Remediation of Dyes in Water using Green Synthesized Nanoparticles.

Akanksha Pandey*, Pooja Shukla, Pankaj Kumar Srivastava

DOI: 10.18811/ijpen.v6i01.08

International Journal of Plant and Environment, Volume 6 Issue 1 (2020); ISSN: 2454-1117 (Print), 2455-202X (Online)

A B S T R A C T
With the rapid growth of population and increasing urbanization and industrialization, environmental pollution is becoming a serious concern worldwide. Different type of pollutants is released into the water bodies enormously from the expansive range of industries. Among all the pollutants, dyes are the major used noxious waste discharged by these productions. Even at minute content (< 1ppm), dyes are posing a detrimental threat to the ecosystem and human health risks. Recently, nanotechnology has emerged as an efficient technology for the remediation of environmental pollutants from water. Green synthesis of nanoparticles (NPs) can be done to degrade molecules of dyes in wastewater. Various nanoparticles such as iron, palladium, and cerium dioxide using Camellia sinensis, Boswellia serrata, and Azadirachta indica extracts have been reported successfully for the remediation of various dyes like rhodamine B, methylene blue, etc. Removal of dyes from the wastewater using green synthesized nanoparticles with the help of microbes or plant extracts is a sustainable technique, i.e., by the use of this technique, our environment will not get polluted, and its quality will also be maintained. The present review discusses the classification of dyes, nanoparticle formation by using microbes or plant extract, and, finally, the remediation of dye using such nanoparticles.

Keywords: Dye pollution, Green synthesis, Nanoparticles, Nanotechnology, Remediation.


INTRODUCTION
Along with growing urbanization, industrialization, and rapid advancement of population, environmental pollution, and other crucial difficulties are becoming critical globally. Various types of pollutants discharged from the diverse industries are the major source of pollution (Yang et al., 2010; Tang et al., 2014; Chen et al., 2015; Wu et al., 2017; He et al., 2018). These industrial pollutants modify the quality of water bodies. Wastewater discharges from chemical industries contain toxic substances such as heavy metal ions, dyes, and organic pollutants. One of the harshest water pollution sources is dye effluent discharge from various industries (Mua and Wang, 2016). A large amount of dyes is produced annually from the different industries such as textile, paint, cosmetic, paper, plastic, leather, agricultural research, hair coloring, photo-electrochemical cell, light-harvesting array, pharmaceutical and nutrition industries. However, the exact estimation of the amount of dyes that are discharged from these industries is a tough task (Khataeea and Kasiri, 2010). Approximately 70,000 tons is the worldwide annual production of dyes, whose commercial types are around 100,000 (Robinson et al., 2001). Discharge of dyes into water bodies without proper treatment has caused serious problems to aquatic life and human health (McKay, 1982; Shimada et al., 2010; Khan et al., 2013).

Dyes are commonly observed to be carcinogenic and mutagenic, as well as pernicious in nature. In the natural environment, dyes retain their color and structural stability as well as show strong resistance to microbial degradation under the exposure to sweat, sunlight, soil and bacteria (Banat et al., 1996; Robinson et al., 2001; Baban et al., 2010; Pathakoti et al., 2018). Rate of photosynthesis reduces because these dyes prevent the penetration of light across the water bodies, therefore the level of dissolved oxygen of entire aquatic ecosystem getting affected which cause aesthetic damage to the water bodies (Imran et al., 2015; Hassan and Carr, 2018; Lellis et al., 2019). When dyes enter into the drinking water system, they impart serious health hazards. Dye effluent contains chemicals that are carcinogenic, mutagenic, or teratogenic, which can cause damage to genetic material in various organisms (Weisburger, 2002; Umbuzeiro et al., 2005). In humans, some dyes have been linked to bladder cancer; dysfunction of the kidneys, reproductive system, liver, brain and central nervous system (Medvedev et al., 1988; Kadirvelu et al., 2003; Dinçer et al., 2007; Shen et al., 2009). Only 1.0 mg L\textsuperscript{-1} of dye concentration in drinking water could impart a significant color, making it unfit for human consumption (Malik et al., 2007). So the remediation of dyes is essential even though at a very minute concentration of theirs is present in the environment.

Dyes have complex structures, stable, non-biodegradable, and remaining ecosystems for a longer time. For their complete degradation, there is a constant need to have an effective...
method that can efficiently remove these dyes from wastewater. However, such a method for dye removal has remained a challenge for scientists because conventional methods for dye removal were not very efficient and economical. Many conventional treatment methods applied for the remediation of dyes from wastewater include physical decolorization (sedimentation, filtration adsorption, and reverse osmosis), chemical decolorization (neutralization, recovery, chemical oxidation, ion exchange methods), and biological decolorization by using bacteria, fungi, and actinomycetes (Morshedhi et al., 2013). The drawback of physical methods is high operational cost, while drawback for the chemical method is the production of a concentrated sludge (Robinson et al., 2002). The biological method takes a long time for degradation, and for some dyes, this method has a low degradation efficiency. Moreover, the management and start-up of biological techniques is a tricky process (Lin et al., 2008; Shan et al., 2008; Yadav et al., 2012). Consequently, there is an urgently needed technique for dye remediation, which should be cost-effective, eco-friendly, and have high removal efficiency for decolorization of wastewater discharges from the various industries.

