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Selenium-based nanomaterials: green and conventional synthesis methods, applications, and advances in dye degradation

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The rapidly expanding industrialization and global increase in economic activities have drawn attention to the concerning accumulation of waste. The textile industry plays a significant role in environmental pollution, especially in and water pollution. Harmful dyes used during the fabrication process are mixed with water bodies through sewage or wastewater ejected from industrial factories. These toxic dyes are not only applied in textile industries but also used in other industries like pharmaceutical companies and rubber manufacturing. Therefore, scientists have adopted alternative techniques for the degradation of organic dyes because of eliminating the drawbacks from the traditionally used techniques. Catalytic degradation of organic dyes with the help of a safe and easy nanocatalyst is one of the best alternatives. Accordingly, the use of biomaterials or waste materials offers an easy, cost-effective and eco-friendly approach for the synthesis of such nanocatalysts. Several nanocatalysts have been used for the degradation of dyes present in industrial wastewater. The well-known semi-conductor selenium has several important properties, viz., optoelectronic, photovoltaic, thermoconductivity, and anisotropy, and has drawn significant research attention for its catalytic application in

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Institute of Technology (VIT), India, as a junior research fellow in 2018 under the supervision of Dr Priyankar Paira, MRSC, Associate Professor, Department of Chemistry. There, he focused on the development of various anticancer organometallic drugs by studying different cancer cell death pathways. He is now a senior research scholar. His research interest involves the development of mitochondria targeting Ru(II)/Ir(III)/Re(I)-based half-sandwich and cyclometallated complexes for chemodynamic therapy. Currently, he is a member of the Society of Biological Inorganic Chemistry (SBIC). He has 27 publications in various ACS, RSC and Elsevier journals with 514 citations and an h-index of 13.



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characterization and evaluation of various arene-N[^]N heterocycles and their Ru(II)/Ir(III) complexes on anticancer treatment and sensing.



dye degradation. Considering all these points, selenium nanoparticles synthesized via green techniques provide the best possible alternative catalyst for the degradation of organic dyes in industrial wastewater. The current review covers various aspects of the biosynthesis of selenium nanoparticles; their application as a catalyst for the degradation of harmful organic dyes, viz., methylene blue, methyl orange, rhodamine B, alizarin S, malachite green, sunset yellow, fuchsin, safranin T, Congo red, and bromothymol blue; and their mechanism for the degradation process. This review will also shed light on the importance of using green chemistry towards the synthesis of selenium nanoparticles and different biosynthesis procedures and explores all aspects of the interesting catalytic activity towards the dye degradation mechanism. Hence this article will be beneficial to both industrialists and academicians bridging the gap between industrial and academic scientists.



Priyankar Paira

Dr Priyankar Paira, MRSC, Associate Professor, Vellore Institute of Technology (VIT), Vellore, Tamilnadu, India, has completed his PhD from Indian Institute of Chemical Biology (IICB) in medicinal chemistry in the year of 2010 and undergone Post Doctoral training from National University of Singapore (2010–2013) in Bio-organometallic Chemistry under the supervision of Prof. Giorgia Pastorin and Prof. Ang Wee Han.

His postdoctoral training was on the development of target specific organoruthenium complexes for cancer therapy and application of bionanomaterials in drug delivery. He was appointed as Assistant Professor in Vellore Institute of Technology in 2013 and promoted to Associate Professor in the year 2022. He has 15 years research experience in the field of Bioinorganic and Medicinal Chemistry. His research interest lies in the area of transition metal complexes in cancer therapy and diagnosis. Currently, he is involved in many independent and collaborative projects includes A3 receptor targeting phototoxic transition metal complexes for cancer diagnosis and therapy, heterobimetallic biotin conjugates and their encapsulated MWCNT for target delivery and organelle specific cyclometalated complexes for photo-theranostic application. He has more than 100 publications in internationally acclaimed journals includes Journal of Medicinal Chemistry, Chemical Communication, Inorganic Chemistry, Chem. A Eur. Journal, Dalton Transaction, Journal of Inorganic Biochemistry, European Journal of Medicinal Chemistry, etc. Research conducted in his laboratory has been featured as editor's choice and cover page articles. Under his mentorship, several UG students completed their final year thesis project, and four scholars received their PhD degree. Dr Paira has secured 3 patents in Medicinal Chemistry and has successfully completed the DST-SERB-Young Scientist project, DST-SERB-EMR, DST-SERB-CRG project and two ICMR projects under Govt. of India. At present, he is working on CSIR-EMR project (Govt. of India) in the field of Ru(II)/V(V)-based Multinuclear Complexes as Cancer Therapeutic Agent. He is associated as a reviewer with several RSC, ACS, Willey and Elsevier journals. Currently, he is serving as an Executive Guest Editor in Current Organic Chemistry and a Review Editor in Frontier in Chemistry. He is associated as a professional member in RSC, ACS and SBIC.



Rinku Chakrabarty

Dr Rinku Chakrabarty embarked on her academic journey at Kalyani University, West Bengal, India, followed by her PhD under the guidance of Prof. Shyamaprosad Goswami from the Indian Institute of Engineering Science and Technology, Shibpur, India in 2011, focusing on molecular recognition and supramolecular chemistry. She spent two years at the University of Witwatersrand, Johannesburg, South Africa, for her post-

doctoral studies, where she was involved in the synthesis of rare earth-based molecular systems and their extensive application as MRI agents. Her passion for academia led her to assume the role of an Assistant Professor in the Department of Chemistry at Ali-purduar University. Her published works encompass an impressive collection of research papers. Her research pursuits are centered on nanomaterials, dye degradation, molecular sensing and bio-inorganic chemistry, showcasing her unwavering commitment to the advancement of the field of chemistry.



1. Introduction

The significant increase in industrialization, along with the growing population and environmental pollution, has become a major global concern.^{1,2} Globally, the prevention and reduction of pollution have become major challenges. A considerable amount of wastewater is discharged into water bodies every day. The dyes present within the wastewater generated by the effluents of the various industries show cytotoxic, neurogenic, teratogenic and carcinogenic effects.^{3,4} Thus, the treatment of water through different techniques such as sedimentation, reverse osmosis, anaerobic treatment, membrane filtration, adsorption, filtration, ionization, ion exchange, and degradation using bacteria, fungi, *etc.* is mandatory to eliminate these harmful organic dyes and other waste materials present in the industrial effluents.^{5,6} All these physical, chemical and biological methods for the removal of dyes are generally costly, and the concomitant production of toxic sludge is another concern. The effectiveness of these treatments is sometimes questionable because these stable organic synthetic dyes are very resilient towards the biodegradation process that occurs naturally with the help of microorganisms.⁷ Synthetic organic dyes present in wastewater have complex chemical structures, which makes them resistant towards removal techniques generally applied by physical and chemical methods.¹ Thus, metallic nanocatalysts are considered as effective candidates for catalysing the dye degradation.⁸

Nanoscience is a branch of science that deals with materials at the nanoscale. Metal nanoparticles have gained considerable attention due to their diversified applications in the field of research catalysis, sensors, medicine, optics, electronics, *etc.*^{9,10} They are also effective in toxic gas sensing and the removal of heavy metals.^{11–14} Different varieties of metal nanoparticles, *e.g.*, copper, zinc, silver, gold, iron, platinum, palladium, titanium, magnesium, *etc.*, have been synthesized, and their biological applications, *e.g.*, anticancer, antifungal and antimicrobial,

have been studied extensively.¹⁵ The presence of a large surface-to-volume ratio is a special characteristic feature of the metallic nanoparticles, which makes them a strong candidate for application in the optical and chemical fields.¹⁶ Two methods are generally employed for the synthesis of nanomaterials: top-down method and the bottom-up approach. The top-down approach is mainly applicable to physical techniques like ball-milling method, vapour deposition and laser ablation. By comparison, the bottom-up approach includes chemical techniques like pyrolysis, sol-gel method, microwave irradiation, solvothermal method, *etc.*, and biological techniques like synthesis using plant extracts, fungi, microorganisms, *etc.*¹⁷ The use of chemical and physical methods is less common nowadays because of their harmful side effects. Rather, the biological synthesis procedure is more cost-effective, safe, simple and environmentally friendly.¹⁸ In the green synthesis approach, emphasis is given on the reduction or decreased use of chemicals, especially harmful ones. Furthermore, the production of less toxic products is taken into account, along with the twelve principles of green chemistry.

