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REVIEW

Bioremediation of heavy metals from wastewater using nanomaterials

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Abstract

One of the key reasons for water pollution is the existence of heavy metals in wastewater. Industrial wastewater and domestic sewage are one of the top reasons to cause water pollution. Increasing water pollution is a major concern for humans as it is not only affecting our health but also disturbing the economy and sustainable growth all around the world. Heavy metals affect human health as well as flora and fauna of the region because they are non-biodegradable. Heavy metals induce mutagenesis, cancer, and hereditary genetic disorders because they bind to the same sites in which essential metal ions bind and lead to the destabilization of structures and biomolecules. Conventional methods are well-established for the removal of heavy metals, but they have several drawbacks. Therefore, there is a requirement of alternative methods that can efficiently remove heavy metals. Nanoparticles hold immense potential, and they are used as adsorbents for heavy metal removal. Due to its unique properties like high selectivity and adsorption capacity, they are effective sorbents and extensively used for heavy metal removal from wastewater. This review addresses the significant issue of global wastewater crisis. Various methods of heavy metal remediation (HMR) and wastewater treatment are discussed including the application of microbes, plants, and nanoparticles in HMR. This review also highlights real-time applications and economic aspects of HMR. It has been concluded that the application of nanomaterials both, in the existing technologies and novel methods, will help in increasing efficiency, better operational costs, and enhanced outcomes.

Keywords Heavy metals · Microbes · Treatment · Nanoparticles

1 Introduction

Water is counted as a necessity to maintain the livelihood of any living being, especially humans who constitute 70% water. Drinking water is a basic source yet lacked by 785 million people, which includes 144 million people dependent on surface water for their

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survival. Worldwide, people are facing issues with water crisis due to its contamination with various pollutants (Verma et al. 2020). As per a recent report, at least 2 billion people use contaminated water for drinking purposes (World Health Organization 2019). To fulfill the human needs and desires for energy generation and various other functions, natural resources and the environment have been exploited which caused the degradation of water quality and environmental pollution leading to ecological imbalance. Harmful toxic pollutants present in the wastewater consist of a variety of compounds which leads to cause a serious threat to the ecosystem. Wastewater constitutes elements like phosphorus, nitrogen, and carbon which can lead to the growth of undesired life in aquatic bodies. It also contains dissolved inorganic constituents like sodium, calcium, suspended solids, biodegradable organics, pathogens, and heavy metals. Wastewater treatment can resolve this concern (Ferroudj et al. 2013). Heavy metal removal is one of the challenging issues and traditional methods possess some disadvantages (Qu et al. 2013). Conventional remediation methods generally include the physical elimination of pollutants. Physical remediation methods are not cost-effective and often disturbing the environment. (Mosa et al. 2016). To overcome the current situation, we need an efficient method for the elimination of heavy metals.

Nanotechnology is one such alternative way which can be used for heavy metals removal from polluted bodies. It is a rapidly growing sector and combined along with the major traditional methods for removal of heavy metals from wastewater (Yang et al. 2019). Nanoparticles are those materials which have size ranges from 1 to 100 nm and possess unique properties due to their high surface area to volume ratio. These materials have the capability to react with pollutants/contaminants (Chen et al. 2017). They can penetrate deeply into the contaminants which lead to the enhancement of their reactivity and ultimately increasing its efficiency to remove contaminants (Bystrzejewski et al. 2009). A range of nanomaterials has been developed with unique features and properties for wastewater treatment and decontamination of industrial effluents, surface water, groundwater, drinking water, etc. (Anjum et al. 2016). For heavy metal removal, various nano-materials are utilized. These materials are cost-effective, easily regenerated, and possess better removal efficiency. In the last few years, various advancements in the novel and cost-effective nanomaterials for environmental remediation, including wastewater treatment has been reported in literature. Therefore, its worth discussing application of nano-materials for wastewater treatment and effective heavy metal elimination. This review addresses various methods used for heavy metal remediation (HMR) and wastewater treatment. It provides details about application of microbes, plants, and nanoparticles in HMR. The application of nanoparticles and nanomaterials in HMR is listed for overcoming obstacles, improvement in efficiency, and overall enhancement of the process.