Nanotechnology is an emerging field that is being used in several applications to improve the quality of the environment. It is a field of applied science that is concerned with materials and systems whose structure and components exhibit novel and significantly improved biological, chemical, and physical properties, owing to their nanosized structure. Generally, nanotechnology refers to materials of size 100 nanometer (nm) or smaller in at least one dimension, and it involves the development of materials or devices in this size range (Rawtani et al., 2018). Various nanomaterials, such as a nanoparticle, nanofiber, nanotubes, nanowire, nanorods, nanoribbon, etc. are used for remedial techniques. But out of these, nanoparticles are of great scientific interest for the remediation because of their small size and relatively large reactive surface area. Different methods such as physical, chemical, biological, and hybrid processes are used to synthesize myriad nanoparticles (Pandey et al., 2016; Rawtani et al., 2017; Tharmavaram et al., 2017, 2018; Rawtani et al., 2019). However, physical methods are too expensive, while chemical methods create some adverse effects on our environment and are very harmful to living organisms as well as human health (Panigrahi et al., 2004; Narayanan and Sakthivel, 2010; Thakkar et al., 2010). These methods are not much suitable for wide-scale production because of demerits such as high preparation costs, consumption of extraordinary energy, use of hazardous organic solvents, production of hazardous intermediates, and harmful waste products, which leads to environmental pollution and several biological risks. During the formation of nanoparticles, aggregation of particles occurs due to attractive forces between the nanoparticles. Consequently, there is a requirement to add some capping agents to prevent aggregation and attain the uniformity of the product. All these incidents are responsible for the necessity of improved or appropriate alternative technology, which is consistently good for the development of nanoparticles and also is environmentally friendly. For the remediation of different pollutants from the environment, green technology is recommended as the superior-most technique because in this technique biogenic substances or natural substances such as plants or microbes are used as a reducer and capping agents. Nanoparticles derived from green synthesis using microbe or plant extract have no toxic substances, and their by-products are also eco-friendly. So as far as remedial processes are concerned, it is evident that green synthesis of nanoparticles is the best technique.

In this regard, this review focuses on the recent developments for the remediation of dyes from industrial wastewater by using nanoparticles, which are synthesized by greener routes involving extract of plants, microbes, and other natural products. Previous studies majorly focused on the remediation of various dyes using nanoparticles synthesized by physical and chemical methods. The novelty of present review summarizes the classification of dyes of various aspects such as on their sources, attached chromophore and their applications in various sectors, synthesis of nanoparticles with the help of green technology, and these nanoparticles applied for the remediation of various dyes which was not focused by the past reviews.

**Categorization of Dyes**

Organic compounds which have been colored substances called as dyes. When these colored substances or dyes applied to some substrates, these colored substances get tied up or bind to these substrates chemically and impart permanent color to these substrates. Any type of substrate such as fur, hair, paper, plastics, cosmetics, textiles is used for the coloration from dyes. The imparted color is not removed by washing with water, detergents, or exposure to light. Dyes are used by diverse industries such as plastic, paint, textiles, food, etc. (Chincholi et al., 2014; Yagub et al., 2014). Various types of manner occur for the categorization of dyes such as categorized by the material source, i.e., dyes obtained from which kind of source, naturally or synthetically; categorization by the attached chromophores; and categorization by application (Fig. 1).

**Categorization by the Material Source**

This type of categorization is very familiar. According to this categorization, dyes are of two types: one is a natural dye, and the other is a synthetic dye.

**Natural dyes**

These dyes or colorants are derived from plants, animals, and minerals. As the name suggests, natural dyes are derived naturally from diverse plants or plant parts (wood, root, bark, etc.) that are categorized as a natural dye.
and stem), fungi, and lichens. Some minerals (sangraj, lajerd, gem, sindur, and sajeda) are also used as natural dyes.

**Synthetic dyes**
Now a day, synthetic dyes are used extensively in almost all places. The production of synthetic dyes is economical, as well as they are very bright in color, and their application to textile is uncomplicated. These reasons make synthetic dye’s usage to be ubiquitous. Classes of synthetic dyes are acid dyes, azo dyes, basic dyes, and mordant dyes.

**Categorization by the Attached Chromophore**
Dyes are categorized by chromophores, which are found in the structure of dyes.