Natural organic compounds, including various types of polyphenols, alkaloid, terpenoids, *etc.*, present in plants act as both reducing and capping agents during the synthesis of nanomaterials using the green technique. Different parts of plants, fungi, and microorganisms are used for this purpose. The biomolecules present in the plant extract get adsorbed on the surface of the produced nanoparticles, reducing the possible toxicity of the nanomaterials.¹⁹ In many cases, more stable and less toxic nanomaterials are generated using the green technique compared to other methods.²⁰

Based on the green technique, the use of fungi or plant extract has recently become quite popular. The process described in Fig. 1 shows the step in which parts of the plants are used without further modification. In this process, parts of a particular plant are collected, washed properly, chopped, air-

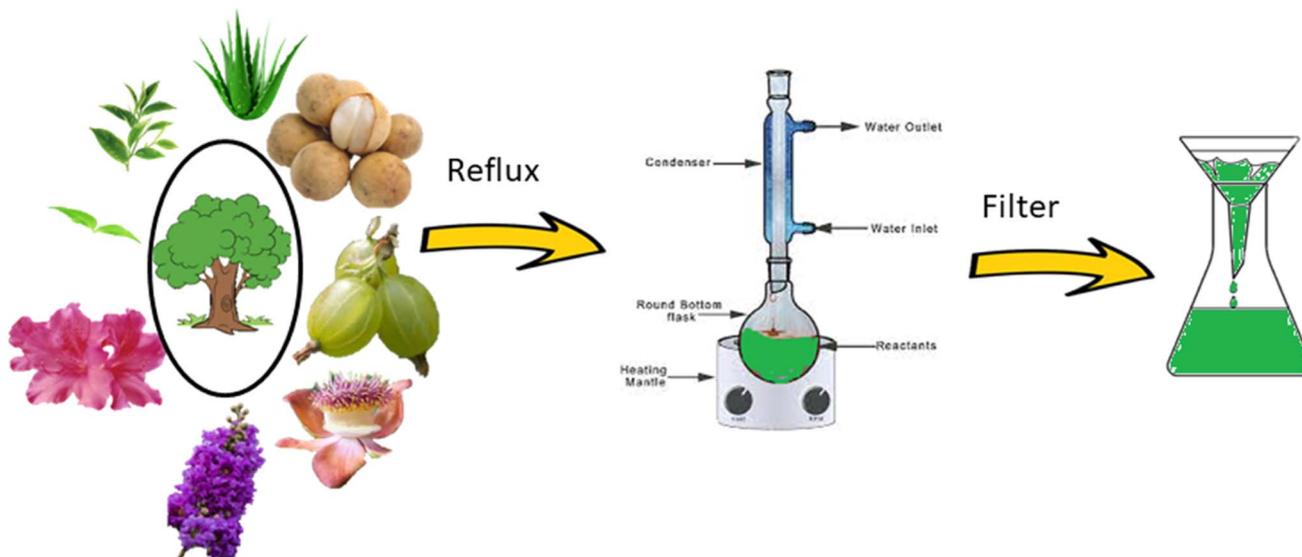


Fig. 1 Schematic diagram for the extraction of different parts of plants.



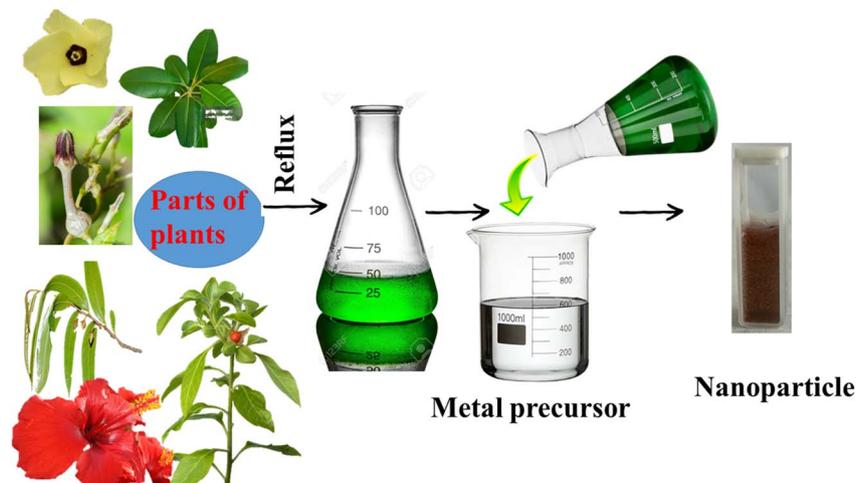


Fig. 2 Schematic representation of the biosynthesis of selenium nanoparticles.

dried, and weighed. A water extraction is performed in a round-bottom flask under refluxing condition, followed by cooling and filtration. The extract is then used for the synthesis, from the corresponding metal salt as precursor (Fig. 2).

Selenium is a trace micronutrient and an essential element for most living organisms. The presence of selenium in lower concentrations within the human body may affect the immune system. Selenium is found to be present in certain functional proteins, which are involved in many important activities like promoting anticancer activities within the body and enhancing the immune system. Se increases the antimicrobial effects of the body by reacting with the peroxides present in the membrane and producing oxygen-free radicals.²¹ Se is a good semiconductor, possessing superior thermoconductivity, high photoconductivity, and anisotropy. Selenium nanoparticles have important applications as catalysts in organic synthesis and semiconducting materials.²² It has widespread application in areas utilizing optoelectronic and photovoltaic properties, owing to the photocatalytic nature of selenium nanoparticles. Selenium is known to possess comparable size and similar properties to other nonmetals like phosphorous. It has excellent stability in air and moisture. It has strong metal coordination properties. Its unique properties, like photoconductivity and semiconducting nature, make it different among other chalcogens, also known as the oxygen family. Its melting point and boiling point do not follow the trend of this family.²³ Due to its distinct physical and chemical properties, there has been a remarkable upsurge of interest in the biogenic synthesis of selenium nanoparticles and their widespread application.²⁴ During the biogenic synthesis of selenium nanoparticles, Se(IV) is converted to Se(0). Selenium nanoparticles produced using the green technique are found to possess important biological properties, like anti-microbial, anticancer, anti-fungal properties. It acts as a nutritional supplement, and is extensively used in drug delivery.^{25,26} It has also been known to exhibit superior biodegradability and biocompatibility compared to other metal nanoparticles synthesized using biomaterials.²⁷ Se nanoparticles have strong affinity towards certain metals. This

property has been utilized for the adsorption of heavy pollutant metals like Cd(II), Cu(II), Hg(0), Zn(II), *etc.* Amorphous Se and crystalline Se possess a bandgap of ~ 1.8 eV, which makes it an ideal photocatalyst for the degradation of organic pollutant dyes.

Amidst previous attempts²¹ to only summarize the catalytic applications of biosynthesized selenium nanoparticles, a review of the synthesis, detailed mechanism, applications and all other related topics is required under one umbrella is required to organize myriad information regarding selenium nanoparticle, which will be helpful for researchers for further studies. Emphasis has been given on the synthetic procedure, including the source of the metal nanoparticle in the current review article.

In this review, the degradation of organic pollutant dyes [methylene blue, methyl orange, rhodamine B, alizarin S, malachite green, sunset yellow, fuchsin, safranin T, Congo red, bromothymol blue] (Fig. 3) using biosynthesized selenium nanoparticles will be discussed with their plausible mechanism of action (Tables 1–9). Due to the intense dark colour of the organic dyes, researchers have studied the degradation process by keeping track of their optical properties, which can easily be studied *via* the absorption properties of the organic dyes with the help of UV-Vis spectroscopy. The surface plasmon resonance vibration of selenium nanoparticles appears in the 250–500 nm range. The λ_{max} value of selenium nanoparticles appears at ~ 270 nm, as reported by various research groups.

2. Degradation of organic dyes

2.1 Methylene blue

Methylene blue is a synthetic organic blue-coloured dye, and is highly water-soluble. Methylene blue is used as a dyeing agent in industries, like the paper industry, cotton industry, *etc.*, as well as in medication. The dye, methylthionium chloride or methylene blue is used as a chemotherapeutic agent, and in the treatment of shock states. It is used for treating methemoglobinemia, staining lymph nodes, treating vasoplegia, and



