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Production of TiO2 nanoparticles by green and chemical synthesis-A short review

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Abstract—From the past few years, many scientists have been investigating to find eco-friendly techniques for the production of nanoparticles. Nanoparticles have a huge demand for a wide variety of applications with its ambit ranging from areas like mechanics and biomedical sciences apart from playing a pivotal role in uprising fields like nanobiotechnology. The enthusiasm towards titanium dioxide nanoparticles reached its zenith among researchers due to its remarkable photocatalytic activity and antibacterial activity in addition to being a good semiconducting material. They can be synthesized by either physical, chemical or biological methods. The present review describes and analyzes the synthesis of TiO2 nanoparticles by various chemical means like sol-gel process, electrodeposition etc and also their synthesis from different plant extracts in an environmentally friendly manner termed "Green synthesis". The use of plants as a source for the synthesis of nanoparticles is advantageous when compared to the use of microorganisms due to their faster rate of biosynthesis. In addition, it can be clearly stated that the green synthesis by using plants is beneficial than production by chemical methods. The present review throws some light on the incorporation of TiO2 nanoparticles to produce nano paints and nanocoatings. This review also presents a detailed information regarding several production processes and parameters involved, in addition to the particle size and coating thickness obtained.

Index Terms—eco-friendly, titanium dioxide nanoparticles, photocatalytic activity, Green synthesis, biosynthesis, nano paints, nanocoatings, semiconducting material

1 INTRODUCTION:

1.1 Chemical Methods:

Chemically, titanium dioxide is one of the most versatile and stable element having an outstanding photocatalytic activity [1] in addition to being a good semiconducting material [2] . The titanium dioxide is employed in, dye- sensitized solar cells [3] [4] , solar water splitting [5] and is also used for photocatalytic degradation [6] of harmful pollutants which are organic in nature. According to a re- cent study done by P.Y.Zhang et al, [7] the titanium dioxide nanocoatings, when applied on surfaces, gave better results than those which employed titanium dioxide powders.

The presence of high grain size and high grain boundary volume fraction [8] resulted in the nanomaterials acquiring excellent mechanical properties in addition to physical properties. Nanocoatings are produced by condensing the size of the particles from the very basic molecular level so as to result in a more dense product. The incorporation of nanoparticles in coatings results in a wide range of applications and also enhancing the coatings with additional beneficial characteristics.

Conventional methods present like PVD and CVD are being used for the preparation of nanocoatings by changing the existing experimental parameters that are used for the production of microcrystalline coatings [9] in addition to using nano grained structured powders.

Thermally activated processes like HVOF is also being used to produce crystalline nanocoatings [10] [11] . A nanocoating is said to be effective when it has the combined characteristics of organic polymers such as elastic nature

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and being resistant to water and characteristics of inorganic materials like hardness and permeability [12] . Nanostructures help in superior adhesion to the substrate by forming a protective oxide layer [13] .

Hydroxyapatite nanoparticles based nanocoating pro- vides a better amount of corrosion protection and the titanium can be used for the making of biomedical im- plants [14] . The characteristic feature of nanocoatings is the wear resistance that is achieved because of the presence of combined strength and ductility. The addition of nanoparticles to coatings helps in increasing the surface area and simultaneously the size and volume of the pores, in turn increasing the roughness of a surface [15] .

By incorporating specific nanoparticles such as titanium dioxide nanoparticles, it is possible to develop nanocoatings that not only have the self-cleaning ability but also helps in imparting biocidal activity [16] [17] .

UV resistant and antibacterial self-cleaning paints have been developed by the use of nano titanium dioxide particles. The hiding power of the titanium dioxide nanoparticles is highest and its value is at 250nm particle size [18].
The degradation of the paint coatings by UV rays is the most common cause for their destruction, that is due oxidation and degradation of the polymer film in addition to organic and inorganic pigments. And the use of titanium nanoparticles helps in reflecting back the harmful rays.

