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REVIEW

Mechanistic removal of environmental contaminants using biogenic nano-materials

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Abstract

Materials of nano-dimensions are gaining popularity due to their inherent properties such as high reactivity, mobility and surface area. Environmental bioremediation by employing microbial platforms is one of the most rapidly growing areas of nano-biotechnology. Nanoparticles synthesized using biological entities such as yeast, bacteria, fungi, algae and plants are referred to as biogenic nanoparticles. Owing to their nontoxicity, biologically synthesized nanoparticles have emerged as a sustainable alternative to chemically synthesized nanoparticles. In the past few years, several biogenic nanoparticles have been developed for potential application in medicine and environmental remediation. Biogenic nanoparticles such as biogenic manganese oxide (BioMnOx), biogenic nano-magnets, bio-palladium nanocrystals and biogenic iron species have proven to be effective for the removal of several micro-pollutants, heavy metals, recalcitrant pollutants and halogenated compounds. Nano-bioremediation could emerge as a better, safer, ecofriendly and cost-effective technology, which can greatly influence the domain of environmental remediation in the long run. This study reviews the synthesis, classification and applications of microbial nanoparticles for environmental bioremediation.

Keywords Biogenic metals · Nano-biotechnology · Nanoparticles · Nano-toxicity

Introduction

In recent years, nanotechnology has emerged as one of the most intriguing branches of science with extensive applications in various sectors (Iverson et al. 2013; Sen et al. 2012a, b). Professor Richard Feynman first gave the concept of nanotechnology in his talk “there’s plenty of room at the bottom” (Feynman 1959), and the term nanotechnology was coined by Professor Norio Taniguchi (Taniguchi 1974). Particles in the size range of 1–100 nm having different shapes such as triangular, circular, rod, spherical and star are referred to as nanoparticles (Menon et al. 2017). Nanoparticles possess inherent properties such as uniform shapes and large surface area-to-volume ratio. Owing to their unique size-dependent physical and chemical properties, new advances in the synthesis of nanoparticles are gaining much interest among researchers worldwide. Nanoparticles can be synthesized by either physical or chemical methods via the top-down approach or the bottom-up approach. Top-down approach includes physical methods such as irradiation, diffusion and arc discharge, whereas bottom-up approach encompasses various chemical and biological methods. Due to several inherent drawbacks of physicochemical methods, such as addition of toxic chemicals and formation of toxic by-products, high-cost, biological methods for the synthesis of nanoparticles are gaining popularity (Davis et al. 2017).

Nanoparticles synthesized using fungi, yeast, algae, bacteria and plants are referred to as biogenic nanoparticles (Yadav et al. 2017). Biological entities used in the synthesis of nanoparticles are referred to as “Bio-nanofactories” and act as a driving force in their synthesis. These biological entities are composed of biomolecules and secrete proteins that further leads to the reduction of metal ions, thereby leading to the synthesis of nanoparticles (Rai et al. 2011). Such biogenic nanoparticles have potential applications in diverse fields such as chemical, electrochemistry, medical, food industry, biotechnology and environmental remediation

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(Sharma et al. 2015). These nanoparticles are also found to have wide-ranging applications in wastewater treatment, soil remediation, air remediation, water disinfection, sensing and detection. Due to an extensive urban development and industrialization, soil and ground water pollution has become highly pervasive. Each year, fuel and power industries generate about 2.4 million tonnes of heavy metal waste, while agriculture and waste disposal add another 2 million tonnes/year (Dhillon et al. 2012). These organic and inorganic pollutants usually enter into the environment, transforms into toxic compounds and contaminates water bodies and soil. Heavy metals such as arsenic, lead, cadmium and mercury, which are categorized as priority pollutants by the Environmental Protection Agency (EPA), gain entrance into the environment via the industrial manufacturing sector. In addition to these, remediation of other pollutants such as polynuclear aromatic hydrocarbons (PAHs), trichloroethylene (TCE) and perchloroethylene (PCE) is very challenging through biological route because of their inherently high toxicity (Dhillon et al. 2012). Nanoparticles have proven to be effective for remediation of several pollutants such as pesticides (Das et al. 2009), halogenated compounds (Hennebel et al. 2009b), dyes (Aziz et al. 2015), pharmaceutical products (Furgal et al. 2014) and heavy metals (Castro et al. 2018) from water and soil matrix.

The environment-friendly biogenic nanoparticles due to its excellent adsorptive and catalytic properties are proving to be an efficient and emerging tool to remove environmental contaminants. The present review article is an attempt to compile and summarize studies related to the application of biogenic nanomaterial in the field of water and soil remediation. In addition, this review deals with an in-depth discussion on the synthesis of nanoparticles by employing microorganisms and their role in environmental remediation (Fig. 1). Role and mechanism of action of various biogenic nanoparticles and engineered nanoparticles using only microbes for the removal of contaminants from water and soil have also been discussed. This study also addresses the limitations related to biogenic nanoparticles which could be avoided for better application to remove various environmental contaminants.

Advantages of using biogenic nanoparticles

Nature has provided alternative clean and green routes for the synthesis of materials in the nano-range. Nanoparticles synthesized using biogenic agents such as bacteria, algae and fungus are better, superior and successful alternatives in many ways than using physical and chemical methods (Fig. 2). Biogenic nanoparticles are cheaper than nanoparticles synthesized using physicochemical methods as they employ biomolecules as reducing agents, thus eliminating the requirement for expensive chemical reductants such as sodium borohydride and hydrazine. Although nanoparticles synthesized using chemical methods are large in quantity, they entail production of toxic wastes that are harmful to the environment and human health, whereas biogenic mechanism does not produce such harmful toxic wastes. Furthermore, nanoparticles synthesized using biogenic routes possess greater surface area that considerably enhances adsorption capacity for the removal of environmental

