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The possible mechanism of eco-friendly synthesized nanoparticles on hazardous dyes degradation

N.T. Nandhini[a], S. Rajeshkumar[b], S. Mythili[a,*]

[a] School of BioSciences and Technology, VIT, Vellore, 632014, TN, India
[b] Department of Pharmacology, Saveetha Dental College and Hospitals, SIMATS, Chennai, 600077, TN, India

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ABSTRACT

The quality of natural water resources has been depleting due to the lack of proper treatment of effluent discharged from textile dyeing units. To impart color to the fabrics, synthetic dyes have been used which pose a serious threat to the environment due to their toxicity. The Complex structure of dyes has made them difficult to degrade. Therefore a perpetual method is needed to eradicate the dyes. Conventional methods arouse but they are not efficient as the derivatives of the complex dyes remain in the water even after the treatment and are expensive. In recent times, nanoparticles are found to be wholly effective. Notably, nanoparticles which are synthesized by biological methods took up many applications such as wastewater treatment, drug delivery, biosensors etc. Biological methods are eco-friendly, easily approachable and cost- effective. Biologically synthesized nanoparticles were found to have the ability to degrade toxic dyes. This review emphasizes the biological sources used for the synthesis of various metal nanoparticles, mechanism of degradation and their dye degradation efficiency.

1. Introduction

In this neoteric world, some of the renewable resources are getting polluted as we failed to conserve them. One of them is water resources. Water is the vital constituent of natural resources and has been playing an efficacious part as one of the basic needs of living organisms. Nearly 75% of the earth's surface is covered by water. Only 5% of this remains fresh and can be utilized by living creatures (Odlare, 2014). As technology gets developed, human beings and other mortal beings have been falling on to the prey of its downside effects. Water resources are being polluted by industries like the textile industry, leather industry, and paper and pulp industry. Discharging untreated effluent into the water streams will turn out to be a serious threat to living beings (Gupta et al., 2011; Gupta and Saleh, 2013). Textile industries are listed one among them. Dye effluent has become a major threat to the environment. Dyes have been playing a vital role in textile industries. Textile dyes are either natural or synthetic substances that add color to the fabrics. Unless a proper treatment, toxicological impacts of the textile dye effluent will never get reduced (Brown, 1987; Ghaedi et al., 2015).

Various chemicals are being used in dyeing and printing processes and most of them are highly noxious (Laing, 1990). Some of the textile dyes are grouped into azo, diazo, acidic, basic, metal-complex, reactive and anthraquinone. Whilst discharging the effluent some non-biodegradable dye fixing agents (formaldehyde), softeners (hydrocarbons) and dyeing chemicals reside in the water streams (Banat et al., 1997; Bhatt and Rani, 2013). Traditional dyeing method utilizes 30–50 L of water to dye per Kg of yarn and merely 15–20% of water containing dyes is released into the water streams as effluent (Junejo et al., 2014; Kant, 2012). After the dyeing process, nearly 280,000 tons of textile dyestuffs have been discarded as wastes globally (Jin et al., 2007). Eliminating these non-biodegradable hazardous dyes has become an unavoidable challenge.

Azo dyes are generally made up of aromatics and heterocyclic compounds with –N = N– bonding and recalcitrant structures (Sudha et al., 2014). The complex structures of these compounds are hard to degrade and eradicate completely. It builds up the adverse effects such as COD (chemical oxygen demand), BOD (biological oxygen demand), colour, heavy metals, etc., while discharging the effluent into the water bodies without proper treatment. To cut down the difficulties, researchers have been working in natural dyes to replace synthetic dyes. Conventional methods like degradation by UV-light, flocculation, activated carbon sorption, redox treatment and electrocoagulation were found to be ineffective as they are expensive, involves the usage of toxic chemicals, time-consuming and generation of by-products (Mohammadi et al., 2011; Selvam and Sivakumar, 2015). Biological methods are considered to be the only way to eradicate the effluent as

* Corresponding author. SBST, VIT, Vellore, 632014, India.
E-mail address: smythili@vit.ac.in (S. Mythili).

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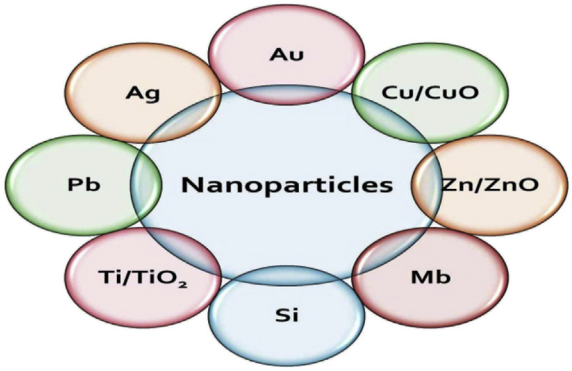

Fig. 1. Types of metal nanoparticles obtained from biological routes.

they are cost-effective and efficient in action. Utilizing nanoparticles in bioremediation could be an effective method to eradicate toxic dyes. Different types of nanoparticles have been synthesized from biological sources as given in Fig. 1. This review focuses on the degradation of highly hazardous dyes using biologically synthesized nanoparticles.