Several chemical methods have been employed for the coating and deposition of the titanium dioxide nanocoatings such as sol-gel processes [19] [20] , vapor deposition [21] [22] in addition to thermal spraying [23] [24] and sputtering. When the process of preparation of these nanocoatings involves high temperatures like the commonly employed temperature of 300-2000 °C[25] ,the microstructure of the titanium dioxide nanoparticles may change resulting in hindering its potential in photochemical applications. In addition to the already present chemical methods, nanocoatings can also be applied to the surfaces with the help of techniques like electro-spark deposition, and laser beam surface treatment. When agglomerated titanium dioxide nanopowders are used as shown in previous study conducted by C.J.Li et al [26] ,the nanocoating had optimal photocatalytic activity. Among the main parameters which influence the coatings of nanoparticles upon surfaces, the pivotal role is the methods of preparations of those coatings.

2 DESCRIPTION OF DIFFERENT CHEMICAL METHODS :

According to the study conducted by S.-Q. Fan et al., one of the latest methods involving the coating of surfaces with nanoparticles, resulting in a thick layer of titanium dioxide nanoparticle deposition is the process of vacuum cold- spraying. Two types of titanium dioxide nanoparticle powders were employed for their deposition as coatings on stainless steel substrates and similarly on conducting glass substrates [27] .

In this study, vacuum cold spray(VCS) was developed and employed for the deposition of titanium dioxide nanoparticle powders with average diameters of 25nm and 200nm on the surfaces of conducting glass and stainless steel substrate respectively and then both their characteristics were crosschecked and analyzed. The developed VCS system consisted of many components such as a vacuum chamber and a vacuum pump, an aerosol room, an accelerating gas feeding unit, a particle-accelerating nozzle, a two- dimensional worktable and in addition a control unit.

Helium gas under the influence of high pressure was made to accelerate the titanium dioxide particles. The de- posited titanium dioxide nanocoatings were further characterized by X-ray diffraction and scanning electron micro- scope. It was also further found that the thickness of the deposited titanium dioxide nanocoating could be increased by increasing the number of spray passes. Using a load of 20 gm, an average Vickers microhardness [28] of 235 HV for the titanium dioxide nanocoating was obtained by using 200nm powder. Due to the repeated employment of a number of spray passes, there was a tamping effect that was created resulting in the increased density of the nanocoating as done by the cold spray process [29] [30] . The titanium dioxide nanocoating deposited by the 25 nm powder was found to have a higher density when compared to the deposition by 200nm powder. This study also resulted in having coatings with low values of microhardness implying the presence of weak bonds among the nanoparticles.

One of the economic methods used for the production of metal nanoparticle coatings is by electrodeposition. Properties of nanocoatings such as resistance to electricity, wear resistance and hardness is attributed to its grain size. One of the commercial aspects regarding the role of nanoparticles is their incorporation into paints to form nano paints. During the process of painting of the automobiles, the nanoparticles keep floating in the paint, but once the temperature of the automobile body is raised, the nanoparticles cross-link to form a dense network providing a substantial amount of scratch resistance. According to Shen et al. [31] the presence of hydrophobic coatings also have an added advantage as they offer low wetting to the surface upon which it is coated offering greater corrosion resistance even in moist environments. This hydrophobicity of the nanocoatings is due to its porous nature resulting in air particles getting trapped in those nanopores thus limiting the access to water particles and thus offering resistance to corrosion. In addition, corrosion resistance can be increased by incorporating the nanoparticles into the hybrid sol-gel systems due to the resulting presence of decreased cracking potential and lowered porosity. [32]

With reference to a recent study done by Cai et al. [33] , it has been found that a uniform layer of sol-gel coating of titanium dioxide can be formed by the technique of corona treatment.

The preparation of nano-composites which was aimed for the protective coating of biodegradable packaging materials which are hydrophilic in nature was done by M. Ioelovich et al. [34] The first step involved in it was to hydrolyze the cellulose in the presence of an acidic catalyst. Then precipitators were introduced into the acidic slurry of nano-cellulose to make the pH value of the slurry to be in between 6 and 7. This resulted in inorganic nanoparticles getting precipitated into the slurry. This is then followed by mixing the hydrophilic biodegradable polymers with the slurry containing nanoparticles. A high-pressure homogenizer was used as a method for mechanically disintegrating the nanoparticle agglomerates to obtain uniform particles of 100-300nm in size. The coating of this nano-composition imparts additional strength and increased resistance to water and grease without any impact on their biodegradability properties.