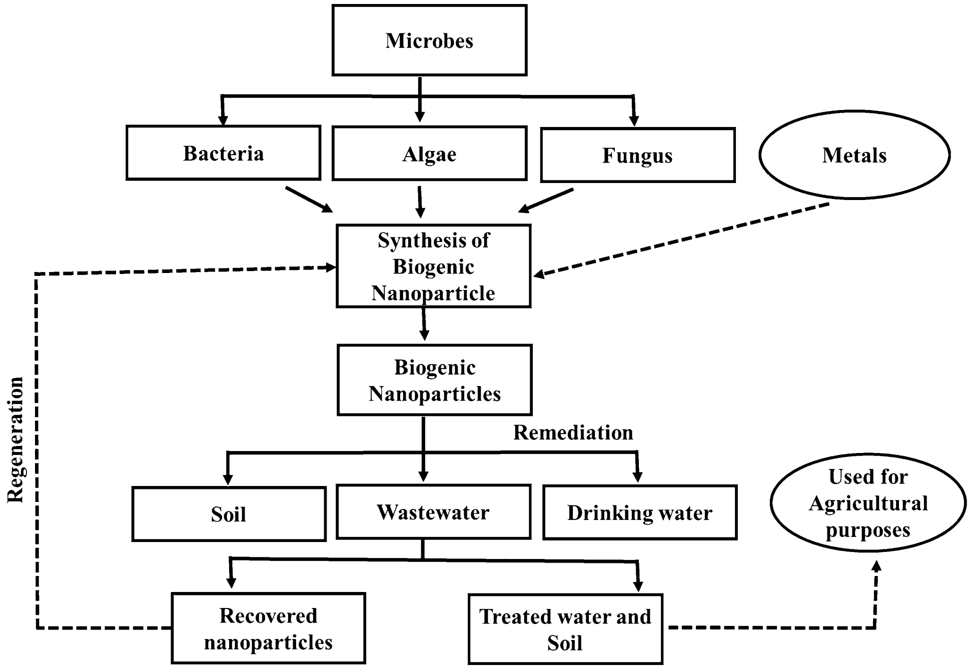

Fig. 1 An outlook of the proposed review work

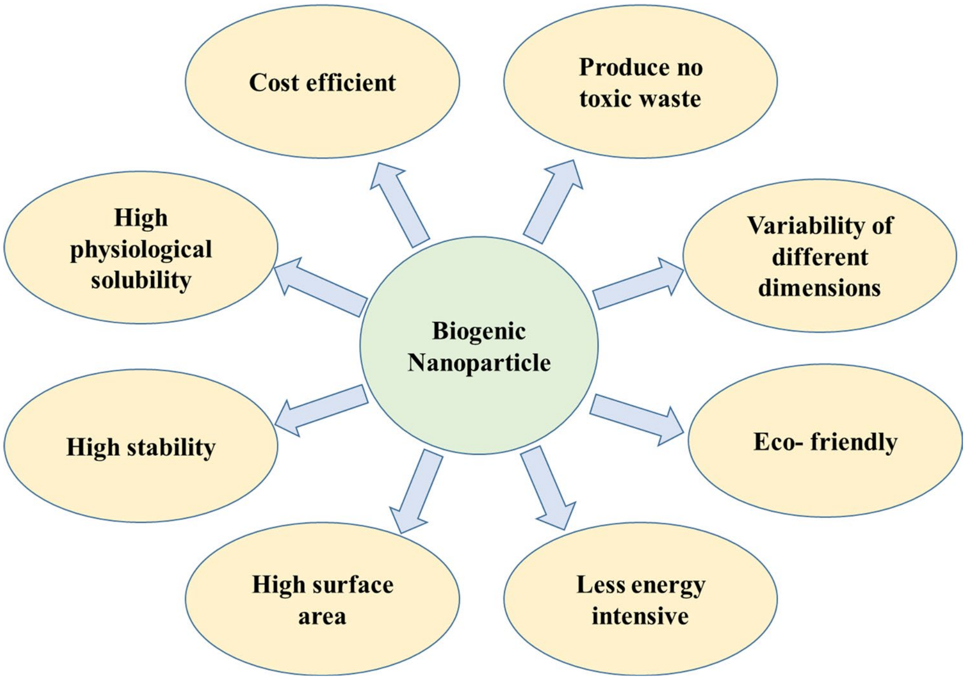

Fig. 2 Advantages of using biogenic nanoparticles over chemically synthesized nanoparticles

contaminants. Many of the biogenic nanoparticles contain lipid bilayer which provides stability and possesses better physiological solubility, thus making them apt for several biomedical applications. Furthermore, the size and shape of nanoparticles could be manipulated by changing the pH, substrate availability and contact time of reaction (Li et al. 2011). Biogenic nanoparticles therefore emerge as an eco-friendly, cost-efficient, less energy intensive and superior alternative to physicochemical methods for the synthesis of nanoparticles in terms of cost, human health and environmental impact.

Biological synthesis of nanoparticles

Microbes can synthesize nanoparticles either by intracellular or by extracellular processes. In intracellular processes, positively charged metal ions get diffused into the negatively charged cell wall by electrostatic interactions. In addition, the cytoplasmic influx of heavy metals is also facilitated through endocytosis, carrier channels and ion channels. Thereafter, the enzymatic machinery in the cell wall converts these toxic metals into non-toxic nanoparticles. The extracellular processes are exemplified by enzymes such as nitrate reductase synthesized by fungus, which converts metal ions into metal nanoparticles (Menon et al. 2017). Biosynthesis of nanoparticles is typically associated with characterization of nanoparticles through different techniques. Characterization of nanoparticles gives a clear idea about their shape, size, surface area, chemical composition and dispersity. Synthesized nanoparticles are usually characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), UV–visible spectroscopic analysis and Raman spectroscopy.

Bacterial synthesis of nanoparticles

Various species of bacteria have proven to be potential biofactories for the synthesis of nanoparticles such as gold, silver, copper, iron, zinc, manganese, palladium and several other engineered nanoparticles (Table 1). Bacteria are capable of mobilization, immobilization and precipitation of metals, thus facilitating the synthesis of nanoparticles. In a study reported by Klaus et al. (1999), *Pseudomonas stutzeri* AG259 isolated from silver mines was capable of reducing silver ions when placed in a solution of silver nitrate, and the accumulated silver nanoparticle was observed within the preplasmic space of cell. He et al. (2007) reported the formation of spherical gold nanoparticles of size ranging between 10 and 20 nm in an acidic environment by *Rhodopseudomonas capsulata. Bacillus subtilis* isolated from rhizosphere soil samples have been found to be capable of biosynthesis of iron oxide nanoparticles (Sundaram et al. 2012).

Algae-based synthesis of nanoparticles

Algae are photoautotrophic, oxygenic and eukaryotic microorganisms which possess metal accumulating

Table 1 Synthesis of biogenic nanoparticles by employing bacteria

Type of NPs	Bacteria	References
Gold (Au)	*Streptomyces* sp. VITDDK3	Gopal et al. (2013)
	Rhodopseudomonas capsulate	He et al. (2007)
	Pseudomonas aeruginosa	Husseiny et al. (2007)
	Thermomonospora sp.	Ahmad et al. (2003)
	Klebsiella pneumonia	Malarkodi et al. (2013)
	Brevibacterium casei.	Kalishwaralal et al. (2010)
Iron (Fe)	*Bacillus subtilis*	Sundaram et al. (2012)
	Klebsiella oxytoca	Anghel et al. (2012)
Copper (Cu)	*Pseudomonas stutzeri*	Varshney et al. (2010)
	Pseudomonas fluorescens	Shantkriti and Rani (2014)
	Escherichia coli	Singh et al. (2010)
Silver (Ag)	*Staphylococcus aureus*	Nanda and Saravanan (2009)
	Escherichia coli	Gurunathan et al. (2009)
	Streptomyces rochei	Selvakumar et al. (2012)
	Bacillus thuringiensis	Jain et al. (2010)
	Brevibacterium casei	Kalishwaralal et al. (2010)
	Bacillus subtilis	Saifuddin et al. (2009)
	Streptomyces sp. ERI-3	Zonooz and Salouti (2011)
	Pseudomonas stutzeri	Klaus et al. (1999)
	Enterobacteria	Shahverdi et al. (2007)
	Streptomyces albidoflavus	Prakasham et al. (2012)
Zinc (Zn)	*Lactobacillus plantarum VITES07*	Selvarajan and Mohanasrinivasan (2013)
	Actinomycetes	Rajamanickam et al. (2012)
	Aeromonas hydrophila	Jayaseelan et al. (2012)
Bio-palladium	*Desulfovibrio vulgaris*	Martins et al. (2017)
Biogenic manganese oxide nanoparticles (BioMnOx)	*Pseudomonas putida*	Furgal et al. (2014)