**Azo chromophore**
Azo dyes have gained the most significant among all the dyes available. They are extensively useful in industries such as textiles, food, and leather. In the structure of these dyes, the azo group is present, which is normally named as azo. Sometimes, the dye may also contain two, three, four, and more azo groups, which are named as disazo, trisazo, tetrakisazo, and polyazo, respectively. Azo dyes can supply yellow/red and blue/brown dyes mostly. Various azo dyes are solvent yellow 14, disperse red 13, disperse blue, reactive brown 1, acid black 1, direct green 26, and direct black 19.

**Anthraquinone chromophore**
This class of dyes is the second most significant of all the dyes. Some dyes of anthraquinone are very old, and they were used in the process of mumification. Almost all the major natural red dyes are anthraquinones (Gordon and Gregor, 1983). Anthraquinone group, which is generally colorless, is present in the ring structure, and their position defines the anthraquinone dyes. When these dyes are used commercially, some amino or hydroxyl groups are added in the ring structure at α position. Anthraquinone dye imparts the combined properties, and generally, these dyes are used for the shades of red and blue.

**Indigoid chromophore**
For the coloration of different textiles such as cotton and wool indigoid, dyes are very utilitarian. Many indigoid dyes have been synthesized using only indigo. These dyes are used mainly for denim jeans and also jackets for the coloration. Various expensive, branded, and luxurious clothes were dyed-through these dyes. Some dyes of this class were so costly that poor community was not capable of affording garments that were dyed with these dyes.

**Nitroso and nitro dyes**
Nitroso dyes are those compounds which carry chromophore named as nitroso and -OH as auxochrome. This nitroso group involved in a carbon or nitrogen atom. Sometimes, this nitroso group in some substances gets involved with an oxygen atom, and then named as nitrates, while sometimes called nitrosyls when involved with a metal ion. The molecules of these dyes were perfect for the penetration of polyester fibers, for example, disperse dyes. These dyes are also very useful for the coloration of papers, for example: Acid Green 1.

**Triarylmethane dyes**
Triarylmethane dyes were produced synthetically and derived from the triphenylmethane. Auxochromes (amino, hydroxyl) present in these dye are responsible for their deep color. Some examples of these are methyl violet, malachite green, and phenol dyes.

**Categorization by the Application**

**Reactive dyes**
The reactive group is found in the structure of reactive dyes; that is why these dyes are named as reactive dyes. These are the only dyes that carry the reactive groups in their structure, and this reactive group is responsible for the establishment of a covalent bond between the dye molecule and respective fiber such as cotton, wool, and nylon.

**Disperse dyes**
The solubility of disperse dyes in water is very low, and are sometimes called insoluble or non-ionic dyes. Polymers, nylon, acrylic are the target fibers for dyeing with these dyes. The requirements at the process of dying are that these dyes need a dispersing agent, high temperature, and acidic condition. Disperse dyes are derived from nitro, anthraquinone, and azo groups.

**Direct dyes**
Generally, direct dyes are also termed as substantive dyes, i.e., these dyes are attracted to the textiles by some physical forces. Substantivity is quantified by the proportion or the degree of attraction that occurs between the molecules of dyes and the textile. These dyes are soluble in water, and during the process of dying, these dyes need an alkaline medium.

**Vat dyes**
Cellulose fibers are the target fibers for dyeing by using vat dyes. Vat dyes are poorly dissolved in water, but for the dying process, it needs to be in its soluble form, which is attained by the aid of reducing agents (e.g., sodium dithionite). After attaining its soluble form, they attached to the respective fiber and imparted the strong color to the fabric.

**Sulfur dyes**
Like vat dyes, sulfur dyes are also water-insoluble, and these dyes also require reducing agents (sodium sulfide, sodium hydrosulfide) for attaining their soluble form. During the process of dying, the reducing agent aid in the dissolution of dye particles and facilitate the absorption of dyes into the fabric.

**Cationic (basic) dyes**
These dyes are also named as cationic dyes. The reason behind the name of cationic dye is the color production. At the time of ionization of the salts of organic bases, the positively charged cation and negatively charged anion are produced, and the produced cation is responsible for the production of color. The uses of basic dyes are mainly in the textile industry, where they are employed to color the fabrics. The target fibers of these dyes are wool, silk, cells/tissues of humans (e.g., safranin and crystal violet).
Acid dyes
The solubility of acid dyes is very high in water. The target fibers are silk, wool, and protein. Various types of bonds (van der Waals, ionic, and hydrogen) are established by the molecules of dyes with the respective fibers.

Solvent dyes
Solvent dyes are those dyes which do not solubilize in water and are much soluble in organic solvents. The uses of solvent dyes are that they utilize the coloration of organic solvent, waxes, fuels, plastics, and glass. Most of the solvent dyes are azo dyes, e.g., red and yellow dyes, and anthraquinone dyes, e.g., green and blue.

