Chapter 9
Biological Synthesis of Metallic Nanoparticles and Their Application in Photocatalysis

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Abstract Removal of dyes from wastewater using the photocatalysis process gets more attention because of its suitability to completely remove of dyes under normal or moderate temperature and pressure, and thus, it overcomes the drawback of the conventional water treatment processes. Metal and metal oxide nanoparticles show valuable magnetic, electrical, optical and catalytic properties. Their unique properties allow them to be used in wastewater treatment as photocatalyst. Firstly, this chapter will focus on the biological synthesis of metallic nanoparticles. Mechanism for the bio-synthesis of metallic nanoparticles, advantages and disadvantages of biogenic route will also be discussed. Secondly, the mechanism of photocatalysis, factors affecting photodegradation, and role of photocatalysis against different water pollutants shall be explained. Different types of photocatalysts will be briefly presented in the next sections, and finally, the discussion will be highlighted with the future perspective and conclusions.

9.1 Introduction

Our drinkable water is under a serious threat. The reason for this threat is not only due to global climate change, but different industry activities and continuous population growth that limit the current natural water reserves. It is stated that about 1.2 billion people are unable to access drinkable water and millions died due to polluted water (Ahuja et al. 2021). Pointing out to industrial activities shows that the existing organic and inorganic pollutants from chemical accidents, or waste and illegal agriculture practices contaminant the available water source and arise the main hazardous for our ecosystem (Liang and Zhang 2019; Mane et al. 2018). Dyes are considered one of examples of organic pollutants that are toxic to our environment. On one side, they represent a major concern because their wide use in different industries such as food, textiles, plastic and pharmaceuticals industries. However, on the other side,

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it is observed that about 15% of the dyes used in textile manufacturing process are wasted and are discharged into the nature. Thus, it represents a serious damage to the environment due to their recalcitrance nature (Ratna 2012). The contaminated water from toxic chemicals, hazardous textile dyes and pesticides causes long-term adverse effects on aquatic and human life. For instance, the organic dyes used in textile industry are highly toxic, carcinogenic and non-degradable. They can cause several diseases such as skin diseases, allergies and cancer (Daniel and Shabudeen 2014; Vasantharaj et al. 2019). Therefore, there is a crucial need to treat this polluted water before disposal to environment.

Currently, there are various conventional wastewater treatment methods like chemical transformation, biological treatments, distillation, reverse osmosis, coagulation and flocculation, ultraviolet treatment and many others. These methods are efficient with various pollutants. However, they are costly, require specific equipment and high energy input (Sahu and Singh 2019; Saharan et al. 2014). Thus, a demand for an alternative water treatment process has risen to tackle these challenges. One of the alternative processes is called Advanced alternative processes (AOPs). In this process, a generation of the hydroxyl radical is needed to be used as an oxidant to destroy the polluted compounds and degrade to carbon dioxide and water (Saharan et al. 2014; Deng and Zhao 2015). In different contexts, AOP could also refer to a series of processes such as photocatalytic oxidation, electron-beam irradiation, ultrasonic cavitation and Fenton's reaction (Samuel et al. 2011). A concern about using AOP in water treatment process is that most of the dyes are resistant to AOPs degradation (Deng and Zhao 2015). The photocatalytic process is another alternative way to treat wasted water and it has more advantages over AOPs because the use of visible light or near-UV as irradiation is cost-effective and there is no sludge produced during the process (Singha et al. 2019). The definition of photocatalysis or photodegradation is process in which the chemical reaction rates change under the action of light and in the presence of substances called photocatalysts.

Photocatalysts absorb light and contribute to transform of the reactants. They must be stable, nontoxic, inexpensive and highly photoactive in order to attract more attention. Removal of dyes from wastewater using the photocatalysis process gets more attention because of its suitability to completely remove of dyes under normal or moderate temperature and pressure and thus, it overcomes the drawback of the conventional water treatment processes. Furthermore, it includes interaction between the catalyst and visible or UV light to generate reactive species such as hydroxyl radicals and oxygen radicals which could interact with organic pollutants and result in removal of organic pollutants (Fagier 2020). Involving catalysts in photocatalysis process opened the door to study the effect of different kinds of catalysts in water treatment processes. It is noticed that using nanoparticle catalysts showed superior photocatalytic effectiveness if they are compared to normal photocatalysts (Osuntokun et al. 2019).

Nanoparticles (NPs) refer to materials with sizes dimensions between 1 and 100 nm. Their sizes, distributions, crystal structures and surface-to-volume ratio give them superior properties (Rathnasamy et al. 2017). Metal and metal oxide nanoparticles (M/MO-NPs) show valuable magnetic, electrical, optical and catalytic properties. Their unique properties allow them to be used in several different applications such as solar cells, light-emitting devices, biomedicine, catalysis, soil stabilization, biosensors and water treatment (Afsharian and Khosravi-Daran 2019; Hardani et al. 2015). Next to Gold and silver metal oxide NPs, TiO_2, ZnO, SnO_2 and CeO_2 are used as photocatalysts in water treatment process.

Synthesis of nanoparticles can be described from structure point of view. Following structure approach, there are two main approaches; Top-down and Bottom-Up. Top-Down approach involves break of bulk or big materials down into nano-sized materials. However, with such approach, it is difficult to control the size of generated particles. It results in wide size distribution and variation of morphologies. The second approach, Bottom-Up approach is opposite to Top-Down approach as it involves growing of nanoparticles from single atom into bigger size material. Bottom-up approach is more common as it results in better-controlled size nanomaterials (Dhandapani et al. 2012). Regardless of the structured approach for synthesizing nanoparticles, Those two approaches may include physical and/or chemical methods. Synthesize nanoparticles by physical approach (it is also called mechanical approach) follow Top-down structure approach. Examples of physical methods are pyrolysis, using laser ablation and attrition. Contrary to physical methods, chemical methods usually follow Bottom-Up structure approach. Physical methods have an advantage of producing narrow particle size nanoparticles. However, it requires expensive instruments such as lasers, it also consumes high energy and the production of nanoparticles is lower if it is compared to chemical method. In chemical methods, we usually use wet chemical protocols. Common chemical methods may include sol–gel process, sonochemical methods, polyol process and reverse micelles method. The chemical methods are better than physical methods in terms of the nanoparticle production volume and they are relatively cheaper. The drawbacks of chemical methods are the use of toxic chemicals and the formation of by-products that might be hazardous and dangerous. Due to the limitations of physical and chemical methods, there is a need to find a green (or biological) method that can overcome the cost, production yield, energy consumption and eco-friendly. Not only because of its environmental benefits, but the green synthesis allows to produce nanoparticles in large quantities and with defined shape and size than the regular production methods offer (Isa et al. 2021a).

The green method of synthesizing nanoparticles means the use of natural materials like the extracts of plants and microorganisms (i.e. bacteria, fungus, yeast and algae) in the synthesis process. It is possible to classify the synthesize process into two categories; bioreduction and biosorption. Bioreduction means that chemical reduction is used to achieve stable metal ions using biological means and it is accomplished by dissimilatory metal reduction. Biosorption means that the metal ions are bonded to the cell wall or synthesized peptides by microorganisms or plants assembles into stable nanoparticle structures. A decision over which method to follow for biosynthesize nanoparticles depends on several variables (Dan et al. 2020).The green method of preparing nanoparticles is Bottom-Up approach. Various plants such as Aloe vera, lemon, Coriander and Oat contain heavy metals and biomolecules. They are utilized to synthesize silver and gold nanoparticles. Bacteria is easy to manipulate and so it is widely used in biotechnological applications. Bacteria such as Escherichia coli, Bacillus amyloliquefaciens, Bacillus cecembensis and Lactobacillus casei have been used to synthesize different nanoparticles silver, zinc and cobalt nanoparticles. Metal and metal oxide nanoparticles can be biosynthesized by fungi that play the role of biological agents. Biosynthesis of nanoparticles using fungi yields bigger amounts of nanoparticles in comparison to bacteria. eukaryotic cells have yeasts such as Saccharomyces cerevisiae and it is used to synthesize silver and gold nanoparticles. Like yeast, marine algae is used to prepare gold nanoparticles (Jagpreet et al. 2018).

Firstly, this chapter will focus on the biological synthesis of metallic nanoparticles from plant, microorganisms and animal-derived products. Mechanism for the biosynthesis of metallic nanoparticles, advantages and disadvantages of biogenic route will also be discussed. Secondly, the mechanism of photocatalysis, factors affecting photodegradation and role of photocatalysis against different water pollutants shall be explained. Different types of photocatalysts will be briefly presented in next sections and finally, the discussion will be highlighted with the future prospective and conclusions.

9.2 Preparation of Metallic Nanoparticles

Three methodologies such as; physical, chemical and biological are used to prepare metallic nanoparticles. Again in a broader way based on the structural point of view, the above-mentioned methods are classified as 'bottom-up' and 'top-down' approaches. In top-down approach slicing or a bulk material undergoes successive cutting or slicing to achieve nano-sized particles and this can be done by various mechanical or chemical methods. The major drawback of top-down approach is the produced metallic nanoparticles often have structural defects, which significantly alter the physical properties and surface chemistry behaviour.