capabilities. Algal species commonly used for the synthesis of nanoparticles are listed in Table 2. There are several inherent advantages of employing algae for the biosynthesis of metallic nanoparticles, which include metal bioaccumulation ability, high tolerance, ease in handling and economic viability. Moreover, large-scale secretion of algal extracellular enzymes enables industrial-scale production of enzymes (Thakkar et al. 2010). Marine brown algae secrete fucoidans (polysaccharides) from their cell wall, which is known to have anticancer, anti-inflammatory, anti-viral and anticoagulant properties. Fucoidans have also been reported to play a key role in the synthesis of gold nanoparticles, thus providing a cleaner alternative to conventional chemical-intensive methods (Lirdprapamongkol et al. 2010). Cell walls of brown algae are also rich in mucilaginous polysaccharides and carboxyl groups which play a key role in metal uptake, and thus are popularly employed in the biosynthesis of nanoparticles (Khandel and Shahi 2016).

Nanoparticle synthesis using fungi and yeast

Fungi have also been extensively used for the synthesis of nanoparticles (Table 3). These are relatively easy to handle and are good source of extracellular enzymes, which facilitate the synthesis of nanoparticles. Nanoparticle synthesis using fungus is economically viable and produces large amounts of nanoparticles when compared to bacteria and algae. Moreover, filamentous fungus possesses high bioaccumulation ability and high metal tolerance, is ease in downstream processing and is economically viable. Fungi have been reported to be capable of intracellular synthesis of gold nanoparticles (AuNPs), in which ultra-thin sections of fungal cells showed the presence of gold nanoparticles in the vacuoles of cells (Menon et al. 2017). Mukherjee et al. (2001) reported intracellular synthesis of silver nanoparticles (AgNPs) in *Verticillium*. Exposure of fungal biomass to aqueous solution containing Ag^+ led to the reduction of metal ions and formed AgNPs of size 25 ± 12 nm. TEM

Table 2 Synthesis of algal-based biogenic nanoparticles

Type of NPs	Algae	References
Gold (Au)	*Tetraselmis kochinensis*	Senapati et al. (2012)
	Chlorella vulgaris	Annamalai and Nallamuthu (2015)
	Lemanea fluviatilis	Sharma et al. (2014)
	Turbinaria conoides	Rajeshkumar et al. (2013)
	Stoechospermum marginatum	Rajathi et al. (2012)
	Sargassum muticum	Namvar et al. (2015)
	Padina gymnospora	Singh et al. (2013)
	Laminaria japonica	Ghodake and Lee (2011)
	Euglena gracilis	Dahoumane et al. (2016)
Iron (Fe)	*Sargassum muticum*	Mahdavi et al. (2013)
	Euglena gracilis	Brayner et al. (2012)
Copper (Cu)	*Bifurcaria bifurcate*	Abboud et al. (2014)
Silver (Ag)	*Caulerpa racemosa*	Kathiraven et al. (2015)
	Turbinaria conoides	Rajeshkumar et al. (2012)
	Chlamydomonas reinhardtii	Barwal et al. (2011)
	Caulerpa racemosa	Kathiraven et al. (2015)
	Cystophora moniliformis	Prasad et al. (2013)
	Sargassum muticum	Azizi et al. (2013)
	Sargassum longifolium	Devi et al. (2013)
Zinc (Zn)	*Sargassum muticum*	Azizi et al. (2014)

images further confirmed that the synthesized Ag nanoparticles are spherical in morphology.

Few yeast strains have also been exploited for the synthesis of nanoparticles. In a study by Sen et al. (2011), two different strains of *Saccharomyces cerevisiae* have been exploited for the synthesis of gold nanoparticles. In situ reduction of Au^{3+} to Au(0) was facilitated by providing small doses of γ-energy in the cell cytoplasm, and nano-sized Au^{3+} were observed within the nucleolus. Reductants extracted from yeast have been used as a reagent for the synthesis of gold nanoparticles. However, a smaller number of yeast species have been reported to be capable of nanoparticle synthesis.

Application of biogenic nanoparticles in environmental remediation

Nano-biotechnology-based environmental remediation is gaining popularity in recent years. Microorganism, being a biological entity, is considered to be a renewable source, which is easy to handle, cost-effective and demonstrates high metal tolerance (Narayanan and Sakthivel 2011). A list of biogenic nanoparticles and their application in removal of environmental contaminants are given in Table 4. The use of microbial platform for metal nanoparticle synthesis is a sustainable approach for the treatment of environmental pollutants. Several laboratory-based studies and field-level application of biogenic nanoparticles are being conducted to address various environmental issues. Recent advances in nano-bioremediation entail removal of heavy metals, inorganic and organic pollutants from groundwater, surface water, wastewater and soil. Nanoparticles produced via biological route display high reactivity and possess higher surface area than the chemically synthesized nanoparticles and have been reported to behave as oxidants or reductants, catalysts and adsorbents. Iron-reducing and iron-oxidizing bacteria are popularly being used for the preparation of nanoparticles. Biogenic iron oxides not only remove metals such as chromium, arsenic and cobalt through adsorption, but also reduce organic contaminants (nitro-aromatics) and promote dechlorination of aliphatic compounds. Iron oxides significantly remediate contaminants via oxidation and reduction processes (Castro et al. 2018). Biologically synthesized silver nanoparticles have been quite extensively studied and are reported as having good antibacterial and catalytic properties. Photo-catalytic degradation via silver nanoparticle has become a cost-effective and environmentally friendly technique for remediation of toxic organic contaminants from the environment (Aziz et al. 2015).

Removal of heavy metals

Heavy metals, by virtue of their teratogenic and carcinogenic properties, cause serious health issues to humans and other organisms. It therefore becomes imperative to find a route which removes heavy metals from environment in a sustainable way. Heavy metals such as arsenic and copper

