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Treatment of Water Effluents Using Silver Nanoparticles

Abstract

The water from industries with potential hazardous organic matters when discharged into the water bodies cause undesirable effects to the environment, aquatic life and human health. So it is necessary to treat waste water prior to their disposal. Degradation of organic pollutants is a major concern in the present scenario due to its stability, fastness to sunlight, resistance to degrading agents or microbial attack. It is mainly achieved by silver metal nanoparticles synthesised by green route. Degradation of dyes using metal nanoparticles is an environmental benign method. Silver metal nanoparticles show high catalytic potential due to its unique property of smaller structure and large surface to volume ratio. This review provides a detailed report of the degradation of various organic pollutants by phyto synthesised silver metal nanoparticles.

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Introduction

Water pollution is an environmental issue which is gaining global attention in the recent years. The major source of water pollution are the effluents from textile dyeing and finishing industries. Because of drastic changes in customer's demands, the textile industry is a challenge to use high quantity of dyes and auxiliaries that are necessary for modern textile processing. The used water contains various constituents such as dyes and chemicals which are directly released into the sources of water which gets contaminated and thus resulting in water pollution. The discharge of untreated waste into the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals. In our day to day demand for potable water is increasing, which is placing an increasing burden on nature's availability of water resource, has forced for new and efficient methods for water treatment.

Sources and effect of dye pollutants

Synthetic dyes and organic colorants used in paint, plastic, paper, printing, textiles, drug, leather and food related industries are the major organic pollutants in water.[1–3] Nitrophenols and their derivatives are produced from agricultural and industrial sources including those manufacturing dyes, explosives, pesticides and other products.[4,5] Dyes are the chemical substances used to impart colour to fabrics, foods and other objects for their beautification and distinction. They are capable of getting fixed to the fabrics permanently and are resistant to the action of water, sunlight, soap, acid and alkalies. The colour of a dye is mainly due to the presence of chromophores and auxochromes. Depending upon the characteristic structural units constituting the dyes, these are classified as azo, phthalein, triphenyl methane, indigoid, anthraquinone and nitro dyes. The dyes are also classified on the basis of their characteristics like fastness to light, resistance to acids and alkalies and the kind of fibre they can dye as acidic, basic, direct, disperse, vat, insoluble azo and mordant dyes. More than 7 x 10^5 tons of approximately 1,00,000 types of dyes are produced annually.[6] The toxic and carcinogenic effect of dyes causes eutrophication, reduces reoxygenation, and makes severe damage to the aquatic organisms by hindering the infiltration of sunlight and interfering the growth of aquatic species.[7,8] Dyes are not readily biodegradable as they are resistant to microbial attack, aerobic digestion and are stable to heat, light and oxidising agents. The highly persisting nature of organic contaminants even at their very low concentrations make the water more detrimental for use. Therefore, it is essential to remove or minimize dyes to permissible concentration prior to discharge.

Different methods for removal of dye effluents in water bodies

a) Physical

Adsorption is the most efficient method for the removal of dyes, odors, organic, and inorganic pollutants from industrial effluents and is found to be superior to other techniques in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants.[9] Adsorption does not require an additional pre–treatment step before its application and process does not result in the formation of any harmful substance. In ion exchange treatment of dye–containing effluents, wastewater is passed over the ion exchange resin until the available exchange sites are saturated.[10] Both cation and anion dyes can be removed from dye–containing effluent using this approach.[11] Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. Membrane separation including ultrafiltration, nanofiltration and reverse osmosis have been increasingly used recently for the treatment of effluents due to its ease of operation.[11] Electrotreatments such as electrodialysis has also contributed to environmental protection.[12]

b) Chemical

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe(II)/$Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes.[13–16] These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem.[17] Although these methods are efficient for the treatment of water contaminated with pollutants, they are very costly and commercially unattractive.