2. Effects of dye effluent

Due to the toxicity and carcinogenicity of dyes, the need for eradication of dyes has also been increased. This is because these dyes are made up of highly hazardous chemicals (Fig. 2). The impacts of textile dye effluent are: depletion of dissolved oxygen in the water (Banat et al., 1997), conversion of dyes into carcinogenic or toxic products that can cause cerebral abnormality and intestinal cancer (Sudha et al., 2014), inhibits the growth of microorganisms, allergic reactions and some of the dyes even cause a genetic mutation that leads to malignant tumor formation (Tsuboy et al., 2007). Dyes that are present in the effluent may be toxic or carcinogenic as they are made up of some aromatic compounds like benzidine. Removing hazardous has been gaining importance as their presence would create many incurable diseases to living creatures (Banat et al., 1997).

3. Biological and chemical synthesis of nanoparticles

The biological and chemical methods of nanoparticles synthesis have been explained in Fig. 3. Chemical synthesis of nanoparticles involves chemicals like 16-mercaptohexadecanoic acid, trisodium citrate, diethanolamine, etc. which act as reducing agents (Karthikeyan et al., 2019). Owing to the usage of toxic chemicals and expensive processes, the necessity of biological methods arouses. Plants as nanofactories have been gaining importance because of its non-toxicity, availability and simple processes in synthesizing metal nanoparticles. Phytochemicals and amino acids present in plants function as reducing agents and

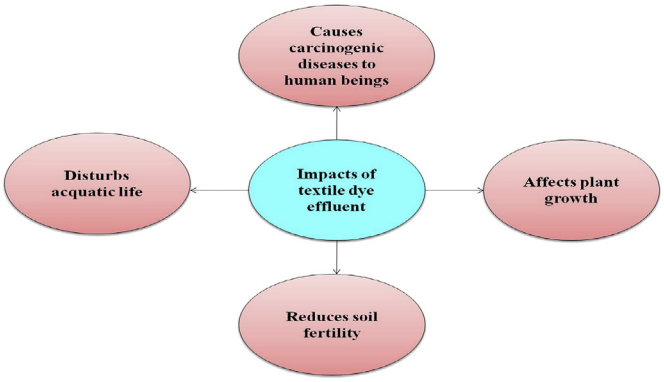

Fig. 2. Impacts of textile dye effluent.

reduce metals salts effectively (K. et al., 2015). Similarly, microorganisms have been used for the synthesis of various metal nanoparticles. Metal salts are entrapped by reductase enzymes which reduce metal salts to metal ion nanoparticles (Hasan, 2014; Singh et al., 2016).

4. Dye degradation by nanoparticles

Nanoparticles have been used in reductive degradation of harmful and toxic dyes because they possess unique physical and chemical properties that cannot be found in bulk materials as depicted in Fig. 4. Versatile nanoparticles can be used in various applications including wastewater treatment, medicines, energy generation and bioremediation (Jyoti and Singh, 2016). Nanoparticles act as effective catalysts in reductive reactions (Vanaamudan et al., 2016). Various nanoparticles such as Ag (Silver) (Kavitha et al., 2014), Au (Gold) (Paul et al., 2016), Zn (Zinc) (Inamur et al., 2013), Silica (Badr et al., 2008) etc., have been synthesized from biological sources and are being utilized in various fields.

4.1. Silver nanoparticles

Ag nanoparticles are extensively used because of its excellent antimicrobial and catalytic properties. Ag metal has the ability to synthesize stable nanoparticles and also being used in various fields such as biological labelling, catalysis, biosensors, optoelectronics and photography (Kearns et al., 2006; Smith et al., 2006). Ag nanoparticles are having good dye degrading capability mentioned in Table 1. Ag nanoparticles that are synthesized by *Actinidia deliciosa* fruit extract degraded the toxic dye methylene blue completely in 33 mins in the presence of a catalyst (Naraginti et al., 2017). The complete degradation of methylene blue and rhodamine B was achieved by Ag nanoparticles synthesized by the biomass of *Parkia roxburghii* leaf extract in 12 mins (Paul et al., 2015).

4.2. Gold nanoparticles

Au nanoparticles are being used in drugs, treatment of some cancers, drug delivery and gene delivery. Au nanoparticles effectively involved in the degradation of dye (Table 2). Toxic dyes like methylene blue and rhodamine B were strongly degraded by Au nanoparticles synthesized by *Paderia foetida Linn* within 12 mins (Dutta, 2017). *Sterculia acuminata* mediated Au nanoparticles degraded the organic dyes such as methyl orange, methylene blue, and direct blue and the reaction time was observed to be 4 mins (Kumar et al., 2015).

4.3. Zinc oxide nanoparticles

ZnO nanoparticles are being extensively used owing to their high surface area, non-toxicity, stable structure, photosensitivity, higher reactivity and cost-effectiveness (Xie et al., 2011). In dye degradation ZnO nanoparticles have been used as catalysts and they are considered to be effective photocatalysts (Table 3) (Peng et al., 2013; Suchithra et al., 2013). *Artocarpus heterophyllus* leaf extract is found to have essential compounds to synthesize ZnO nanoparticles and the nanoparticles wholly degraded rose bengal dye in 1 h (Vidya et al., 2016). ZnO nanoparticles are biologically synthesized by the fungus *Aspergillus sp.* and effectively degraded the methylene blue dye (Jain et al., 2014).

