent the strong interaction existing with MWNTs itself and epoxy chains, limiting the movement of polymer and chains [24].

In this technology world we are using many kinds of composites for different purposes. Polymer composites have a wide range of applications in various fields. Polymer composites with metal ions embedded in the matrix changes the character of the polymer and increases its applications. Conducting polymer like polyaniline, copolymer of polyaniline with other polymers and copolymer composites with metal ions have a good applications in dye degradation, super capacitors, fuel cells, corrosion studies, etc. Composites containing iron is used for the degradation of dyes, corrosion inhibitors, compact capacitors and anti static coating. Metal atoms present in the composites can undergo redox reactions and it makes useful for the catalytic degradation. So copolymer composite made up of aniline, o-nitroaniline and ferric chloride was chosen for the dye degradation studies. Malachite green dye was chosen for the studies by electro coagulation method. This method is chosen because it is a cheap method and less time consuming.

Materials and Methods

Chemicals Required

Aniline was bought from Spectrum reagents and chemicals of 99% purity and used as such. o- nitroaniline was bought from Loba chemie which is of 98% purity. 99.96 % pure ferric chloride was bought from Spectrum reagents and chemicals. Hydrochloric acid was bought from Isochem laboratories. Potassium per disulphite, and malachite green were bought form Merck.

4.2 Synthesis of the composite

About 0.01 mol of aniline and 0.01 mol of ortho nitroaniline were taken in 200ml of 1M HCl and stirred for 10 minutes for dispersion. Ferric chloride in 50 weight percentage of aniline and potassium per disulphite of about 0.015mol were added to the mixture. Within 5 minutes colour change to green was noted. The stirring was continued for four hours. Then the mixture was kept in the refrigerator 48 hours. It was then filtered and washed for several times using water and dried in room temperature for one week. The obtained green lumps obtained were ground in a mortar to fine powder.

4.3 Electro coagulation of Malachite green

0.01mol of the dye Malachite dye was prepared in distilled water. 100 ml of the dye was taken in beaker and it is electro coagulated using aluminium electrodes with the applied potential of 25mV and the concentration of the dye was measured for every five minutes using a single beam UV-Visible spectrophotometer in the wavelength of 617 nm.

Again 100 mL of 0.01 mol malachite green solution was taken in a beaker along with 0.01 g of the composite and electro coagulated using aluminium electrodes by applying 25mV potential and absorbance values were measured for every five minutes using single beam UV-Visible spectrophotometer in the wavelength of 617 nm.

4.4 UV- Visible Spectral analysis

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

4.5 FT-IR Spectral Analysis

FTIR spectra were recorded for the composite using Nicolet Si5 spectrometer using KBr pellets in the range of 4000 – 400 cm^{-1}

The copolymer was synthesized with aniline and o-nitro aniline in the ratio 1:1. When the concentration of the o- nitroaniline is increases, it will make the yield low. The reason for the low yield is due to the electron withdrawing nature of the nitro group. Also due to the intermolecular interaction of the nitro groups which are present near the amine group to the polaronic nitrogen atom in the polymer chain may create a six membered chelate ring, which in turn will reduce the conductivity of the formed polymer rings [25].

Potassium per disulphate was used as an oxidant and ferric chloride is used as co-oxidant. Ferric chloride will act as a dopant as well as oxidizing agent [26]. Zhang et.al found that, the addition of ferric chloride does not change the shape of the particles, but it increases the yield and reduces the time needed for the formation of the particles. The yield of polymer increases with increase in the concentration of ferric chloride [27]. Also it was reported that the conductivity of polyaniline formed by ammonium perdisulphate and ferric chloride are similar [28].