Bottom-up approach means building up of nanomaterials from the bottom, i.e. by self-assembly of atoms, molecules or clusters. Here in this approach at first, the building units are produced and consequently, those building units are transformed into the nanostructured materials. The major advantages of bottom-up approach are nanomaterials are produced by this method have homogenous chemical compositions and no structural defects. Both approaches play very important role in modern industry and most likely in nano technology as well (Adam and Gabriela 2011).

9.2.1 Physical Methods

There exist four methods such as evaporation/condensation, pyrolysis, laser ablation and attrition that are mostly used as physical or mechanical methods. In evaporation/condensation technique the inert gas atoms are condensed and formed metallic nanoparticles. In the beginning, very high temperature is applied into reaction chamber to evaporate the metal atoms from the substrate. Evaporated metal atoms gain very high kinetic energy and collide with inert gas (carrier gas) atoms into the reaction chamber. These interatomic collisions resulted into loss of kinetic energy of metal atoms and condense in the form of small crystals. In pyrolysis method, the precursor is burnt into the furnace at very high temperature in presence of inert gases and with limited supply of oxygen under atmospheric pressure conditions. The precursor atomizes inside the furnace and then produced metallic nanoparticles by following either of the following methods; condensation, precipitation, thermal decomposition and intraparticle collisions. In laser ablation technique pulsed laser is used to produce metallic nanoparticles. The metallic precursor is irradiated by pulsed laser in liquid or gas environment, which causes formation of high mobility metal oxide atoms and finally, metallic nanoparticles are produced by condensation in presence of liquid nitrogen. All the above-mentioned methods are typical representatives of ‘bottom-up’ approach. The advantage associated with these methods is metallic nanoparticles with narrow particle size distribution can be produced while the limitation is these are costly methods as very expensive equipments like lasers, furnaces, inert atmosphere, etc. are necessary to proceed the reactions.

In attrition method, a size-reducing mechanism like ball milling is applied to ground the bigger particles into the nano-sized particles. The obtained metallic nanoparticles by this method are affected by various conditions, like the nature of starting material, time of drilling and reaction medium. This method typically represents ‘top-down’ approach (Adam and Gabriela 2011).

The limitations associated with these methods are low production rate as compared to chemical methods, higher energy consumption to maintain the pressure and temperature during the reactions.

9.2.2 Chemical Methods

The second approach is chemical method which is usually a ‘bottom-up’ method. Chemical method is actually the wet chemical procedure where the metal salt precursor is dissolved in a suitable solvent and undergoes controlled reduction procedure in defined reaction conditions such as at particular temperature and pH. This procedure allows the successive formation of clusters or aggregates of metal oxide nanoparticles in gel or precipitation form. In next step, the gel or precipitate is subjected to ageing and calcinations at very high temperature in muffle furnace, where it is transformed into a solid mass by vaporizing completely the water molecules and other volatile solvents. In this step, the gel network is contracted and solvent from gel pores gets ejected. At high temperatures ($T > 800$ °C) densification and decomposition of the gels occur and during these steps, the porous parts of the gel network get distorted and residual organic solvents are volatilized. Several methods such as the sonochemical method, the polyol process, the solvent-reduction method, the template method and the reverse micelles method have been developed for the preparation of nanoparticles. Seed-mediated growth is another chemical method to prepare metallic nanoparticles. In this method, small particles which are prepared by other methods are used as seeds and reducing agents are utilized to reduce metallic ions. Reduced metallic ions grow on the surface of the seed particles (Samanta et al. 2010). Based on the purposes of the metallic nanoparticles synthesis, required properties, types, sizes of n- MOs different reducing agents are used. Examples of few reducing agents are $NaBH_4$, $SnCl_2$, sodium citrate, methoxy polyethylene glycol, ascorbic acid, sodium hydroxide, etc. For instance, to prepare nano ZnO, NaOH can be used as reducing agent. The chemical methods are associated with few advantages such as; (i) these are relatively cost-effective methods for high volume, (ii) very simple to execute.

However, the disadvantages are; (i) Highly toxic chemicals are used (ii) Greater chance of contamination between precursor materials and reducing agents, (iii) There is a chance of development of hazardous by-products (Adam and Gabriela 2011).

9.2.3 Biological Methods

Both physical and chemical methods are associated with few limitations and therefore there is a burgeoning need to develop a new method, which will be eco-friendly, rapid, high percentage of yield, occur under normal air pressure and room temperature, energy-saving and nontoxic by-products. Biogenic route for metallic nanoparticle synthesis serves all these purposes. Recently, biological ways mediated by living organisms have become an easy way to synthesize metallic nanoparticles as we have variety of organisms available in nature. Plants and plant products, algae, yeast, fungi, virus and bacteria play important roles in this purpose. Many inorganic materials are derived by using intra or extracellular organisms and it has been a well-known method for almost 30 years (Wilbur and Simkiss 1979). Biomaterials are not only used for the easy, fast synthesis of nanoparticles but also they have a great application field in the removal of toxic materials. Many microorganisms such as bacteria and algae are used in this purpose (Pérez-de-Mora et al. 2006). In this way, a comparatively novel nature-derived process for the development of metallic nanoparticles by microorganisms and other living beings has been established. Biogenic synthesis of nanoparticles is known as an emerging route of synthesis which is designed by overlapping nanotechnology and biotechnology. In the last few decades, it has gained an ample of attention of the researchers because of its capability to develop environment-friendly methodologies in material science. Till now plethora of both unicellular and multicellular organisms have been utilized to yield metallic nanoparticles. However, this method also has many limitations and few of these are listed below:

(i) Biological approach using living cells are an extremely complicated method as cells contain thousands of molecules with variety of functional groups such as; hydroxyl, emine, amine, hydrides, etc. Each of these functional groups has separate role in the reduction of metal salts. Therefore, it is quite hard to explain a specific mechanism responsible for the growth of metallic nanoparticles.

(ii) The resulting solution contains a mixture of various biological components, metallic nanoparticles and other molecules. Therefore, the purification method of metallic nanoparticles is very much complicated.

(iii) Presence of large number of protein molecules in the resulting solution destabilized the nanoparticles and also can influence their properties.

(iv) Few salts are toxic for biological materials and therefore cannot be allowed to use at higher concentrations (Fig. 9.1).

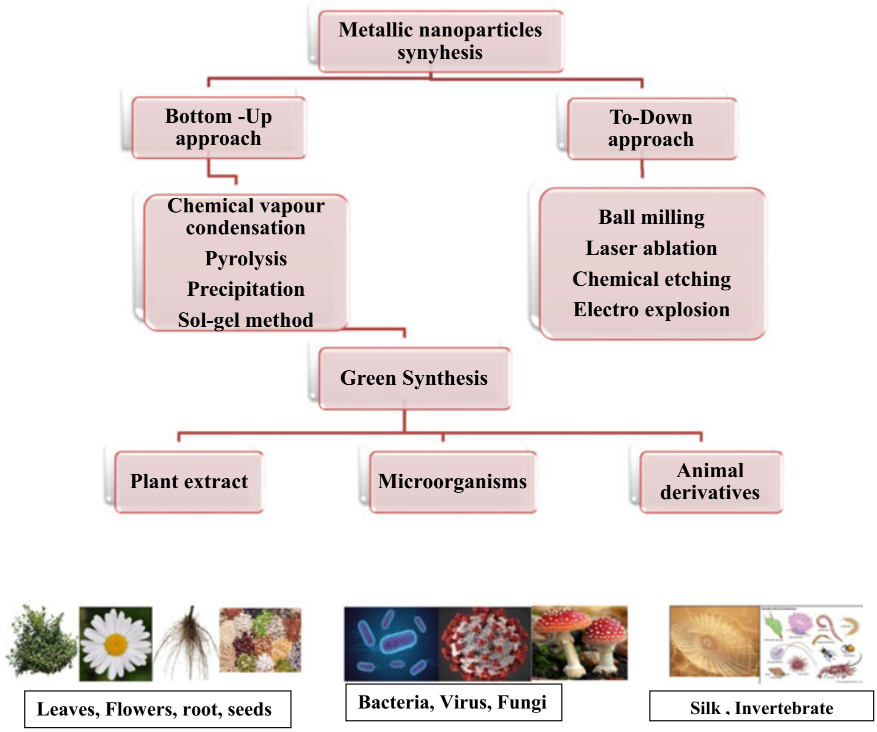

Fig. 9.1 Synthesis route of metal nanoparticles

9.3 Biological Synthesis

9.3.1 Plant Components in Metallic Nanoparticles Synthesis

It has been noticed that plants are the better option for the synthesis of metallic nanoparticles as plant molecules act as a natural capping agent and the particles present in plant sources are nontoxic. Extensive research on plant-medicated synthesis of metallic nanoparticles with different parts of plants belonging to different taxonomic groups has divulged the ability of green synthesis and capping activities as well (Vithiya and Sen 2011).