4.4. Other nanoparticles

Metal nanoparticles such as Nickel (Ni), Silica (Si), Molybdenum (Mb), Titanium (Ti), Copper (Cu) etc., have been emerging out due to their unique properties (Table 4). Palladium (Pd) nanoparticles have been synthesized by *Catharanthus roseus* leaf extract and showed efficient degradation of phenol red (Kalaiselvi et al., 2015). Leaves of *Lagerstroemia speciosa* have been used for the synthesis of zirconium oxide

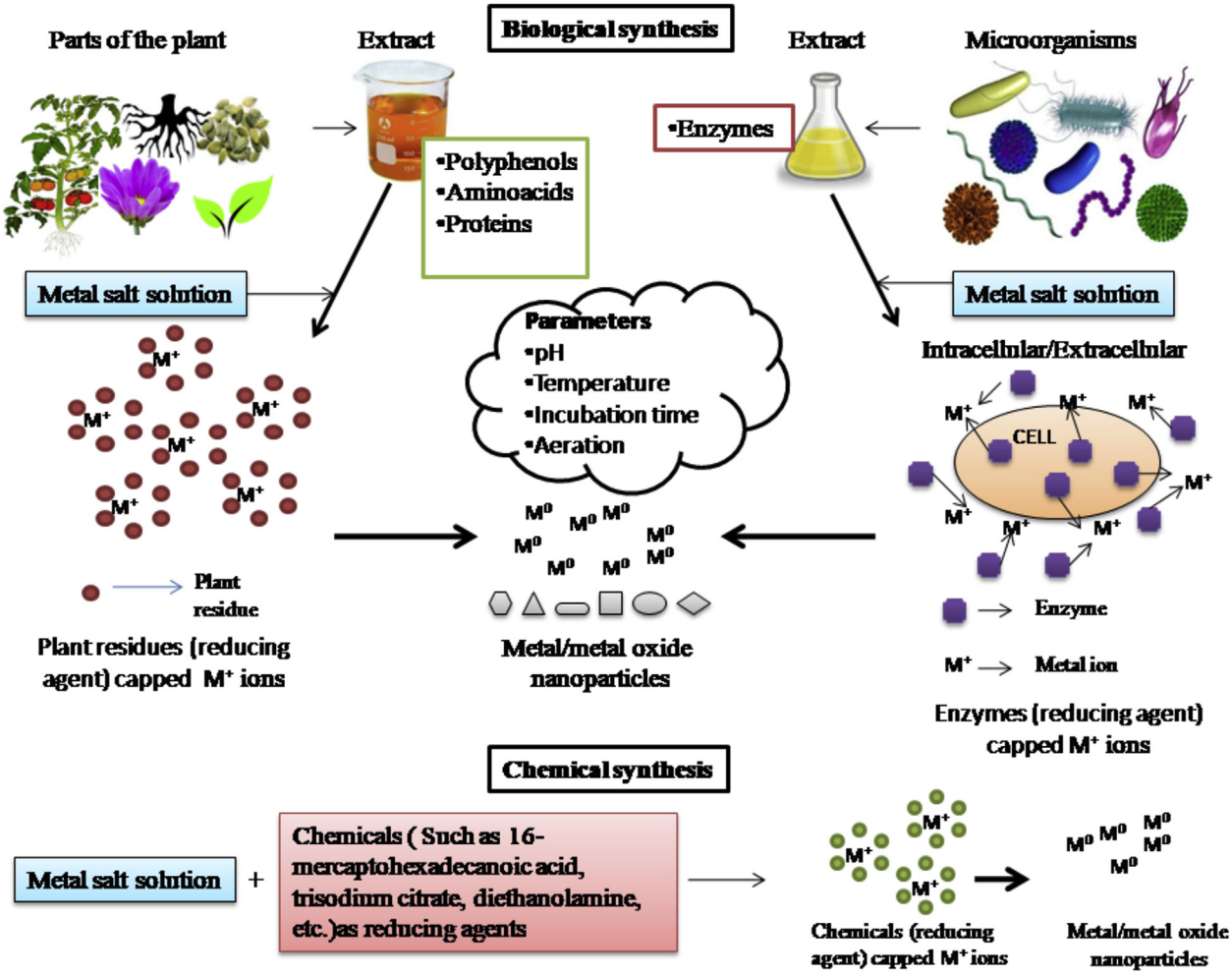

Fig. 3. Methods of nanoparticles synthesis.