5.1 UV- Visible spectral studies

The UV-Visible spectrum of poly(Aniline-co-o-nitroaniline) –$FeCl_3$composites are given in fig. 5.1. Peaks are present at 238nm, 366nm, 398nm, 410nm and 560- 820nm

The first absorption band at 366nm was due to the π to π* transition of the benzenoid ring present in the composite [29, 30].The peak due to polar on to π* transition is found at 410nm. The peak obtained due to band gap excitation is present at 398 nm [31]. This peak depends on the level of doping of the polymer composites and it depends on the transition of oligo anilines that lead to different wavelength in the UV- Visible spectra [29]. For poly (Aniline- co-o – nitro aniline) copolymer, a charge transfer from the HOMO of the benzenoid ring to the LUMO of the quinonoid ring was reported in the range 605 – 635 nm by Keueston et.al.[25] A broad peak in the range of 560 – 820nm is seen in the spectrum. That is due to the charge transfer from the HOMO of the benzenoid ring to the LUMO of the quinonoid ring of the metal composite. This band is very much broadened due to the presence of iron in the polymer matrix. Broad bands for excitation of quinonoid ring in the presence of metals was reported.

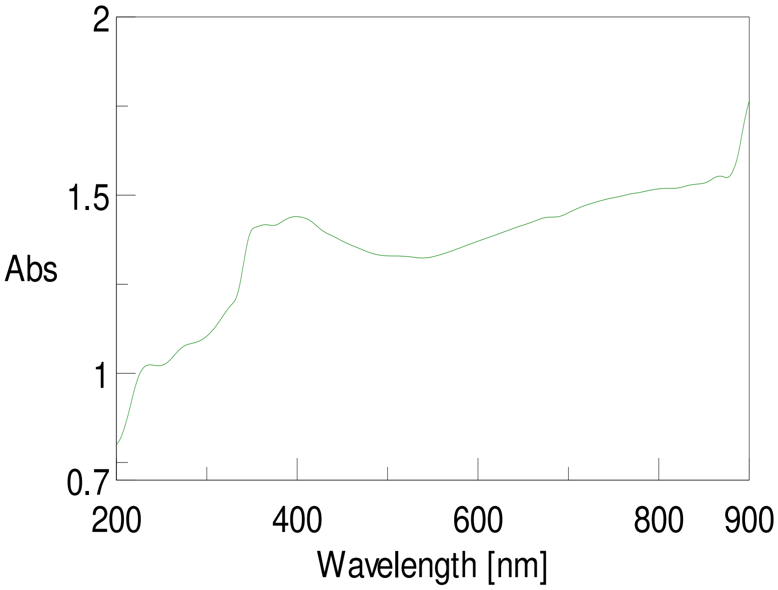

Fig. 5.1 UV – Visible spectrum of poly(Aniline-co-o-nitroaniline) –$FeCl_3$ Composite

5.2 Fourier transform Infrared spectral studies

FTIR spectrum of poly(Aniline-co-o-nitroaniline)- $FeCl_3$ composite is given in figure 5.2.