9.3.1.1 Angiosperms Mediated

Angiosperms are generally considered as best of plant evolutionary family and therefore they are extensively used in the green synthesis of metallic nanoparticles (Ratul et al. 2017). Various benefits of angiosperm joined together and have made this group more attractive in pursuing scientific studies. Few of those are listed below:-

(i) Worldwide availability and easy access have made this group of plants more persuasive for nanoparticle synthesis and other biological applications.
(ii) Angiosperm has played an essential role as natural remedy for various kinds of diseases of humans and other animals (Petrovska 2012).
(iii) Angiosperm species are edible in nature and that makes them even more important material for scientific research.

In terms of biogenic synthesis of metallic nanoparticles, angiosperms, being extremely rich in nontoxic plant bioresources, have better natural reducing capability of metallic ions and this pushed it more towards the rapid expansion of green field of science. It has been observed that high reducing potentials of plant phytochemicals react with metallic cations (M^{n+}) and reduced them to neutral atoms (M) for metal nanoparticle synthesis. Metallic cations with higher standard reduction potentials are reduced by the plant molecules with lower ionization potential values. This also proves nature's ability of reduction without the use of hazardous reducing materials.

Highly explored angiospermic plant species for the synthesis of metallic nanoparticles are Azadirachta indica, Camellia sinensis, Aloe vera, Centella asiatica, etc. as capping behaviour of the phytochemical molecules present in the above-mentioned plants can produce biocompatible metallic nanoparticles, have excellent medicinal values (Afaepour et al. 2009; D'Britto et al. 2012). However, overall biocompatibility of metallic nanoparticles depends on the size and shape of them (Alkilany and Murphy 2010). Metallic nanoparticles having size range less than 100 nm are highly desirable for biomedical applications and managing desired size and shape of metallic nanoparticles during the synthesis is a real challenge for the scientists working on green synthesis. Researchers suggested that morphology of nanoparticles is dependent on reaction parameters like plant extract concentrations, metallic ion concentrations, pH, temperature and, time taken for the reaction (Mishra et al. 2014).

Cost-effective synthesis of metallic nanoparticles with Asparagus racemosus under sunlight is an amazing attempt because external energies are not required to carry out the reaction and the whole synthesis can be done at room temperature. Other plant species Camellia sinensis (tea) and Coffea Arabica (coffee) are well-explored plants for green synthesis mechanism study because of isolation and purification of the tea and coffee biomolecules, viz. catechins, thea-flavins, other phenolic compounds, fibres and alkaloids are easy and less time-consuming. Moreover, effective capping and reduction can be done by teac and coffee biomolecules. Commercially available pure tea polyphenol (from Sigma) has been applied for the green synthesis of Pt nanoparticles (Alshatwi et al. 2015). These results support in designing large-scale production of metallic nanoparticles. Involvement of phenolic compounds in the synthesis of metallic nanoparticles such as; Fe_2O_3, ZnO, CuO, Ag and Au are reported in literature (Ratul et al. 2017; Wang et al. 2014). Other plant species like Jatropha curcas L, Azadirachta indica Kernel, Camellia sinensis leaves are also used to reduce metal cations using their biomolecules at room temperature. The reaction mechanisms using angiosperms claim that common phytochemical constituents, such as phenols, alkaloids, terpenoids and some pigments, are mainly responsible for the green synthesis of different metallic nanoparticles (Ratul et al. 2017). It has been reported that gold and silver nanoparticles can be derived from geranium extracts (Chandran et al. 2006). Literature has also reported that gold nanotriangles and silver nanoparticles can be synthesized using Aloe Vera plant extracts (Singaravelu et al. 2007). Huang et al. (2007) derived silver and gold nanoparticles in a simple way by using the sundried Cinnamomum camphora leaf extract (Huang et al. 2007). Most of the reports available on the derivation of silver or gold nanoparticles utilize broths obtained from the boiling fresh plant leaves. Well-defined silver nanowires were synthesized by reducing silver nitrate solution in presence of broth of sundried Cassia fistula leaf at room temperature without any additive (Lin et al. 2010). However, it should be noted that not all randomly selected plant species can be used for biological synthesis of metallic nanoparticles.

9.3.1.2 Bryophytes Mediated

Bryophytes are known as the most ancient and second-largest group of land plants in the world. Bryophytes are essential in understanding the plant origin and following the plant transition to land. These are the less explored plant groups in green synthesis of metal nanoparticles. Bryophytes can emit biologically active compounds which are used to protect themselves from other living organisms and because of the presence of these active biological components bryophytes are used in the synthesis of metallic nanoparticles. Studies showed that simple organization of makes the process facile. Literature showed that gold nanoparticles of various shapes viz.; spherical, triangular and hexagonal with the size in the range of 42–145 nm can be synthesized using the extract bryophyte gametophyte at 37 °C. Various metal oxide nanoparticles have been synthesized using plant bodies (thallus) of bryophytes (Acharya and Sarkar 2014).

9.3.1.3 Pteridophytes Mediated

Pteridophytes plants have excellent antibacterial activity and therefore over 350 million years, they have been investigated in research studies as an interesting topic. Extracts of these plants are used in the green synthesis of nanoparticles to get nanoparticles with antibacterial activity. Studies showed that (Britto et al. 2012) three different pteridophyte plants of pteris genus were used in the green synthesis of silver nanoparticles with excellent antibacterial activity. Antibacterial activities against bacterial pathogens have been shown by various nanomaterials derived from fern, Nephrolepis exaltata (Bhor, et al. 2014). Literature studies have shown that nanoparticles synthesized from pteridophytes have excellent antibacterial activity and this might be due to the different natural antioxidant and antibacterial properties of the plants themselves. However, the actual mechanism of biosynthesis of metallic nanoparticles from different plant species and their antibacterial properties are yet to be studied.

Presence of various phytochemicals, such as; flavonoids, alkaloids and terpenoids in pteriodophytes makes the plant extracts highly oxidant and helps in the production of metallic nanoparticles. Literature studies also revealed that flavonoids act as both reducing agents and stabilizers during the production of nanoparticles and have enhanced antioxidant effects (Singh 2013). Extract of Azolla pinnata can be used to derive silver-based nanoparticles with different size and shape with enhanced antibacterial effects (Korbekandi et al. 2014).

9.3.1.4 Gymnosperms Mediated

Gymnosperms can be found in everywhere on earth and a large diversity of them makes each plant family unique, well organized and different valued. The biomolecules present in plants can reduce metal ions to form metal nanoparticles and recent research suggested that, like prokaryotes, eukaryotes are also capable of producing metal nanoparticles by biosorption and bioreduction methods. Literature has shown many examples of the formation and bioaccumulation of metal nanoparticles by gymnosperms mediated methods using various reducing and stabilizing agents. Literature showed that these reduced and stabilized metal nanoparticles can be utilized as catalyst in detoxifying pollutants (Cirtiu et al. 2011). Researchers claimed that copper (Cu) is essential as micronutrient for plants, but high concentration of Cu is detoxified by plants by reduction of Cu ions into Cu(0) and ultimately into Cu nanoparticles (Ratul et al. 2017). Research revealed that, the mechanism of the formation, size, morphology and quantity of metal nanoparticles dependent on the plant type, phytochemicals, pH of the solution and bioavailability of metals (Ratul et al. 2017). The general mechanism of metal ion reduction, stabilization and formation of nanoparticles by phytochemicals of angiosperms has been studied thoroughly but not in case of gymnosperms but as the phytochemicals are almost similar among plant groups, therefore by studying the mechanisms of angiosperms the reaction mechanisms of gymnosperms can be explained. Jha and Prasad (2010) showed the formation of AgO nanoparticles from $AgNO_3$ solution using antioxidative system of Cycas plant. Researchers also claimed that leaves of Cycas plant contain phenolic compounds, carbonyl and thiols groups, which are responsible for the biosynthesis of metal nanoparticles. Green synthesis of spherical Au nanoparticles is reported by Noruzi et al. (2012) utilizing the aqueous extract of cypress leaves and they observed that the reaction got completed within 10 min at room temperature and the average size of the synthesized nanoparticles depended on the pH and concentration of leaves extract (Noruzi et al. 2012). An eco-friendly synthesis of Cu nanoparticles using Ginkgo biloba Linn leaves extract as a reducing and stabilizing agent at room temperature has been studied (Nasrollahzadeh and Sajadi 2015). Kalpana et al. (2014) derived Ag nanoparticles from Torreya nucifera leaves extract and they found that temperature and concentration of extract played a vital role in the determination of size and shape of nanoparticles (Kalpana et al. 2014). Velmurugan et al. (2013) reported that in pine family of gymnospermic plant leaves and bark contain high concentration of phenolic compounds and hydroxyl and carboxyl groups of phenolic compounds are involved in metal nanoparticles synthesis. Another study proved that polyphenolic functional groups and proteins present in plant biomolecules are responsible for the metal ion reduction and as stabilizing agents of the metal nanoparticles and high temperature, pH and total time is taken for the growth can positively influence the properties of the synthesized nanoparticles (Ratul et al. 2017). Hence, it can be said that the biomolecules of gymnospermic plant extract have an essential role in the formation and stabilization of metal nanoparticles and the route is eco-friendly and efficient alternative to conventional methods.