In the study undertaken by Geetha Subbiah et al., [35] the titanium dioxide nano paint was prepared by incorporating the titanium dioxide nanoparticles into an alkyd resin matrix by employing a high energy ball mill. The choice of titanium dioxide in this study was because of the presence of antibacterial nature, and excellent photocatalytic activity in addition to being biocompatible. [36] [37] [38] [39]

The size reduction method was employed to obtain the titanium dioxide nanoparticles by the process of high energy ball milling which was performed for 9 hours. [40]

Nano paints differ from the existing conventional paints mainly in the nature and properties of the binding agent used. In the case of a nano paint, the binding agent is an inorganic-organic hybrid polymer whereas in the conventional paints it is organic in nature. Pigments and binders make up the main components in the nano paints which play a role in imparting the color to the paint and in the process of its formation respectively [41] .

For the preparation of the TiO_2 nano paint, the titanium dioxide nanoparticles were used as a pigment utilizing the alkyd resin as a binder in addition to using nanosized zinc oxide as a stabilizer. This process was done in a ball mill which employed both the balls and the bowl made up of tungsten carbide and at 300 rpm which resulted in a white colored titanium dioxide nano-paint.

The obtained titanium dioxide nanoparticles had in its composition, the presence of mixed phases like anatase, ru-

TABLE 1
Synthesis of Nano particles using various techniques and their parameters

AUTHOR	PARTICLE SIZE/COATING THICKNESS	KEY CHARACTER-STICS	TECHNIQUE USED	REFERENCE
SQ Fan et al	Thickness obtained: <10µm	Temperature: 300-2000°**C** Pressure: 2000Pa Helium flow rate : 3liters/minute TiO_2 powder size: 25nm and 200nm.	Vacuum deposi-6tion(vacuum cold spraying)	
V s saji et al	Particle size (Nanocoating): 4-300 nm Thickness of coating:<2mm Nickel Nano ceramic–Al_2O_3,TiO_2 co-Deposition particle size: 10-30 nm	Use of Sol-Gel technology.	High velocity thermal spraying (HVOF)	9
M ioelovich et al	Particle size: 100-300nm Average size: 170 nm	pH: 6-7 Homogenisation Pressure: 100MPa. Number of circulations: 10. Viscosity measured at 20rpm.	Use of an acidic catalyst to hydrolyze the cellulose. Use of hydrophilic biodegradable polymers. Nanocoating imparts resistance to : Water and Grease	34
Geetha Subbiah Et al	Particle Size: 20-30 nm	Alkyd resin-Binder Nanosized ZnO-Stabilizer Material used: Balls and bowl-Tungsten carbide Shape of nanoparticles: Cubic shape Ball/powder ratio: 10:1	Ball mill process And agar dilution.	35

tile, and srilankite due to the milling induced phase trans- formation [42] . The atomic phase microscopy results explicated the presence of titanium dioxide nanoparticles to be in cubic shaped and the micrographs showed the size to be in the range of 20-30nm. The prepared titanium dioxide nano paint was made to apply on the substrate using the brush coating method.

Upon applying the nanopaint onto the substrates, the mechanism of its drying is based on the unsaturated fatty acids to undergo lipid autooxidation reaction in the alkyd resin and in the presence of oxygen [43]. The process of drying can be speeded up by using additives which act as external drier and an internal drier [44] [45]. The obtained titanium dioxide nanoparticles were studied for their antibacterial properties by using the method of agar dilution [46] [47].

One of the interesting properties of nanoparticles is their high surface area to volume ratio and this leads to paints having high performance due to the presence of nano- additives [48] . Some of the nanoparticles like nano-ZnO, nano-alumina have been used to enhance the UV- blocking and corrosion resistance [49] . Silanes based nanocoatings have superior performances as they do not use any toxic solvents or raw materials and come under the category of "green coatings" [50] [51] . The presence of silver nanoparticles in paints makes them antimicrobial in nature. These silver ions penetrate the bacterial cells and deactivate their enzymes, in turn, killing them [52] [53] . Nano-silica diox- ide in paints improves their scratch resistance and water repellence nature giving them a glossy finish [54] .