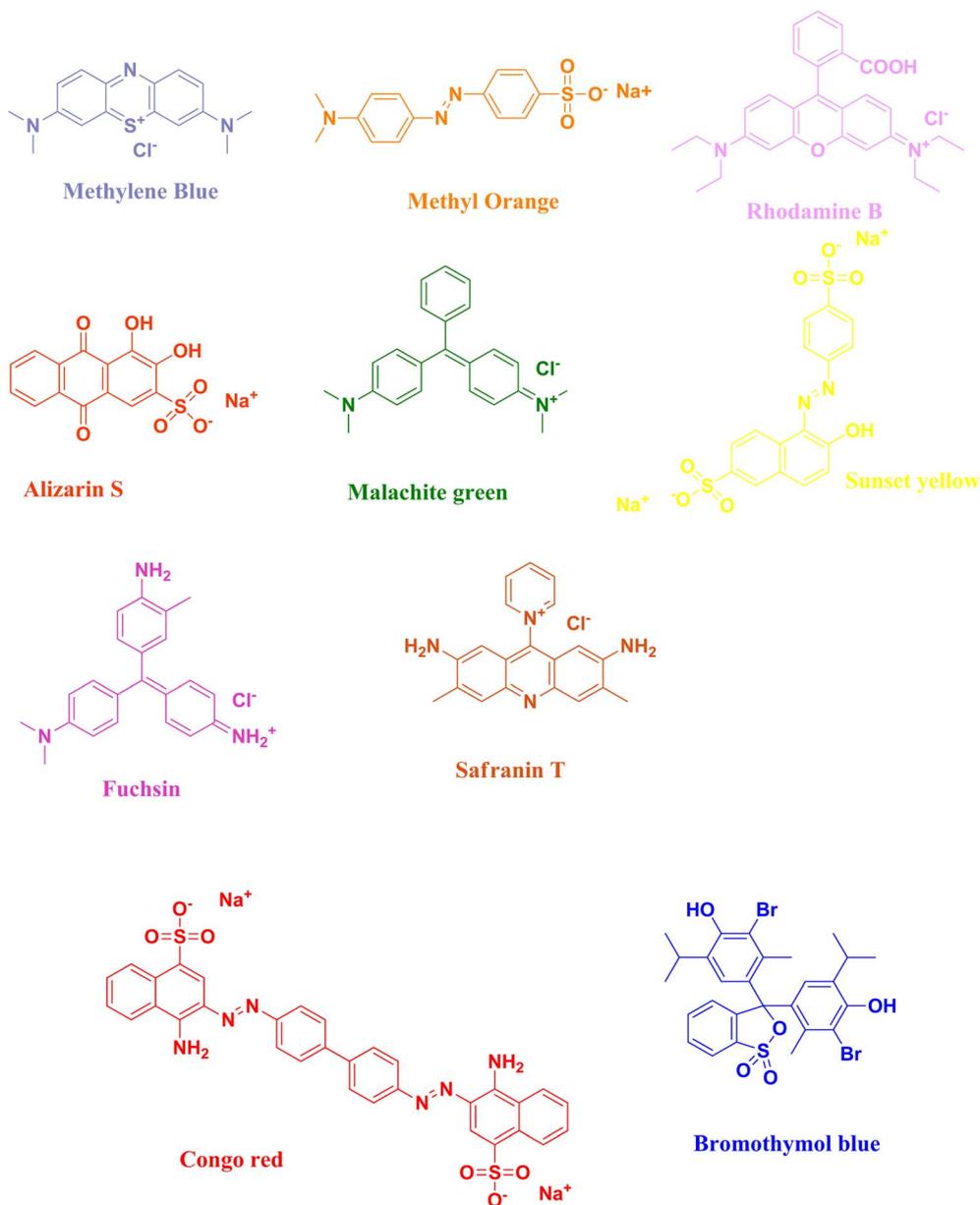


Fig. 3 Structures of organic pollutant dyes.

Table 1 Summary of the degradation of methylene blue dye using selenium and selenium-based biosynthesized nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	Yeast	Na ₂ SeO ₄	170–240	Rod	Visible	—	31
2	<i>W. somnifera</i>	H ₂ SeO ₃	45–90	Spherical	Sunlight	—	32
3	Sodium formaldehyde sulfoxylate	SeO ₂	100–200	Rod	Visible	H ₂ O ₂	33
4	<i>F. benghalensis</i>	Se powder, sodium sulphide	45–95	Spherical	UV	—	34
5	<i>M. purpureus</i>	Na ₂ SeO ₃	46.58	Round	Sunlight	—	35
6	<i>C. bulbosa</i> tuber	H ₂ SeO ₃	55.9	Spherical	Halogen lamp	—	36
7	<i>G. wightii</i> , AA	Na ₂ SeO ₃	80	Spherical	Sunlight	—	37
8	<i>A. paradoxum</i>	Na ₂ SeO ₃	37.5	Semi-spherical	—	NaBH ₄	38
9	<i>H. esculentus</i>	Na ₂ SeO ₃	62	Spherical	—	NaBH ₄	39
10	<i>H. rosa-sinensis</i>	NiCl ₃ , Se powder	26	Spherical	Visible	—	40
11	<i>Nyctanthes arbor-tristis</i> L.	Na ₂ SeO ₃	44.57	Spherical	—	—	41

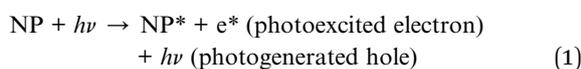


anaphylaxis. It is also used as a disinfectant, biological stain, optical probe in the biophysical systems, pH and redox indicator, and for the determination of anionic surfactants. Methylene blue is a highly pollutant dye having carcinogenic and mutagenic properties. Exposure to excess amounts of methylene blue causes serious damage to the nervous system. Furthermore, it causes irritation to the eyes, respiratory infections, affects the digestive system, and can cause vomiting and nausea.^{28,29} Therefore, methylene blue is a serious threat to living organisms. Its removal from aqueous media is necessary.

The reduction of methylene blue is generally carried out using either nanoparticles as catalyst using sodium borohydride as a reducing agent or using only metallic nanoparticles as a photocatalyst (Table 1).

The plausible mechanism of the reduction of methylene blue using sodium borohydride as a reducing agent and selenium nanoparticles as catalyst is delineated in Fig. 4. Methylene blue dye shows its absorption maximum at ~660 nm, which is slowly decreased with time in the presence of the reducing agent sodium borohydride. However, in the presence of the selenium nanoparticle catalyst, the time for the reduction of methylene blue decreases and the blue-coloured dye is converted into its colourless leuco form. Here, the synthesized selenium nanoparticle acts as in electron relay during the whole reduction process. The selenium nanoparticle generally acts as an electron donor and the dye molecule acts as an electron acceptor.

The detailed mechanism of the photocatalytic degradation of methylene blue has been established by Kalaycıoğlu *et al.*³⁰ for the CeO₂ nanoparticle. Metal nanoparticles (NPs) absorb the photons and reach the excited state. During this process, the photoexcited electron in the conduction band and photo-generated hole in the valence band are produced (eqn (1)). Methylene blue (MB) is excited to directly produce the reactive intermediate, and is then oxidized by photogenerated holes (eqn (2)).



Indirectly, it has been shown that the oxygen and water are adsorbed on the surface of the nanoparticle used as catalyst. Then, they react with the photoexcited electron and photo-generated hole to produce reactive oxygen species (eqn (3) and (4)). Methylene blue, in the presence of a hydroxyl radical and superoxide ion produced *in situ*, is converted to carbon dioxide and a water molecule (eqn (5)).



The blue colour of methylene blue originates from the π electron transfer from the N and S atoms. The λ_{max} of methylene blue appears due to this transition. In the structure of methylene blue, the positively charged S atom is attacked by the electrons, followed by the opening of the aromatic ring (Fig. 5). During this process, after the reduction process, the electron transfer between the S and N atoms is diminished and the whole solution becomes colourless.

Goud *et al.* synthesized rod-shaped selenium nanoparticles using fermented yeast broth from agricultural waste, and characterized the product by different spectroscopic techniques. Yeast fermented broth was derived from agricultural waste. This fermented yeast has been used as a reducing agent for synthesis purposes. Addition of this broth to the aqueous solution of sodium selenite yielded stable selenium nanoparticles. The fabricated nanoparticles had a size of 170–240 nm. For the decomposition study, 50 mg of biosynthesized catalyst were incorporated into 50 μL of the dye solution, methylene blue, and irradiated under visible light for 3 h. For this purpose, they set up a visible annular-type photoreactor with a tungsten lamp of 300 W. They also studied the use of their nanoparticles for biological applications, and showed that

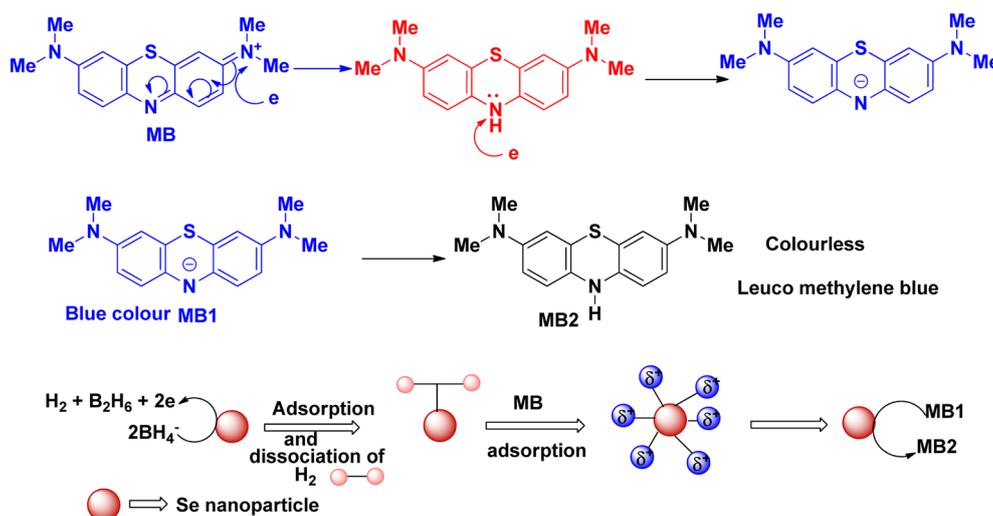


Fig. 4 Schematic representation of the plausible mechanism for the reduction of methylene blue dye in the presence of selenium nanoparticles.