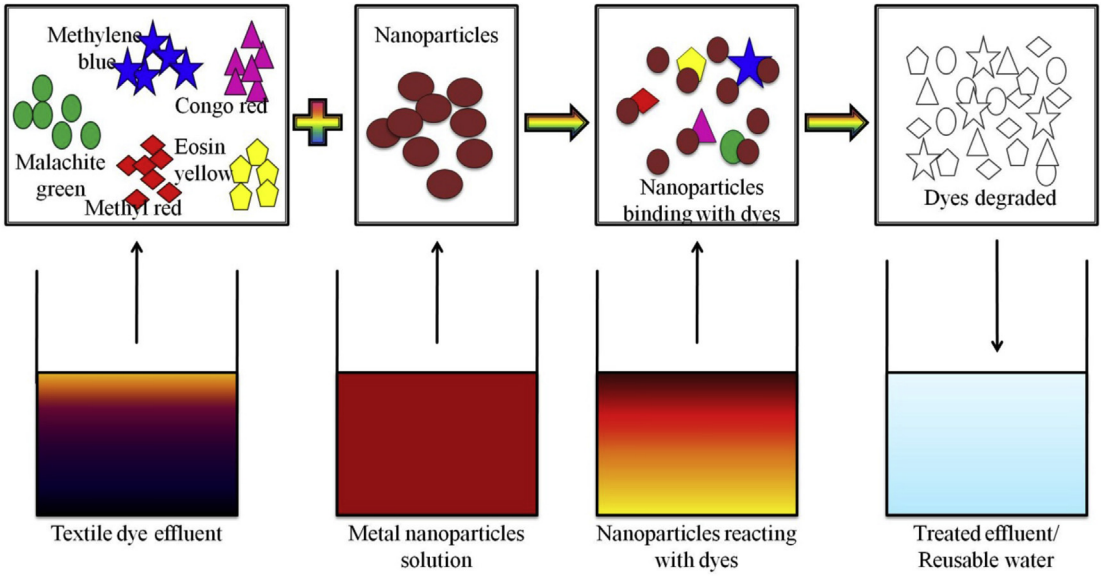

Fig. 4. Dye degradation by nanoparticles.

Table 1
Dye degradation by silver nanoparticles.

S. No	Source used for Ag nanoparticles synthesis	Dyes degraded	Size of nanoparticles	Reaction rate and speed	Reference
1	*Leuconostoc lactis*	Methyl orange, Congo red	30–200 nm	Degradation achieved in 240mins	Saravanan et al. (2017)
2	*Gmelina arborea*	Methylene blue	8–32 nm	Completely degraded in 10 mins	Saha et al. (2017)
3	*Zanthoxylum armatum*	Safranine O, Methyl red, Methyl orange and Methylene blue	15–50 nm	Dyes are degraded in 24 h	Jyoti and Singh (2016)
4	*Borassus flabellifer*	Reactive Blue-21, Reactive Red-141, Rhodamine 6G	55 nm	RB-21 took 6 h to degrade, RR-141 degraded in 3.5 h and Even after 24 h Rh-6G did not degrade	Vanaamudan et al. (2016)
5	*Cicer arietinum*	Methylene blue, Congo red	88.8 nm	Methylene blue and Congo red were degraded in 16 and 14 mins respectively	Arya et al. (2017)
6	Green tea waste	Methylene blue, Ethyl violet	51.32 nm	Degradation was achieved more than 65%	Qing et al. (2017)
7	*Mussaenda erythrophylla*	Methyl orange	50–80 nm	Completely eradicated	Thivaharan et al. (2016)
8	*Anacardium occidentale*	Congo red, Methyl Orange ($NaBH_4$ assisted)	25 nm	Methyl orange degraded in 20 mins and congo red took 30 mins for complete degradation	Edison et al. (2016)
9	*Biophytum sensitivum*	Methylene blue ($NaBH_4$ assisted)	20–50 nm	Remarkably competent catalysts in degrading dyes.	Joseph and Mathew (2015a)
10	Grape seeds	Direct Orange 26	54.8 nm	Only 10% degradation occurred (10 mins). Clearly depicts that degradation decreases with increase in temperature and size of nanoparticles	Ping et al. (2017)
11	*Lagerstroemia speciosa*	Methyl Orange, Methylene blue	12 nm	10% degradation was observed in the presence of sunlight after in 310 mins	Sai Saraswathi et al. (2017)
12	*Camellia japonica*	Eosin Y	12–25 nm	Excellent catalytic activity with 97% degradation in 60 mins	Karthik et al. (2017)
13	*Ulva lactuca*	Methyl orange	50 nm	Completely degraded within 12 h	Kumar et al. (2013)
14	*Terminalia chebula*	Methylene blue	25 nm	Significant degradation of dye was observed within 30 mins	Edison and Sethuraman (2012)
15	*Coccinia grandis*	Coomassie Brilliant Blue 250-G	20–30 nm	Exhibited good photo catalytic activity and the dye was found degraded in 90 mins	Arunachalam et al. (2012)
16	*Cordia dichotoma*	Methylene blue, Congo red	24 nm and 36 nm	Methylene blue was degraded with time period of 6 h and Congo red dye was degraded in 20 mins	Kumari et al. (2016)
17	*Catunaregum spinosa*	Amaranth	38 nm	The dye was degraded up to 94.07%	Haritha et al. (2017)
18	*Salvadora persica* stem extract	Methylene blue	1–6 nm	Methylene blue was decomposed up to 96% in 80 mins	Tahir et al. (2015)

nanoparticles and methyl orange dye was degraded up to 94.5% (Sai Saraswathi et al., 2017).