Table 3 List of yeast- and fungus-derived nanoparticles

Type of NPs	Fungus and yeast	References
Gold (Au)	*Candida albicans*	Chauhan et al. (2011)
	Fusarium semitectum	Sawle et al. (2008)
	Epicoccum nigrum	Sheikhloo et al. (2011)
	Cylindrocladium floridanum	Narayanan et al. (2013)
	Neurospora crassa	Castro-Longoria et al. (2011)
	Hormoconis resinae	Mishra et al. (2010)
	Penicillium brevicompactum	Mishra et al. (2011)
	Saccharomyces cerevisiae	Sen et al. (2011)
	Fusarium oxysporum	Mukherjee et al. (2002)
Iron (Fe)	*Fusarium oxysporum*	Mirzadeh et al. (2013)
	Pleurotus sp.	Mazumdar and Haloi (2017)
Copper (Cu)	*Hypocrea lixii*	Salvadori et al. (2013)
	Aspergillus sp.	Cuevas et al. (2015)
Silver (Ag)	*Cladosporium cladosporioides*	Balaji et al. (2009)
	Aspergillus tamarii	Kumar et al. (2012)
	Aspergillus clavatus	Verma et al. (2010)
	Fusarium solani	Ingle et al. (2009)
	Amylomyces rouxii	Musarrat et al. (2010)
	Aspergillus niger	Gade et al. (2008)
	Fusarium semitectum	Basavaraja et al. (2008)
	Fusarium oxysporum	Ahmad et al. (2003)
	Aspergillus flavus	Jain et al. (2011)
	Verticillium	Mukherjee et al. (2001)
	Trichoderma reesei	Vahabi et al. (2011)
	Aspergillus oryzae	Phanjom and Ahmed (2015)
	Aspergillus clavatus	Verma et al. (2010)
Zinc (Zn)	*Candida albicans*	Mashrai et al. (2017)
	Saccharomyces cerevisiae	Mala and Rose (2014)

are common occurrences in industrial wastewaters emanating from mining and metallurgical processing industries. In a recent study, iron nanoparticles synthesized from natural consortium were reported to be capable of adsorbing arsenic, copper, zinc and chromium from wastewaters (Castro et al. 2018). Biogenic precipitates obtained from the cultures were magnetite (Fe_3O_4), vivianite ($Fe_3(PO_4)_2{\cdot}8H_2O$) and siderite ($FeCO_3$). These biogenic adsorbents demonstrated higher adsorption capacity and higher affinity for arsenate than for chromate. Copper and zinc were also adsorbed by organic components bound to the nanoparticle.

Groundwater and surface waters containing high concentrations of arsenic, Fe(II) and Mn(II) adversely affect the aquatic ecosystem and human health (Davolos and Pietrangeli 2013). Manganese (II)-oxidizing bacterium, *Pseudomonas* sp. QJX-1, isolated from soil of manganese mines was used in the synthesis of biogenic Fe–Mn oxides (BFMO). These oxides were found to be capable of oxidizing and adsorbing arsenic. The proposed mechanism involves an initial precipitation of BFMO on the surface of which Fe(II) was chemically oxidized to FeOOH and Mn(II) was biologically oxidized to form MnO_2, which together co-precipitated as Fe–Mn oxide to adsorb and oxidize As (Fig. 3). FeOOH has higher adsorption capacity with lower oxidation capability which is complemented by BMO which possesses higher effectiveness for oxidation. FeOOH and BMO, in consonance, bring forth the production of BFMO, which facilitates adequate adsorption and oxidation of As(III) and As(V). Simultaneously, BMO is also capable of oxidizing Fe(II) to FeOOH, which in turn further adsorbs remaining As(III) and As(V) (Bai et al. 2016), hence remediating three contaminants, viz. As (III or V), Fe(II) and Mn(II) in the groundwater.

Sulfate-reducing bacteria (SRB) could also be utilized to treat wastewater containing chromium (VI). These bacteria also facilitate removal of sulfate and chemical oxygen demand (COD) of wastewater by utilizing the organic compounds as their carbon source. Sorption experiments conducted on simulated wastewater under optimized conditions resulted in reduction of 81.9% COD, 89.2% Cr(VI) and 95.3% sulfate from synthetic wastewater (Verma et al. 2015). Saunders et al. 2018 also reported the use of SRB

Table 4 Bio-nanoparticles employed in the remediation of environmental contaminants

Nanoparticles	Organism	Remediation	References
Biogenic manganese oxide (BioMnOx)	*Pseudomonas putida*	Organic micro-pollutants (estrone, 17-α ethinylestradiol, diclofenac, ibuprofen)	Furgal et al. (2014)
	Pseudomonas putida MnB1	Heavy metals	Zhou et al. (2015)
	Pseudomonas putida MnB6	Pharmaceutical micro-pollutants	Forrez et al. (2011)
	Manganese-oxidizing bacteria (MOB) named as C-S1	1,2,4-triazole from chemical industrial wastewater	Wu et al. (2017)
	Desmodesmus sp.	Bisphenol A (BPA)	Wang et al. (2017a, b)
Biogenic Fe–Mn oxide (BFMO)	*Pseudomonas* sp. QJX-1	Arsenic-contaminated groundwater	Bai et al. (2016)
Nanoparticle synthesized using sulfate-reducing bacteria (SRB)	Sulfate-reducing bacteria	Arsenic-contaminated groundwater	Saunders et al. (2018)
		Chromium (VI), sulfate and COD removal from wastewater	Verma et al. (2015)
		Sorption of contaminants from mine drainage water	Jencarova and Luptakova (2012)
Biogenic palladium (bio-Pd) nanoparticles	*Klebsiella oxytoca* GS-4-08	Azo dyes containing wastewater	Wang et al. (2018)
	Shewanella oneidensis	Dehalogenation of ICM	Forrez et al. (2011)
		Trichloroethylene (TCE) from groundwater	Hennebel et al. (2009a)
Bio-Pd nanoparticle doped with gold (bio-Pd/Au)	*Shewanella oneidensis*	Dechlorination of halogenated micro-pollutants	De Corte et al. (2012)
Biogenic platinum nanoparticles (Bio-Pt)	*Desulfovibrio vulgaris*	Pharmaceutical products removal	Martins et al. (2017)
Algae-derived silver nanoparticle	*Chlorella pyrenoidosa*	Methylene blue (MB) dye	Aziz et al. (2015)
Biogenic gold nanoparticles (bio-AuNPs)	*Saccharomyces cerevisiae*	Quinclorac degradation	Shi et al. (2017)
	Cylindrocladium floridanum	Degradation of 4-nitrophenol to 4-aminophenols	Narayanan and Sakthivel (2011)
Nanogold bioconjugate (NGBC)	*Rhizopus oryzae*	Organophosphorus pesticides	Das et al. (2009)
Biogenic selenium nanoparticle	*Citrobacter freundii* Y9	Mercury from soil	Wang et al. (2017a, b)

for bioremediation of arsenic-contaminated groundwater. Biogenic iron sulfides also have the potential to remove zinc ions from mine drainage water, suggesting that this technique can remediate real wastewater too (Jencarova and Luptakova 2012). Hence, it could be concluded that SRB can be utilized as an efficient bio-adsorbent for the removal of sulfate and heavy metals from wastewater and groundwater.