9.3.1.5 Algae Mediated

Algae-mediated method provides eco-friendly reducing agent, nanoparticle stabilizing agent and capping agent but still a very few algae-mediated synthesis of nanoparticles are reported in literature. In the synthesis of gold-based nanoparticles, marine algae were used and the process took relatively short time period compared to other biosynthesizing processes. Similarly, Palladium and platinum-based nanoparticles using meta chloride salts have been investigated (Jagpreet et al. 2018).

Bioreduction process of algae showed a great potential in the green synthesis of different metallic nanoparticles, such as copper oxide, zinc oxide, iron oxide, silver, gold, palladium, etc. (Jagpreet et al. 2018). Algae is capable of controlling size and shape of the synthesized nanoparticle and therefore gaining more interest in the biological synthesis of metallic nanoparticles. During the synthesis, metal ions are entrapped on the surface of the plant cells by an electrostatic force of attraction between the positive metal ions and negatively charged carboxylate groups present on the cell surface. In next step, metal ions get reduced by cellular enzymes and form new nuclei, which later on undergo self-assembly process to grow and converted to nanoparticles. Single-celled green algae have a strong binding ability toward gold and silver nitrate salts and afterwards reduced the metal ions into Au (0)/Ag (0).

Various functional groups, such as hydroxyl (–OH) from polysaccharides and different amino acids (such as tyrosine) and carboxyl anions (–COOH–) from various amino acids such as aspartic acid (Asp) present on the cell surface are the most active functional groups for the reduction of metal ions to form metal oxide nanoparticles. Literature reported that several metallic nanoparticles, such as; Fe_2O, MgO, NiO, Ag, Au, Pt and Pd can be synthesized by using algeas (Jagpreet et al. 2018).

9.3.2 Microbial Components in Metal Oxide Nanoparticle Synthesis

9.3.2.1 Fungi Mediated

Use of fungi extract for the green synthesis of metal/ metal oxide nanoparticles is an efficient method and in this route nanoparticles with mono-dispersed phase, well-defined morphology and excellent properties can be synthesized. Fungus are having a large variety of intracellular enzymes, which make them a good mediator for the green synthesis of nanoparticles as, those enzymes are used as reducing, capping and stabilizing agents for the synthesized products. The major advantages associated with fungi mediated route are;

(i) Total yield by fungi mediated route is much more higher than bacteria mediated route.
(ii) Fungus have variety of enzymes, proteins and reducing agents on their cell surfaces, which help in the synthesis.

The probable mechanism for the synthesis of metal/metal oxide nanoparticles using fungi extract is enzymatic reduction on the cell surface or inside the fungi cells.

To synthesize gold nanoparticles Fusarium oxysporum releases enzymes into the aqueous solution of $AuCl_4^-$ ions with NADH and these enzymes act as reducing agents. Binding of protein through cysteine and lysine linkage provides long-term stability to the synthesized nanoparticles (Mukherjee et al. 2002). Fusarium oxysporum can also synthesize crystalline zirconia nanoparticles by hydrolyzing metal salts in presence of K_2ZrF_6 aqueous solution. Synthesis of silica and titania nanoparticles from their aqueous anionic complexes by using Fusarium oxysporum are also reported in literature. When F. oxysporum gets exposed to equimolar solution of AuCl4 and $AgNO_3$, it can derive Au–Ag nanoparticles (Senapati et al. 2005). Platinum nanoparticles can be derived by inter and extracellular formation in the presence of H_2PtCl_6 (Riddin et al. 2006). The size and shape of all nanoparticles derived by using fungi can be manipulated by altering pH and temperature during growth conditions. Aspergillus flavus and C. versicolor, a white-rot fungus, are used in the large-scale production of high-stability Ag nanoparticles (Ratul et al. 2017; Vigneshwaran et al. 2007). The silver nanoparticles can be synthesized by fungus, where glucose is used as stabilizing agent. Researchers proved that these silver nanoparticles could be used as water-soluble metallic catalysts for living cells. Advantages associated with fungal mediated synthesis are,

(i) regenerative capability
(ii) eco-friendly and energy-conserving nature
(iii) large-scale production of metal nanoparticles
(iv) commercial feasibility of the synthesized nanoparticles (Ratul et al. 2017).

9.3.2.2 Bacteria Mediated

Bacteria has a wide range of applications in biotechnology field, such as; bioleaching, bioremediation, genetic engineering, etc. Because of the relative ease of manipulation of bacteria, a variety of it is widely used in the biogenic synthesis of metal/metal oxide and other novel nanoparticles.

Bacterial cell wall plays an essential role in the synthesis of metallic nanoparticles. During the reaction, metal ions penetrate through the cell into the cytoplasm and again transferred back to the wall for extracellular liberation. The cell wall contains a large number of metal-binding sites, such as; carboxylic acid, amines, etc. and they are responsible for stoichiometric interaction between metal and other biomolecules followed by deposition of metal. The crystallinity and non-crystallinity of nanoparticles are affected by the morphology and intra-extracellular environment of bacteria. The formation of metal nanoparticles depends on various parameters, such as; pH, temperature, composition of growth medium and growth in light or dark conditions. The biosynthesized metallic nanoparticles can be produced using metal-containing bacteria and they have excellent optical and electrical properties with potential future applications. Metals can be recovered from waste by biosorption process onto the bacteria which ultimately resulted in n bioreduction of metals into nanoparticles and therefore, this method is gaining more interest for the recovery and production of nanoparticles by industries.

Prokaryotic and actinomycetes bacterium are mostly used bacterial strains for the green synthesis of nanoparticles. *Escherichia coli, Pseudomonas proteolytica, Lactobacillus casei, Bacillus amyloliquefaciens, Arthrobacter gangotriensis, Bacillus indicus,* etc. are few examples of bacteria strains extensively used in the synthesis of silver oxide nanoparticles with distinct morphologies and properties. Similarly, to synthesize gold oxide nanoparticles *Bacillus subtilish168, Escherichia coli* DH5a*, Rhodopseudomonas capsulate,* etc. are extensively exploited (Jagpreet et al. 2018).

9.3.2.3 Virus Mediated

In bacteria and fungi mediated routes for the synthesis of nanoparticles protein cages, DNA recognizing linkers and surfactant assembled pathways are used but all these techniques have their own limitations. It has been observed that to produce metallic nanoparticles the above-mentioned routes are facing difficulties and hence virus-mediated method comes under consideration. This method can produce self-assembled semiconductor materials with exceedingly oriented quantum dots structures with mono-dispersed shapes and sizes in nanoscale dimensions. Literature recorded the use of genetic selection and molecular cloning techniques by the genetically engineered phage-based tobacco mosaic virus to yield 3D inorganic nanoparticles (Shenton et al. 1999). The storage stability of the fabricated viral films is upto 7 months without any bacterial infection and it can be utilized to store high-density engineered DNA and in other medicinal applications (Mao et al. 2003).

9.3.2.4 Yeast Mediated

Yeasts can be found in eukaryotic cells and they are unicellular microorganisms. Till date around 1500 varieties of yeasts is identified. Metallic nanoparticles have been synthesized biologically by numerous groups by using yeast as the mediator. Literature revealed that silver and gold-based nanoparticles can be synthesized biogenically by using silver-tolerant yeast strain and Saccharo-myces cerevisiae broth.

9.3.3 Animal Components in Metal Oxide Nanoparticle Synthesis

9.3.3.1 Animal-Derived Materials Mediated

Recently, many animal-derived materials such as; bones, shells, horns, etc. have gained attention of the researchers in the synthesis of metallic nanoparticles. In addition to that cellular organisms are also capable of producing inorganic nanoparticles in oxide form. For instance, various unicellular organisms are used to produce magnetite nanoparticles and inorganic composite materials can be yielded from many multicellular organisms.

9.3.3.2 Invertebrate Mediated

Various kinds of sponges and starfishes have mineralized biological materials which facilitate the green synthesis of nanoparticles and the synthesized materials have medicinal uses also. These biological materials are used to stabilize amorphous minerals and to yield metallic nanoparticles. The most used biomaterials are the hydroxyapatite and the bio-silica. The hydroxyapatite can be obtained from fish bones and it has natural minerals in the form of calcium apatite. This mineral is the main compound in nano-sized collagenous and noncollagenous proteins and has biomedical applications. Many aquatic organisms, such as sponges, diatoms, radiolarians and choanoflagellates can produce glassy amorphous biogenic silica and in sponges, it is formed by the enzyme silicatein (Stupp and Braun 1997). This method happens by appositional layering of lamellae consisting of silica nanoparticles (Müller et al. 2009). Gunduz (2014) synthesized nano-hydroxyapatite from corals by thermo-gravimetry method and used it in medical applications such as osteogenesis (Gunduz 2014). Many nano metaloxide particles have been synthesized from different kinds of worms. In this method, the extracts of worms are used as reducing agents as well as stabilizer in the production of the nanoparticles. Invertebrate chitin can release chitosan peptides which can be used to produce metallic nanoparticles/chitosan nanocomposites and can be used as photocatalysts.