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c) Biological

Biological methods for degradation of dyes found to be more economical than physical and chemical methods. Biodegradation methods such as fungal decolourization, microbial degradation, adsorption by microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants.[18,19] However, their application is often restricted because of technical constraints such as requirement of large land area, less flexibility in design and operation.[20] Although many organic molecules are degraded, many others are recalcitrant due to the complexity of their structure and also due to their synthetic organic origin.[21] In particular, due to the xenobiotic nature, azo dyes are not totally degraded.

d) Photocatalytic degradation

Sunlight is an abundantly available natural source of energy which can be conveniently exploited for the photodegradation of pollutants and can make the process economically more viable.[22,23] Dyes can be degraded in the presence of photocatalyst such as metal nanoparticles upon irradiation with visible light because of their absorption in the visible region and is advantageous due to its quick oxidation, without the formation of polycyclic products and oxidation of pollutants. UV irradiation acts as another source for organic dye degradation by photocatalysts including TiO_2 [24] and ZnO.[25] TiO_2 is of particular interest due to its low cost and high stability. But they show a relatively large energy band–gap and only absorbs UV region, while the UV light only contribute to less than 10% of total solar radiations; the visible light, on the other hand, contribute to 50% of the solar radiations. It is a crucial drawback for the TiO_2 based photo catalysts.[26] ZnO is unstable due to incongruous dissolution to yield $Zn(OH)_2$ on the ZnO particle surfaces and thus leading to catalyst inactivation.[27] Photocatalysts like SnO_2, ZrO_2, CdS, MoO_3,WO_3, RuO_2, Co_3O_4, Cu_2O, SiO_2, α–Fe_2O_3, Mn_2O_3 and Fe_3O_4 have shown negligible activity.[28] The photocatalytic activity of these could be improved under UV and visible illumination by incorporation of metal nanoparticles of silver, gold or iron to broaden the absorption of solar radiations.[29] The size, shape, large surface area to volume ratio and mass dependent reactivity has made metal nanoparticles as effective catalyst.[30] Conventional chemical synthesis of these nanoparticles is not an eco–friendly method. Thus, a cost effective, clean, non–toxic and biogenic approach of synthesis of nanoparticles gain importance.

e) Catalytic degradation by metal nanoparticles with the aid of reducing agent

An alternative method for organic dye reduction utilises the electron donating capacity of transition metal nanoparticles such as silver, gold, iron, nickel, palladium and platinum in the presence of reducing agents like $LiAlH_4$, $NaBH_4$ or H_2O_2. Silver metal nanoparticles have high efficient catalytic activities because of their unique properties such as extreme small dimensions, large surface to bulk ratio, large dispersitivity and ability to transfer electrons between the donor and acceptor electon relay system.[30,31] Nowadays biogenic silver nanocatalysts are widely used for the effective removal of dye contaminants.

Need for the green synthesis of silver nanoparticles

Metal nano particles can be synthesised by using top–down (physical) and bottom–up (chemical and biological) methodologies. Most popular physical and chemical nanoscale synthetic methods involve laser ablation, mechanical grinding, photochemical, solvothermal, co–precipitation, microemulsion, sol–gel, physiochemical reduction, electrochemical and sonochemical process.[32,33] Majority of these methods involve the use of toxic chemicals and severe reaction conditions, which causes chemical toxicity and environmental pollution.[34] This increases the focus on synthesis using biomediated green routes. Biosynthesis of metal nanoparticles are eco friendly which involves the use of plant extracts, enzymes, cell cultures or microorganisms such as bacteria, fungi, algae, yeast and virus.[35,36] Among these, plant products is the most adopted method as phytochemicals are the natural resource for the synthesis of metal nanoparticles, much safer to handle, widely available and ability to act as both stabilization and reduction agent.[37] *Azadirachta indica* leaves, *Camellia sinensis, Capsicum annuum L., Cinnamomum camphora* leaves, *Datura metel, Emblica officinalis* fruit, *Ocimum sanctum* leaves are few among them.[38,39] Moreover, use of plant extracts also reduces the cost of microorganism isolation and culture media preparation. The following gives the account of degradation of organic pollutants by biogenically synthesised silver nanoparticles.

Mechanisms of dye degradation

Catalytic degradation by silver nanoparticles using reducing agents

The process of dye degradation by silver nanocatalyst through reducing agent like $NaBH_4$ can be explained by electron transfer mechanism. During degradation, the catalysis process occurs on the surface region of metals, therefore the surface area availability will increase significantly and in turn improve the efficiency of the catalyst.[40] The reductant molecules and dye molecules are probably adsorbed on the large surface of silver nanoparticles without affecting their activity. When the reducing agent $NaBH_4$ is adsorbed on the nanoparticles, its reductive potential decreases, as $NaBH_4$ is a strong nucleophile. On the other hand, when dye molecules get adsorbed on nanoparticles, their reduction potential increase, as the molecules are electrophilic in nature and hence, when both the species are adsorbed on nanoparticles they become more negative for $NaBH_4$ molecules and more positive for dye molecule. The biogenic silver nanoparticles support the "electron shuttling" from the donor to the acceptor molecules and thus act as an effective substrate for the electron relay process.[41] During electron transfer reaction, the BH_4^- ions are simultaneously adsorbed on the surface of metal nanoparticles and thus electron transfer occurs from BH_4^- ions to dye through the nanoparticles, resulting in the destruction of the dye chromophore structure to form small species such as acetamide, CO_2, H_2O, which are less hazardous than the organic pollutant.[42]