Green Synthesis of Nanoparticles
Nanoparticles can be synthesized by various methods that are categorized into two approaches: top to down and bottom to up (Figs 2 and 3). By the employment of the top-down approach, the nanoparticle is synthesized by the reduction of size from minute particles, and these minute particles are formed from the bulk material. Different techniques utilized in the nanoparticle formation through this approach include arc discharge, pulsed laser ablation, spray pyrolysis, evaporation-condensation, and lithography (Rafique et al., 2017). These are the physical methods, where physical forces are involved in the attraction of nanoscale particles and the formation of a large, stable, well-defined nanostructure. Limitations of the physical method involve the use of expensive equipment for the synthesis, high temperature, and pressure (Chandrasekaran et al., 2016), large space area for setting up of instruments, defective surface formation, and low production rate.

By the employment of the bottom-up approach, nanoparticles are obtained by the use of chemical and biological methods. Under this approach, atoms clump and form clusters or new nuclei, which at last develop into a nanoparticle. Different techniques occur in the nanoparticle synthesis by chemical methods such as solvothermal, pyrolysis, co-precipitation, sonochemical, and electrochemical (Ealias and Saravanakumar, 2017). Chemical synthesis methods are not eco-friendly and involve the usage of toxic chemicals, formation of hazardous by-products, which create biological risk and contamination from precursor chemicals (Thakkar et al., 2010; Vijayan et al., 2016). On the whole, the conclusion is that these conventional methods for nanoparticle synthesis have certain drawbacks at the time of the fabrication process of nanoparticles. In addition, the major limitation is when these synthesized nanoparticles are applied to certain fields like medical, agriculture, where they create toxicity and alter the quality of our ecosystem (Ahmed et al., 2016). Consequently, there is a growing exigency to establish clean, non-toxic, and environment-friendly procedures for nanoparticle synthesis.

Nanoparticle synthesis by green route is fascinating all investigators because the use of the green route for the generation of nanoparticles has overcome all the downsides or limits which come when the chemical or physical method is adopted for the development of nanoparticles. In the chemical methods, chemicals which were used in the process of nanoparticle synthesis were too expensive, and also, they are toxic as well as their by-products are also very hazardous, but if we select the green route for nanoparticle genesis, this problem is controlled because, in the development of nanoparticles through green route, the process is completed by the use of non-toxic natural products. Physical methods of nanoparticle synthesis consume more energy; which was also not good, and that can also be overcome by green synthesis. The generation of nanoparticles by the green route method or biological method adopts the bottom-up approach. In the process of synthesizing nanoparticles from the biological method, three most important selections are required: choice of the solvent medium which is for the development of nanoparticles; choice of environment-friendly reducer; and choice of stabilizer agent which acts as capping agent (Narayanan and Sakhthivel, 2011; Singh et al., 2011).

For the production of advanced nanoparticles, nature has provided many ways, and sometimes these biogenic or natural products which are helpful in the generation of nanoparticles are termed as the laboratory of the natural products especially in the fabrication of metallic and metal oxide nanoparticles (Sharma et al., 2019). The biological approach includes different types of microorganisms such as bacteria (Shivaji et al., 2010), fungi (Chan and Mat Don, 2013), yeast (Kumar et al., 2011), and plant extract (Akhtar et al., 2013) (Fig. 4).

Nanoparticle Synthesis using Microorganisms
In the generation or synthesis of diverse type of nanoparticles, different microbes have acted as utilitarian agents in the development of desirably sized nanoparticles. Different microbes are used in the process of nanoparticle genesis due to their simplicity to work, medium for the evolution of microbes is cheap, and they are maintainable. In previous years, the synthesis of nanoparticles using microbes has enlarged comprehensively due to its immense application. The generation of metallic nanoparticles through microbes is an appropriate approach. Gold, silver, and cadmium sulfide nanoparticles are extensively...
Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).

Some other nanoparticles; synthesis has also been reported in previous literature by using bacterial strains such as cadmium sulphide (CdS NPs) nanoparticles using Klebsiella aerogenes (Holmes et al., 1995), Enterobacter cloacae (Sharma and Kaur, 2018), Stenotrophomonas malophilia (Sharma et al., 2012), E. coli K12 (Srivastava et al., 2013), Geobacillus sp. strain ID17 (Narayanan and Sakthivel, 2008), Thermomonospora sp. (Kasthuri et al., 2008), Rhodococcus sp. (Park et al., 2011), and Delftia acidovorans (Johnston et al., 2013).
polysaccharide named fucoidans, which is secreted from the cell wall of algae, is very advantageous since it has properties such as anti-cancerous, anti-viral agent, slow aging agent, and anti-inflammatory. Metabolites are present in the algal cells, which perform the role of stabilizing and reducing agents for attaining the size of NPs at the range of nanometer. Various algal species were reported successfully in the generation of diverse nanoparticles. Silver NPs were produced by Chaetomorpha linum (Kannan et al., 2013), Pterocladia capillacea, Jania rubins, Ulva fasciata, and Colpomenia sinusa (El-Rafie et al., 2013), Hypnea musciformis (Selvam and Sivakumar, 2015), and Enteromorpha flexuosa (Yousefzadi et al., 2014). Sargassum muticum was used in the production of gold (Au) NPs (Namvar et al., 2015), Tetraselmis kochinensis (Senapati et al., 2012), Ecklonia cava (Ghodake and Lee, 2011), Chlorella vulgaris (Annamalai and Nallamuthu, 2015), Padina gymnospora (Singh et al., 2013), and Fucus vesiculosus (Mata et al., 2009). Sargassum myriocystum, Caulerpa peltata, and Hypnea valencia were used in the production of zinc oxide (ZnO) NPs (Nagarajan et al., 2013), Gracilaria gracilis (Francavilla et al., 2014). Ferric oxide (Fe$_2$O$_3$) NPs have been synthesized by Sargassum muticum (Mahdavi et al., 2013), copper oxide NPs by Bifurcaria bifurcate (Aboud et al., 2014), cadmium sulfide NPs by Phaeodactylum tricornutum (Scarano and Morelli, 2003), and ferricydrite NPs by Euglena gracilis (Brayner et al., 2012).