9.3.3.3 Silk Protein-Mediated

Silk fibroins are the amino acids, such as glycine, alanine and serine, produced by a variety of insects and spiders. Different kinds of silks are produced by spiders, such as non-sticky, dry, strong and spiralling threads. Silkworms can also produce silk fibroin, which has commercial uses also. Other species like the larvae of Hymenoptera and Trichoptera can produce silk in their adult stage during metamorphosis. Silk also can be obtained from South American tree ants. All these kinds of silk fibroins have various applications in textile and clinical fields. As silk fibrons are nontoxic and bio-degradable in nature, therefore, in medicinal field they are utilized as material for tissue engineering for blood vessels, skin, bone, ligament and nerve tissue regeneration. Several nanocomposites are produced using fibroin as component, as fibroin-TiO_2 (Feng et al. 2007), nano-hydroxyapatite/ silk fibroin (Wang et al. 2008).with near about 100 nm length. Sericin, a waste material, which is discarded into the wastewater from silk industries, can be used for production of metallic nanoparticles. In this method, sericin is extracted from wastewater and reduced by rotation to yield a concentrated sericin solution. Nano-sericin powder can be obtained by ultrasonication (Ratul et al. 2017). Metallic nanoparticles produced by these kinds of fibers show antibacterial activities, biocompatibility, oxidation resistance and UV resistance.

9.4 Mechanism of Biological Synthesis of Metallic Nanoparticles Using Plant Extract

For the synthesis of metallic nanoparticles heated plant extract (A) and metal salt solution (B) is taken and heated to 70–80 °C using a stirrer-heater for about 30 min. NaOH is added sometimes drop-wise to the mixture for adjusting the pH of the solution to 10–12 and then heated for more than one and half hours until it is reduced. The solution is then filtered using filter paper and the residue is kept overnight in an oven. Next day the material is carefully collected and mashed in a mortar-pestle to get a finer powder on metallic nanoparticles. Various parameters are responsible to control the rate of the reaction, size and stability of the nanoparticles. Those parameters are pH, temperature, concentration of plant extract, concentration of metal salt extract and phytochemicals. Bacteria, algae, fungi mediated methods require longer time of incubation to reduce metal ions, whereas phytochemicals present in plant extracts take lesser time to reduce metal ions and therefore metallic nanoparticle synthesis using plant extract is considered as an excellent method. In addition to that, plant extract has dual character in whole procedure. They act as a reducing agent as well as stabilizing agent during the reaction. Phytochemicals play an important role in this process. Various kinds of phytochemicals like sugars, ketones, aldehydes, carboxylic acids, terpenoids, flavonoids, etc. are responsible for the synthesis of metallic nanoparticles. Sugars such as glucose and fructose help in the synthesis of metallic nanoparticles of different shapes and sizes. Flavonoids contain large number of functional groups and during the synthesis because of tautomerism active hydrogen atoms get released from enol and converted it to keto form. This enol-keto transformation reaction is responsible for the synthesis of many plant extracts, like basil extract. Plant extract also contains protein biomolecules with functionalized amino acids, heterocyclic compounds which also help in the synthesis of metallic nanoparticles. The steps involved in the synthesis of metallic nanoparticles using plant extract are (i) the activation phase—bioreduction of metal salts followed by nucleation process of the reduced metal ions, (ii) the growth phase—self-assembly of small particles and (iii) termination phase—the final shape and size of the nanoparticles are defined (Jagpreet et al. 2018) (Fig. 9.2).

9.5 Advantages and Disadvantages of Biological Synthesis of Metallic Nanoparticles

Chemical methods for the synthesis of metallic nanoparticles are based on harsh chemicals, non-polar solvents and therefore chemically synthesized nanoparticles have some restrictions in clinical and biomedical applications. Toxic chemicals are used to reduce metal ions, as capping agents, to stabilize nanoparticles, etc. and those chemicals and their by-products contaminate soil and water. Another drawback of

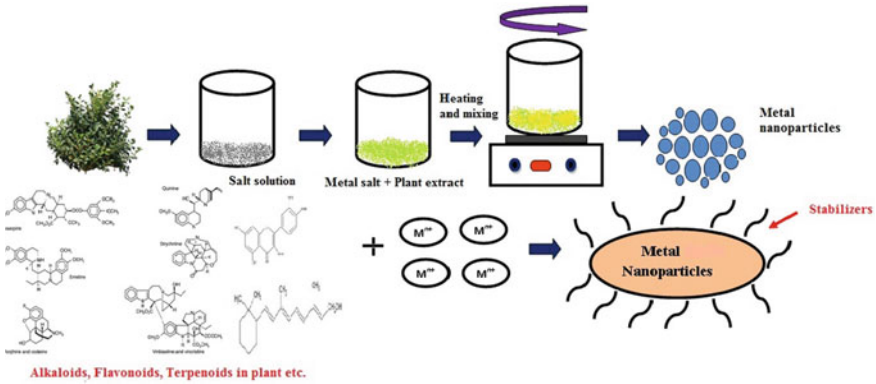

Fig. 9.2 Biological synthesis of metallic nanoparticles using plant extract

chemical methods are those are more capital and energy-consuming. Therefore, eco-friendly and green methods for the synthesis of metallic nanoparticles are in demand now and unlike chemical methods, lack of toxic chemicals in biological methods makes it a more environmentally friendly, consumes no energy and cost-effective route. The biogenic route involves synthesis of metallic nanoparticles from plant extract and the use of different microbes, such as fungi, bacteria and yeast. The whole process of synthesis depends on the enzyme and biomolecules activities when the microbes or the gigantic phytochemicals grab the target metallic ions and reduce them by controlling their sizes. Highly stable, well-characterized nanoparticles can be synthesized by green method. Biologically synthesized metallic nanoparticles are more polydispersed than chemically synthesized metallic nanoparticles. Controlling shape and size of the metallic nanoparticles are easier in biological method and as the fundamental properties of nanoparticles such as; optical, catalytical, magnetic, electronic, etc. are size-dependent properties, therefore, biogenic route is more convenient than chemical route for the researchers. Moreover, the bioproducts of these methods are non-hazardous and can be utilized for clinical and biomedical applications.

Nonetheless, the limitation associated with the biological synthesis is the total time required for the production as the microbes and other phytochemicals grow or work under natural conditions to synthesize metallic nanoparticles (Fig. 9.3).

Toxicity issue during biological synthesis

Compared to chemically synthesized metallic nanoparticles, green synthesized metallic nanoparticles have a broad range of applications such as; biosensors, water purification, drug delivery, cancer treatment, DNA analysis, gene therapy, magnetic resonance imaging, antibacterial agents, slow vaccine release, tissue engineering, etc. As chemical methods use harsh chemicals for the synthesis of metallic nanoparticles, therefore, this kind of vast field of applications cannot be accomplished by chemical synthesis. In biological method for the synthesis of metallic nanoparticles hazardous chemicals like, organic solvents and inorganic metal salts are used in very

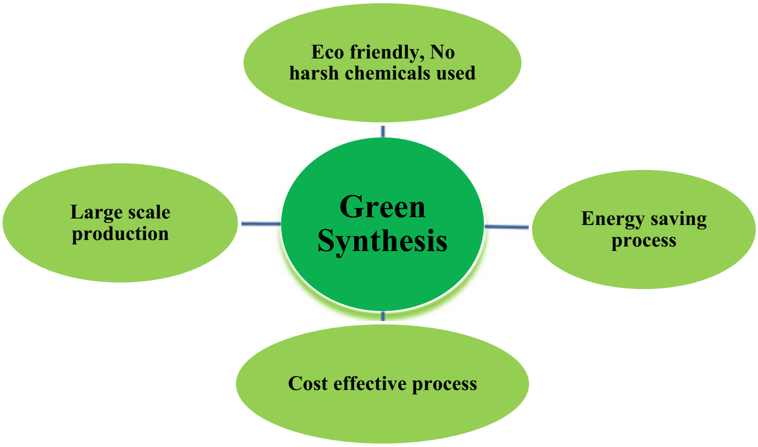

Fig. 9.3 Benefits of green synthesis

low concentrations, therefore, this kind of synthesis is known as green synthesis. However, it is quite impossible to prepare extracts of microorganisms and few plants without any organic solvents. Use of water as only one solvent during the extraction of biological substances and during the synthesis of metallic nanoparticles is still under investigation.