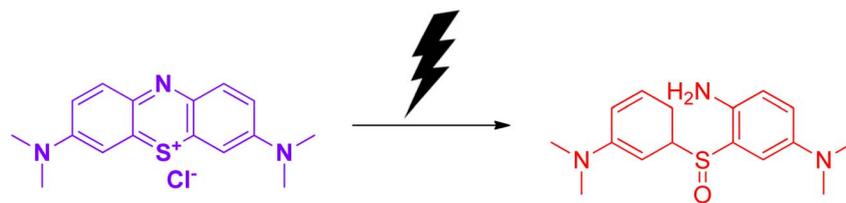


Fig. 5 Photocatalytic degradation of methylene blue.

their catalyst is effective as an anticancer and antibacterial agent.³¹

Venkatesan and co-workers³² have synthesized amorphous and spherical-shaped selenium nanoparticles having a diameter in the range of 45–90 nm using *Withania somnifera* extract. Selenous acid was used as the starting material. Suitably washed and chopped leaves were boiled in a beaker with distilled water, followed by filtration and centrifugation to obtain the extract, which was then added to a sodium selenite solution and stirred at room temperature for the completion of the reaction. The nascent nanoparticles were centrifuged and washed with water and acetone, then suspended in PBS with the help of ultrasonication at neutral pH, and centrifuged again to obtain red pellets of selenium nanoparticles. The band gap of the nanoparticles was determined, and shown to be higher than that of the commercial selenium powder and bulk selenium. Decomposition of methylene blue was studied under sunlight after 30 minutes. The synthesized selenium nanoparticles also possess antioxidant, antimicrobial and antiproliferative properties.

The green approach has been adopted by Xia *et al.*³³ to synthesize trigonometric selenium nanowires with the diameter ranging between 100–200 nm, and their potential application as a catalyst for the reduction of methylene blue dye was studied. A Xe lamp of 300 W was used for the visible light source. Selenium dioxide was used as the starting material, and sodium formaldehyde sulfoxylate was used as the reducing agent for the synthesis. The bandgap determined for the synthesized selenium nanoparticle was slightly lower than that of the bulk selenium. Degradation of methylene blue was carried out with the oxidation process using H₂O₂ as an oxidizing agent, and it took 3 h to nearly complete the degradation process.

Spherical-shaped polycrystalline selenium nanoparticles have been synthesized by Tripathi and co-workers³⁴ using *Ficus benghalensis* leaf extract from selenium metal powder and sodium sulphide having particle sizes in the range of 45–95 nm. The leaves were chopped and boiled in distilled water, followed by filtration through a muslin cloth to obtain the bioextract. Selenium sulphide was synthesized separately from the reaction of selenium and sodium sulphide under heating condition. Further reaction of the plant extract with sodium selenite solution afforded the desired nanoparticles, which was indicated by the dark reddish orange colour. The bandgap calculated for their synthesized nanoparticles is higher than that of the commercial Se powder, which affects their quantum confinement and the effect of the capping agents present on the surface of the metal nanoparticle. The degradation of

methylene blue under UV light irradiation was studied, achieving ~58% degradation after 40 minutes. The degradation process follows first-order kinetics with the calculated rate constant of 0.02162 s⁻¹.

Another research group synthesized highly stable single-phase crystalline selenium nanoparticles through the green technique using *Monascus purpureus* ATCC16436 fungi extract from sodium selenite as a starting material at room temperature with a zeta potential value of 24.01 mV. The application of the biogenic synthesized selenium nanoparticles towards the degradation of organic dye, methylene blue, was successfully carried out with sunlight at the catalyst concentration of 4 mg mL⁻¹. This catalyst also possesses antioxidant, antimicrobial and anticancer activities.³⁵

Ceropegia bulbosa tuber extract was used by Cittrarasu *et al.* with selenous acid to synthesize uniformly spherical selenium nanoparticles, which was fully characterized using PXRD, FE-SEM, EDX, HRTEM, DLS, *etc.* The *C. bulbosa* tuber extract was initially obtained from distilled water, diluted to a 1:9 ratio, and used for the synthesis. The diluted extract was added to a 40 mM solution of selenous acid solution, and was stirred for another 24 h. After completion of the reaction, which is indicated by the change of colour to a brilliant ruby red, the product was further purified by washing with distilled water several times after centrifugation. The obtained solid was dried in a refrigerator for further studies. The synthesized selenium nanoparticles can degrade 98% of methylene blue dye through photocatalysis in 80 min. The synthesized nanoparticles have been proven to exhibit antimicrobial, antimosquitocidal and cytotoxic activity.³⁶

Goniothalamus wightii extract was used by Santhosh and co-workers³⁷ to synthesize selenium nanoparticles through green technique. Sodium selenite was used as the precursor of selenium metal nanoparticles of average size distribution at 80 nm. Leaves of the plants were collected from Kalakad Mundanthurai Tiger Reserve Forest, Tirunelveli, India, and were washed, dried and ground to obtain the powder form of the leaves. The powder was then soaked in distilled water for half an hour, and filtered using a Whatman-1 filter paper for the plant extract. This plant extract was then added to the solution of sodium selenite, followed by the addition of ascorbic acid for 24 h to obtain an orange-coloured solution, which was then centrifuged and dried at 60 °C in a hot air oven to obtain selenium nanoparticles in powder form. The produced nanoparticles were characterized through different spectroscopic techniques, *viz.*, PXRD, SEM, EDX, TEM, *etc.* Sunlight was then used for the photocatalytic degradation of methylene blue in 150 minutes. This



synthesized nanoparticle possesses anticancer and radical scavenging properties.

Allium paradoxum aqueous extract was used by Alizadeh and colleagues³⁸ very recently for the green synthesis of semi-spherical shaped selenium nanoparticles with an average size of 37.5 nm. Sodium selenite was used as the precursor for selenium metal. Common spectroscopic techniques like PXRD, SEM, EDX, TEM were applied for the characterization of the synthesized nanoparticles. Degradation of methylene blue dye using sodium borohydride as a reducing agent was carried out over a reasonable time period. It followed the pseudo-first order kinetics, and the rate constant values were calculated. It also possesses antibacterial, antioxidant, anticancer, antifungal, and iron-chelating properties.

Hibiscus esculentus L. extract has been proven by Ebrahimpzadeh *et al.*³⁹ to be effective for the biosynthesis of hexagonal crystals of spherical-shaped selenium nanoparticles having a size of 62 nm. Sun dried plant pieces of *Hibiscus esculentus* L. were added to distilled water, and treated with heat and sonication for the preparation of the extract. The obtained filtrate was added to the sodium selenite solution, which was stirred under heating at ~ 50 °C for two days until the solution changed to a red colour. It was then centrifuged and underwent several washing with distilled water and methanol, followed by drying in a hot air oven at ~ 60 °C to afford the selenium nanoparticles. Colloidal selenium nanoparticles were used for the degradation of methylene blue using sodium borohydride as a reducing agent in 21 minutes. This degradation process follows pseudo first order kinetics, and the rate constant value calculated for this process was found to be 0.1023 min^{-1} .

Velayutham *et al.*⁴⁰ used *Hibiscus rosa-sinensis* extract for the biosynthesis of spherical shaped selenium based nanoparticle having particle size of 24 nm using the hydrothermal process. Dried chopped leaves of *Hibiscus rosa-sinensis* was boiled for 2 h to get the extract, which was then added to an equimolar mixture of selenium powder and nickel chloride. The whole reaction mixture was then stirred and put into a thermal reactor at 120 °C for 24 h, followed by centrifugation and calcination at 500 °C for 2 h. The collected precipitate was washed and dried to afford NiSe nanoparticles. The produced nanoparticle has a bandgap of 1.74 eV, which is helpful for the generation of the photoexcited electron in the conduction band and photo-generated hole. The synthesized nanoparticle is active towards the degradation of methylene blue. It also exhibits good antibacterial properties against the well-known bacteria, *Staphylococcus aureus* and *Escherichia coli*.