Photocatalytic degradation by silver nanoparticles

The photocatalytic mechanism can be related by two parts namely, photo and catalysis. The first portion related to photon absorption, charge carrier creation and dynamics. The second portion is related to surface radical formation and surface reactivity between O_2, H_2O and organic molecules.[43] Upon photon absorption by silver nanoparticles, an electron gain energy and get excited from valence band (VB) to conduction band (CB), leaving a positively charged hole in the valence band (h^+_{VB}). The valence band holes react with the chemisorbed H_2O molecules to form reactive species such as $OH^\bullet$ radicals. An electron in the conduction band (e^-_{CB}) of the nanoparticles reacts with dissolved oxygen molecules in the reacting medium and

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converted into oxygen anion radicals.[44] $HO_2^{\bullet}$ radicals were generated on protonation of superoxide radical anions $O_2^{\cdot -}$. The molecular oxygen, adsorbed on the surface of the photocatalysts prevents the hole–electron pair recombination process.[45] Recombination of hole–electron pair decreases the rate of photocatalytic degradation. The hydroxyl radicals ($OH^{\bullet}$) and super oxide radical anions ($O_2^{\bullet -}$) are powerful oxidizing agents capable of attacking dye molecules and degrade them into small molecules such as CO_2, H_2O, and NH_3, which are not particularly toxic.

The degradation mechanism is as follows

1. Absorption of photons by silver nanoparticles

$$Ag\ nanoparticles + hg \rightarrow h^{+}{}_{VB} + e^{-}{}_{CB}$$

2. Production of OH radicals

$$OH^{-} + h^{+}{}_{VB} \rightarrow OH^{\bullet}$$

$$H_2O + h^{+}{}_{VB} \rightarrow OH^{\bullet} + H^{+}$$

3. Oxidation of the organic pollutant via successive attack by the OH• radicals

$$dye + OH\bullet \rightarrow dye^{\bullet}\left(intermediates\right) + H_2O$$

$$dye + h^{+}{}_{VB} \rightarrow dye^{+\bullet} \rightarrow Degradation\ products\ NH_4{}^{+},\ SO_4{}^{2-}, CO_2$$

4. Oxygen reduction

$$O_2 + e^{-}{}_{CB} \rightarrow O_2^{\bullet}$$

Degradation of methylene blue

Methylene blue degradation at 664 nm corresponding to $n-\pi^*$ transition is studied using UV–vis. spectrophotometer, in the presence and absence of different biogenic silver nanocatalysts. The colour change from blue to colourless leuco methylene blue infer the complete degradation of dye. Silver nanoparticles acts as a electron mediator between donor ($NaBH_4$) and electron acceptor (Methylene blue dye). Silver nano catalyst is believed to have redox potential in between the values of acceptor and donor.[46] In the catalytic degradation by *Convolvulus arvensis* mediated silver nano, reaction was completed within 20 minutes and rate of the reaction is 0.108 min^{-1}.[47] The high catalyic efficiency of silver nanoparticles is due to the large number of active sites provided by high surface area of the very small nanoparticles.[47] The catalytic action of silver nanoparticle is attributed to the 'electron relay effect'. Reduction of dye by $NaBH_4$ without nano catalyst is not effective and required months for the degradation. The reduction of dye by sodium borohydride in the presence of *Soymida febrifuga* silver nanocatalyst was completed in less than 20 minutes.[48] In the absence of *Aglaia elaeagnoidea*[49] mediated catalyst, reduction of dye was not effective as the original colour persisted for more than 20 minutes. In the presence of catalyst, degradation completed within 5 seconds. Addition of nano catalyst lowers the bond dissociation energy and causes efficient electron transfer between borohydride ions to the dye acceptor. [50] The decolurisation of dye by *Dillenia indica*[51], *Polygonum hydropiper*[52], *Cucurma longa*[53] mediated silver nanocatalyst was completed within 30, 15 and 60 minutes respectively. As the concentration of the *Biophytum sensitivum* synthesised AgNP increased between 0.020 to 0.050 mg/ml, keeping the concentration of dyes and $NaBH_4$ a constant, the rate of dye degradation increased and were 0.9066 and 1.3080 min^{-1} respectively. As concentration of $NaBH_4$ is much higher than that of dyes, its concentration remains practically constant and the degradation reaction is considered to follow pseudo first order kinetics.[54] The degradation by *Punica granatum* nanocatalyst with $NaBH_4$ followed first order kinetics and rate of degradation is 0.1904 min^{-1}.[55] The degradation constant for the efficient reduction catalysed by *Zanthoxylum armatum* derived silver nanoparticle is 1.44 x 10^{-3} min^{-1}.[56]