2 Heavy metals and their toxic effects

Heavy metals are elements that have a density of more than 5.0 g/cm^3. Chromium, Cadmium, Arsenic, etc. are common heavy metal sources (Coelho et al. 2015) (Fig. 1). Heavy metals have great biological significance in the functioning of both plants and animals, but only below the standard consumption concentration approved by the WHO. Heavy metal pollution is a major concern for developing and developed countries due to improper disposal (Roy and Bharadvaja 2020). Heavy metals are generally coming into wastewater by industrial and commercial activities (Emenike et al. 2018). The ones

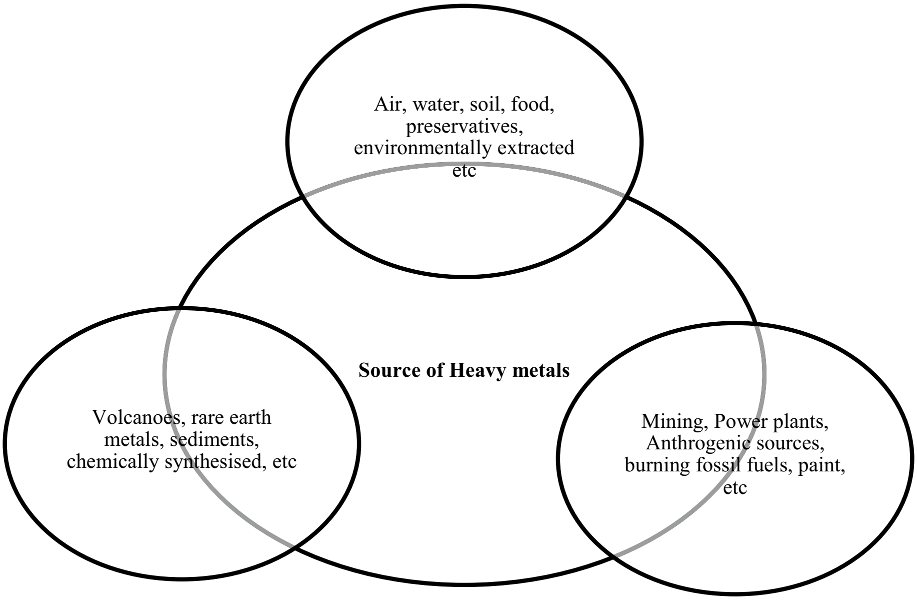

Fig. 1 Source of heavy metals

which enter via natural activities like volcanic eruptions, forest fire etch are generally less harmful than those entering into the environment via anthropogenic sources like mines, smelters, foundries, etc. (Jaishankar et al. 2014). They are one of the topmost pollutants found in wastewater and pose great harm to the environment, aquatic life, plants, and humans. Heavy metal pollution is caused due to anthropogenic activities like mining, untreated industrial wastewater disposal, as well as usage of pesticides and fertilizers made up of heavy metals in agricultural activities (He et al. 2013). The presence of heavy metal in higher concentrations can cause cell membrane damage, reduce seed viability, decrease pollen grains, and adversely affect both flora and fauna. These are very toxic as well as non-biodegradable in nature (Coelho et al. 2015). They possess a strong binding affinity toward the same sites which are used by the essential metal ions for various cellular structures. This causes de-stabilization and induces replication defects, consequent mutagenesis, and cancer (Perpetuo et al. 2011). Various physiological and biochemical activities are disrupted by heavy metals, and they not only induce harm to cells due to free radical population but also denature microbes. It can also reduce the bioremediation capacity of microbes (Bernard et al. 2018). Heavy metals such as copper in both forms copper (Cu (I) and Cu (II)), causes yield of reactive oxygen species (ROS) and that acts as soluble electron carriers. This led to high damage to various cellular components like cytoplasmic molecules, DNA, lipids, etc. (Giner-Lamia et al. 2014). Similar effects are also seen in the case of lead. Aluminum (Al) stabilizes superoxide radicals and leads to DNA damage (Booth et al. 2015). Heavy metals interact with substrates that can stop vital enzymatic functions and cause configurational changes in enzymes (Gauthier et al. 2014). Imbalance of ions caused due to adherence to the surface of the cell and entry via channels or carriers is also very common due to heavy metals (Chen et al. 2014). The harmful effects of heavy metal are listed in Table 1.