Biogenic manganese oxide (BMO) synthesized from *Pseudomonas putida* MnB1 was employed for the removal of heavy metals present in the environment. BMO proved to be an excellent heavy metal adsorbent compared to the chemically synthesized manganese oxide (birnessite). The structural characterization (TEM and EDX analysis) of BMO produced is shown in Fig. 4a, b (Zhou et al. 2015). Figure 4c depicts amorphous, irregular and nano-sized materials which were different from chemically synthesized birnessite (regular shaped, crystalline having stick-like structure) as shown in Fig. 4d. The amorphous nature, high surface area and small size of BMO make it a good

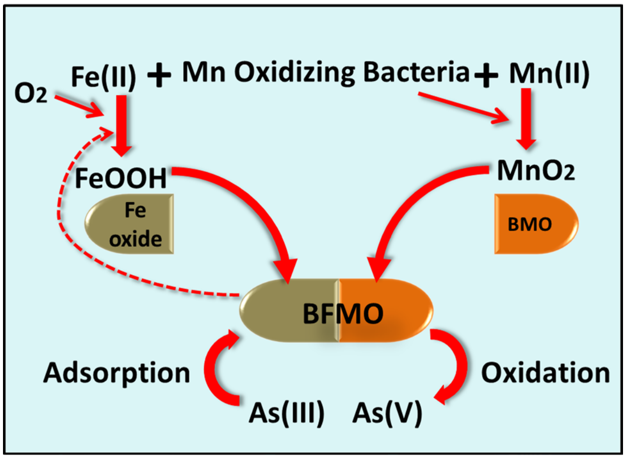

Fig. 3 Proposed mechanism of adsorption and oxidation of As(III) by BFMO

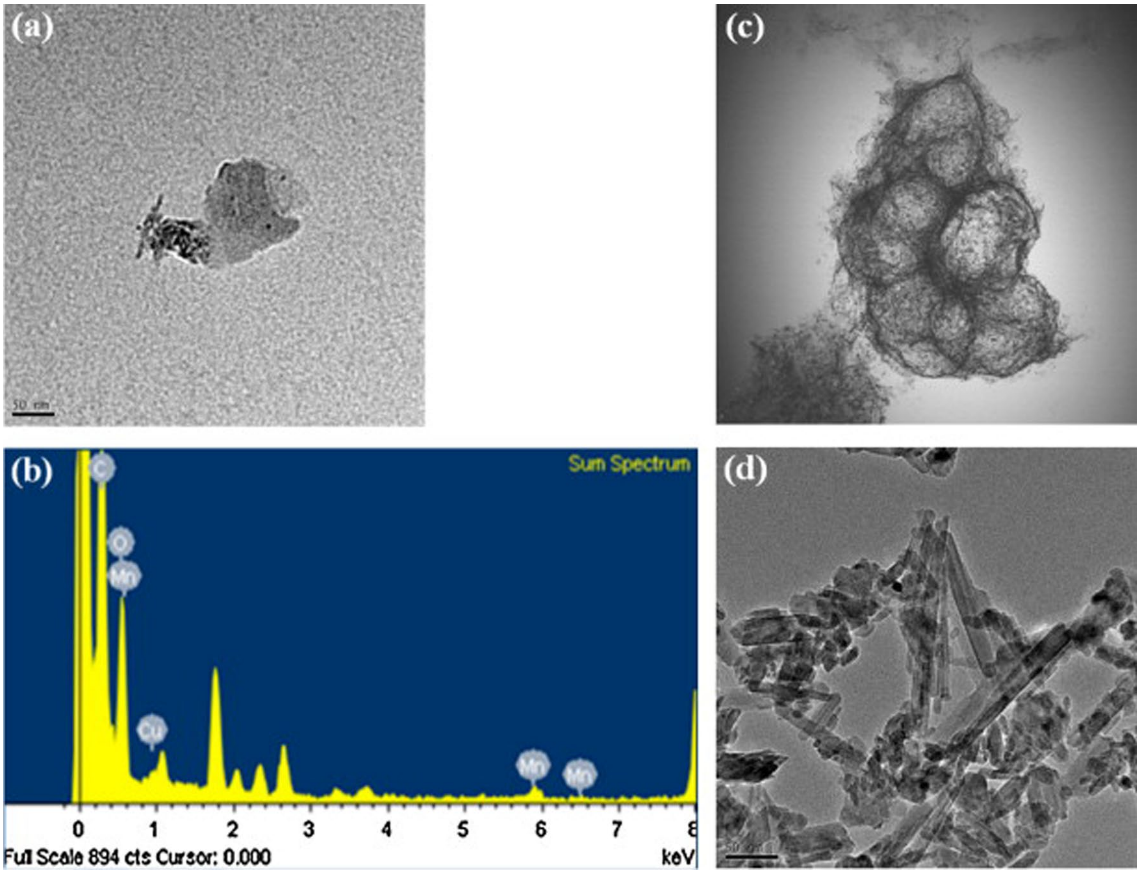

Fig. 4 TEM images and EDX analysis. **a** TEM image of BMO; **b** EDX analysis of BMO; **c** TEM image of BMO generated on the cell; **d** TEM image of birnessite. Reprinted from Zhou et al. (2015), Copyright (2015), with permission from Elsevier

adsorbent. The adsorption capacities of BMO for zinc, lead and cadmium were 7–8 times higher than those of birnessite and the adsorption capacities of heavy metals increased when pH and temperature were increased from 3 to 6 and 15 to 30 °C, respectively. The increase in adsorption capacity at higher temperatures also suggested that the adsorption was endothermic in nature (Zhou, Kim and Ko 2015).

Removal of organic pollutants

The use of biogenic nanoparticles for remediation of organic micro-pollutants is extensively being studied these days. This includes remediation of pharmaceutical products, dyes, halogenated contaminants and organophosphorus pesticides.

Removal of pharmaceutical products

The release of pharmaceutical products and other organic compounds into aquatic environment is a serious issue which has attracted the attention of researchers worldwide (Kümmerer 2009). Wastewater treatment technology using conventional methods mainly dealt with removal of BOD, COD and nutrients in higher concentration (ppm), but it has been found that these methods fail to remediate micro-pollutants in ppb levels. Pollutants in lower concentrations therefore find entry into aquatic bodies and the surrounding environment through effluents of wastewater and sludge (Ternes et al. 2004). The biogenic manganese oxide nanoparticles (BioMnOx) synthesized using *Pseudomonas putida* were used for the removal of organic micro-pollutants such as steroid hormones estrone, 17-α ethinylestradiol, diclofenac, ibuprofen and other micro-pollutants. Almost complete removal of estrone and 17-α ethinylestradiol was attained by employing biogenic manganese oxide nanoparticles. These particles were capable of removing organic micro-pollutants present in lower concentrations (ppb level) (Furgal et al. 2014).

Two biologically derived nanoparticles, namely BioMnOx produced by *Pseudomonas putida* MnB6 strain and biopalladium (Bio-Pd) synthesized by bacterium *Shewanella oneidensis*, were capable of removing several micro-pollutants from sewage treatment plant effluent. These nanoparticles were employed in laboratory-scale membrane bioreactors (MBR) to remove contaminants via oxidation or reduction techniques. In BioMnOx-MBR, significant reduction of naproxen (95%), ibuprofen (95%), diuron (94%), codeine (93%), N-acetyl-sulfamethoxazole (92%), chlorophene (> 89%), diclofenac (86%), mecoprop (81%), triclosan (> 78%), clarithromycin (75%), iohexol (72%), iopromide (68%), iomeprol (63%) and sulfamethoxazole (52%) was observed. Bio-Pd acts as a nano-catalyst to remove highly persistent iodinated contrast media (ICM) and dehalogenated compounds with novel reductive techniques (Forrez et al. 2011).