Due to large surface areas, the nanoparticles help in carrying corrosion inhibitors. Presence of reactive groups in the nanoparticles helps them cross-link giving more stability and durability to the coating [55]. According to the "continuum theory", effective dispersion and distribution of nanoparticles help in the optimal performance of the coating. But the piling of the nanoparticles is undesirable as it loses its large surface area [56] [57] [58] [59]

In many processes, antifouling treatment of the surfaces can be done resulting in substantial energy savings. Once they are economical in nature, these antifouling coatings can be used in many domestic systems and also in industries. To prevent the accumulation and deposition of marine organisms on immersed structures, environment- friendly antifouling coatings were developed. This antifouling property was achieved by modifying the resin resulting in the conversion of the hydrophilic epoxy surface into a hydrophobic one. This was done by introducing nano additives which made the coatings to have suitable proper- ties. Both the nano-additives helped to reduce the surface energy of the coatings and also have an effect on the elastic modulus of the substance on which it is coated.

3 AN OVERVIEW OF GREEN SYNTHESIS:

From the past few years, many scientists have been in- vestigating to find eco-friendly techniques for the production of nanoparticles. Rapid growth and progress in the field of nanotechnology have resulted in the uprising of new fields like applied microbiology and nanobiotechnology [60] . Based on the demands for various applications in biomedicine, bioscience, and biosensors, nanotechnology serves as a reliable alternative to manipulate and engineer the nanomaterials to achieve the desired properties [61] . A large number of metal nanoparticles and metal oxide nanoparticles that are being synthesized are highly useful due to their high surface area to volume ratio which is of utmost use in mechanical, optical, medical and many other applications.

One of the priorities in the field of nanotechnology re- search in producing nanoparticles is to keep in view the pa- rameters affecting the size, the shape and the stability of the obtained metal and metal oxide nanoparticles [62]. [63] Among many sources, one of the widely preferred organ- isms is plants as they can be used for large-scale production of metallic nanoparticles due to their low cost of production. One of the major advantages of using plants rather than other microorganisms for the production of metallic nanoparticles is that in plants, the biosynthesis is much faster and the particles thus obtained are of various shapes and sizes [64] . The production of nanoparticles is gaining much importance in many areas like mechanics, optics, biomedical sciences, drug-gene delivery and also photoelectrochemical applications [65] . Nanoparticles are extremely useful compared to their other bulk counterparts due to their extremely small size and large surface area to volume ratio [66] [67] [68] .

As a result of commercial revolution [69] , nanomaterials have bagged significant importance in the production of many new products in the market gaining much attention due to their broad involvement in many innovative applications which is mainly attributed to their distinct physical and chemical properties [70] [71] . Amid a wide range of metal and metal oxide nanoparticles present today, there is great demand for titanium dioxide nanoparticles due to their notable and diverse ability in decomposing chemical compounds and also it's character in imparting antibacterial properties [72] .

The green synthesis of metallic nanoparticles is by the biosynthesis of the nanoparticles in an environmentally friendly manner without using any toxic and harsh chemicals. One of the advantages of using nanoparticles is their antimicrobial nature and thus instead of producing it by chemical means, their green synthesis is preferred. The organisms that are used for the biosynthesis of metallic nanoparticles vary from simple prokaryotic microorganisms to multicellular eukaryotic organisms including plants. Some of the important aspects that have to be taken into consideration for the biosynthesis of nanoparticles are selecting the best organisms to use as a host and considering their growth conditions apart from taking into view their reaction conditions.

The need to develop biologically synthesized nanoparticles is because their production is more environmentally friendly and also their mode of action will not have any ad- verse effects in the application it is being used for. A wide variety of nanoparticles can be synthesized by using some of the most common plants like aloe vera, neem, lemon grass etc.