Satpathy and coworkers have reported the synthesis of selenium nanoparticles using the extract of leaves of a plant having medicinal value, *Nyctanthes arbor-tristis* L., which is also known as tree of sorrow. Washed and dried leaves were stirred, and the aqueous solution was heated at 60 °C for half an hour, followed by centrifugation and filtration using a Whatman filter paper. The extract was then added to the solution of sodium selenite, and incubated for 24 h at 37 °C. The obtained solid was centrifuged, washed and dried at 80 °C. The average size of the nanoparticle was 44.57 nm with a spherical shape. These synthesized nanoparticles possess antioxidant, antimicrobial

and anti-biofilm activities. A cytotoxicity study showed that the synthesized selenium nanoparticle possesses minimal toxicity. It was found to be effective in the photocatalytic degradation of the environmentally toxic dye methylene blue in 80 minutes.⁴¹

2.2 Methyl orange

Methyl orange is a sulphonated anionic azo dye. It is a yellow powder with the melting point of >300 °C. It is highly soluble in warm water, and sparingly soluble in water at ambient temperature. It is also an acid–base indicator. It shows a red colour in acidic medium, and is orange in colour in basic medium. The high chemical stability of methyl orange dye makes it less biodegradable, and thereby increases its toxicity to a certain extent.⁴²

Methyl orange shows its absorption maxima at ~ 460 nm. The absorption maxima decrease during the photocatalytic degradation process using selenium nanoparticles as the catalyst. The mechanism for the photocatalytic degradation (Fig. 6) is similar to that described earlier in the case of methylene blue.

Degradation of methyl orange in the presence of the reducing agent sodium borohydride using selenium nanoparticles follows similar mechanistic pathways, and is shown in Fig. 7. Methyl orange is reduced to its corresponding colourless form. The addition of hydrogen atoms occurs at the azo group, which then eventually gets dissociated into small molecules in some cases.

Ahluwalia and co-workers synthesized selenium nanoparticles using *Bacillus* sp., taking sodium selenite as the starting material. Here, selenium nanoparticles were used as the cocatalyst. It improved the activity of ZnS through photocatalytic pathways. A mixture of selenium solution and *Bacillus* sp. was incubated on a rotary shaker for 48 h at 120 rpm. Centrifugation was followed by repeated washing with ethanol, yielding selenium nanoparticles, which were then used for wet impregnation method with ZnS nanoparticles. The reaction mixture was stirred overnight, followed by calcination to yield the final nanocomposite. It was shown to be effective for the degradation of methyl orange dye. The selenium nanocomposite synthesized through green technique, applying calcination at ~ 200 °C, has been fully characterized through PXRD, SEM, TEM, *etc.*, and showed an average particle size of ~ 40 – 80 nm. The degradation of methyl orange dye followed

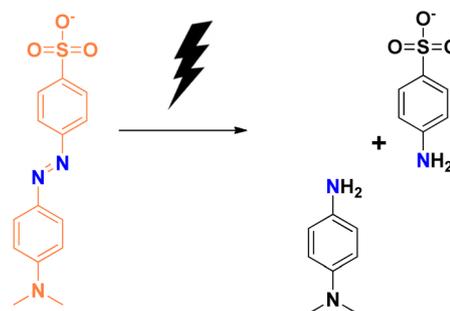


Fig. 6 Photocatalytic degradation of methyl orange.



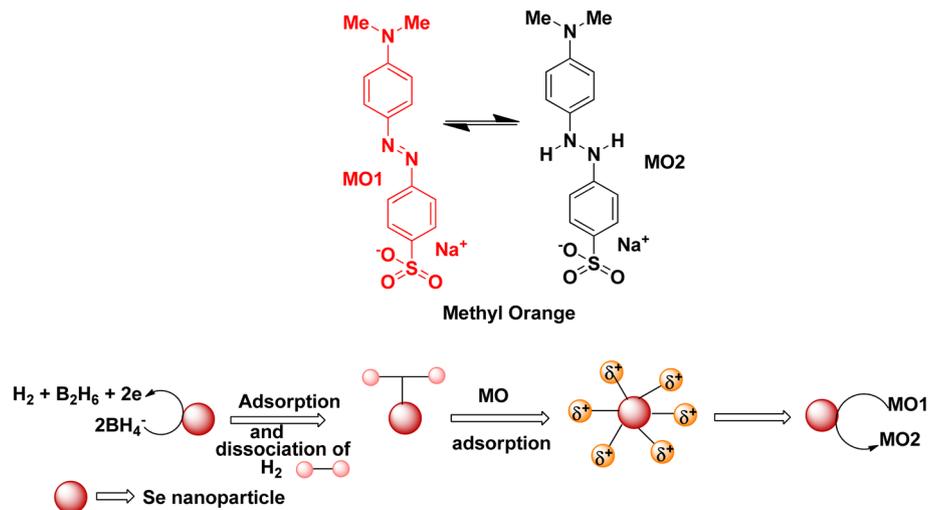


Fig. 7 Schematic representation of the plausible mechanism for the reduction of methyl orange dye in the presence of selenium nanoparticles.

Table 2 Summary of the degradation of methyl orange dye using the green selenium nanocomposite

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>Bacillus</i> sp.	Na ₂ SeO ₃ , ZnNO ₃ , L-cysteine	40–80	Cluster form	UV	Calcination	43

pseudo-first order kinetics and the calculated rate constant value was 0.00842 min⁻¹ (Table 2).⁴³

2.3 Rhodamine B

Rhodamine B is considered to be one of the most toxic dyes present in wastewater from textile industries. It is highly stable and nonbiodegradable in nature. In the UV-vis spectra, the λ_{\max} appears at ~550 nm. This cationic dye is highly soluble in water. It is also highly carcinogenic in nature, and has mutagenic and neurotoxic properties. Excess exposure to rhodamine B dye can cause respiratory infections, vision problem, and hemolysis. This dye can cause liver and kidney diseases. Death of planktons has resulted from the presence of this toxic dye in water bodies. Due to the mixing of rhodamine B dye in the water bodies, pollution occurs that affects light transmission. It prevents the penetration of sunlight into the water bodies, thereby reducing the dissolved oxygen level in the water bodies and affecting the aquatic life. Like other dyes, rhodamine B dye is also very stable and resistant to other biological decomposition processes.^{44,45}

The photocatalytic degradation of rhodamine B (Fig. 8) and the degradation of rhodamine B using sodium borohydride as a reducing agent with the help of selenium nanoparticles (Fig. 9) follow similar mechanistic pathways as that shown in the case of methylene blue, where it is converted into its colourless form (Table 3).

Che *et al.* used sulfite reductase enzyme in the *Lysinibacillus* sp. ZYM-1 for the synthesis of selenium nanoparticles. Sodium selenite has been used by this research group to afford cubic to spherical-shaped nanoparticles having the size of ~100–200 nm. The addition of the marine sediment slurry into sodium selenite, and incubation for 7 days at ~30 °C yielded a red-coloured product. It was found that upon increasing the concentration of sodium selenite, the morphology of the synthesized selenium nanoparticles drastically changed from a cubic to spherical shape. Photocatalytic degradation of rhodamine B dye was studied under visible light using the biogenic synthesized selenium nanoparticles in the presence of the oxidizing agent H₂O₂ after 300 min. The rate constants determined for the spherical and triangular nanoparticles were

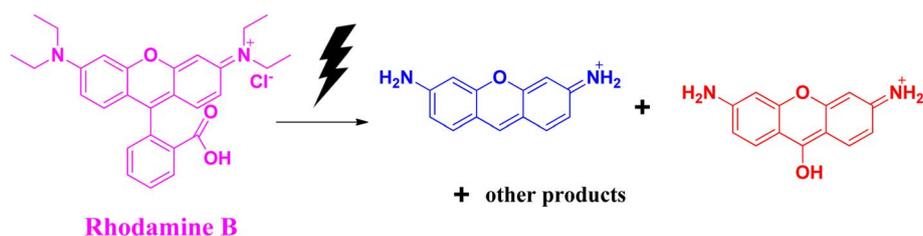


Fig. 8 Photocatalytic degradation of rhodamine B.



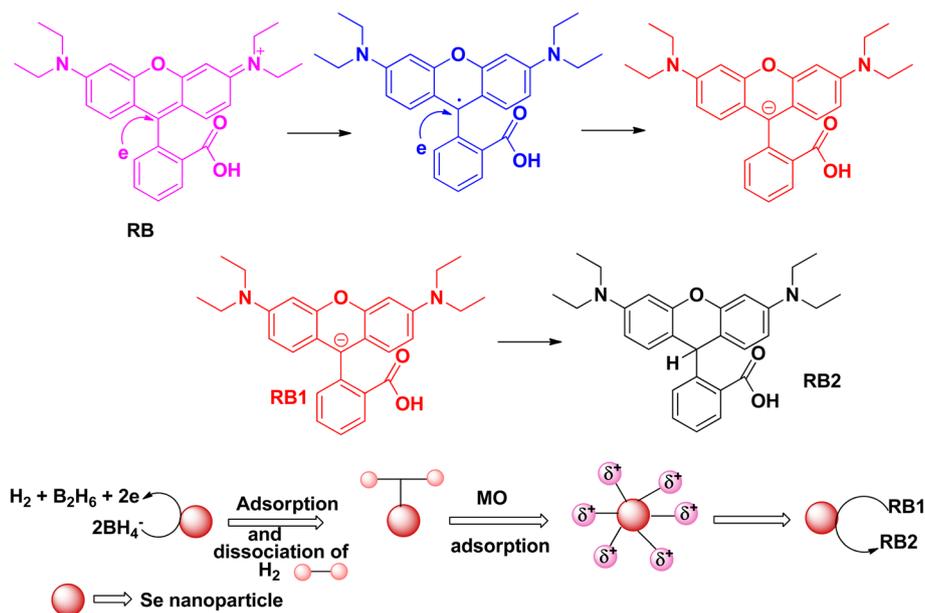


Fig. 9 Schematic representation of the plausible mechanism for the reduction of rhodamine B dye in the presence of selenium nanoparticles.