In the fabrication process of various types of nanoparticles, actinomycetes are also a very fabulous candidate because they have the characters of both fungi and bacteria, and also the genetic modification is very facile for the development of desirably sized nanoparticles. Metallic nanoparticles are produced in large numbers with the aid of actinomycetes. Gold nanoparticles were synthesized by Thermomonospora sp. (Ahmad et al., 2003b) and Rhodococcus sp. (Ahmad et al., 2003a). Streptomyces hygroscopicus (Husseiny et al., 2007), Gordonia amarae (Montes et al., 2011), Gordonia amicalis (Baker and Satish, 2015), Streptomyces fulvissimus (Balagurunathan et al., 2011), Streptomyces sp. (Meyam et al., 2015), and Streptomyces viridogens (Kumar et al., 2011). Actinomycetes such as Streptomyces sp., Pilimeliacolu mellifera, and Rhodococcus sp. have been used in the development of silver (Ag) nanoparticles (Patrtya et al., 2016). Various species of yeast are also used in nanoparticle synthesis. Some reported literature for gold nanoparticles is Pichia jadinii (Gericke and Pinches, 2006), Yarrowia lipolytica 3589 (Ganesh Babu and Gunasekaran, 2009), Hansenua anomala (Waghmare et al., 2014), and Candida guilliermondii (Tripathi et al., 2014), Magnusiomycosinengens (Venkatesan et al., 2014). Cadmium sulfide nanoparticles synthesized by Candida glabarata, and Schizosaccharomyces pombe (Agnihotri et al., 2009). Amorphous iron phosphate NPs by Saccharomyces cerevisiae (He et al., 2009). Saccharomyces cerevisiae was also used in titanium dioxide nanoparticle (Jha et al., 2009a) and antimony trioxide (Sb$_2$O$_3$) nanoparticles synthesis (Jha et al., 2009b).

**Nanoparticle Synthesis using Plant Extract**

The synthesis of plant-based nanoparticles is a simple one-step process. In the plant-based nanoparticle fabrication, a wide range of green reducing and capping agents are used, which can be cost-effective, biocompatible, non-hazardous, and eco-friendly. Biomolecules and the existence of functional groups in the extracts of plant aid in the generation of nanoparticles because during the synthesis process, they perform the role of capping and reducing agents.

As compare to microbes, plant extract could be an efficient approach according to previous reports (Iravani, 2011) because the plant-based synthesis of nanoparticles produces highly stabilized nanoparticles in a single step process and in a very short duration.

Silver nanoparticles were synthesized from the solution of silver nitrate with the help of the various type of plant extracts such as Alternanthera dentate leaf extract (Kumar et al., 2014), Acorus calamus rhizome (Nakkala et al., 2014), tea extract (Suna et al., 2014), Vitis vinifera fruit extract (Gnanajobitha et al., 2013), Salvadoria persica stem extract (Tahir et al., 2015), Vasaka (Justicia adhatoda L.) leaf extract (Bose and Chatterjee, 2015), and beetroot extract (Bindhu and Umadevi, 2015). Gold nanoparticles have been synthesized by Coleus amboinicus, Dillenia indica fruit extract, tuber extract of Dioscorea bulbifera, and leaf extract of Euphorbia hirta, Zingiber officinale, Mentha piperita. Zinc oxide nanoparticles have been synthesized by various plant parts like leaf, stem, root, fruit, and seed. Bio-reduction involves reducing metal ions or metal oxides to 0-valence metal NPs. Other fabulous plant species also reported successfully such as Calatropsis gigantean, Plectranthus amboinicus, Agathosma betulina, Vitex negundo, Nephelium lappaceum, Azadirachta indica, Moringa oleifera, Plectranthus amboinicus, and Anisochilus carnosus (Agarwal et al., 2017; Kumar et al., 2017; Nadeem et al., 2017).
Remediation of Dyes in Water using Green Synthesized Nanoparticles (NPs)