Degradation of azo dyes

Methyl orange, methyl red and congo red are the commonly used azo dyes in textile industries and are also used as indicators in various industries. These are highly toxic and are harmful to plants and human beings. So its effective degradation is a need. The aqueous solution of methyl orange is orange red in colour. The UV–vis. spectrum of aqueous solution of the methyl orange and methyl red showed strong absorptions at 465 nm and 490nm respectively. Congo red in water medium shows surface plasmon resonance bands at 498 nm and 338 nm corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions associated with azo group. An increase in the rate of methyl orange degradation by *Punica granatum* nanocatalyst with the help of $NaBH_4$ was observed because of the excellent catalytic activity of nanoregime particles due to their relative high surface to volume ratios. The degradation followed first order kinetics and rate of degradation is 0.5477min^{-1}.[55] In the absence of nanocatalyst prepared from *Tangerine* peel extract, degradation by H_2O_2 or $NaBH_4$ was found to be negligible slow rate and in its presence the rate became appreciably high.[57] As *Biophytum sensitivum* mediated silver catalyst concentration was varied between 0.02 to 0.040 mg/ml the degradation rate was found to be 0.1953 and 0.2758 min^{-1} respectively. The degradation followed pseudo first order kinetics.[54] Catalytic degradation by the reductant $NaBH_4$ alone results no change in the characteristic absorption peak at 465nm even upto 6 hours. Addition of green synthesised silver nanoparticles using *Mussaenda erythrophylla* into the solution containing dye and $NaBH_4$ caused a rapid dip in the absorbance peak at 465nm.[58] Faster degradation is attributed to the large surface area, "electron shuttling" of electrons between donor and acceptor and assistance in diminishing the activation barrier provided by the silver nanoparticles. Surface plasmon resonance band showed a blue shift in absoption peak from 465 to 440 nm during the dye degradation due to the surface alterations arising due to electron relay process.[58] In presence of tannic acid[59] stabilised catalyst, 82% degradation was completed within 2 minutes. While in uncatalysed reaction, no such significant degradation was observed even after 150 minutes. The catalysed reaction found to be faster due to electron relay of silver catalyst from BH_4^- ions to the methyl orange dye.[55] *Cucurma longa* mediated silver nano showed complete degradation within 3 minutes.[53] The rate constant for the degradation of methyl orange and methyl red by *Zanthoxylum armatum* mediated catalyst were 1.86 x 10^{-3} min^{-1} and 1.03 x 10^{-3} min^{-1} respectively.[56] The degradation of methyl orange and congo red did not even started by the reducing agent $NaBH_4$ without nano catalyst. Only after the addition of silver nanoparticles, catalytic reductive degradation of the dyes commenced and completed within 30 min for both dyes. Absorbance peak of the dyes degraded in a fast manner as the reaction time increased. Dye degradation followed Langmuir Hinshelwood model and pseudo first order kinetics with rate constants 0.0795 and 0.1178 min^{-1} respectively for congo red and methyl orange. Silver nano catalyst was the electron transfer mediator, and provided more catalytic sites due to high surface to volume ratio, lowered activation energy and fast discoloration of dyes.[60] *Hyphaene thebaica*[61] and *Aglaia elaeagnoidea*[49] mediated silver nanocatalysts in the presence of $NaBH_4$ degraded almost 80% and 99% of Congo red. *Amaranthus gangeticus*[62] mediated silver nano catalyst showed high efficiency in catalytic degradation of Congo red by strong ethanolic borohydride reductant. Degradation in the absence of nanocatalyst is very slow due to the inefficient transfer of electron from the reductant to the dye which was usually done by the catalyst.[62] Within 24 hours of incubation, *Phaseolus vulgaris* and *Brassica oleracea capitata* mediated AgNP at varying concentrations showed almost and 50–60% degradations of Congo red. Due to the presence of azo bond and structural complexity of Mordant black 17, the degradation was not much effective by silver nanocatalyst at both the concentrations .[63,64]