It is a well-established fact that plants have the ability to reduce the metal ions that are present both in and on various cells, tissues and even the organs of plants. After a study on the process of the accumulation of metals plants, it has been corroborated that metals exist as nanoparticles in the plant cells. Those metals that have been accumulated can later be retrieved by the processes of sintering and smelting by harvesting the plants and their cells. The phenomenon of obtaining the desired metals from the plants, more specifically the hyperaccumulator plants rather than mining them from land and keeping economic constraints in mind is known as phytomining [73] .

Generally, the synthesis of the nanoparticles takes place by two methods which are either "Top Down" approach or "Bottom Up" approach [74] .In the case of the "Top Down" approach, the main force that plays a role is the size reduction and is achieved by various physicochemical means [75]
. Antithetical to this approach is the "Bottom Up" approach, where small-sized particles like atoms or molecules undergo the process of oxidation or reduction to produce the nanoparticles.

During the process of synthesis of the nanoparticles, there are different stages in which the foremost stage is called as the activation stage where the process of conversion of the metal ions takes place from their monovalent or divalent oxidation states [76] to the zero valent oxidation state. The next stage in the synthesis process is the growth phase where all the surrounding particles coalesce together to form larger sized nanoparticles which are more stable. With respect to the characterization of metal nanoparticles synthesized, there is a color change observed in the reaction due to the reduction of the metal ions and their salts which confirm the formation of the nanoparticles [77] . Once the reaction involving the formation of nanoparticles has taken place, they can further be separated from the reaction mixture by high-speed centrifugation and later characterized. Regarding the characterization of nanoparticles, many techniques such as AFM, SEM, and TEM are used for the determination of the size and morphological properties of the obtained nanoparticles [78] [79] [80] [81] .

4 DESCRIPTION OF VARIOUS METHODS USED FOR BIOSYNTHESIS OF TIO2 NANOPARTICLES:

M.Sundrarajan et al. [82] synthesized titanium dioxide nanoparticles by a simplistic and environmentally friendly method from Nyctanthes arbor-tristis leaf extract. Com- pared to all the other metal oxide nanoparticles, titanium dioxide nanoparticles are highly sought after for air and water purification, as a result, they are highly useful for nanocoating purposes imparting high anticorrosive property among others. In addition to their purifying properties, the titanium dioxide nanoparticles also have antimicrobial and antibacterial properties. Their wide use in industrial applications as pigments and photocatalysts come from their high chemical stability and catalytic properties [83] [84] [85] [86] [87] The synthesis of titanium dioxide nanoparticles can also be done by some of the chemical methods like chemical vapor deposition, microemulsion, and sol-gel methods, but they are not as widely used as biological methods due to the involvement of high cost, their toxic nature and the requirement of high pressure and high energy making their separation difficult and the process highly hazardous [88] . Another important factor to be considered for the synthesis of nanoparticles by chemical means is the requirement of additional capping agents which help to stabilize the size of the particles. Whereas in the case of their biosynthesis from plants, the plants naturally have the capping agents in them cutting off the need to add them additionally [89] . The presence of microbial enzymes and plants with phytochemicals having antioxidant or reducing properties are mainly used for the synthesis of the nanoparticles. Nanoparticle synthesis can take place by bacteria, fungi and also plant extracts only if they are compatible with the green chemistry principles [90] [91] .

One of the major limitations that may hinder the experimentation for biosynthesis of metal nanoparticles from plants occurs when the plant extracts have been isolated from the plants taken at different geographical locations in different seasons. This could result in changing the size and properties of the obtained nanoparticles due to the different compositions of the plant extracts.

According to the experimental procedure done by Sundrarajan et al., the leaves of nyctanthes arbor-tristis were collected and were cut into fine pieces, ground and sieved and were then extracted and filtered after mixing with ethanol. And for the production of the titanium dioxide nanoparticles, this leaf extract was made to react with titanium tetraisopropoxide which was further subjected to centrifugation under suitable conditions. the obtained sample was then evaluated under a scanning electron microscope to reveal spherically shaped nanoparticles with an average size between 100-150nm.