Table 3 Summary of the degradation of rhodamine B dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	Sulfite reductase in <i>Lysinibacillus</i> sp. ZYM-1	Na_2SeO_3	100–200	Cubic and spherical	Visible	H_2O_2	46
2	Chitosan <i>Justicia adhatoda</i>	Na_2SeO_3	87–152	—	—	—	47
3	GA, AA	Na_2SeO_3	20–24	—	UV-A	—	24
4	Chitosan, AA	Na_2SeO_3	20–27	Rod	UV	—	48

determined, and the calculated values were 0.0048 min^{-1} and 0.0011 min^{-1} , respectively. A plausible mechanism for the degradation process has been determined using LC-HRMS.⁴⁶

The Britto research group prepared selenium nanoparticles by green technique. They utilized *Justicia adhatoda* leaf extract from the sodium selenite precursor. The leaves of the plant were ground using a mortar and pestle by adding water, and the supernatant liquid obtained by centrifugation was added to the sodium selenite solution for the preparation of the selenium nanoparticles, which was then allowed to react for an additional 24 h and incubated under dark conditions. They also prepared chitosan–selenium nanoparticles. Chitosan in acetic acid solution was added to the aqueous solution of sodium selenite, followed by the addition of ascorbic acid to obtain chitosan–selenium nanoparticles. The Langmuir isotherm model was used to study the degradation process of rhodamine B dye using chitosan–selenium nanoparticles. The process was studied by varying the different conditions, like the absorbent material, temperature, dye concentration, pH, etc. The adsorption process was utilized in this research study. The adsorbent limit was reported as 34.5 mg g^{-1} for the rhodamine B dye.⁴⁷

Velayati and coworkers produced selenium nanoparticles from gum Arabic. Sodium selenite was used as the precursor material of the selenium nanoparticle. An aqueous solution of

sodium selenite and gum Arabic mixture was heated at $\sim 80^\circ \text{C}$ for 24 h to obtain the desired selenium nanoparticles, which was obtained after centrifugation and subsequent washing. The used biomaterial can act as both reducing and capping agent. Various spectroscopic techniques have been used to characterize the synthesized hexagonal selenium nanoparticles with an average size $\sim 20\text{--}24 \text{ nm}$, including UV-vis, FTIR, PXRD, EDX, FESEM, and TEM. A photocatalytic study was carried out under UV-A light. It was shown that 85% degradation of rhodamine B was completed after 135 min. The reaction kinetics were assumed to be pseudo-first order, and the value of the rate constant was calculated accordingly.²⁴

The same research group used the biopolymer, chitosan, for the synthesis of highly crystalline hexagonal rod-shaped selenium nanoparticles with a size of $\sim 20\text{--}27 \text{ nm}$. The photocatalytic degradation of rhodamine B was achieved under UV light after 120 min. The biosynthesized selenium nanoparticle is proven to exhibit potential anticancer activity on the cancer cell lines tested, viz., HT-29 and CT-26.⁴⁸

2.4 Alizarin red

Alizarin S (or alizarin red S) or 1,2-dihydroxyanthraquinone-3-sulphonate is a red-coloured dye. It has been widely used as



a synthetic dye for dyeing textile fabrics. Alizarin red dye was first extracted from the roots of the madder genus plant. It is the first synthesized dye. This dye is used as a staining agent in biological research. Studies have shown that it has toxic effects if it comes in contact with the skin or is swallowed. It is carcinogenic and mutagenic in nature. It affects the respiratory system and can damage eyes. Alizarin red S absorbs at the λ_{max} of 271 nm.

Alizarin red S can be degraded under a photocatalytic pathway to form a dicarboxylic acid and dihydroxy compound, which are then further dehydrated and form small degraded products that are eco-friendly in nature (Fig. 10).

Haewon *et al.* synthesized trigonal-shaped selenium nanoparticles from the leaf extract of *Tectona grandis* with an average size of ~ 45 nm. The leaves were washed, air-dried, smashed, and the extract was prepared using distilled water. Then, the sodium selenite solution was added to the leaf extract solution, and kept in a hydrothermal oven for 9 h at 180 °C. After centrifugation, the obtained solid product was subjected to calcination for 1 h at 300 °C. Their green synthesized selenium nanoparticle is proven to be active against the toxic industrial dye alizarin red. A recyclability study proved that the synthesized nanomaterial is active after five consecutive cycles. The biosynthesized selenium nanoparticle is active against alizarin red dye; it takes 90 minutes to achieve 87% degradation. This nanoparticle is found to be active as a catalyst for use in the photocatalytic degradation of dyes, like crystal violet, reactive black and rhodamine B. The research group used sunlight for the photocatalytic degradation technique (Table 4).⁴⁹

2.5 Malachite green

A triphenylmethane-based cationic dye, malachite green is widely used worldwide in the aquaculture industry for the treatment of fungal and protozoan infections among aquatic animals. Its excess use and high solubility in water contribute to its water pollutant nature. Like rhodamine B, malachite green also affects the dissolved oxygen level in water bodies by preventing the transmission of sunlight into the water surface.^{50,51} It affects the photosynthesis process of algae present in the aquatic system. It absorbs at 618 nm, which can be detected by UV-vis spectroscopic technique. Excess exposure to malachite

green dye can damage the nervous system, cause eye irritation, hamper breathing, and affect the kidney and brain. It is carcinogenic in nature.^{50,51}

Photocatalytic degradation of malachite green follows similar pathways, as in the case of methylene blue (Fig. 11).

Aspergillus terreus pure cells were used for the synthesis of spherical-shaped selenium nanoparticles having a size of ~ 10 –100 nm by Saied and coworkers, where *Aspergillus terreus* acts as a bioreactor. Calcination at 200 °C for 24 h furnished the powdered selenium nanoparticles. The studies were successfully carried out for the degradation of 89% of rhodamine B for 240 min under sunlight. It also displayed weak antifungal effects, but strong antibacterial properties (Table 5).⁵²

2.6 Sunset yellow

Sunset yellow is an azo dye that is widely used in confectionaries, including candies, some dairy products, soft drinks, chocolates, *etc.* It has some adverse side effects like allergies. It affects the respiratory system, liver, kidney, and digestive system, and has cytotoxic effects. Due to its structural stability, it is resistant to biodegradation. At acidic pH values, sunset yellow exhibits the λ_{max} value at 480 nm. It shows its absorption peak at λ_{max} at ~ 480 nm.^{53–55}

Hassanien *et al.* synthesized selenium nanoparticles with the help of the bioextract, starting from sodium selenite salt. They have used *Moringa oleifera* extract to obtain spherical-shaped selenium nanoparticles with an average size ranging between 23 and 35 nm. Addition of the plant extract to the sodium selenite solution changes the colour from a light yellow to a brick red colour, indicating the formation of the selenium nanoparticle. The reaction mixture was further allowed to incubate at room temperature for another 24 h. The bandgap value for their synthesized nanoparticles was also determined, and was found to be 2.3 eV, which was higher than that of the bulk selenium and commercial selenium powder. The higher band gap can be attributed to its quantum size effects. Sunset yellow dye degradation (Fig. 12) was studied using their synthesized nanomaterial under UV light irradiation, as well as under solar light irradiation at slightly acidic pH range, and the dye degradation was successful after 10 h. This degradation process was reported to take place *via* pseudo-first order

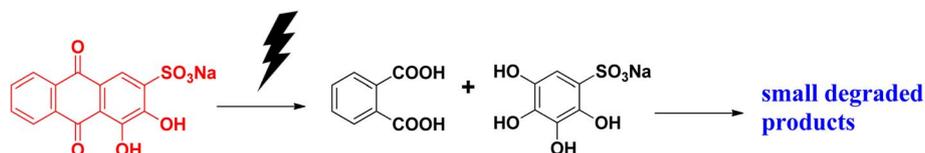


Fig. 10 Photocatalytic degradation of alizarin red S.