Table 1 Effect of various heavy metals

Heavy metal	Source	Toxic effects	Reference
Arsenic	Found with other metals in trivalent atomic state. Found in soil and water, pesticides, deep well water, mining sites, emission from coke oven	Increased risk of diabetes, mellitus, and hypertension, skin lesions, subjective neurological impairments, CNS damage in children, oxidative stress	Mochizuki (2019)
Lead	Paint, Dust, Water, Soil, Toys, Tableware, Folk medicines and cosmetics, Occupational sources and metal costume jewelry	Impairment of nervous system, blood disorders, Effect on kidneys and brain, cognitive behavioral disturbances, increases oxidative stress, interference with CNS system	Debnath et al. (2019)
Cadmium	Air, water, soil, and, sludge, sewage, Ni–Cd battery, plating	Affects cell proliferation, differentiation, and apoptosis. inhibits the activity of antioxidant enzymes, accumulates in kidney and liver, carcinogenic in humans, nephrotoxicity	Rafati et al. (2019)
Nickel	Found in abundance in the earth's crust and core. occurs in air, water, sediments, and soil	Respiratory cancer risks, Contact dermatitis; headaches; gastrointestinal manifestations; respiratory manifestations; lung cancer; epigenetic effect	Buxton et al. (2019), Genchi et al. (2019)
Chromium	Road dust containing chromium, metal treatment use, wood preservative, oil drilling sites, burning fossil fuels, oxidative pigment	Lung; the kidneys, liver, skin, and immune system may also be affected Cause gastrointestinal, cardiovascular, hepatic, hematological, reproductive and mutagenic problems Cr(VI) is termed as group 1 carcinogen	Shahisini et al. (2019)
Copper	Food, drinking water	Cause acute gastrointestinal symptoms, liver toxicity, infants can suffer from copper, tumor promoter	Taylor et al. (2020)
Tin	Anthropogenic sources as well as meat, sea food and some sweets as well	Divalent tin salts causes gastrointestinal irritation besides anemia and pain in the abdomen area	Filippini et al. (2019)
Europium	Nuclear rods, anthropogenic sources, rare earth metals	Dust of europium metal compounds can cause fire and explosive hazards. Europium chloride and Europium nitrate have high lethal values	Rim et al. (2013)
Cobalt	Naturally found in various forms and a part of numerous anthropogenic sources. Occupational, dietary and medical intake are some other sources of exposure	Hematological, endocrine dysfunctions and in extreme cases, malfunctioning MoM hip implants	Leyssens et al. (2017)

Table 1 (continued)

Heavy metal	Source	Toxic effects	Reference
Germanium	Mined, chemically synthesized or environmentally extracted	Germanium chloride cause irritation in eyes and germanium hydride is highly toxic. It can cause hemolysis and in severe cases can lead to death	Chen et al. (2011)
Mercury	Elemental for, inorganic form, organic form, volcanoes, caustic soda, Coal-fired power plant,	Blood level poisoning, lower intelligence quotient-IQ, huntell-russell syndrome, Hg vapors can cause serious respiratory diseases	Muthusaravanan et al. (20180

3 Conventional methods for wastewater treatment

Treating wastewater involves techno-economic, environmental, and social aspects. These aspects are taken into consideration before developing any method. Heavy metal removal requires its immersion as well as isolation because these contaminants are not easily deprived by any means of biological, physical, or chemical processes (Naz et al. 2015). The conventional methods which are in practice right now include chemical precipitation, photocatalysis, ion exchange, membrane filtration, and adsorption of inorganic materials, chemical oxidation, reduction, reverse osmosis, electrodialysis. Table 2 summarizes various methods and techniques for heavy metal remediation from wastewater. The methods included conventional methods, microbial methods, plant-based degradation, and nanomaterial-based heavy metal remediation and treatment of wastewater. This table helps to understand the difference better and draw out strategies to enhance the existing methods, while leaving scope for the development of novel methods.

These methods hold various superiorities like good controllability and resilience to a high amount of heavy metals present. The most commonly used method to treat wastewater is based on the activated sludge process in which carbonaceous and nitrogen compounds are oxidized by suspended bacteria to produce an effluent that is within the legal standards and poses minimal effect on the environment (Carolin et al. 2017). Contaminants occupy active sites by chemisorption or physisorption, whereas in polymer-based adsorbents, complexation and electrostatic attraction play important role in adsorption (Lata and Samadder 2016). Conventional methods have various disadvantages such as the production of waste by-products that are difficult to manage, high energy requirements, etc. These methods can be harmful to the environment as the material utilized is obtained from non-renewable resources. Physiochemical methods are very costly which makes it difficult to be applied in under-developed and developing countries. These methods also lead to secondary pollution, reducing soil fertility, hence making them unfit for agricultural practices (Sharma et al. 2018). Conventional methods also have major drawbacks like high-energy requirements, incomplete elimination of pollutants and production of toxic side-products. Therefore, use of microbes, i.e., bioremediation combined with other methods of treatment like physical methods can lead to better remediation techniques (Muthusaravanan et al. 2018) (Fig. 2).