Martins et al. (2017) in a recent study investigated the potential of employing two biocatalysts (bio-platinum and bio-palladium) synthesized from *Desulfovibrio vulgaris, a* sulfate-reducing bacterium for remediating four pharmaceutical products (PhP): ibuprofen, 17b-estradiol, ciprofloxacin and sulfamethoxazole. Bio-Pt was found to be capable of higher catalytic role for the removal of PhP than Bio-Pd nanoparticles. Removal of 70% ciprofloxacin, 85% sulfamethoxazole and 94% of 17b-estradiol was reported. Moreover, Bio-Pt greatly reduced the estrogenic activity of 17b-estradiol, thus suggesting that a lesser toxic effluent was produced using this biocatalyst. Ibuprofen was, however, not removed by either Bio-Pt or Bio-Pd, but was biotransformed by using whole cells of *D. vulgaris,* fostering the idea that ibuprofen could be completely removed by sulfate-reducing bacteria in an anaerobic environment. Diclofenac, an anti-inflammatory drug, also finds its way into surface and drinking water in very low concentrations (nanogram/liter or microgram/liter) and is very sparingly biodegradable. Techniques such as ozonation have been adopted to degrade this contaminant, but it resulted in the formation of various by-products which were mutagenic in nature. The bio-Pd nanoparticles were therefore found to degrade some pharmaceutical compounds (Forrez et al. 2011), while others were not efficiently degraded. The catalytic activity of bio-Pd nanoparticles was improved by doping these biocatalysts with Au (0) (bio-Pd/Au) to remove diclofenac (De Corte et al. 2012). *Shewanella oneidensis* was employed for co-precipitation of bimetallic bio-Pd/Au nanoparticles, which later proved to be a good dechlorination agent for diclofenac. Bisphenol A (BPA), an endocrine disrupter, was degraded by algae-derived BioMnOx nanoparticles produced from *Desmodesmus* sp. WR1. The algae-generated BioMnOx were capable of degrading organic pollutants, similar to that of bacterial-derived BioMnOx (Wang et al. 2017a, b). These nanoparticles effectively removed approximately 72% of BPA through oxidative degradation.

Removal of dye and other pollutants from wastewater

Palladium (0) nanoparticle (bio-Pd) was produced using *Klebsiella oxytoca* GS-4-08 in fermentative condition and was found to reduce the azo dye. This may be helpful in designing and operation of bioreactor for the removal of azo dye from wastewater (Wang et al. 2018). Methylene blue (MB) is a recalcitrant organic compound which is highly toxic to aquatic organisms. Biological removal of methylene blue is very challenging due to its high toxicity. Aziz et al. (2015) evaluated the photo-catalytic activity of biologically synthesized silver nanoparticle (biogenic AgNPs) for degradation of MB dye under visible light irradiation and reported the synthesis of biogenic AgNPs using algal platform featuring *Chlorella pyrenoidosa*. The biogenic AgNPs demonstrated better photo-catalytic degradation of methylene blue when compared to commercially synthesized silver nanoparticles. Photo-catalytic activity of AgNPs is initiated by irradiation with visible light, thus enabling the movement of photoelectrons from the valance band to conduction band of nanoparticles. This leads to the formation of band gap, electron hole (e^-) in conduction band and creation of hole pair (h^+) in the valance band. High band gap increases the photo-catalytic activity of silver nanoparticles by forming non-radiative recombination of hole pairs and electron holes which are effective reducing and oxidizing agents, respectively. Oxygen adsorbs toward the conduction band of nanoparticles, entraps electrons and gets reduced to form anionic superoxide radical (O^{2-}). The superoxide radical thus formed id capable of accepting protons and forms hydrogen peroxide (H_2O_2), which further dissociates into hydroxyl radicals ($OH^{\cdot}$). Simultaneously on the other side, water is taken up by hole pairs and is oxidized to form hydroxyl radicals in the valence bands. The hydroxyl radicals and anionic superoxide attack the aromatic rings, hydroxylated rings and azo bonds, thereby leading to the degradation of MB to CO_2, H_2O, SO_4^{2-}, NO_3^- and NH_4^+ ions (Fig. 5).

Nitroaromatic compounds such as nitrophenols are also considered to be highly toxic contaminants and are commonly found in the effluent of dye industries, which find their way into the local water bodies. 4-nitrophenol is highly soluble and stable in water, posing significant environmental and public health risks as these have carcinogenic and mutagenic properties. Their degradation takes prolonged duration and may be accumulated deep in soil for an indefinite period. Nitrophenols have been listed as “priority pollutants” by USEPA (United States Environment Protection Agency), and their maximum allowable concentration is approximately 20 ppb. Thus, it becomes important to degrade these pollutants efficiently. The biogenic gold nanoparticles synthesized from filamentous fungal biomass, *Cylindrocladium floridanum*, have proven to be helpful in the catalytic degradation of toxic 4-nitrophenols into non-toxic 4-aminophenols (Narayanan et al. 2013).

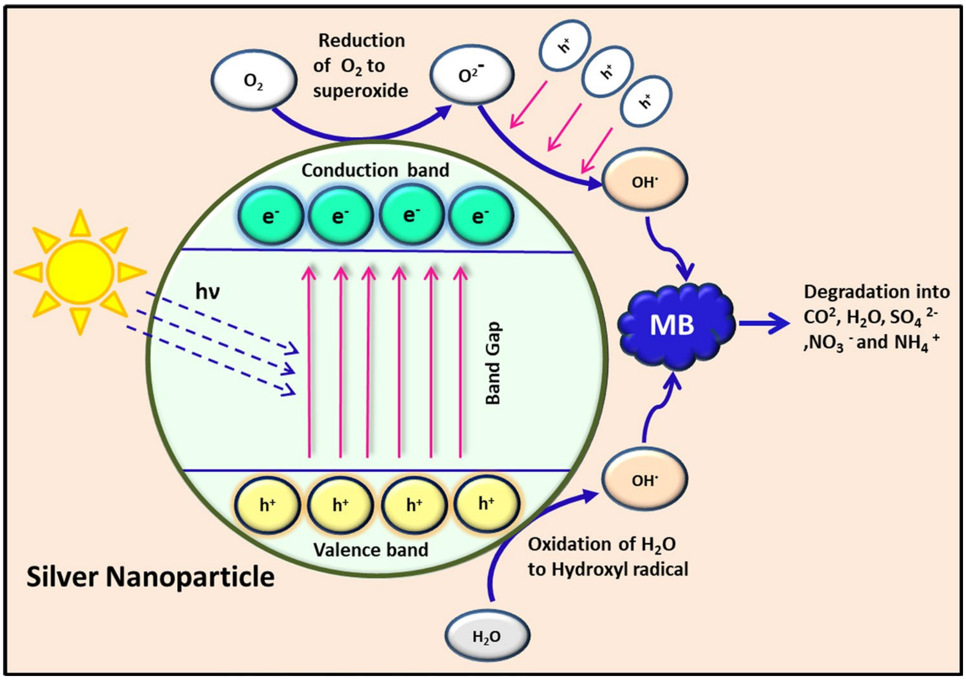

Fig. 5 Proposed mechanism of biogenic silver nanoparticle-mediated photo-catalytic degradation of methylene blue (MB)

Removal of halogenated contaminants

Trichloroethylene (TCE) is a chlorinated solvent and one of the most persistent pollutants in the groundwater. TCE finds its way into the groundwater through metal industry and textile industry effluents, as it is commonly employed to remove grease from textile and metal parts. A fixed bed reactor with encapsulated bio-Pd (biologically precipitated by *Shewanella oneidensis* grown on polyacrylamide, polyurethane, silica, alginate or coated on zeolites) resulted in 98% removal of trichloroethylene (Hennebel et al. 2009b). This technique could be used as an alternative to the existing remediation technology for TCE-contaminated groundwater and wastewater.