Degradation of nitro compounds

Plant based metal nanoparticles are effective for the degradation of nitro compounds (Table 1). Characteristic absorption peaks of o–nitro anilines are at 283 nm and 412 nm. In the presence of sodium borohydride, degradation was very slow. Upon the addition of *Indigofera tinctoria* mediated nanocatalyst in presence of the reducing agent, o–nitro aniline was reduced to 1, 2 benzenediamine. Intensity of the characteristic peak of p–nitroaniline at 380 nm decreased and a new peak was formed at 240 nm which indicates the complete conversion of p–nitroaniline to phenelenediamine. Both reductions follow puseudo first order kinetics with high correlation coefficients. Rate constants for the respective reactions are 0.0975 min^{-1} and 0.1823 min^{-1}.[65] The nano catalyst took part in the electron relay between the electron donor (borohydride ions) and organic electron acceptor moieties.[46] *Elephantopus scaber* mediated silver nanoparticles showed effective reduction of 4–nitrophenol, o–nitro aniline, p–nitro aniline by sodium borohydride. All reductions followed pesuedo first order kinetics and rate constants for the respective reduction reactions are 0.2794, 0.0751, 0.2788 min^{-1}.[66] The aqueous solution of 4–nitro phenol is pale yellow in colour and its UV–vis. Absorption spectrum showed peaks at 317 nm and 227 nm respectively due to n → π* and π → π* transitions. Majority of organic pollutants like nitro–phenol and their respective derivatives are chiefly formed during the production of pesticides, insecticides, herbicides and synthetic dyes in their industries.[67] In the presence of $NaBH_4$ as reducing agent, the colour of 4–nitro phenol solution instantly changed to greenish yellow and the absorption maximum at 317 nm was red shifted to 400 nm due to the formation of 4–nitrophenolate ions in the alkaline condition caused by the addition of $NaBH_4$.[68] Hydrogenation of 4–nitro phenol to 4–amino phenol was carried out by alkaline tapioca starch[69] and *Lawsonia inermis*[70] capped silver nano using $NaBH_4$. In the presence of catalyst, peak at 400 nm vanished along with the decolouration of bright yellow colour of 4–nitro phenolate ions and a new peak at 298 nm emerged due to the formation of 4–amino phenol.[71] Though the reduction of 4–nitro phenol to 4–amino phenol by aqueous $NaBH_4$ is thermodynamically favorable, the presence of the kinetic barrier due to large potential difference between donor and acceptor molecules decreased the feasibility of this reaction.[72] The metal nanoparticles catalyzed this reaction by facilitating electron relay from the donor BH_4^- to acceptor 4–nitophenol to overcome the kinetic barrier and results in the appearance of a new adsorption peak at 298 nm corresponding to the formation of 4– aminophenol.[49] Both BH_4^- and 4–nitro phenolate ions are adsorped on the catalytic surface. Reduction was achieved by the lowering of activation energy and thus nanoparticles acted as efficient catalysts.[70] *Chenopodium aristatum L.* capped silver nanoparticles was effective catalyst for the reduction of 4–nitro phenol. Plot of $\ln(C_t/C_o)$ with time for degradation in presence of silver nano catalyst gave a linear relation and followed Langmuir and Hinshelwood model kinetics.[73] Since the amount of $NaBH_4$ used in reduction greatly exceeds that of 4–nitrophenol, the concentration of $NaBH_4$ stayed practically constant throughout the course of the reaction.[71] The degradation followed pseudo–first order kinetics with respect to 4–nitrophenol concentration. The *Hyphaene thebaica*,[61] *Dillenia indica*,[51] *Actinidia deliciosa*72 mediated silver nanoparticles could facilitate electron transfer from BH_4^- ion to the 4–nitrophenol, lead to 4–aminophenol formation. Fast electron transfer occured in presence of catalyst, which gave rise to fast reaction process.[51]