4 Application of microbes in heavy metal removal

Many microorganisms can decompose metals without any chemical interruption, but this is inadequate on a larger scale. Remediation efficiency is a factor of microbial resistance against stress due to heavy metals (Naz et al. 2015). Henceforth, genetically engineered microbes can be a potential solution to this issue. Genetic engineering is a basic step in modifying the metabolic pathways used by these microorganisms. It will also prohibit harmful action due to the modulated activity of heavy metals. Modified microbes alter inorganic form to organic form by applying reactions such as by using oxidation–reduction (Coelho et al. 2015). Genetic engineering is useful in altering properties of microorganisms to gain desirable features, for example—speeded growth, resilience in harsh surroundings, variation in pH, as well as cultivation at minimum price. It also allows the progression of metabolic structure in microbes, while enabling heavy deposition of metals

Table 2 Comparison table between various methods of HMR

Name of method	Mechanism	Advantages	Disadvantages	Reference
Conventional methods	Chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption	Good controllability and resilience to high amount of heavy metals present	Low metal removal efficiencies for high operational costs production of waste by products that are difficult to manage, high energy requirements, lead to secondary pollution, reducing soil fertility	Renu et al. (2017), Kaushal et al. (2017) Muthusaravanan et al. (2018)
Microbial treatment	Biosorption and Bioaccumulation, passive and active mechanisms	Reduces energy consumption and cost, inhibits pathogens, eliminate odor and improves air quality	Low in process, limited due to presence of non-biodegradeable contaminant and may also cause toxicity of microbes	Anjum et al. (2016), Coelho et al. (2015)
Plant-based treatment	Phytodegradation, phytoaccumulation, phytoextraction, phytovolatilization, phytostabilization	Cost-effective, efficient, easy maintenance, and eco-friendly	Leaching of metals into groundwater besides persistence of soil amendments Produces waste requires wide area, proper set-up and location, lengthy process	Singh et al. (2015)
Nanomaterial based treatment	Single stage-treatment method, chelation, metal adsorption	Extraordinary adsorption capacity and reactivity due to surface effect, small size effect, quantum effect, and macro quantum tunnel effect	Agglomeration, few real life applications, use of toxic chemicals lack of extensive study, experimentation and documentation	Yang J et al. (2019), Qu et al. (2013)

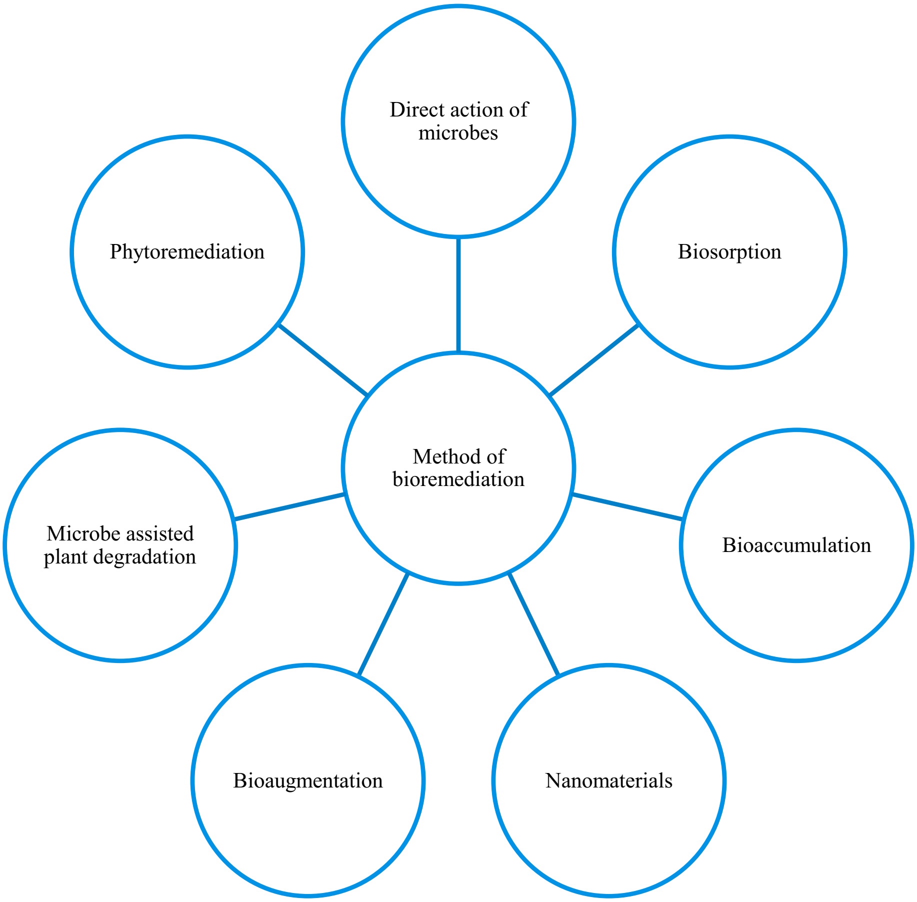

Fig. 2 Method of bioremediation

or reducing the harm produced by these metals, hence enhancing the depuration of water bodies (Wasilkowski et al. 2012).