Quinclorac is a highly selective herbicide applied to control weeds in rice and turf fields. Its residues in soil after the harvest of paddy crops harm other susceptible crops and make their way to the aquatic system, manifesting adverse impacts on aquatic organisms (Resgalla et al. 2007). Several quinclorac degradation techniques such as microbial degradation, photodegradation and degradation via metal nanoparticles have been carried out, but all these methods have certain limitations. Shi et al. (2017) used gold nano-catalyst (AuNPs immobilized on NaOH-pretreated yeast, Au/SC_M) synthesized from pretreated *Saccharomyces cerevisiae* for reductive degradation of quinclorac. The chemical synthesis of AuNPs is costly and toxic (Narayanan and Sakthivel 2011). However, the microbial community provides a suitable platform for the synthesis of nanoparticles, making its synthesis inexpensive, rapid and environmentally friendly. One such microbe is yeast whose unique porous morphology makes it a potential bio-sorbent for the removal of organic pollutants and transformation of heavy metal ions. The Au/SC_M demonstrated increased catalytic activity and effectively led to dechlorination of quinclorac to 8-quinoline-carboxylic acid, which could also be reused for two consecutive dechlorination cycles.

Removal of organophosphorus pesticides from water along with disinfection

Nanogold bioconjugate (NGBC) synthesized using *Rhizopus oryzae* strain has been employed for the removal of organophosphorus pesticides and some microorganisms from water in a single-step treatment method (Das et al. 2009). Laboratory experiments were conducted using simulated wastewater containing *E. coli* (~ 103 cells/mL) and malathion (10 µg/L), parathion (5 µg/L), chlorpyrifos (12 µg/L) and dimethoate (8 µg/L). Five grams of NGBC was added to 100 mL of this wastewater and was incubated at 30 °C for different time intervals. At the end of the desired incubation period, NGBC was aseptically filtered using glass wool. After filtration, *E. coli* cell count and concentration of pesticide in the filtrate were analyzed. The concentration of the pesticides (Table 5) and *E. coli* density (Fig. 6b, c) in treated water were found to decrease significantly within 10 min as compared to control (Fig. 6a). The level of pesticides was found to be below the detection limit (< 1 µg/L), and *E. coli* disappeared completely (Fig. 6d) after 30 min of incubation. The control experiment with pure *R. oryzae* mycelia (without embedded gold nanoparticle) failed to kill *E. coli*. It was therefore concluded that NGBC could be used

Table 5 Concentration of pesticides and *E. coli* in simulated wastewater after NGBC treatment (Das et al. 2009)

Incubation time (min)	Malathion (µg/L)	Parathion (µg/L)	Chlorpyrifos (µg/L)	Dimethoate (µg/L)	*E. coli* (cell/mL)
Control (no biomass)	10	5	12	8	1.2×10^3
5	5	1.5	4	2	40
10	1.5	Not detected	1.2	Not detected	15
30	Not detected	Not detected	Not detected	Not detected	Not detected

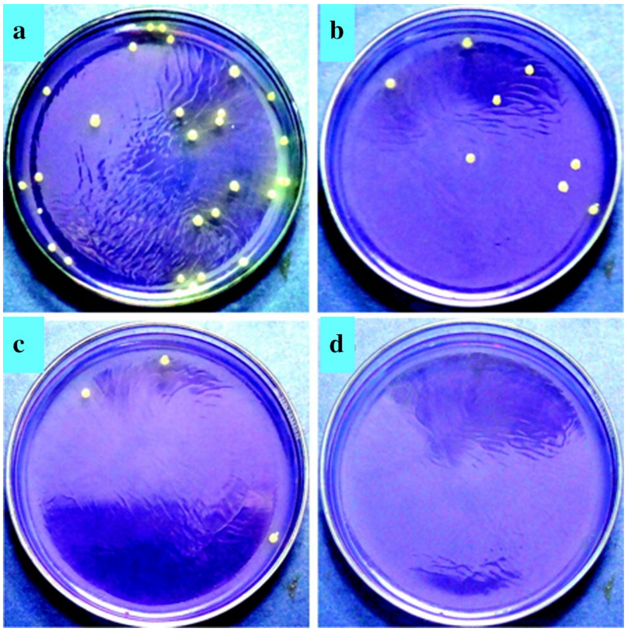

Fig. 6 NGBC-treated E. coli cells at different incubation periods: **a** 0 min, **b** 5 min, **c** 10 min, **d** 30 min. Reprinted with permission from Das et al. (2009), Copyright (2009) American Chemical Society

for one-step purification process for the removal of organophosphorus compounds.

Removal of contaminants from soil

Heavy metal contamination of soil is a cause of great concern. Fossil fuel combustion and its atmospheric transport result in an increase in soil mercury (Hg) concentration by a factor of 3–10 times (Xu et al. 2014). Several remediation techniques such as soil washing (Dermont et al. 2008), stabilization or solidification (Mulligan et al. 2001), thermal treatment (Busto et al. 2011) and biological techniques (Permina et al. 2006) have been employed to treat mercury-contaminated soil. Bioremediation of Hg-contaminated soil by biogenic selenium nanoparticles synthesized from *Citrobacter freundii* Y9 (isolated from an anaerobic sulfate-reducing bioreactor) was recently reported by Wang et al. (2017a, b). The characterization (SEM micrographs, EDS spectrum, XRD pattern, TEM micrographs) of *C. freundii* Y9 and selenium nanoparticles is shown in Fig. 7. In the presence of elemental mercury and elemental selenium, non-reactive HgSe was reportedly formed which is less toxic and chemically inert. Additionally, nano-selenium (0) can capture Hg (0) in soil under both aerobic and anaerobic conditions. Therefore, use of nano-selenium for immobilization of mercury is an efficient way to remediate such contaminated soils.