Table 4 Summary of the degradation of alizarin S dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>Tectona grandis</i>	Na_2SeO_3	45	Trigonal	Sunlight	—	49



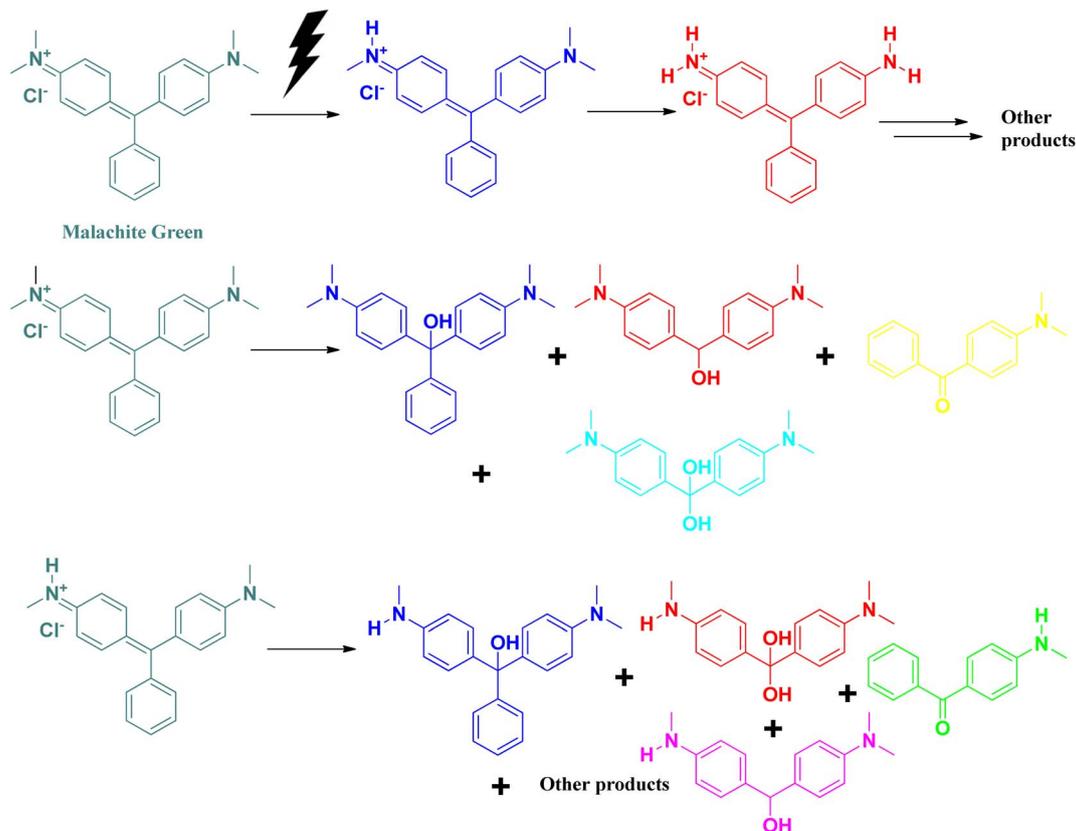


Fig. 11 Probable products of malachite green after photodegradation.

Table 5 Summary of the degradation of malachite green dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>Aspergillus terreus</i>	Na ₂ SeO ₃	10–100	Spherical	Sunlight	—	52

kinetics. The rate constant was determined from the equation applicable for the pseudo-first order reaction, and was found to be 0.173 min⁻¹ (Table 6).⁵⁶

2.7 Fuchsin

Fuchsin is a dye that is basic in nature. It belongs to the triarylmethane family. It is highly flammable in nature. Fuchsin dye

is popularly used in textile industries for the dyeing of clothes, leather, silk fibre, *etc.* This dye also possesses fungicidal, bactericidal and anaesthetic properties. Its high stability is attributed to its non-biodegradability issues. It is carcinogenic and affects the digestive system, as well as the respiratory system. In spite of its many positive sides, fuchsin is considered

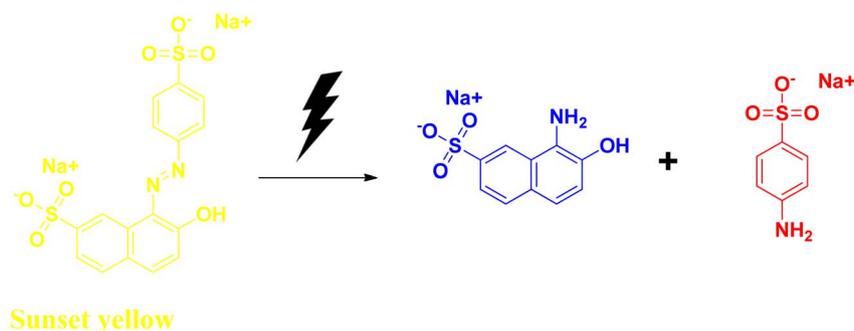


Fig. 12 Probable products of sunset yellow after photodegradation.



Table 6 Summary of the degradation of sunset yellow dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>M. oleifera</i>	Na ₂ SeO ₃	23–35	Spherical	UV, solar	—	56

as a water pollutant. Therefore, the removal of fuchsin from the aqueous system is a big challenge.^{57–59}

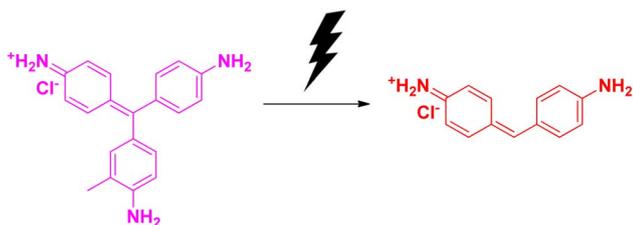
Badreah and coworkers synthesized semi-spherical selenium nanoparticles having a diameter ranging between 8 and 22.5 nm. The photocatalytic degradation of fuchsin dye was successful after 34 min when the catalyst dose was 10 mg. The effects of changing the concentration of catalyst on the degradation efficiency were studied under visible light irradiation. When a significant amount of selenium nanoparticles was used, the degradation (Fig. 13) process was found to follow the pseudo-first order kinetics. This biosynthesized selenium nanoparticle is effective towards the generation of hydroxyl radicals, which is responsible to improve the degradation process leading to the removal of contaminant dyes ultimately from the wastewater effluents (Table 7).⁶⁰

2.8 Safranin T

Safranin T is an important class of basic dye, belongs to the phenazinium dye family. This azine dye has widespread application as a synthetic dye in research as a spectroscopic analysis tool and as an indicator.^{61,62} This reddish brown-coloured powder is highly soluble in water. The cationic charge in the structure of safranin T facilitates its permeability into proteins and DNA molecules, thereby making it more toxic.⁶³

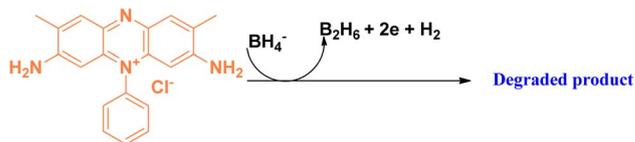
In the degradation of safranin T in the presence of the reducing agent sodium borohydride, adsorption on the surface of the nanomaterial is an important step. It follows a similar mechanism to that of methylene blue, and is depicted in Fig. 14.

Xia *et al.* utilized the *Escherichia coli* strain for the biogenic synthesis of irregular sphere-shaped selenium nanoparticles.



Fuchsin

Fig. 13 Probable products of fuchsin after photodegradation.



Safranin T

Fig. 14 Probable degradation of safranin T in the presence of the reducing agent sodium borohydride.

The *E. coli* culture was treated with sodium selenite and incubated for 36 h. The suspension was washed in distilled water and sonicated. Centrifugation yielded selenium nanoparticles, which were suspended again in 80% sucrose, and then centrifuged and washed with distilled water to obtain the pure product. A detailed study revealed that changing the pH of the system changed the zeta potential value. Safranin T absorbs at 520 nm, which gradually decreases during the degradation process with the biosynthesized selenium nanocatalyst. With increasing pH, the efficiency of safranin T dye degradation was increased. It was found that the optimum pH was 10 for safranin T dye degradation, which was achieved after 25 minutes. Temperature also has a significant effect on the dye removal efficiency of the synthesized nano-catalyst. The adsorption technique was used to determine the dye removal efficiency, which was 1911.0 mg g⁻¹ for safranin T dye. Pseudo-second order kinetics was followed. Reusability of the bio-catalyst is an important characteristic. It was demonstrated that the catalyst could be reused for more than five dye removal cycles with the help of 200 mM NaCl. This selenium nanoparticle could be used simultaneously for the degradation of Congo red dye as well as methylene blue dye, and was found to be very effective (Table 8).²⁵

2.9 Congo red

Congo red is a synthetic azo dye. Congo red absorbs at a λ_{\max} value of 497 nm. The stable aromatic nature of the dye makes it a more potent bio-pollutant. Congo red is carcinogenic in nature, and requires number of years to be decomposed. Due to its toxicity, it has been banned in a number of countries. Therefore, it is very urgent to treat wastewater containing Congo red dye to eradicate this pollution issue.^{64,65}