Some fungi like, *Aspergillus* and *Penicillium* and some yeasts, for example, S. cerevisiae has shown the ability to eliminate pollutants, especially heavy metals from certain bodies. Microorganisms like E. *coli*, *Bacillus subtilis*, and Saccharomyces *boulardii* have also been applied in the elimination of heavy metals from wastewater (Gupta et al. 2016). Biologically driven heavy metal remediation technologies use biomass to eliminate heavy metals from effluents and it is a cost-effective, eco-friendly, and simple process. The mechanism used for metal to bind a particular spot in the biomass influences the efficiency of a bioremediation process. Microorganisms use passive and active mechanisms to eliminate metals from the solution. The proficiency of these methods is related to factors like the experimental conditions, the target pollutant, etc. In the process of bioremediation, microbes having biological activity, for example, algae, are used in their natural forms. Bioremediation is a solar-driven process that is more practically applied and publicly accepted. It works for both hydrophobic and organic compounds and eliminates secondary air and groundwater pollution as well. The method bioremediation can be broadly categorized in biosorption and the other as bioaccumulation (Coelho et al. 2015).

The mechanism followed by biosorption can be defined as a passive adsorption mechanism that is quick and of reversible nature. Physicochemical interaction, like adsorption, and crystallization which occurs between the metal and functional groups found on the surface of the cell retains the metals (Gadd et al. 2009). Factors like ionic presence in the solution, pH of the solution, its ionic strength, and biomass concentration along with temperature and particle size affects biosorption. According to Fomina and Gadd (2014), around a pH of 7, the extracellular surface of microbes contains anionic groups that provide binding spots to cationic heavy metals. Biosorption is not dependent on cell metabolism, hence suits for both living and dead biomass. Development of recent research technologies in the field of genomics could make it possible to study organisms having potential biosorption capacities which might have an ample number of bioremediation applications in the future. The process of bioaccumulation is defined by intracellular as well as extracellular processes where passive uptake has a limited role. This method does not work for dead mass (Kapahi et al. 2019). The complex process of accumulation varies according to the route of metabolism which is directed depends on the amount of metal present in the body (Fukunaga et al. 2011). Choi (2015) and Tan (2015) proved microbes having potential bioaccumulation capacities to help in improving bioaccumulation efficiency. The role of significant genes that are involved in bioaccumulation has been described by transcriptomics analysis (Shi et al. 2015).

Biosorption is less expensive than bioaccumulation because bioaccumulation takes place in the residence of living cells which need to be sustained, while biosorption can take place with industrial waste. The major costs in biosorption are contributed by transportation and production of biosorbent. Another significant factor is pH, which influences both the processes. Biosorption can work in a wider range of pH, while bioaccumulation is restricted to a specific pH range and any significant change will affect the living cells. Selectivity is better in the case of bioaccumulation, whereas the rate of removal is better in biosorption as mechanisms occur at a faster rate as compared to the intercellular accumulation which is required in bioaccumulation (Malini et al. 2020). The reuse of bioaccumulation is limited, whereas biosorbents can be regenerated and reused. Bioaccumulation requires more energy than biosorption due to energy demands by the living cells. In the case of bioaccumulation, biomass cannot be used for other purposes (Fosso-Kankeu et al. 2014). Microbial treatment of wastewater has many advantages like it reduces energy consumption and cost. This method inhibits pathogens, eliminate odor, and improves air quality. Different microorganisms adapt various pathways to survive and interact with inorganic metals, like heavy metals. Biological wastewater treatment is widely accepted, but they have some major drawbacks like slow in the process, limited due to the presence of a non-biodegradable contaminant, and may also cause toxicity of microbes (Anjum et al. 2016).