Plants as a source for the production of gold and silver nanoparticles were reported for the first time by Gardea- Torresdey et al [92] [93] . As of today, many researchers have shown that plant leaf extracts can be used for the production of metallic nanoparticles [94] [95, 96] . It was also reported that the reduction of silver ions to produce silver nanoparticles to produce silver nanoparticles was also seen in Nelumbo nucifera [97].Silver nanoparticles of size 20 to 30 nm have been produced by using Acalypha indica leaf extract [98] .

By using the plant-derived substances like latex and other phytochemicals and plant proteins, many metal nanoparticles can also be fabricated as it does not involve the culturing of cells extracted from the plant tissue and their maintenance thus reducing their cost. According to the experimental procedure done by Manish Hudlikar et al. [99] the latex was obtained from the green stems of the plant J.curcas L. and was treated with deionized water. Then a small amount of the sample was made to react with the aqueous solution of $TiO(OH)_2$ and heated till the titanium dioxide nanoparticles were seen to be deposited at the bottom. The size of the nanoparticles that were obtained was in between 25-100nm in size with the majority of them having a spherical shape.

Utilizing the Catharanthus roseus leaf extract, the synthesized titanium dioxide nanoparticles were found to possess antiparasitic activities. Subsequent analysis of the synthesized titanium dioxide nanoparticles was done by XRD, FTIR, SEM, AFM [100] . These nanoparticles have widespread usage in the fields of drug delivery, sensing, imaging, tissue engineering, and other related areas as well [101] .In the experimental procedure done by Velayutham et al. [100] , the leaf extract of C.roseus was used to prepare a broth solution and after boiling and extrac- tion, it was filtered and the extract was made to react with TiO_2 powder and its stirring under suitable conditions resulted in the formation of titanium dioxide nanoparticles. The obtained titanium dioxide nanoparticles were irregularly shaped and the size ranged from 25 to 110 nm. The average size of the obtained nanoparticles was detected to be 65 nm in size.

In process of biological synthesis from plants, the plant extracts serve as both capping as well as reducing agents. Rajakumar et al. [102] used Eclipta prostrata L. commonly known as False Dasiy to produce titanium dioxide nanoparticles by aqueous reduction method. For the synthesis of titanium dioxide nanoparticles, the aqueous leaf extract of Eclipta prostrata L. was then boiled, filtered and mixed with $TiO(OH)_2$ and stirred to form the nanoparticles which were confirmed by a color change under room temperature. The obtained titanium dioxide nanoparticles were then analyzed by FTIR, XRD, AFM, and FESEM. Analysis of the obtained sample showed spherical nanoparticles with a size ranging from 36 to 68 nm and an average size of 49.5nm.

Selvaraj et al. [103] biosynthesized titanium dioxide nanoparticles using the fruit peel extract of A.squamosa. considered as an agricultural waste product. On the basis of the surface plasmon resonance (SPR), it has been corrob- orated that the titanium dioxide nanoparticles have modifiable optical properties. With regard to the experimental procedure performed, the peels of Annona squamosa were collected and made into a powdered form after drying. The extract was then filtered with the help of millipore hydrophilic filter and used for further experimentation. Then for the preparation of the nanoparticles, 5mM $TiO(OH)_2$ was mixed with the aqueous extract and stirred under suitable conditions. It is assumed that the titanium ions have been reduced to the titanium nanoparticles be- cause of the phytochemicals present in the peel extract of A.squamosa. The TEM images confirmed the nanoparticles to be spherical and polydispersed having the size of the 23±2nm range. Based on the experimental procedure performed on J.curcas L. it has been found out that the latex used for the biosynthesis of titanium dioxide nanoparticles contained an enzyme curcain and cyclic peptides like curcacycline A which is an octapeptide and curcacycline B, a nonapeptide are the possible reducing and capping agents. The green methods employed for the synthesis of the nanoparticles are generally direct methods of synthesis without any requirement to supplement additional reducing and capping agents, templates etc [104] .