5. Mechanism of dye degradation by nanoparticles

In recent times, degradation using biological sources has become a suitable alternative to remove dyes from the polluted water and soil. Researchers have been utilizing engineered metal nanoparticles from different sources to degrade the dyes (Lavanya, 2014; Shanker, 2017). The possible dye degradation mechanism by various metal nanoparticles in the presence of light is depicted in Fig. 5.

After dye degradation by nanoparticles, the presence of degraded products was spotted. HPLC-MS (high performance liquid chromatography-mass spectrometry) was used for the detection of degraded products. Orange G was degraded by Fe–Ni bimetallic nanoparticles that generated degraded products such as naphthol amine and aniline derivatives (Bokare et al., 2008). It was also reported that unknown intermediate by-products were observed by HPLC-MS after the degradation of methyl red dye by immobilised TiO_2 and ZnO nanoparticles (Comparelli et al., 2014). TiO_2 nanoparticles were found to degrade acid red 88 with various by-products such as 4-amino naphthalene sulfonic acid, napthalene-2-ol, 2-sulfobenzoic acid (IV) or 3-sulfobenzoic acid (V) and 4-(2-hydroxy-naphthalene-1-ylazo)-naphthalene-1-sulphonic acid (I) (Sathishkumar et al., 2011).

5.1. Methyl orange

Methyl orange (an organic sulfosalt dye) has been widely used as an indicator in various fields. The excessive usage of this dye leads to several environmental and health hazards (Fu et al., 2017). Reductants like $NaBH_4$ (Sodium borohydride) are being used to reduce methyl orange to small organic molecules and non-toxic compounds. Since the rate of reduction is very slow, metal nanoparticles have the ability to accelerate the reaction. Ag nanoparticles have been extensively used as catalysts in the dye degradation process (Joseph and Mathew, 2015b). Fe nanoparticles synthesized by *Trigonella foenum-grecum* seeds were used as catalysts in degrading methyl orange. It is observed that the particle size of Fe nanoparticles is directly proportional to the reaction time. The degradation of the dye involves both oxidation and reduction reaction. Electron transfer occurs from $NaBH_4$ to the dye in the presence of sunlight which leads to the degradation of the dye and the formation of hydrazine derivatives (Ali et al., 2018). Kumar et al.(2013) reported that the Ag nanoparticles synthesized using *Ulva lactuca* were effectively used as a catalyst in degrading methyl orange. It was found that there was no peak change in the absence of Ag nanoparticles. Initially, the reaction was slow and the rate of degradation was gradually increased with increase in time due to the excitation of Surface Plasmon resonance between Ag ions and dielectric medium (Kumar et al., 2013). Azo group (-N = N-) in methyl orange acts as chromophore which is responsible for the strong orange colour. In the presence of biologically synthesized ZnO nanoparticles using *Nephelium lappaceum* peel extract, the colour change from strong orange to colourless was observed. This is because of the breaking up of the chromophoric group in the presence of light (Karnan et al., 2016). An experiment by Sha et al. (2016) showed that hollow Co (Cobalt) nanoparticles easily degraded the dye due to its simple structure and low molecular weight. Co atoms present on the surface of Co nanoparticles likely to access the molecule with low molecular weight and relatively smaller in size. The molecules with higher molecular weight would block the active sites of the catalysts (Sha et al., 2016).

5.2. Methylene blue

The usage of methylene blue (a heterocyclic aromatic dye) in textile industries has been increased in the past few years. The blue colour of the dye is due to its oxidized state and becomes colourless on reduction

Table 2
Dye degradation by Gold nanoparticles.