9.6 Photocatalysis

Release of industrial wastewater containing organic dyes into the main water bodies is highly objectionable because the coloured dye materials and their dissociated products are extremely toxic and carcinogenic in nature. Various methods have been evolved to remove dye particles from water but they all are non-destructive and as a result of that toxic dye particles are removed temporarily and in due course of time those get transformed into other toxic substances. Advanced oxidation processes (AOPs) have gained interest in this regard because of the formation of nontoxic by-products after oxidation of the pollutants. Degradation of organic pollutant through AOPs occur by using reactive oxygen species such as hydroxyl (·OH) and superoxide ($\cdot O_2^-$) radicals which are generated in several steps.

AOP follows four different pathways and those are, photolysis, ozonation, Fenton process and photocatalysis. To generate active radical species photolysis and ozonation methods use hydrogen peroxide in presence of ultraviolet and ozone, respectively. Hydrogen peroxide along with ferrous ions as catalyst are used in Fenton process to get radicals. In photocatalysis, radical species are generated in presence of light and semiconducting materials, where semiconductors absorb photons from light and produce active radicals. Among these four methods, recently photocatalysis process using semiconducting nanoparticles has attracted much more attention of the researchers as nanoparticles can degrade very low concentration organic pollutants in presence of photons and produces nontoxic degraded products, utilizes renewable solar energy and do not use harsh chemicals. Therefore, photocatalysis is considered as safe, green and sustainable process (Eleen et al. 2021).

9.6.1 Mechanism of Photocatalysis

Photocatalytic reaction rate depends on the catalyst structure that is used in reaction and the photons energy of visible or UV light. Depending on the electronic structure of the catalyst, it plays a role as a sensitizer for the irradiation of light-stimulated redox processes. Reaction mechanism of pollutant degradation photocatalysis process follows two ways; direct and indirect ways but indirect way is the most commonly used to explain the reactions. Indirect reaction process starts with photoexcitation. The general mechanism is that the electrons of valance band will excite to conduction band upon absorbing photons only if the band gap of the catalyst is equivalent or less than the incident light energy. When electrons move from valence band to conduction band, they leave holes (h^+) which play the key role to oxidize the donor molecules. An additional example is a strong oxidizer hydroxyl radical (·OH) is produced when H_2O reacts with these holes. After the electrons reach the conduction band, they are absorbed by the water molecules and produce superoxide ions ($.O_2{}^-$) which are reducing agents. Consequently, it is acceptable to say that the free electrons and holes are responsible for the redox reaction with any kind of pollutants which come into the contact with the catalyst and convert it into the desired products (Muhammad et al. 2020). The schematic representation of pollutant degradation by photocatalysis is shown in Fig. 9.4

The photocatalytic reactions of pollutants (P) in the presence of photocatalysts (metallic nanoparticles n−M) and light source are given below:

$$P + h\upsilon \rightarrow P*$$

$$P* + n - M \rightarrow (n - M)* + P^+ \quad P * + n - M \rightarrow P + h^+ + e^-$$

$$(n - M)*\left(e^-\right) + O_2 \rightarrow .O_2^- + n - MOs \quad h^+ + H_2O \rightarrow OH^- + H^+$$

$$O_2 + H^+ \rightarrow HO_2 \quad 2HO_2 \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + O_2^- \rightarrow HO\cdot + OH^- + O_2 \quad H_2O_2 + e^- \rightarrow HO\cdot + OH^-$$

Organic and inorganic pollutants + reactive oxygen species → Degradated into harmless products.

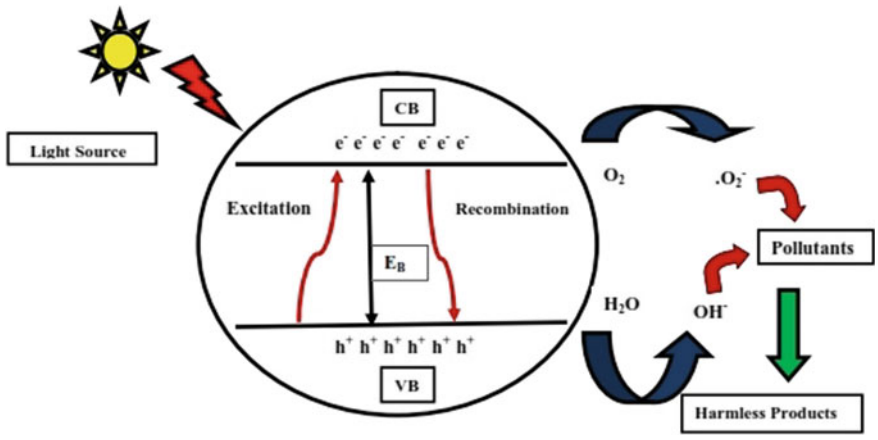

Fig. 9.4 Mechanism of photocatalysis process

9.6.1.1 Oxidation Mechanism

Light generates electron–hole pairs in the catalyst and it captures water molecules. When water molecule is oxidized and results into hydroxyl and oxygen radicals. Hydroxyl radicals have oxidizing powers that can decompose all organic pollutants. If oxygen radical is involved in the process, it creates chain reactions with organic molecules' intermediate radicals and results into carbon dioxide and water (Muhammad et al. 2020).

9.6.1.2 Reduction Mechanism

Oxygen is easily reduced by pairing reaction. When it is reduced, it produced hydrogen. The reduction reaction mechanism of oxygen is that electrons in the conduction band form superoxide ion by reacting with oxygen it is also possible that the anion attaches with intermediate to produce peroxides in an oxidation reaction and then produce water. Therefore, when the concentration of organic matter increases, the probability that number of holes which reduces the recombination rate of the carriers increases as well (Muhammad et al. 2020).

9.6.2 Factors Affecting Photocatalysis Process

There are different factors that can affect on the photocatalytic activity process for treating wastewater. Electron–hole pair separation rate, the structure of the catalyst, pH, amount of catalyst, intensity of the incident light and temperature are the factor that affects the performance of the photocatalyst. In case of electron–hole pair separation rate, a good catalyst should utilize in secondary reaction before recombination because the life of the electron–hole pair in semiconductor catalyst is small. In order to have a deal photocatalyst, it must have a wide band gap and electron recombination as low as possible. For instance, in TiO_2 holes are considered as good oxidizing agents while electrons are acted as reducing agents in valance band (Muhammad et al. 2020).

9.6.2.1 Structure of the Catalyst

The structure of the catalyst plays an important role in the photocatalytic reactivity. TiO_2 has three different structures, they are rutile, brookite and anatase. Each of them has different impact on the photocatalytic activity. It is observed that anatase is more effective than others. This is attributed to its structure stability, conduction band position and its high adsorption. Another example is zinc oxide which has two different shapes; spherical and rod shapes. The degradation efficiency is higher in spherical form than in rod form and this is because of its high surface area. In general, materials are used in their nano form instead of bulk state because their size dimension gives them an advantage in terms of reactivity rate. The enhancement of reaction rate in case of nanomaterials is because they have higher surface area or surface-to-volume ratio is high which permits reactants and catalysts to react together (Muhammad et al. 2020).

9.6.2.2 pH

Photocatalyst efficiency is pH-dependent. pH affects the surface charges of the photocatalyst and that can be observed in the electrostatic phenomena that are between pollutant and charged particles. The impact of different pHs on the photocatalysts has been studied. It is reported that in acidic medium, pH less than 5, photocatalyst does not have high-efficiency level l and the reason is that the high concentration of protons H which limits OH radicals that are used to degrade the dyes. If pH is in range of 5–10, the efficacy of the photocatalyst increase and it can reach its maximum if pH is at 10 which is alkaline medium because the amount of OH radicals is bigger and that help in degrading the dyes pollutant. However, if pH is above 10, such in range of 11–13, it is observed that there is a drop in the efficiency of the photocatalyst and it is attributed to the increased level of OH radicals in the process and that avoids them to react with the dyes in the medium (Muhammad et al. 2020).

9.6.2.3 Amount of Catalyst

There is direct relationship between the amount of catalyst and photocatalytic activity which means when the amount of catalyst increases, the degradation rate will increase as result of the increase of generated radicals. There is an optimal amount of catalyst after which the increase of amount of catalyst will not change the degradation rate because it will avoid the light to penetrate (Muhammad et al. 2020).

9.6.2.4 Intensity of Incident Light

The intensity of incident light on the catalyst surface has an impact on the photocatalytic degradation rate as well. When light incident increases, it leads to an increase in the quantum yield, i.e. the ratio of reaction rate and absorption rate. To illustrate, an example is TiO_2 which has 3.2 eV bandgap and absorbs UV light. Comparing light intensity, when it is 0–20 mW/cm, the degradation rate increases. However, when high-intensity light helps in the recombination of electron–hole pairs then the rate of the reaction decreases (Muhammad et al. 2020).