The knowledge of the potency of plant extracts in the biosynthesis of metal nanoparticles was known since the inception of 1900 but the reducing agents involved in the process was not understood to the researchers [105] . The source from which the plant extract has been taken influences the characteristics of nanoparticles that can be synthesized as different extracts contain different concentrations and compositions of the organic reducing agents [106] [107]
. Titanium dioxide nanoparticles possess many useful optical and antimicrobial properties in addition to catalytic properties and high chemical stability [108] [109]. Titanium dioxide nanoparticles were also produced from the leaf ex- tract of Eclipta prostrata and were reported by Rajakumar et al. These produced nanoparticles also showed extensive antibacterial activity against E.coli [110] . From the investigation of Marimuthu et al.it [111] was found out that biosynthesis of Tio2 nanoparticles from the aqueous extract of the flower C. gigantea showed to have excellent acari-

cidal activity. The scanning electron micrographs of the titanium dioxide nanoparticles produced from Calotropis gigantea had spherically shaped particles having the size of 160-220nm. According to the experimental procedure done by Rajakumar et al. [112] , the fresh leaves of Solanum trilobatum L. were dried and powdered and further filtered with Millipore hydrophilic filter and mixed with TiO (OH)2 solution. The titanium dioxide nanoparticles were formed after the resulting color change was observed to be green. SEM images displayed NPs that were spherical, oval in shape, individual, and some in aggregates with an average size of 70 nm. The results from scanning electron microscope showed spherical and oval-shaped nanoparticles with an average size of 70nm. In the experimental procedure as done by Sankar et al. [113], the leaves of Azadirachta indica were collected and dried to make it into a powdered form. Then under suitable experimental conditions, an aqueous leaf extract was prepared. In the next step for the synthesis of the titanium dioxide nanoparticles, the aqueous leaf extract with mixed and made to re- act with 5 mM titanium isopropoxide solution kept at a pH of 1.5. This mixture was stirred at a temperature of 50 degrees centigrade till there was the formation of a high intensity dark brown color which confirmed the formation of titanium dioxide nanoparticles [114]. The results from the scanning electron microscopy and dynamic light scattering analyses revealed the obtained titanium dioxide nanoparticles to be spherical in shape and interconnected with each other with the average sizes of the particles to be 124nm. With reference to the experiment performed by Sankar et al., it has also been inferred that the titanium dioxide nanoparticles can be the right choice for their use in photocatalytic reactions due to their strong oxidizing potential, and non-toxic nature and remaining highly photo-stable in reactions apart from being abundant and affordable [115] . The titanium dioxide nanoparticles synthesized from the leaves of Azadirachta indica can also take the role as an effective photocatalyst in the remediation of pollution. With reference to the experimental procedure done by Santhoshkumar et al [69] ., an aqueous leaf extract of Psidium guajava was prepared and then further filtered with the help of millipore hydrophilic filter. And then for the synthesis of titanium dioxide nanoparticles, the aqueous leaf extract was made to react with 0.1mM TiO(OH)2 and stirred under suitable conditions until a light green color appeared confirming the formation of titanium dioxide nanoparticles. FESEM images were measured and topo- graphical analysis was performed based upon the surface study. Synthesized TiO2 NPs were smooth and spherical in shape. The results from the field emission scanning electron microscope were analyzed on the basis of the topography of the nanoparticles. It showed the nanoparticles to be smooth and spherical in shape with the average size to be 32.58 nm. The titanium dioxide nanoparticles were analyzed by XRD, FTIR, FESEM, and EDX.

Titanium dioxide nanoparticles were also produced from the rice straw by sol-gel method. Tio2 nanoparticles that are extensively used for photocatalysis was produced by using rice straw as a soft biotemplate as it was a source of lignocellulosic waste material [116] . Apart from the biosyn- thesis of the TiO2 nanoparticles, there are many chemical processes like chemical vapor deposition, microemulsion etc [117] [118] . In the method used by Donya et al [116] . titanium isopropoxide was made to dissolve in the deionized water using glacial acetic acid as a chelating agent where different concentrations of rice straw powder were introduced. This resulted in the production of titanium dioxide nanoparticles of sizes up to 20nm. In addition to thermogravimetric analysis, the structural properties of the ob- tained nanoparticles were studied further by Raman spec- troscopy and UV-visible spectroscopy. The high photo- catalytic activity of the synthesized TiO2 nanoparticles re- ported under UV light irradiation was due to an increase in the surface area resulting in increased porosity [119] .