S. No	Source used for Au nanoparticles synthesis	Dyes degraded	Size of nanoparticles	Reaction rate and speed	Reference
1	*Momordica cochinchinensis*	Congo red, Methylene blue, Rhodamine B, Eosin Y, Methyl Orange	10–80 nm	Dye decolorisation occurred between 4 and 8 mins	Paul et al. (2016)
2	*Sueda fruciotosa*	Methylene blue	6–8 nm	Completely degraded in 40 mins	Khan et al. (2017)
3	*Plumeria alba*	Methylene blue, Eosin Y, Methyl red, Congo red	28 ± 5.6 and 15.6 ± 3.4 nm	Decolourised	Mata et al. (2015)
4	*Morinda tinctoria*	Methylene blue	79–96 nm	Effectively degraded	Vanaja et al. (2014)
5	*Sterculia acuminata*	Methyl orange, Methylene blue, Direct blue 24	9.37 nm–38.12 nm	Methyl orange and methylene blue degraded in 12 mins, Direct blue 24 degraded in 18 mins	Kumar et al. (2015)
6	*Piper longum*	Methylene blue, Methyl red, Crystal violet, Acridine orange	56 nm	Methylene blue and methyl red showed 64 and 28% degradation respectively after 28 h, crystal violet and Acridine orange exhibited 39 and 34% of degradation respectively at 28 h	Nakkala et al. (2016)
7	*Cladosporium oxysporum*	Rhodamine B, ($NaBH_4$ assisted)	72.32 ± 21.80 nm	Decolourised wholly in 7 mins	Bhargava et al. (2016)
8	*Aspergillum sp.*	Cationic Red X-GRL, Acid Orange II, Acid Scarlet GR, Cation Red, Acid Yellow 11, Reactive red, Acid Red B, Reactive Red X–3B, Acid orange G, Acid black 10 B, Reactive green KE-4B, Reactive Black 100	10–100 nm (H2O system), 12–48 nm (PBS system)	All dyes were degraded in 7 mins. Highest degraded dye (96.4%) was observed to be acid scarlet GR and lowest degraded dye was found to be acid orange G. Acid orange G dye was dye degraded in 20 s	Qu et al. (2017)
9	*Trichoderma sp.*	Acid brilliant scarlet GR, Acid Red B, Acid Orange G, Acid Black 1, Reactive Red X–3B, Reactive Black, Reactive Red, Cation Red	100 nm	Effectively degraded. Acid dyes (82.9%–94.7% in 120 mins), reactive azo dyes (46.1%–73.3% in 100–180 mins) and a cation azo dye (41.7% in 180 mins). 94.7% of degradation was achieved in the acid brilliant dye.	Qu et al. (2016)
10	*Flammulina velutipes*	Methylene blue	< 20 nm	Effectively degraded in 23 mins	Badri et al. (2015)
11	Longan fruit juice	Methylene blue	25 nm	76% of the dye was degraded in 55 mins	Ullah et al. (2016)

Table 3
Dye degradation by zinc nanoparticles.

S. No	Source used for Zn/ZnO nanoparticles synthesis	Dyes degraded	Size of nanoparticles	Reaction rate and speed	Reference
‘’1	*Artocarpus heterophyllus*	Rose Bengal	15–25 nm	Nearly 85% of dye degradation observed	Vidya et al. (2016)
2	*Aspergillus sp.* NJP02	Methylene blue	40–80 nm	Remarkable photocatalytic degradation was observed	Bhargava et al. (2016)
3	*Azadirachta indica* (leaf extract)	Methylene blue	9.6–25.5 nm	Water polluting dye is completely degraded	Bhuyan et al. (2015)
4	*Eucalyptus globulus*	Methylene blue, methyl orange	10–20 nm	Degraded up to 98.3% at 30 mg of catalyst doses	Balaji and Kumar (2017)
5	*Artocarpus heterophyllus*	Congo red	~25–30 nm (800 °C), ~15–25 nm at (600 °C), ~10–15 nm at (400 °C)	Maximum of 90% degradation of 20 ppm dye in an hour	Vidya et al. (2017)
6	*Plectranthus amboinicus*	Methyl red	50–180 nm	Degraded up to 92.45% in 180 mins	Fu and Fu (2015)
7	*Cassia fistula*	Methylene blue	5–15 nm	Increase in pH concentration decreases the photo degradation efficiency. The degradation efficiency was found to be 96.26% at pH-2 and 98.71 at pH-4	Suresh et al. (2015)
8	*Anisochilus carnosus* leaf extract	Methylene blue	30–40 nm	Degraded completely	Anbuvannan et al. (2015)

Table 4
Dye degradation by other nanoparticles (Cu, CuO, Ni, etc).

S.No	Nanoparticle	Source	Dyes degraded	Size of nanoparticles	Reaction rate and speed	Reference
1	Cu	*Azadirachta Indica* (leaf extract)	Methyl Orange (peroxodisulfate and peroxomonosulfate assisted)	48 nm	92% and 98% of degradation achieved in 60 mins and 30 mins respectively	Nagar and Devra (2017)
2	CuO	*Tinospora cordifolia*	Methylene blue	6–8 nm	80% of the dye degraded	Nethravathi et al. (2015)
3	Pd	Catharanthus roseus (leaves methanolic extract)	Phenol red	38 nm	Effectively degraded	Kalaiselvi et al. (2015)
4	ZrO_2 (Zirconium oxide)	*Lagerstroemia speciosa*	Methyl orange	14 nm	Azo dye was degraded up to 94.58%	Sai Saraswathi et al. (2017)
5	TiO_2	*Bacillus amyloliquefaciens*	Reactive Red 31 (Ag, La, Zn and Pt doping)	22.11–97.28 nm	90.98% of dye degraded (Pt-doped)	Khan and Fulekar (2016)
6	TiO_2	Actinobacterial isolates (PVS-1 to PSV-5), PSV-3 (*Streptomyces bluensis*)	Acid Red 79 (AR-79), Acid Red 80 (AR-80)	3.5–92 nm	PSV-3 possessed 88% for AR-79 and 81% for AR- 80 of dye degradation	Priyaragini et al. (2014)
7	Ni	*Camellia sinensis* (leaves extract)	Crystal violet	43.87–48.76 nm	99.5% of CV dye degradation	Bibi et al. (2017)
8	SnO_2 (Tin oxide)	*Erwinia herbicola*	Methylene blue, Methyl orange and Erichrome black T	10–42 nm	93.3, 94.0, and 97.8% of Methylene blue, Methyl orange, and Erichrome black T dyes were degraded	Srivastava and Mukhopadhyay (2014)