Table 1 Catalytic degradation by biosynthesised silver nanoparticles using $NaBH_4$ as reducing agent

Plant species	Plant part	Organic effluent	Remarks	Ref.
Anacardium occidentale	Testa	Congo red, Methyl orange	Followed Langmuir- Hinshel wood model kinetics.	60
Aglaia elaeagnoidea	Flower	Methylene blue, Congo red,4-Nitro phenol	Followed pseudo first order kinetics.	49
Biophytum sensitivum	Leaf	Methylene blue, Methyl orange	Followed pseudo first order kinetics	54
Soymida febrifuga	Leaf	Methylene blue	Degradation completed within 20 minutes	48
Tangerine	Peel	Methyl orange	Degradation was fast in presence of nanocatalyst	57
Zanthoxylum armatum	Leaf	Safranine O, Methyl red, Methyl orange, Methylene blue	Degradation constants are 1.02x10-3,1.03x10-3, 1.86x10-3,1.44x10 -3 min-1 respectively	56
Mussaenda erythrophylla	Leaf	Methyl orange	Degradation was mainly due to nanoparticle mediated transfer of electrons	58
Tannic acid	Analytical grad	Methyl orange	82% degradation complete within 2 minutes	59
Cucurma longa	Tubes	Methyl orange, Methylene blue	Degradation completed within few minutes	53
Convolvulus arvensis	Leaf	Methylene blue	Rate constant is 0.108 min-1	47
Aglaia elaeagnoidea	Flower	Congo red	Shown 99% degradation	49
Gmelina arborea	Fruit	Methylene blue	Complete reduction occur within minutes	50

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Table Continued....

Plant species	Plant part	Organic effluent	Remarks	Ref.
Amaranthus gangeticus	Leaf	Congo red	Degradation completed within few minutes	62
Phaseolus vulgaris	Fruit	Congo red	Showed 50% degradation	63
Brassica oleracea capitata	Fruit	Congo red	Showed 50-60% degradation	64
Punica grantum	Fruit	Methylene blue, Methyl orange, Eosin yellow	Followed first order kinetics	55
Polygonum hydropiper	Leaf	Methylene blue	Degradation completed within 15 minutes	52
Dillenia indica	Bark	Methylene blue,4-Nitro phenol	Degradation complete within 30 minutes	51
Hyphaene thebaica	Fruit	Congo red, 4-Nitro phenol	80% degradation occur within 10 minutes	61
Actinidia deliciosa	Fruit	Methylene blue, 4-Nitro phenol	Degradation completed within few minutes	72
Chenopodium aristatum	Stem	4-Nitro phenol	Followed Langumir and Hinshel wood model kinetics	73
Tapioca starch	Analytical grade	4-Nitro phenol	Reduction completed within 15 minutes	69
Lawsonia inermis	Leaf	4-Nitro phenol	Reduction completed within 15 minutes	70
Indigofera tinctoria	Leaf	Ortho and para Nitroanilines	Followed pseudo first order kinetics	65
Elephantopus scaber	Leaf	Ortho and para Nitroanilines, 4-Nitro phenol	Followed pseudo first order kinetics	66