According to Barizaoa et al. (2020), tartrazine and Bordeaux red dye can be removed by iron oxide nanoparticles using two agro-industry residues: Cucurbita moschata leaves and Beta vulgaris stalks. The synthesized nanoparticles with an estimated diameter of 2 and 20 nm, were observed by diffraction peaks in X-ray Diffraction (XRD). In the adsorption process for dye, equilibrium was achieved after 6 minutes, with a color change from yellow to colorless. The dye was degraded up to 95.08% in 56 minutes of reaction time. As per Wang et al. (2018), Klebsiella oxytoca GS-4-08 is an anaerobic bacteria that was used in the generation of palladium nanoparticles (5–20 nm) in the existence of glucose. These bio-Pd nanoparticles were efficient for the removal of azo dyes (methyl orange, acid blue 113, reactive black 5, and acid red 1). The reduction efficiency was about 96.54 ± 0.23% in 24 hours. The enhancement of the reduction rate of azo dyes obtained by the use of anthraquinone-2-disulfonate (AQS). The reduction rate in the presence of AQS achieved at 68.55 ± 0.21% only in 2 hours, while in the absence of AQS, the reduction rate was only 58.35 ± 0.45%. According to Kora and Rastogi (2016), Palladium nanoparticles are also produced from palladium chloride (PdCl₂) via gom olibanum (Boswellia serrata) with an average size of about 6.6 nm. By the use of these nanoparticles, the reduction in the concentration of the synthetic dyes such as rhodamine B, coomassie brilliant blue G-250, and methylene blue with NaBH₄ was observed. The whole reduction process completed within 6 minutes, with a color change from yellow to colorless.

According to Ismail et al. (2018), silver nanoparticles were synthesized by taro (Colocasia esculenta) plant rhizome powder with a mean size of about 68 ± 12 nm. These nanoparticles showed high degradation efficiency towards the organic azo dyes such as methyl orange (MO), congo red (CR), methyl red (MR), and rhodamine B (RbB) by NaBH₄. 100% degradation of methyl orange was achieved in the presence of NaBH₄ with green synthesized silver nanoparticles only in 7 minutes. The discoloration of congo red (96.9%) was achieved in 12 minutes by NaBH₄ in the presence of active catalysts silver (Ag) nanoparticles. Sodium borohydride in the presence of catalyst reduced congo red molecule at the azo sites (-N=N-) by producing hydrazine derivative compounds. Similarly, 96.29% of methyl red reduction took 14 minutes, and 97.78% reduction of rhodamine B took just 6 minutes. The prepared silver nanoparticles also showed a great reduction of the mixtures of dyes. Complete reduction obtained of the mixture of methyl orange and methyl red only in 9 and 10 minutes for the mixture of methyl orange, methyl red, and congo red. The general hypothesis behind nanoparticle fabrication and dye removal is shown in Fig. 7. Some other literature works have been shown in Table 1.
Table 1: Green synthesized nanoparticles for dye remediation

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Plant extract/microorganism</th>
<th>Nanoparticle (NPs)</th>
<th>Characterization techniques</th>
<th>Size/ diameter of NPs (nm)</th>
<th>Targeted dye</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cucurbita moschata leaves <em>Beta vulgaris</em> stalks</td>
<td>Iron oxide</td>
<td>UV-VIS, FTIR, TEM, XRD</td>
<td>2–20</td>
<td>Tartrazine, Bordeaux red</td>
<td>Barizaoa et al. (2020)</td>
</tr>
<tr>
<td>2</td>
<td>Leaf extract of <em>Teucrium polium</em></td>
<td>Iron oxide</td>
<td>TEM, PSA, XRD, FTIR, VSM, TGA</td>
<td>5.68–30.29</td>
<td>Methyl orange, Congo red</td>
<td>Kouhbanani et al. (2019)</td>
</tr>
<tr>
<td>4</td>
<td>Fruit extract of <em>Duranta erecta</em></td>
<td>Copper</td>
<td>UV-VIS, XRD, EDX</td>
<td>70</td>
<td>Methyl orange, Congo red</td>
<td>Ismail et al. (2019)</td>
</tr>
</tbody>
</table>