Table 7 Summary of the degradation of fuchsin dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	SeNPs, AA, polyvinyl alcohol	Na ₂ SeO ₃	8–22.5	Semi-spherical	Visible	—	60



Table 8 Summary of the degradation of safranin T dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>E. coli</i>	Na ₂ SeO ₃	60–105	Irregular spheres	—	Adsorption	25

The degradation mechanism of Congo red follows similar pathways as that of methylene blue, both through the photodegradation pathways and reduction pathways using sodium borohydride as reducing agent. The breaking and reduction of the azo bond occur during this process. During the photocatalysis process, the aromatic structure is destroyed in the final stage, followed by the production of CO₂ and H₂O, thereby removing the colour and the toxicity of the dye. The products that can be formed after the degradation pathways have been delineated in Fig. 15 and 16.^{25,66–70}

Xia and coworkers synthesized selenium nanoparticles from sodium selenite, and used the *E. coli* extract for the synthesis process. Details have been discussed earlier in the case of safranin T dye. Congo red has a λ_{\max} at 437 nm, which decreases during the degradation process. The optimum pH for degradation was observed at pH 5, and it took 35 min for the whole degradation process. The adsorption capacity was found to be 1577.7 mg g⁻¹, which was about 6% higher than that of the commonly used bio-based materials. Recyclability and kinetics are similar to that in the previously discussed dye, safranin T.²⁵

Turna *et al.* synthesized selenium nanoparticles of 9.969 nm from leaf waste of *Prunus armeniaca* L., by obtaining the leaf

extract with distilled water, followed by filtration and treatment with sodium selenite. Different spectroscopic techniques were utilized for characterizing the adsorption of toxic dye Congo red. Two different kinetics models and four different isotherm models were studied. It was proven that their adsorption phenomena followed pseudo-second order kinetics, and the Freundlich isotherm model was the best fit for their study with R^2 values of 0.996. The calculated maximum adsorption capacity was 96.59 mg Congo red per g of the synthesized nanocatalyst.⁷¹

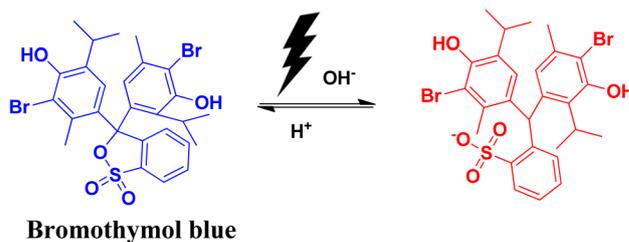


Fig. 17 Probable mechanism of the photocatalytic degradation of bromothymol blue.

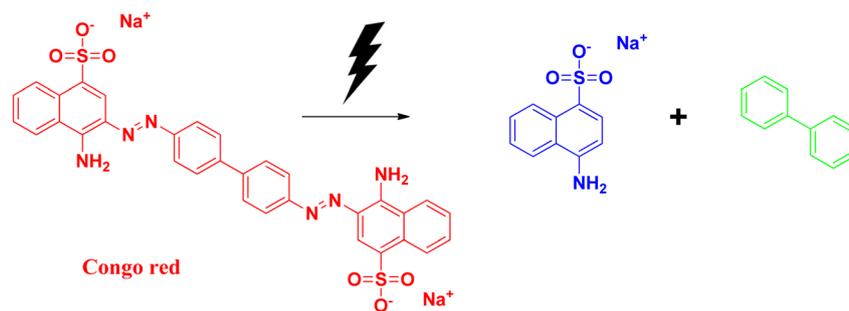


Fig. 15 Probable mechanism of the photocatalytic degradation of Congo red.

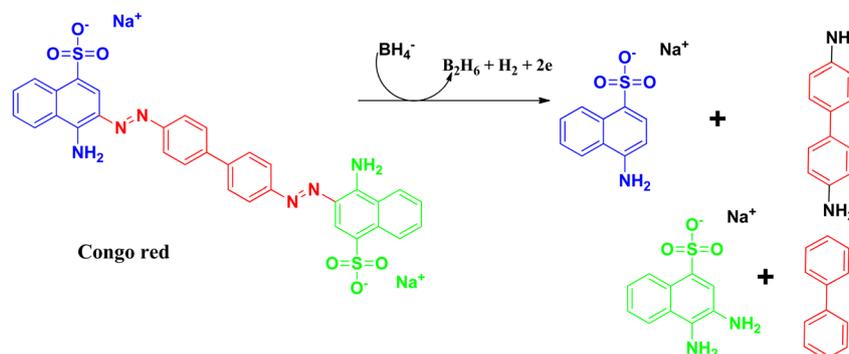


Fig. 16 Probable degradation of Congo red in the presence of the reducing agent sodium borohydride.



Table 9 Summary of the degradation of bromothymol blue dye using biosynthesized selenium nanoparticles

Sl no.	Biosources used	Precursor taken	Size (nm)	Shape	Irradiation	Condition	References
1	<i>S. griseobrunneus</i>	SeO ₂	73.8	Spherical	UV	H ₂ O ₂	74

2.10 Bromothymol blue

Bromothymol blue is a widely used pH indicator. It is used for the identification of carbonic acid in liquid packaged items. Its important use is in the detection of fungal asparaginase enzyme and in many biological applications, including the rupture of membrane in cases of obstetrics and in gynecology. A change in pH has an impact on the colour of bromothymol blue. Changing the pH from acidic to basic pH causes the solution to change from yellow to blue colour. The λ_{max} in the UV-vis spectra also shows a shift from 427 nm to 602 nm. Excess exposure to this dye can have adverse health effects, like infection in eyes and skin. It can also affect the functioning of the respiratory system.^{72,73}

The photocatalytic degradation of bromothymol blue produces the aromatic degraded product shown in Fig. 17.

Ameri and coworkers reported on the synthesis of selenium nanoparticles using the bioextract of *Streptomyces griseobrunneus*. Cultivation of the bacterial strain in CG broth medium was treated with SeO₂ for 5 days, followed by centrifugation and grinding in liquid nitrogen with the help of a mortar and pestle. Finally, ultrasonication and centrifugation yielded the desired selenium nanoparticles. Selenium dioxide was used as the starting material to produce trigonal selenium. Photocatalytic degradation of bromothymol blue in buffer solution was completed in 60 min for under UV irradiation *via* oxidation with H₂O₂ (Table 9).⁷⁴

3. Conclusion

In the last few decades, increased interest has emerged in the field of biogenic synthesis of nanoparticles using plant extracts or microorganisms. The green technique has snatched more attention due to its cost-effectiveness, availability, non-toxicity, and safe nature. The high surface-to-volume ratio and tuneable surface plasmon resonance make the nanoparticles more effective towards the catalytic activity for the degradation of dyes present in the effluents from various industries. Among the different types of nanoparticles used for the application of dye degradation and other biomedical applications, selenium nanoparticles possess unique characteristics. Furthermore, Se nanoparticles exhibit superior biodegradability and biocompatibility. The tremendous escalation in industrialization has resulted in increased water pollution, which not only affects human life, but also disturbs aquatic ecosystems. Physical, chemical and biological methods have been widely used to degrade these detrimental dyes for many years. However, among all of the methods, degradation of organic dyes using nanoparticles as a catalyst has gained much attention and is found to be more effective. Degradation of organic dyes by reduction method using sodium borohydride, or by using

photocatalytic pathways, is quite common and effective. The end products are generally environmentally friendly products, thereby reducing and eliminating the toxic nature of the dyes. This review can shed light on the special features of selenium nanoparticles, its biogenic synthesis, and crucial application in the degradation of toxic pollutant dyes present in wastewater. Their mechanism of degradation and other related information have been discussed here. Synthesis of selenium nanoparticles through green techniques and its important applications as a catalyst in dye degradation, *viz.*, the degradation of methylene blue, methyl orange, rhodamine B, alizarin S, malachite green, sunset yellow, fuchsin, safranin T, Congo red, and bromothymol blue, reported by different research groups, have been summarized here. A number of research groups have reported on the biogenic synthesis of selenium nanoparticles, and extensively studied their dye degradation properties. In spite of the important properties of selenium nanoparticles, this field is still largely unexplored. Along with this, thorough studies on issues like scalability and recyclability can augment the efficiency of the selenium particles to become an effective catalyst. More biogenic sources may be explored, which can improve the synthesis process, including the reduction of the synthesis time and the nanoparticle production yield. We hope that this review will be helpful for academic researchers and industrial scientists, thereby bridging the gap between academia and the industry. Further extensive work can be done on the degradation of other reactive dyes present in industrial effluents that have not been covered yet by the research groups.

Data availability

No new data were generated in this review.

Conflicts of interest

There are no known conflicts to declare.

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