5 Application of plants in heavy metal removal

Phytoremediation is a plant-based technique applied in the removal of heavy metals. It has various advantages like plant vegetation done for this process where plantation avoids soil erosion. It is relatively inexpensive and even contaminated plants can produce 20–30 tons of ash per 5000 tons of soil. It is based on various mechanisms such as phytodegradation, phytoaccumulation, phytoextraction, phytovolatilization, phyto-stabilization, etc. These processes are cost-effective, efficient, and eco-friendly. Phytoremediation can be applied to both genetically modified and non-modified plants to curate contaminate land and water bodies (Singh et al. 2015). Different plant species are selected from a variety of plants based on factors such as their capacity to treat against certain contaminants. Plants that are well adapted with the local conditions of the area have good root structure, the ability to grow in the soil present, rapid growth, and easy maintenance are preferred for this method. Non-native species are avoided, because the plants that are harmless in other environments may raise concerns in a particular environment (Kennen et al. 2015). Plants such as Poplars (*Populus*), Willows (Salix), Eucalyptus, are reported to have phytoremediation capacity (Muthusaravanan et al. 2018). Legumes such as cowpea, clover, and alfalfa play an important role in phytoremediation. *A. fruticosa* was also studied for metal accumulation in contaminated soil, and it was found that more than 15 g kg^{-1} contaminated soil can be remediated (Cui et al. 2016). However, leaching of metals into groundwater besides the persistence of soil amendments is a drawback to this enhancement. Genetically modified plants can be applied for increasing tolerance to certain metals and enhancing their performance in extreme conditions. Various agricultural techniques like adding fertilizers or methods like land farming might also help enhance phytoremediation. Phytoremediation also produces some waste hence, it also needs proper disposal restrictions and management to avoid the contaminated biomass from entering the food chain. Trees are usually cut down after the phytoremediation process and used to make furniture or other wood products (Muthusaravanan et al. 2018). In plant-based remediation, short roots of the plant are unable to decontaminate a higher amount of heavy metals. However, trees those have longer roots and decontaminate better than plants, but still need a better design to work efficiently. It is important to realize that plants that absorb toxic metals will disturb and contaminate the food chain as well. Another drawback of this process is that it needs a wide area, proper setup, and location. The resultant products of the process are non-consumable and the process may take years to decontaminate an area. Phytoremediation can be combined with other branches of bioremediation to produce better outcomes (Parmar et al. 2015). For instance, phytoremediation combined with bio-fortification is a great method for trace element extraction. Bañuelos et al. (2015) extracted selenium from broccoli and carrots growing on land enriched Se-enriched hyperaccumulator *Stanleya pinnata* by biofortification.

6 Application of nanoparticles (NPs) in bioremediation of wastewater

Nanomaterials are classified as materials having 1–100 nm size. Nanoparticles (NPs) are very tiny particles that show quantum effects by confining their electrons. They hold various special and exclusive visible properties due to their size. These hold applications in various fields like photonics, catalysis, electronics as well as biomedicine (Yadav et al. 2017). Nanoparticles can possess significantly varying properties from their bulk counterparts, hence leading us to the opportunity to develop new materials that have a variety of applications in the industry (Fig. 3).

Nanomaterials can make wastewater treatment more energy efficient by using a single-stage treatment method which can eliminate different contaminants present in wastewater (Kamat et al. 2002). Nanoparticles are used as adsorbents in wastewater treatment. Various researchers have reported that nanoparticles possess unique structural properties such as high selectivity and adsorption capacity, due to which it is found effective to eliminate