Recovery and reusability of biogenic nanoparticles

Biogenic nanoparticles show high regeneration efficiency and could be reused several times for the removal of environmental pollutants. NGBC was employed to adsorb pesticides and was reused for up to six cycles with the same removal efficiency (Das et al. 2009). Similarly, quinclorac degradation by dechlorination was carried out using Au/SC$_M$ and it was observed that 1 mg of Au/SC$_M$ could be used for three cycles with a removal efficiency of 61–100% and 46.7% (Shi et al. 2017). Martins et al. (2017) carried out the recovery and recycling of biogenic platinum and palladium nanoparticles for the removal of sulfamethoxazole, a pharmaceutical waste. Nanoparticles were employed for the removal of sulfamethoxazole for three consecutive cycles, and removal efficiencies obtained were 86%, 69% and 78%, respectively. Another study for the recovery of biogenic nanoparticles was carried out on bio-palladium nanoparticles (Hosseinkhani et al. 2015). Aforementioned studies suggest that biogenic nanoparticles have the potential of recovery and can be reused for many cycles, which makes them a promising candidate for the removal of environmental contaminants.

Limitations and future prospects

In comparison with physical and chemical processes, biosynthesis of nanoparticle is a slow process. Future studies should be focused on to reduce the reaction time for nanoparticle synthesis which will make the process more attractive. Furthermore, it is essential to identify and isolate the compound/s, which leads to reduction of metals in the synthesis process so as to make synthesis more efficient. Nano-bioremediation-based approaches reported till date

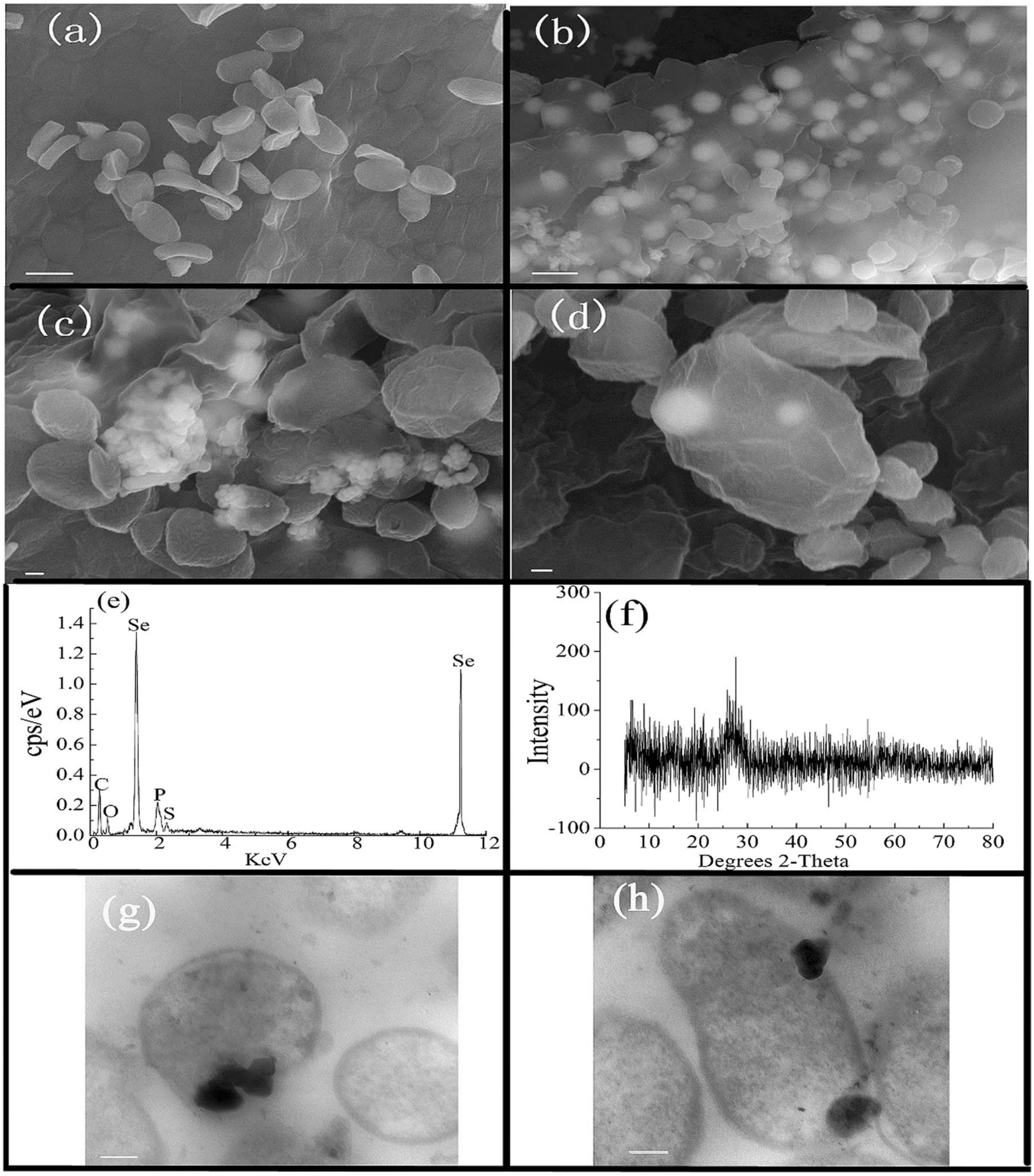

Fig. 7 Characterization of elemental selenium produced using *C. freundii* Y9. **a** Scanning electron microscopic (SEM) images of *C. freundii* Y9; **b**–**d** SEM micrographs of *C. freundii* Y9 grown in 1 mM selenite for 5 days; **e** EDS spectrum and **f** XRD pattern of red selenium particles produced by *C. freundii* Y9 grown in 1 mM selenite for 5 days; **g**, **h** transmission electron micrographs of the cells cultured in 1 mM selenite for 5 days. Reprinted from Wang et al. 2017a, b, Copyright (2017) with permission from Elsevier

have proven to be an effective technique in the treatment of several contaminants, especially micro-pollutants from the environment. However, these studies are limited to laboratory bench-scale studies and their efficiency in wastewater treatment plants is yet to be explored in detail. Synthesis of engineered nanoparticles with better removal efficiencies for priority pollutants is of utmost importance for their successful implementation at an industrial scale. The shape and size of nanoparticles play a crucial role in the bioremediation process, and hence the prospect of genetic engineering to control the particle morphology should be examined (Narayanan and Sakthivel 2011). It has also been reported that nanoparticles that are employed in the remediation of environmental contaminants lead to the formation of intermediate complexes, which imparts toxicity to the aqueous system. Hence, it is imperative to monitor the formation and fate of such complexes at various time intervals during the treatment process, and adequate steps need to be taken to remove these compounds.

Conclusion

Nanotechnology has a potential to mark a revolutionary change in the field of pollution control. Synthesis of nanoparticles using biological entities is a sustainable approach which could lead to nearly zero emission of toxic chemicals. It can be concluded from the reviewed literature that biogenic nanoparticles synthesized from bacteria, fungi and algae are capable of degrading several pollutants from highly contaminated water and soil matrix. Environmental remediation by employing biogenic nanoparticles is an ecofriendly and economically viable alternative to chemical methods, which renders possible solutions to various environmental problems such as removal of pesticides, dyes, halogenated compounds, heavy metals, pharmaceutical wastes from wastewater. Biogenic nanoparticles can efficiently remove heavy metals from contaminated soil. Harmonization of biosynthesis and environmental remediation is a sustainable treatment method that may contribute toward bringing about a revolutionary change in creating a sustainable environment.

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