Fig. 7: Hypothesis behind synthesis of nanoparticle and dye remediation

Cont...
<table>
<thead>
<tr>
<th>No.</th>
<th>Plant/Species</th>
<th>Metal</th>
<th>Method(s)</th>
<th>Size/Range</th>
<th>Dye</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td><em>Parkia speciosa</em> Hassk pod extract</td>
<td>Iron</td>
<td>FTIR, SEM, XRD, HR-TEM</td>
<td>10–80</td>
<td>Bromophenol blue</td>
<td>Fatimah <em>et al.</em> (2020)</td>
</tr>
<tr>
<td>6</td>
<td>Leaf extract of <em>Amarranthus gangeticus</em></td>
<td>Silver</td>
<td>FTIR, SEM, TEM, SAED, UV-VIS</td>
<td>11–15</td>
<td>Congo red</td>
<td>Kolya <em>et al.</em> (2015)</td>
</tr>
<tr>
<td>7</td>
<td>Extract of <em>Clitoria ternatea</em> pods</td>
<td>Silver</td>
<td>FTIR, SEM, XRD, UV-VIS</td>
<td>62.51</td>
<td>Methylene blue</td>
<td>Varadavenkatesan <em>et al.</em> (2019)</td>
</tr>
<tr>
<td>8</td>
<td><em>Klebsiella oxytoca</em> GS-4-08</td>
<td>Palladium</td>
<td>TEM, XRD, EDX</td>
<td>5.20</td>
<td>Azo dyes</td>
<td>Wang <em>et al.</em> (2018)</td>
</tr>
<tr>
<td>9</td>
<td><em>Boswellia serrata</em></td>
<td>Palladium</td>
<td>UV-VIS, DLS, TEM</td>
<td>6.6 ± 1.5</td>
<td>Coomassie brilliant blue G-250, Rhodamine B, Methylene blue</td>
<td>Kora and Rastogi (2016)</td>
</tr>
<tr>
<td>10</td>
<td>Taro (<em>Colocasia esculenta</em>) plant rhizome powder</td>
<td>Silver</td>
<td>SEM, FTIR, XRD, EDX, XPS, XRD</td>
<td>68 ± 12</td>
<td>Methyl orange, Congo red, Methyl red, Rhodamine B</td>
<td>Ismail <em>et al.</em> (2018)</td>
</tr>
<tr>
<td>11</td>
<td><em>Camellia sinensis</em> tea extract</td>
<td>Iron</td>
<td>XRF, TGA, TEM</td>
<td>20–100</td>
<td>Methylene blue, Methyl orange, Bromothymol blue</td>
<td>Carvalho and Carvalho (2017)</td>
</tr>
<tr>
<td>12</td>
<td>Palm dates fruit</td>
<td>Silver-iron bimetallic NPs</td>
<td>UV-VIS, TEM, EDX, XRD, XRF</td>
<td>5–40</td>
<td>Bromothymol blue</td>
<td>Al-Asfar <em>et al.</em> (2018)</td>
</tr>
<tr>
<td>13</td>
<td>Extracts of green tea leaves</td>
<td>Iron</td>
<td>SEM, TEM, EDX, XRD, FTIR</td>
<td>40–60</td>
<td>Methylene blue, Methyl orange</td>
<td>Shahwana <em>et al.</em> (2011)</td>
</tr>
<tr>
<td>14</td>
<td>extract of <em>Cupressus sempervirerens</em></td>
<td>Iron</td>
<td>FTIR, UV-VIS, XRD, TEM</td>
<td>19</td>
<td>Methyl orange</td>
<td>Ebrahiminezhad <em>et al.</em> (2017)</td>
</tr>
<tr>
<td>No.</td>
<td>Plant/Extract</td>
<td>Metal(s)</td>
<td>Methods</td>
<td>Dyes/Colorants</td>
<td>Authors/Year</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>---------------------------</td>
<td>-------------------</td>
<td>---------</td>
<td>----------------</td>
<td>------------------------------</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Green tea</td>
<td>Iron</td>
<td>TEM, SEM, EDX, FTIR, Zeta potential</td>
<td>Remazol brilliant Blue R, Direct red 80</td>
<td>Truskewycz et al. (2016)</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Green tea</td>
<td>Iron</td>
<td>UV-VIS</td>
<td>Malachite green</td>
<td>Abbassi et al. (2013)</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Leaf extract of <em>Azadirachta indica</em></td>
<td>Cerium dioxide</td>
<td>XPS, DSC, TGA, UV-VIS, XRD, SEM, TEM</td>
<td>Rhodamine B</td>
<td>Sharma et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td><em>Angelica gigas</em> ribbed stem extracts</td>
<td>Silver and gold</td>
<td>FTIR, EDX, XRD, FTIR, UV-VIS, PSA</td>
<td>Eosin Y, Malachite green</td>
<td>Chokkalingam et al. (2019)</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Leaf extract of <em>Camellia sinensis</em></td>
<td>Zinc Oxide</td>
<td>UV-VIS, FTIR, XRD, SEM</td>
<td>Malachite green</td>
<td>Batool et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Leaf extract of <em>Camellia sinensis</em></td>
<td>Zinc Oxide</td>
<td>UV-VIS, FTIR, XRD, SEM</td>
<td>Malachite green</td>
<td>Batool et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Mulberry leaves</td>
<td>Iron</td>
<td>DLS, SEM, FTIR, UV-VIS, Zetasizer</td>
<td>Methylene blue, Methyl orange</td>
<td>Lim et al. (2018)</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Datura leaf extract</td>
<td>Iron</td>
<td>SEM, UV-VIS, FTIR, SEM, TEM, SAED, XRD, EDX</td>
<td>Solo chromo black (SCB)</td>
<td>Raju et al. (2017)</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td><em>Zanthoxylum armatum</em> leaves</td>
<td>Silver</td>
<td>UV-VIS, FTIR, SEM</td>
<td>Safranine O, Methyl red, Methyl orange, Methylene blue</td>
<td>Jyoti and Singh (2016)</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td><em>Gymnema sylvestre</em> extract</td>
<td>Silver</td>
<td>UV-VIS, FTIR, XRD</td>
<td>Methylene blue</td>
<td>Kumar et al. (2019)</td>
<td></td>
</tr>
</tbody>
</table>
## Remediation of Dyes in Water using Green Synthesized Nanoparticles (NPs)