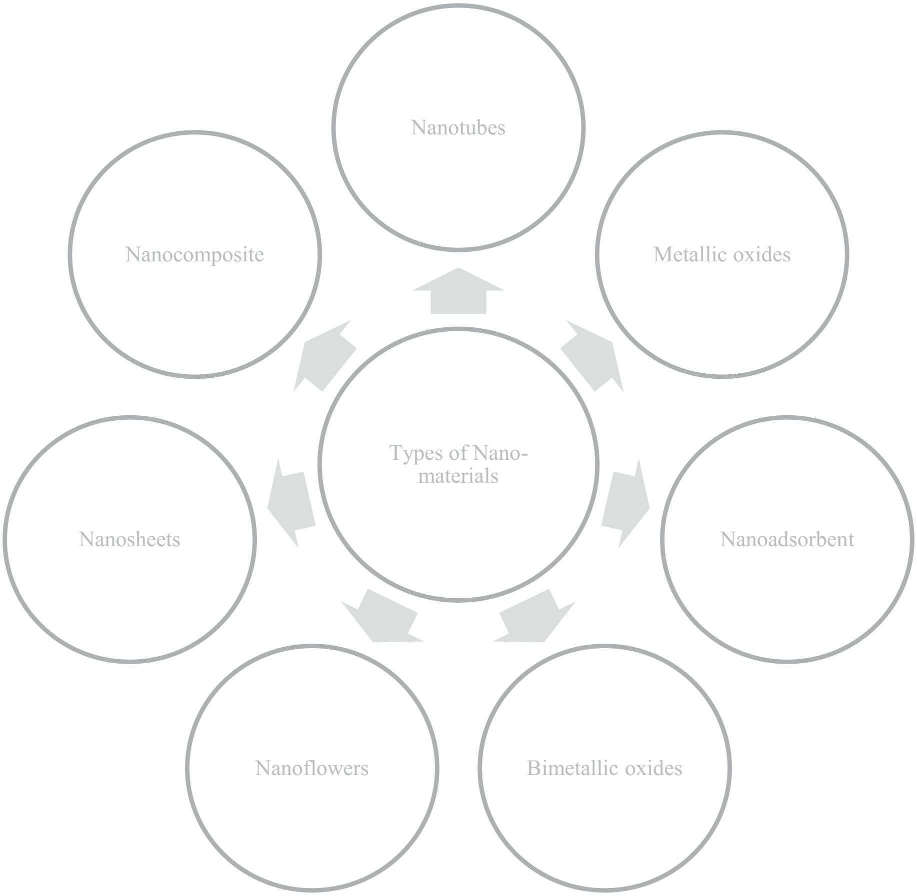

Fig. 3 Types of nanomaterials

heavy metal ions present at low concentrations in wastewater (Mallikarjunaiah et al. 2020). Due to their high surface area to volume ratio, these are suitable for the absorption of heavy metals or other pollutants (Singh et al. 2017). Nanomaterials can penetrate deeper, increases reactivity, and efficiently removes heavy metals (Bystrzejewski et al. 2009). Recent research emphasizes on the potential use of materials like carbon nanotubes, nanocomposite, nano-spheres, nanofibers, and nano-wires combined with conventional technologies for wastewater treatment which can be helpful for the elimination of various organic as well as inorganic pollutants, including heavy metals (Prasad et al. 2019). The diffusion potential of nano adsorbents is influenced by the amount of heavy metal present as well as the external surface area available. Diffusion on pores of adsorbent is followed by diffusion on the external surface (Lata and Samadder et al. 2016). Many factors affect the properties of nano-adsorbents such as the size of the sorbents, surface chemistry, shape, agglomeration state, and fractal dimension they possess, the chemical composition in which they are present, crystal structure as well as solubility (OECD et al. 2010). Unlike bulk materials, nanomaterials offer modifications at the atomic level which opens up many novel characteristics that are not offered by bulk materials (Subramaniam et al. 2019).

7 Nano-adsorbents in heavy metal removal

Nano-adsorbents have various categories such as carbon-based, metal oxide-based, and polymeric nano adsorbents. Nanoadsorbents based on carbon, like carbon nanotubes, are used for its fast kinetics in its oxidized state (Li et al. 2003). Ihsanullah et al. (2016) reported the mechanisms that were used to adsorb heavy metals from wastewater to include physical adsorption, chemical reactions, electrostatic binding, etc. However, adsorption ability in these nano adsorbents might increase by modifying the surface using acid and grafting functional groups. According to Bhanjana (2017), a functional group is a prominent adsorption site for metal ions, promptly by chemical interaction and electrostatic binding. Graphene oxide (GO) is another carbon-based nanomaterial. Modified Hummer's method is used for developing GO nanosheets from graphite and functional groups like hydroxyl and carboxyl, are present on the surface of nanosheets, leading to high sorption efficiency. Graphene oxide has some limitations, like high synthesis cost and the possibility of leaching. Gopalakrishnan (2015) showed that this issue can be addressed by attaching these nanosheets on a mixed matrix membrane. Tabesh et al. (2018) discussed nano adsorbents which are based on metal oxide, like iron oxide, titanium dioxide, nickel oxide, etc. are cost-efficient, have high adsorption capacity, and can easily be regenerated. Adsorption ability possessed by these particles depends on the size of the particle. On decreasing particle size, adsorption capacity increased. These nano adsorbents are regenerated by varying pH or chemical nature of the contaminant body and their efficiency remains the same for several generations (Qu et al. 2013). Iron oxide nano adsorbents are efficient heavy metal eliminators as well as simplifies recovery (Recillas et al. 2011). Besides Fe_3O_4, zero-valent iron-based nano adsorbents might as well be applied in heavy metal removal. Bimetal oxide magnetic nanoparticles like Fe–Mn, Ce-Ti, Mn-Al show higher adsorption capacity than single metal oxide nanoparticles (Babaee et al. 2018). Fe_3O_4, Mn_3O_4, and $MnFe_2O_4$ bimetal oxide nano adsorbent showed exponentially higher arsenic adsorption capacity (Lata and Samadder 2016). Pandey (2015) reported that agglomeration is a common limitation of nanomaterials which can be overcome by the use of polymer-based nanocomposites such as Resin. Resin act as a carrier for zero-valent iron nanoparticles, which in turn adsorb the contaminants, for instance, heavy metals (Fu et al. 2013). Metal interaction between polymer-based nanocomposite and metals is based on the process of chelation between metal ions and carboxylate anions (Shokati Poursani et al. 2017).