Abdul Abduz Zahir et al. [120] used the aqueous leaf extract of Euphorbia prostrata to synthesize the Titanium dioxide nanoparticles in addition to silver nanoparticles. But in this paper, the synthesis of titanium dioxide nanoparticles will only be briefly summarised. For the synthesis of titanium dioxide nanoparticles, the fresh leaves of Euphorbia prostrata were collected and sterilized and an aqueous leaf extract was prepared. This aqueous extract was later filtered by using Whatman filter paper no.1 and made to react with 5mM TiO(OH)2 solution and stirred un- til the change in color to light green indicated the formation of titanium dioxide nanoparticles. The transmission electron microscopy(TEM) of the synthesized titanium dioxide nanoparticles showed the particles to polydispersed and having a spherical shape. The average size of the obtained nanoparticles was found to be 83.22 ±1.50 nm.

Not only are plant leaves employed for the biosynthesis of the metal and metal oxide nanoparticles, but plant root extracts can also be utilized for their synthesis as experimentally established by Nasrollahzadeh et al. [121] . They reported a simple protocol where Euphorbia heteradena Jaub root extract functioned as a reducing agent and stabilizing agent for the synthesis of titanium dioxide nanoparticles.

The root of Euphorbia heteradena Jaub was dried and subsequently powdered after which its aqueous extract was prepared by mixing with sterile distilled water and this aqueous extract was subjected to centrifugation where the supernatant was subjected to separation by filtration. Then for the synthesis of the titanium dioxide nanoparticles, the aqueous leaf extract was made to react with TiO(OH)2 and stirred under suitable conditions. The formation of the nanoparticles was confirmed when there was a color change to light gray. The precipitated titanium dioxide nanoparticles obtained by centrifugation of the light grey colored solution was made to wash with chloroform and ethanol for three times and dried. This is a simple, eco- nomic, nontoxic and efficient green method to synthesize rutile TiO2 NPs. The biosynthesis of the titanium dioxide nanoparticles from the root extract of Euphorbia heteradena Jaub followed the principles of green chemistry as it did not involve the usage of any kind of surfactant or a template or any additional capping agent. In addition, this method of synthesis of nanoparticles is a simple and economical way of producing nanoparticles. UV-visible spectrophotometry was used to study the kinetics of the reaction which showed the surface plasmon resonance (SPR) results to be around 360nm.

In yet another method for the synthesis of the titanium dioxide nanoparticles, Titanium(IV) oxysulfate with the chemical formula TiOSO4 is considered a precursor involving a low cost of production and thus huge efforts are made in that direction [122] . And in this method, instead of using an organic solvent like acetone and alcohol, green sol- vent like water is used [123]. The synthesis of the nanoparticles takes place by the addition of 0.1 M TiOSO4 in dis- tilled water followed by the addition of 0.2 wt% Polyvinyl Pyrrolidone (PVP) which is a capping agent. In the next step, aqueous ammonia was added to form a white gelatinous precipitate. The precipitate was later dried and calcined at various temperatures to obtain the nanoparticles. From the performed scanning electron microscope results, it was corroborated that the size of the obtained titanium dioxide nanoparticles was irregularly shaped with the size ranging from 40-50nm and the average size from the TEM results to be 10 nm.

5 CONCLUSION

The method of biosynthesizing titanium dioxide nanoparticles using "green" approach is a fast process and the particles obtained are of the purest form. It can be concluded that among numerous methods used for the synthesis of titanium dioxide nanoparticles, green synthesis is more favorable and economical when compared to chemical methods. This can be ascribed to the faster rate of nanoparticle synthesis in plants in addition to attaining the particles of desired shapes and sizes. It can also be seen that the nano paints produced by incorporating TiO2 nanoparticles gained additional beneficial properties like resistances to various external factors and antimicrobial activity.

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