<table>
<thead>
<tr>
<th>No.</th>
<th>Plant/Materia/Extraction</th>
<th>Nanoparticle</th>
<th>Dye</th>
<th>TEM</th>
<th>SEM</th>
<th>XRD</th>
<th>EDX</th>
<th>UV-VIS</th>
<th>FTIR</th>
<th>Photoluminescence</th>
<th>Methylene blue</th>
<th>Phenol red</th>
<th>Osuntokun et al. (2019)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Phenol red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Ampicillin</td>
<td>Silver</td>
<td>14.1</td>
<td>Methylene green</td>
<td></td>
<td></td>
<td></td>
<td>Junejo et al. (2014)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td><em>Catharanthus roseus</em> leaf extract</td>
<td>Palladium</td>
<td>38</td>
<td>Phenol red</td>
<td></td>
<td></td>
<td></td>
<td>Kalaiselvi et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td><em>Kashayam, Guggulutiktha</em>, an <em>ayurvedic</em> medicine</td>
<td>Silver and gold</td>
<td>15–50</td>
<td>Methylene blue</td>
<td></td>
<td></td>
<td></td>
<td>Suvith and Philip (2014)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Arabic gum</td>
<td>Zinc oxide</td>
<td>10</td>
<td>Direct blue 129</td>
<td></td>
<td></td>
<td></td>
<td>Fardood et al. (2017)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td><em>Persia americana</em> seed</td>
<td>Tin oxide</td>
<td>4</td>
<td>Phenol red</td>
<td></td>
<td></td>
<td></td>
<td>Elango et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td><em>Helicteres isora</em> extracts</td>
<td>Silver</td>
<td>25–45</td>
<td>Methyl violet Safranin Eosin methylene blue Methyl orange</td>
<td></td>
<td></td>
<td></td>
<td>Bhakya et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Lemon juice</td>
<td>Zinc oxide</td>
<td>21.5</td>
<td>Methyl orange Methylene blue Methyl red Reactive blue 21</td>
<td></td>
<td></td>
<td></td>
<td>Davar et al. (2015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cont...
Remediation of Dyes in Water using Green Synthesized Nanoparticles

**International Journal of Plant and Environment, Volume 6 Issue 1 (2020)**

UV-VIS Morinda morindoides Rhodamine B Methylene XRD SEM Carica papaya Eucalyptus tereticornis Zinc oxide UV-VIS Bifurcaria bifurcata Eosin Y 50–80 UV-VIS 50 Acid black 194 Wang et al. (2014)

**Conclusion**

In the fabrication of nanoparticles, naturally occurring substances are the aptest candidate for playing the role of reducing and capping agent. Green synthesis of nanoparticles has several advantages such as cost-effective, biocompatible, rapid synthesis, high stability, and easily available. One major advantage of green synthesized nanoparticles is that they are environment friendly. The remediation of environmental pollutants using green synthesized nanoparticles has witnessed as an emerging trend in the last decade. The effluent of the dyeing industry poses a threat to the environment because of long term disposal. Conventional and advanced treatment techniques for the remediation of dyes failed because these were not degrading the dye completely, effectively, and economically. This review specially focused on the remediation of dyes by using different sizes and shape nanoparticles, which were synthesized by green nanotechnology because of the protection of the environment. Therefore, for our safe environment, green nanotechnology needs to be explored by further future studies in various fields such as water purification, air purification, agriculture, food science, etc.

**References**


Remediation of Dyes in Water using Green Synthesized Nanoparticles (NPs)


Remediation of Dyes in Water using Green Synthesized Nanoparticles


Kumar, D.A., Palanchamy, V. and Roopan, S.M. 2014. Green synthesis of...
Remediation of Dyes in Water using Green Synthesized Nanoparticles


Tom, R.T., Nair, A.S., Singh, N., Aslam, M. 2003. Freely dispersible AuTiO2, Au@ZrO2, Ag@TiO2 and Ag@ZrO2 core-shell nanoparticles: one-step synthesis, characterization, spectroscopy, and optical limiting properties. Langmuir 19: 3439-3445.


Remediation of Dyes in Water using Green Synthesized Nanoparticles (NPs)