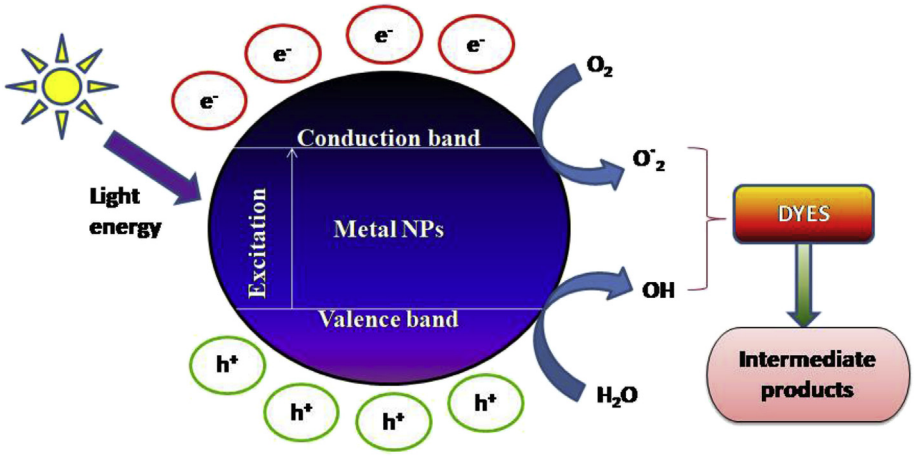

Fig. 5. General mechanism of dye degradation by metal nanoparticles.

(Yang et al., 2018). The maximum absorption peak of methylene blue was found to be 665 nm. The gradual decrease in the absorption intensity was due to the reduction of methylene blue. Incorporation of biologically synthesized Ag nanoparticles increased the rate of methylene blue degradation. In the presence of Ag nanoparticles, the degradation of methylene blue to leuco methylene blue was achieved in 20 min (Qing et al., 2017). Saha et al. (2017) reported that the Ag nanoparticles synthesized using *Gmelina arborea* fruit extract efficiently degraded the dye. It was proved that the Ag nanoparticles acted as mediators in transferring electrons while degrading the dye (Saha et al., 2017). The size of the catalysts considered as an important parameter in dye degradation. The surface of the nanoparticles with smaller size easily adhered to the reactants thus increases the rate of degradation. Green synthesized Ag nanoparticles and Au nanoparticles were effectively degraded the dye by optimizing the size of the NPs (Suvith and Philip, 2014). The magnetic IO nanoparticles which were synthesized by *Cynometra ramiflora* fruit extract showed efficient degradation of the dye. According to Bishnoi et al., 2018 the dye degradation was accelerated by the photonic excitation of NPs (Bishnoi et al., 2018).

5.3. Eosin-Y

Eosin-Y (tetrabromofluorescein or its disodium salt) is a water-soluble dye, extensively used in paper and textile industries. Owing to its toxicity, it can cause a serious threat to the environment. In the absence of Ag nanoparticles, the reduction of the dye was found to be slow and the whole degradation carried off nearly 60 mins. On the inclusion of nanoparticles, the reduction time had been decreased to 10 min (Sengan et al., 2018). Ag nanoparticles synthesized using leaf extract of *Camellia japonica* exhibited excellent degradation eosin-Y. It was documented that the reactive oxidative species oxidizes the dye solution and results in the formation of products (Karthik et al., 2017).

5.4. Congo red

Congo red (anionic dye) has been extensively used in textile, printing, paper, leather and plastic industries. Due to its non-degradability, it causes several environmental problems. To remove the dye effectively, different nanomaterials have been utilized (Hemraj-benny et al., 2018). The maximum absorption spectrum of congo red is 497 nm. The reduction reaction between the dye and $NaBH_4$ was found to be slow. The rate of reduction reaction had been increased when a considerable amount of catalyst was added. The reduction was confirmed by the drop in the maximum absorption peak (Umamaheswari et al., 2018). As stated by Fowsiya et al. (2016), ZnO nanoparticles synthesized using *Carissa edulis* exhibited good catalytic activity. Hydroperoxide, peroxide and hydroxylic radicals play a vital oxidizing property in congo red degradation which was formed by the dissolved oxygen of photogenerated electrons. On oxidation, the dye has been degraded into products which were ascertained through the breaking of the benzene ring, C–S bond, C–N bond, C–C bond and N = N cleavage (Fowsiya et al., 2016).

5.5. Rose bengal

Rose bengal (xanthene dye) has been highly used in textile, photochemical and dyeing industries (Shanker, 2017). ZnO NPs showed the signs of an effective catalyst and degraded the dye completely. The excitation of an electron from valance band to conduction band results in the electron-hole pair where the water molecules react with the hole in the valence band and the adsorbed oxygen accepts the electrons. This results in the formation of superoxide radical anion and further to hydroxyl radicals (oxidizing agent). Finally, the degradation occurs when the radicals react with the dye (Kaur and Singhal, 2014). *Atrocarpus heterophyllus* leaf extract mediated ZnO nanoparticles showed excellent photocatalytic activity. The mechanism in the dye degradation constitutes the reaction between the hydroxyl radicals and the nanoparticles (Vidya et al., 2016).