9.6.2.5 Temperature

Temperature has an influence on the photocatalytic reaction rate. Each nanoparticle has an optimum temperature at which the reaction rate reaches its maximum. reported that 20–80 °C is the optimum temperature range for TiO_2. They observed that the rate of reaction of TiO_2 is decreased at 80 °C as a result of an increase in the recombination rate of electrons and holes increase. In addition, the absorption rate of the catalyst is reduced at this reaction rate. In addition to that, the rate of the reaction declines due to the reduction of the absorption rate of the catalyst at this particular temperature (Muhammad et al. 2020).

9.6.3 Role of Photocatalytic Process Against Different Wastewater Pollutants

Wastewater contains different kinds of pollutants such as heavy metals, microbes, organic and inorganic pollutants. Research has shown that major organic pollutants in wastewater are present in the form of carboxylic acid, alcohol, chlorinated aromatic compounds and phenolic derivatives. In addition to that, leather industry and textile industry are the main sources of dyes pollutants that have major role in polluting water. Dye industries contribute with roughly 20% of the annual dye consumption into the water bodies (Dequigiovanni et al. 2018).

TiO_2, ZnO and CuO semiconducting nanoparticles have a great potential to purify wasted water in presence of dyes (Danwittayakul et al. 2013; Chin et al. 2006). Researchers confirmed that such nanoparticles have an influence in treating wastewater during the photocatalytic reaction process. Liu et al. (2008) reported that TiO_2 reduced humic acid or natural organic matters by 80% and 65%, respectively (Liu et al. 2008). Humic acid substance is a yellow–brown material that has high molecular weight. Not only humic acid and other organic substances are removed by photocatalytic process but also various inorganic substances such as halides, ammonia, cyanide, nitrates and thiocyanate were also can be decomposed photolytically by metal oxide nanoparticles. Hong et al. (2009) reported that TiO_2 was used against $AgNO_3$ (Hong et al. 2009), Joshi and Shrivastava (2011), Bagabas et al. (2013) studied the effect of ZnO against Cr(VI) and potassium cyanide (Joshi and Shrivastava 2011; Bagabas et al. 2013) and Lee et al. (2002) showed that photo-oxidation of ammonia in water by nanotubes (Lee et al. 2002).

Heavy metals in water are a big concern due to its toxicity. The level of heavy metals in water varies and it can threaten the life of human and aquatic creatures. Thus, it is one of elements that is needed to be considered when treating wastewater. But as most of these metals are rare, expensive and valuable than others therefore very often it is preferred to recover those by photocatalysis from polluted water.

Microbes and bacteria are other kinds of pollutants that exist in polluted water. Photocatalysts have an anti-microbial effect. During the photocatalytic process, the catalysts generate radicals that destruct the cell wall of bacteria and thus prevent the growth of microbes and bacteria. Researchers studied the removal of microbes such as S. mutans, S. natuss, S. cricetus, E. coli, S. cerevisisas and L. acidophilus in wastewater by heterogenous photocatalyst. For instance, the growth of Chlorella vulgaris can be controlled by TiO_2 and ZnO is used to inhibit the growth of E. coli and S. aureus (Muhammad, et al. 2020).

9.7 Photocatalysts

9.7.1 Selection of Nanomaterials as Photocatalysts

Like typical redox reactions, photocatalytic reactions include oxidation and reduction steps. There is a need for a catalyst in photocatalytic reaction to support those steps. At electronic level, materials are classified as conductors, semiconductors and insulators. In conductors' class, the electronic valence band is overlapping with conduction band and the best conductors are alkali, alkaline earth metals and transition metals. They are the best conductors because there is no suitable band gap and thus, they are not appropriate for catalytic activity. In case of semiconductors, there is a moderate energy gap between valence band and conduction band which allows for redox reaction to occur. Similar to oxidation mechanism, free electron–hole pairs are generated upon exposure to light.

Semiconductors can be photocatalysts under certain conditions: there must be low recombination rate and the absorption wavelength must lie in range of 350–700 nm in visible region or band gap in 1.5–3.5 eV. The band gap 1.5–3.5 eV is not as large as for typical semiconductors, but this range is what is required to act as photocatalyst in UV–visible region. Examples of semiconductors are metal oxides. They offer properties such as light absorption, structure stability, superior morphology, high surface area, reusability, carrier transportation and band gap that make them good photocatalysts. It is crucial that band gap lies in UV–visible range in order to be an attractive photocatalyst. Examples of metal oxides that have these properties are chromium, vanadium, cerium, zinc and titanium and thus they are widely used as photocatalysts (Muhammad, et al. 2020).

Gold, silver, iron, zinc, nickel and cobalt are examples of metals that exist in metal nanoparticles and when they are combined with hydroxide, chloride, sulphides, phosphate, oxide and fluoride, they form compounds. The synthesis of nanoparticles by photochemical, chemical and electrochemical methods is prepared by using precursors of metals. The band gap of most metal nanoparticles lies in an infrared region and in ultraviolet region. However, this is not suitable to be a photocatalyst. Roy et al. (2015a; b) reported that the band gap of silver nanoparticles shows photocatalytic properties in visible region (Roy et al. 2015a; b). Metal nanoparticles of group IV for instance Si, Ge, group VI, for instance, Se, Te elements and group III–V, II–VI, I–VII, IV–VI, V–VI, II–V compounds such as; GaN, GaO, ZnS, CdSe, ZnO, TiO, Mgo, AgO are semiconducting in nature. They have different properties because of their wide band gap and thus they behave either as metal or non-metal. In addition to metal and non-metal nanoparticles, polymeric nanoparticles are other categories of nanoparticles. They are naturally organic compounds, have structural shapes such as nano-spheres or nano-capsular, the shape of polymeric nanoparticles will depend upon the synthesis method. The difference between nano-capsular and nanosphere is that the morphology of nano-capsular is like core–shell while nanosphere is like matrix structure. Polymeric nanoparticles are mainly used in medical field such in drug delivery and diagnosis (Muhammad et al. 2020). Generally, when metal oxide photocatalysts are irradiated with visible light they absorb photons and electrons from valance band get excited to conduction band and thus create electron–hole pairs. These electron–hole pairs decompose pollutants by redox reactions at the surface of the catalysts and because of this reason metal oxide photocatalysts are gaining more attention in the photodegradation of pollutants.

In case of insulators, they are electrons deficient and there is a band gap between valence band and the conduction band. Consequently, it is difficult for oxidation reaction to carry out in presence of insulators and there is a need for energy to perform redox reactions which make insulators are not good choice as catalyst. In the example of splitting water molecules using insulators, it cannot be achieved unless high energy inputs are utilized. Halogens and noble gases are examples of insulators.

9.7.2 Metal Oxide Nanoparticles Photocatalysts

Recently researchers are more focused on the green synthesis of nanomaterials as this route of synthesis is economical, easy, fast-paced and environment friendly. To produce metallic nanoparticles photocatalysts this methodology makes use of several biological species such as plants, animal products and microorganisms. Furthermore, scientists showed that through biogenic route of synthesis metallic nanoparticles photocatalysts of better size and morphology can be produced.

In this following section, we will be discussing on the green synthesized metal oxide nanoparticles such as zinc oxide, iron oxide and titanium dioxide nanoparticles for the application of photocatalytic degradation of pollutants.

9.7.2.1 ZnO Photocatalysts

A lot of literature suggests adsorption and advanced oxidation processes (AOP) are better methods in the treatment of textile industry disposed wastewaters and in the removal of dye particles from water. Several semiconductor materials have been used as adsorbents and photocatalysts in the removal of dye particles. Recently, an increasing attention has been directed to ZnO nanostructures in waste removal methods from polluted water where nano ZnO are found to be highly effective as it has a wide band gap of 3.37 eV and due to its low cost, low toxicity, antibacterial properties and high surface activity. ZnO can be found in nature within the earth's crust in the form of mineral zincite but it can be obtained through synthesis (Eleen et al. 2021). ZnO has three crystalline structures; rocksalt, wurtzite and cubic (zinc blend) and it can absorb larger fraction of the UV spectrum. AOPs and adsorption methods are used by ZnO in the waste removal method because the high surface area to mass ratios of ZnO nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Various researchers have shown the removal efficiency of ZnO nanomaterials with different types of microorganisms and heavy metals, including Cu, Pb, Cd, Ni, Co, Pb, Hg and As. Literature also shows effective removal of dye particles and toxic organic contaminants from industrial and pharmaceutical wastewater by various groups (Eleen et al. 2021).

Sangeetha et al. (2012) produced ZnO nanoparticles by green route and used it against bacterial and fungal pathogens (Sangeetha et al. 2012). Varadavenkatesan et al. (2019) reported that *Cyanometra ramiflora* leaves extract can be used in the green synthesis of ZnO and the results showed nanoflowers morphology of the synthesized n-MO. This type of synthesized nanoparticles was used to degrade Rhodamine B dye up to 98% in 200 min (Varadavenkatesan et al. 2019). Eleen et al. (2021) have used biopolymer, pullulan to synthesize ZnO nanoparticles to degrade Rhodamine B and Methyl orange dyes completely within 60 min under UV irradiation (Isa et al. 2021b).