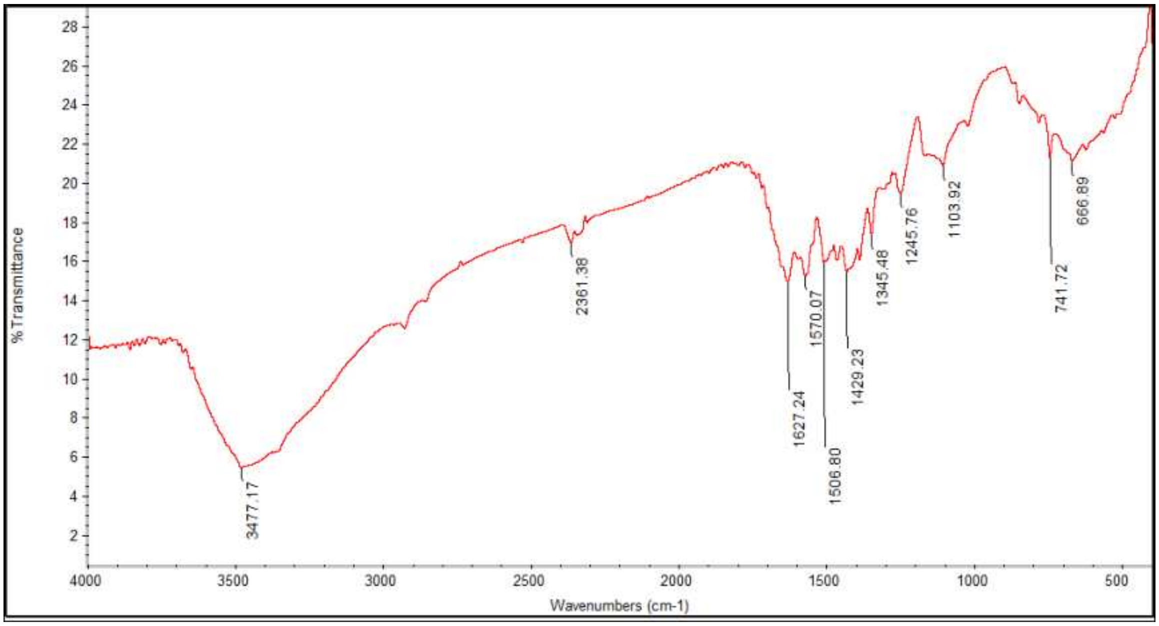

Fig. 5.2 FTIR spectrum of poly(Aniline-co-o-nitroaniline)-$FeCl_3$ Composite

FTIR shows peaks at 666cm^{-1}, 741 cm^{-1}, 1103 cm^{-1}, 1245 cm^{-1}, 1345cm^{-1}, 1429cm^{-1}, 1506cm^{-1}, 1627cm^{-1}, 2361cm^{-1} and 3477cm^{-1}. The band at 3477cm^{-1} is due to –OH stretching [32]. According to the literature the band for Fe – O is present at 420cm^{-1} and 423 cm^{-1} [32]. The Fe –O band may be present in the region of below 500 cm^{-1}

C=C stretching of quinonoid ring is present at 1506 cm^{-1}. C=C stretching of benzenoid ring is present at 1429 cm^{-1} [34]. The band present at1245cm^{-1} is assigned for N-H bending [32, 33]. The very small band present at 815cm^{-1} is due to the C–H out of plane bending vibration. The peaks obtained for this composite is slightly different form the obtained for pure polyaniline indicating π-π* interaction of the vacant p orbital of the polyaniline chains, and Fe^{3+} ion can coordinate with more than one N atom at a time of the same chain or a different chain by of its vacant d orbital [34].

Normally in Infrared Spectroscopy, asymmetric and symmetric stretching bands of NO_2 groups are located at around 1535 and 1345 cm^{-1} [30]. In this composite a strong band at 1345 cm^{-1} is observed in the spectra of the composite and it is due to the N O stretching vibrations of the nitro groups present in the polymer. 1103 cm^{-1} is due to B–(NH^+) =Q structure which is formed during the protonation process. In addition, the peak at 666cm^{-1} is attributed to –NH_2 wagging [33].

5.3 Electrocoagulation of Malachite green

Malachite dye was degraded using electrocoagulation method with the applied potential of about 25mV. Aluminium electrodes were used. Absorbance values of the dye, malachite green was measured using single beam UV- Visible Spectrophotometer at 617nm and the values are given in table 5.1. For malachite green the absorbance values slowly decreases when the potential is applied in electrocoagulation. Colour of the dye malachite green slowly decreased when the time is increased.