5.6. Malachite green

Malachite Green (N-methylated diaminotriarylmethane dye) has been highly used in dyeing fibres such as silk, angora, wool and cashmere. The complex aromatic ring structure of the dye made difficult to degrade (Shanmugam and Ulaganathan, 2017). The biologically synthesized Fe nanoparticles using Oolong tea extracts were able to degrade malachite green dye. The degradation of the dye occurred by breaking up the =C=N- and –C=C- bonds which result in degraded products (Huang et al., 2014). The degradation of the dye by Fe nanoparticles synthesized using green tea extract was found to be effective. The absorption peak of the dye has begun to reduce which shows that the whole chromophore structure has been demolished (Weng et al., 2013). Under visible light illumination, the degradation activity of CdS nanoparticles was investigated. The dye was completely degraded and leuco compounds were formed which confirmed the degradation of the dye (Kaur et al., 2018).

5.7. Methyl violet

Methyl violet (water soluble) has been used in paper, dyeing and textile industries. It is also used as printing ink and disinfectant. Methyl violet is reported to be carcinogenic and hazardous to animals. The

maximum absorption band of methyl violet is 580 nm. According to Bhattacharjee et al. (2016) the dye degradation was effective when SnO_2 nanoparticles were used. On the inclusion of SnO_2 nanoparticles, the decrease in the intensity of the dye was observed which confirms the degradation of the dye (Bhattacharjee et al., 2016). Similarly, the intensity of the dye was decreased when ZnO nanoparticles were added into the solution containing dye. This shows that the nanoparticles as a nanocatalyst play a crucial role in degrading dyes (Jeyasubramanian et al., 2015).

5.8. Rhodamine B

Rhodamine B (water tracer fluorescent) is a colorant that has been enormously used in the food and textile industries. It is proved to be highly carcinogenic and neurotoxic to living beings (Shanker, 2017). The maximum absorption spectrum of rhodamine B is 554 nm. The colour of the dye vanished promptly in the presence of Fe nanoparticles catalyst with $NaBH_4$.In the absence of the catalyst, the reaction remained unchanged. The formation of amino compounds was found after dye degradation which could be the degradation product of the dye (Khan and Al-thabaiti, 2018). In the presence of ZnO nanoparticles as catalysts, the absorption peak of the dye has begun to reduce. The drop in the peak was due to the degradation of the dye chromogen (Akir et al., 2016). The ZnO nanoparticles exhibited good photocatalytic activity. In the presence of the catalyst, there was a decrease in the absorbance intensity with an increase in the time period. The degradation of the dye is owing to the formation of electron-hole pairs between valence and conduction bands of the catalyst (Inamur et al., 2013).

6. Biosafety of nanoparticles

Though nanoparticles are synthesized using biological sources, the existence of nanoparticles in effluent water after degradation has become a big concern. Recovery and reusability of nanoparticles are needed. Kitture et al. (2011) performed cytotoxicity studies of ZnO nanoparticles against SiHa cell lines and also reported these nanoparticles are safer to use (Kitture et al., 2011). Photocatalytic degradation of congo red by Fe_2O_3 nanoparticles was sufficiently good but needs secondary treatment to be used for irrigation purposes (Bharadwaj et al., 2012). It has been reported that after degradation of methyl green dye, Ag nanoparticles could be recovered from the reaction medium and could be reused (Junejo et al., 2014).

7. Conclusion

An enormous quantity of hazardous dyes has been used in textile industries, where those untreated discharge dyes lead to water pollution. To eradicate highly hazardous azo dyes, newer treatment and techniques have been emerging out. Perhaps the usage of conventional methods beyond its limitations; nanoparticles could be used in treating and degrading dyes in an efficient way without limitations. The size, shape and efficiency of nanoparticles made its importance in the dye degrading efficiency. Physical and chemical methods have got some drawbacks like less efficiency, expensive, longer time period, size of the nanoparticles, etc. Methods for synthesizing nanoparticles have concern over the cost and efficiency in degrading dyes. To overcome the drawbacks, biological methods could be used.

Synthesizing nanoparticles using biological sources like plants, algae and microorganisms involveseveral parameters such as pH, temperature, concentration etc. By optimizing these parameters, nanoparticles may be synthesized with high stability and effectiveness. The size of the nanoparticles plays a vital role i.e. smaller the size of the nanoparticles, greater is its efficiency.

Biologically synthesized metal nanoparticles are being used in various fields such as medicine and drugs, nanodevices, nano fabrics, bioengineering, energy, nanotechnology, defence and security, commerce, agriculture, wastewater management and optical engineering. In future, biogenically synthesized nanoparticles would hold its prominent place in wastewater treatment. Industrial effluent may be treated effectively using various metal nanoparticles such as Ag, Cu, Fe, Zn, Sn, Au, etc. Nanomaterials are believed to completely replace the conventional methods in dye degradation.

Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2019.101138.

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