9.7.2.2 Fe(II/III) Oxide Photocatalysts

Iron oxide is known as a transition metal oxide, which can exist in three crystalline forms such as hematite (a-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) but among all these, hematite is the most stable form and most commonly used as photocatalyst (Eleen et al. 2021). According to literature magnetic Fe_2O_3 nanoparticles being a semiconductor has a potential application in photocatalysis and under

UV radiation, electrons excite from valence to conduction band which ultimately resulting into the formation of electron–hole pairs, comparable to the electron–hole pair formation in ZnO nanoparticles. Fe_2O_3 nanoparticles having high specific surface areas, also have unique adsorption properties due to disordered surface regions as well as for different distributions of reactive surface sites. Shiying et al. (2017) reported that iron oxide /biochar nanocomposites loaded with photosynthetic bacteria are effectively used in wastewater treatment (Shiying et al. 2017).

The widespread applications of Fe_2O_3 in the removal of organic and inorganic pollutants by photocatalysis and adsorption methods are studied in detail by Santosh et al. Karunakaran et al. (2018) have shown that magnetism of Fe_2O_3 is a unique physical property that can influence the physical properties of contaminants in water and helps in water purification. Adsorption procedure combined with magnetic separation of Fe_2O_3 nanostructures has therefore been used widely in wastewater treatment (Karunakaran et al. 2018). Researchers reported that synthesized nanorods of iron oxide nanoparticles using Wedelia urticifolia DC. Leaf extract and the synthesized materials were used to degrade methylene blue dye up to 98% in 360 min under visible light irradiation. Literature showed that to photodegrade naphthalene iron oxide nanoparticles were synthesized using the leaves extract of spinny amaranth and 97% degradation efficiency within 150 min under UV irradiation was recorded (Eleen et al. 2021).

9.7.2.3 TiO_2 Photocatalysts

Titanium dioxide nanoparticles is another widely used photocatalyst in recent years and this is all because of their non-toxicity, cost-effectiveness, excellent photosensitivity, photocatalytic stability and plentiful availability. TiO_2 has two phases; anatase and rutile and the band gap value of those phases are 3.2 eV and 3.03 eV, respectively (Eleen et al. 2021). Sonker et al. (2020) reported that nanosheets of TiO_2 nanoparticles can be synthesized using Aloe vera extract. The synthesized materials showed degradation on Rhodamine B dye in 50 min under visible light irradiation and the degradation efficiency was 58% of Sonker et al. (2020). Literature showed that spherical TiO_2 NPs with particle sizes ranging from 50 to 120 nm were synthesized by using *Salvia officinalis* leaves extract. Produced n-MOs were utilized to degrade Reactive Black 5, Reactive Blue 19 and Brilliant Blue R dyes with degradation percentages of 69, 74 and 79%, respectively (Eleen et al. 2021).

9.7.3 Nanocomposites and Other Photocatalysts

Chitosan peptide can be derived from invertebrate chitin. Nanochitosan can be utilized for environmental applications such as removal of pollutants from water. For instance, Fe_2O_3/ graphene/chitosan is an useful material to remove organic dyes from water and this is due to the presence of the large number of hydroxyl and amino groups of chitosan and magnetic property of Fe_2O_3, which in together showed good adsorption capability for certain organic dyes (Sheshmani et al. 2014). Recently, TiO_2/chitosan composite was found to be an efficient photocatalyst in the removal of organic pollutants from wastewaters and also the photocatalytic activity of this catalyst remains almost same after 10 cycles (Xiao et al. 2015). A nanocomposite of Bentonite–chitosan can adsorb and remove synthetic dyes with great efficiency. Chitosan–metal oxide nanocomposites have several industrial and pharmaceutical applications like; in textile industry they can be used for colourizing textiles, in medicine, they can be used as a nano- capsule for slow release of vaccines and cancer treatment (Ratul et al. 2017).

The nanocrystalline semiconductors such as; HgSe, PbSe and CdSe colloids were studied thoroughly for their photocatalytic activity and it has been found that, for less than 50 Å diameters(d), optical absorption edge of HgSe and PbSe was blue-shifted by several volts. The enhanced photocatalytic effects of these above-mentioned quantum size semiconductors are due to the evolution of H_2. The nanocrystalline CdSe particles ($d < 50$ Å) have more stability against photo corrosion compared to HgSe and PbSe and hence were exploited for the reduction of CO_2 in formic acid. It has been observed that large particle-sized CdSe colloids did not show the same results under the same experimental conditions (Beydoun et al. 1999).

One research article showed that, when Zn is mixed with nanocrystalline ZnS, it can enhance the photoreduction of CO_2 by switching from formate to CO, without any loss in its efficiency. Another study on CO_2 photoreduction by the same group explained that CdS had enhanced photocatalytic capability due to the formation of sulphur vacancy on the surface and they also explained that, CO formation process occurred via adsorption of CO_2 to a Cd atom in the vicinity of a sulphur vacancy (Beydoun et al. 1999).

Sato et al. (1996a) showed the use of $H_2Ti_4O_9$/CdS nanocomposites for the photochemical reduction of nitrate to ammonia with and without methanol and it has been observed that addition of methanol increased the reduction rate. Photocatalytic activity of the nanocomposite could also be increased by doping Pt particles into the interlayer. This group also studied on the photocatalytic properties of layered hydrous titanium oxide/CdS–ZnS nanocomposites, where CdS–ZnS was incorporated into the interlayer and it was observed in presence of visible light the photocatalytic activity with the liberation of hydrogen on the surface of nanocomposites was more following compared to unsupported CdS–ZnS (Sato et al. 1996b).

9.8 Future Scope and Conclusion

Green synthesis of metal nanoparticles for their photocatalytic activity has become an interesting topic of research over the last decade. Various kinds of plants, microorganisms, fungi, algae and animal-derived products have been employed for the synthesis but it has been found that plant extract is more efficient in this regard as phytochemicals present in plants can be used as reducing as well as stabilizing agents. This chapter discussed over biosynthesis of metal nanoparticles by using various parts of plants, microorganisms and animal derivatives and also elucidated the mechanism of biosynthesis. Photocatalysts and their mechanism in photodegradation are explained thoroughly in this chapter.

Photocatalysis is initiated by light and completed with the help of catalysts, where nanomaterials are considered as most suitable photocatalyst for photodegradation. Semiconducting metal-based nanomaterials are considered as most efficient photocatalyst due to their excellent photocatalytic activity and wide range of band gaps in visible regions. As recently our focus is on cost-effective and environmentally friendly photocatalyst therefore biosynthesized nanoparticles play a vital role in this field of research. In water pollution treatment photocatalytic technique is the most desirable because of its cost-effectiveness, environmental friendliness and degradation efficiency towards organic, inorganic, heavy metal and microbe's pollutants. However, detail study on photocatalysis by biosynthesized metal nanoparticles has encountered with few existing problems, which can be resolved effectively in future studies.

(1) Few hours are required for complete degradation of pollutants by metal nanoparticles therefore in future more studies should be done to reduce the total time taken for complete photodegradation.
(2) More emphasis should be put on the study based on the concentration of pollutants, reproducibility and stability of the catalysts after several runs.

Biosynthesis of metal nanoparticles for the use in photodegradation studies, is a quite new field of research and it is in the developing stage and because of that, this methodology is encountering with several problems, which can be solved by taking some measures. The initial start problems faced by these methods are related to size, shape, self-assembly, stability and crystal growth of nanoparticles. These kinds of problems are quite common in metal nanoparticle synthesis but however, more and more attention should be drawn towards biological synthesis to wave out those issues in future. Some salient points of green synthesis of nanoparticles comprise the fact that:

(1) The mechanism of biogenic synthesis of metal nanoparticles is still not clear. Therefore future studies must put more concentration on reaction of biomolecules and enzymes during the growth phase. In addition to that details study on the properties of synthesized nanoparticles is much more needed.
(2) Another relatively unexplored area of research is purification of metal nanoparticles. Removal of unreacted metal salts, plant extract and microbes is very essential. For purification, chemical treatment must be avoided to keep the nanoparticles nontoxic. Therefore in future purification processes by physical methods, such as centrifugation, heating, ultrasound and osmotic shock can be investigated.
(3) Large-scale production is another important point to be considered in future as till date metal nanoparticles are synthesized only in laboratory scale via green method.

(4) Future studies must emphasize on cost-effectiveness of the large-scale production of metal nanoparticles. In biogenic synthesis, major expenses are coming from consumable metal salts and microbial growth. In this case, cost can be cut down by using recyclable waste materials and this can be a sustainable approach too.
(5) Future studies must put more stress in the rapid production of nanoparticles.

However, recent studies on biogenic route have suggested that principles of this method can be efficiently applied for the biological synthesis of metal nanoparticles and at the end, we can conclude that photocatalytic technique using green synthesized metal nanoparticles is a sustainable, emerging, efficient and green approach.

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