Table 5.1 Absorbance values of the dye malachite green

Minutes	**Absorbance**
0	0.269
5	0.228
10	0.213
15	0.197
20	0.115

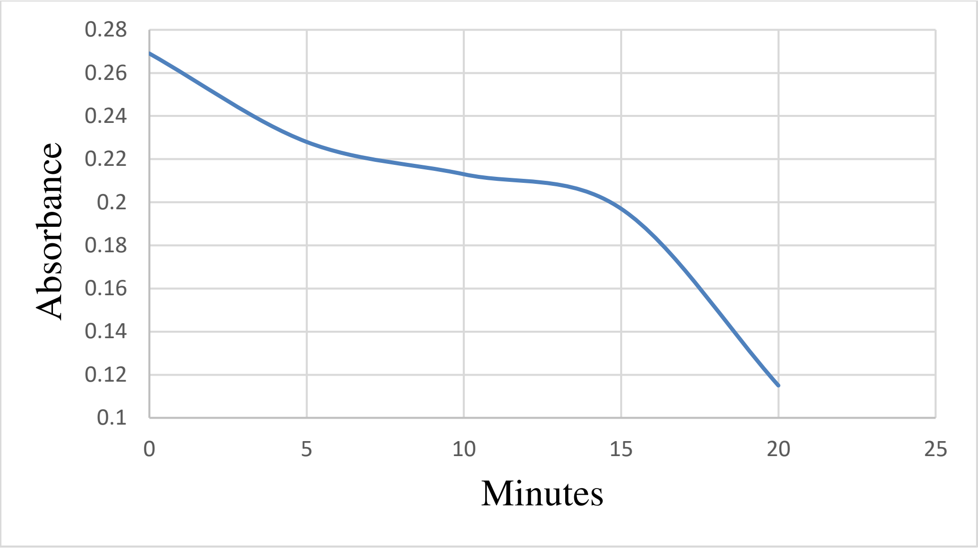

Fig. 5.3 Plot of time versus Absorbance for malachite green

Absorbance values of the dye, malachite green and the composite was measured using single beam UV- Visible Spectrophotometer and the values are given in table 5. 2. The absorbance values decreases when the potential is applied in electrocoagulation. The decrease in the absorbance is more when the composite is added to malachite green. The composite contains ion chloride and it degrades the dye at a faster rate.

Table 5.2 Absorbance values of malachite green and the composite

Minutes	**Absorbance**
0	0.360
5	0.279
10	0.204
15	0.178
20	0.118

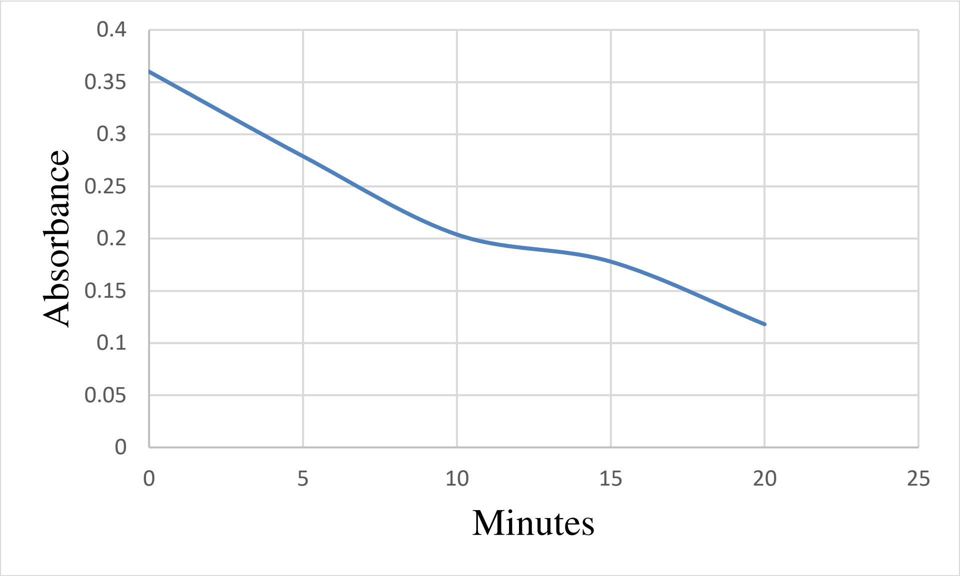

Fig. 5.3 Plot of time versus Absorbance for malachite green and composite

A copolymer composite of polyaniline with o-nitroaniline with ferric chloride was synthesized and characterized. Ferric chloride acts as both dopant and oxidizing agent. Electrocoagulation of the dye malachite green was studied and the results showed that the composite efficiently degrades the dye with the applied potential. So this can be used to clean waste water containing this dye efficiently.

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