Photo catalytic degradation of dyes

The photodegradation of methylene blue dye by silver nanoparticles from *Helicteres isora,*[74] *Anas platyrhynchos*[75] showed decrease in the absorption peak at 664 nm in the presence of light. The degradation reaction followed pseudo first order kinetics. In the proposed mechanism the excited surface electron interacts with dissolved oxygen which produced hydroxyl radicals which helped in the interaction of Ag^+ ions with dyes resulting in effective degradation.[76] Smaller particle size, large surface area and capping phytochemicals effectively reduce the recombination of electrons leading to increase in the photo degradation efficiency of the biosynthesized *Dimoncarpus longan,*[77] *Casuarina equisetifolia*[78] silver nanoparticles. The silver nanoparticles acted as a catalyst by lowering the activation energy.[77] Absorption peak of the dye decreased with increase in time of exposure to sunlight.[79] The visible light irradiation of silver nanoparticles promoted electron from valence band to conduction band.[80] The excited electrons in the conduction band were scavenged by lattice oxygen molecules on the surface of the catalyst to form a superoxide radical anion ($O_2^{\cdot-}$).[81] The newly formed oxygen anions further react with water to generate many oxidative species which causes dye degradation.[82] *Parkia roxburghii,*[83] and *Diplazium esculentum*[84] silver nanoparticles showed effective degradation of methylene blue and rhodamine B through $NaBH_4$, indicating that silver nanoparticles caused structural changes and removed chromophore group from the dye.[83] The high potential difference among the donor and acceptor groups made the reaction kinetically unsuitable. The kinetic barrier could be removed by using silver catalyst that mediates the transfer of electron from donor (BH_4^-) to acceptor molecules.[77] The reductions followed pseudo first order kinetics. The photocatalytic degradation by *Solanum tuberosum,*[85] *Hypnea musciformis*, *Ulva lactuca*[87] silver nanoparticles of methyl orange and *Cordia dichotoma*[76] of congo red solution were initially low and further increased with regular increase in time. The probable mechanism of photocatalytic degradation by silver nanoparticles could be attributed to the surface plasmon resonance effect where the excited surface electrons might interact with the dissolved oxygen molecules and ultimately produce hydroxyl radicals while allowing Ag^+ ions to interact with the anionic dyes.[76] Catalytic degradation process is initiated by the striking of colloidal silver nanoparticles by photons of sunlight and the degradation mechanism involving the excitation of conduction electrons of metallic Ag through surface plasmon resonance effect.[88] Catalytic reduction of Allura red and Congo red, Eosin Y, Green Pls, Bromo phenyl blue under visible light was done using $NaBH_4$ in presence of silver nanoparticles synthesised from *Ekebergia capensis*,[89] *Camellia japonica,*[90] *Dicrostachys cinerea,*[91] *and Cirsium japonicum*[80] extracts respectively. $NaBH_4$ or sunlight alone is unable to bring about effective dye degradation. The presence of silver nanoparticles caused enrichment of the rate of reaction due to its electron relay effect for borohydride ions.[92] A summary of the various photocatalytic processes by silver nanoparticles are given in Table 2.

Table 2 Photocatalytic degradation by biosynthesised silver nanoparticles

Plant species	Plant part	Organic effluent	Remarks	Ref.
Casuarina equisetifolia	Cladode	Methylene blue	Photocatalytic degradation found to be effective	78
Diplazium esculentum	Leaf	Methylene blue, Rhodamine B	Complete degradation within 8 minutes	84
Solanum tubersom	Infusion	Methyl orange	Complete degradation within 8 hours	85

Table Continued....

Plant species	Plant part	Organic effluent	Remarks	Ref.
Anas platyrhynchos	Egg shell	Methylene blue, Methyl violet 6B, Rose Bengal	Shown 98.2%, 98.4% and 97% degradations respectively	75
Helicteres isora	Stem, leaf, root	Methyl violet, Safranin, Eosin, Methylene blue, Methyl orange	Followed pseudo first order kinetics	74
Ekebergia capensis	Leaf	Allura red, Congo red	Complete degradation within 1 hour	89
Hypnea musciformis	Whole plant	Methyl orange	Degradation within 10 hours	86
Ulva lactuca	Whole plant	Methyl orange	Degradation within 12 hours	87
Paederia foetida	Leaf	Rhodamine B	Degradation kinetics fitted into pseudo first order equation	92
Cirsium japonicum	Whole plant	Bromo phenyl blue	Effective degradation was observed	80
Camellia japonica	Leaf	Eosin Y	Complete degradation within 1 hour	90
Azadiracluta indica	Leaf	Methyl violet	Degradation % increased with increase of time of sunlight exposure	79
Parkia roxburghii	Leaf	Methylene blue, Rhodamine B	Complete degradations within 12 minutes	83
Dimoncarpus longan	Seed	Methylene blue, 4-Nitro phenol	Followed first order kinetics	77
Cordia dichotoma	Leaf	Methylene blue, Congo red	Highly potential photocatalytic activity	76
Dicrostachys cinerea	Leaf	Green Pls	Complete degradation within 120 minutes	91

Conclusion

Green synthesis of silver nanoparticles is a compatible, ecofriendly, low cost, and less time consuming process. It is found that the use of natural renewable and eco–friendly reducing agents for the synthesis of silver nanoparticles exhibits rapid and excellent photocatalytic activity against different dyes compared to other degradation techniques like biodegradation. These make them potential candidates for water purification systems and dye effluent treatment. The application of nanomaterials offered opportunities for upgrading the conventional methods or generating innovative methods to deal with the dye contaminants with high efficiency.

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Conflict of interest

Author declares there is no conflict of interest.

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