8 Silver based nanomaterial in heavy metal removal

Various reports suggested that metallic nanoparticles can remove heavy metals. There are some reports available in the literature where silver nanoparticles interact with contaminants such as mercury, cadmium, chromium, etc. A study reported the use of silver nanoparticles in which mercaptosuccinic acid is used and supported by activated alumina for mercuric ion elimination from contaminated waters. It was found that silver nanoparticles showed better mercuric ion uptake efficiency (Sumesh et al. 2011). Ganzagh (2016) used silver supported nano mesoporous silica for the elimination of mercury from wastewater and reported that the nanomaterial was able to absorb the mercury ions effectively. Another study reported the use of zero-valent Ag nanoparticles which can be produced by using leaf extract of *Ficus Benjamina* for effective removal of cadmium. The removal efficiency was increased when the concentration of nanoparticles increases (Al-Qahtani 2017). Shittu and Ihebunna (2017) developed Ag nanoparticles by using leaf extract of *Piliostigma thonningii* besides evaluating the potential role of these particles in heavy metal removal from laboratory prepared wastewater. Ali et al. (2018) indicated the role of Ag nanoparticles impregnated cotton in the removal of mercuric, chromium, cobalt, lead, and nickel ions from contaminated wastewater and found that mercuric ions reported having maximum adsorption capacity on nanoparticles surface. Samrot et al. (2019) synthesized silver nanoparticles from gums of *Azadirachta indica, Araucaria heterophylla*, and *Prosopis chilensis* and demonstrated its potential role in chromium removal. In another report, Ag nanoparticles were developed in a similar manner using leaf extract of *Prosopis juliflora* ,and they are encapsulated using chitosan. Chitosan encapsulated silver nanoparticles showed 81% of copper ion absorption (Malini et al. 2020).

9 Gold based nanomaterial in heavy metal removal

Gold nanoparticles are being comprehensively applied in the detection and elimination of heavy metals. Gold is an excellent choice as a nanoparticle to adsorb heavy metals. Gold nanoparticles showed excellent in the removal of heavy metals and possess high selectivity toward various target species (Fidelis et al. 2014). AuNPs with different sizes and shapes were studied for the effect on the removal of Hg^{2+} (Kamarudin and Mohamad 2010). It was seen that due to the absence of surface protector AuNPs (gold nanoparticles) reusability is affected as they tend to aggregate into clusters (Rodriguez-Perez et al. 2011). This can however be solved by immobilizing them on the surface of Al_2O_3. Adsorption capacity can be increased by applying $NaBH_4$ as the reducing agents for Hg^{2+} from 0.27 to 4.065 AuNPs-poly (dimethylsiloxane) nanocomposite foam has six times higher removal capacity against organic compounds in water that of the poly (dimethylsiloxane) foam without AuNPs (Gupta and Kulkarni 2011). Gold nanoparticle adsorbents have a characteristic binding affinity for Hg^{2+} ions with a dissociation constant of 0.3 nM, while Al_2O_3 adsorbents have slightly less dissociation constant of 52.9 nM. Au NP– Al_2O_3 adsorbents show a great affinity for mercuric species and few other metal ions as well (Lo et al. 2012). This could be due to the synergic effect. The AuNP– Al_2O_3 adsorbent removes mercury species with more than 97% efficiency, and the method is cost-efficient, effective as well as stable (Lin et al. 2013).

10 Iron based nanomaterial in heavy metal removal

Nanocomposites that are made of iron oxide encapsulated in macroporous silica (Fex-MOSF) reported high-arsenic absorption capacity. As compared to other nano-adsorbents, iron-based composites adsorb 46 times higher (Parvin et al. 2019). High sorption affinity is observed by nanoscale hydrated iron (III) oxide (HFO) particles toward both forms of arsenic and the required contact time was also very less (4 min) (Cumbal Sengupta 2005). Tahar et al. (2018) reported that maghemite nanoparticles are highly efficient in the elimination of chromium (Cr (VI) from an aqueous solution than magnetite derivatives nanoparticles. Hence, the competition between then for binding with chromium species against commonly coexisting ions in water such as Na, Ca, Mg, Cu, Ni, NO_3, and Cl is very low (Hu et al. 2005). Nassar (2012) were studied the role of Fe_3O_4 in the elimination of lead ions from contaminated water. The highest adsorption capacity of 36 mg/g for Pb (II) was observed. The application of Fe_3O_4 super-paramagnetic nanocomposites which are coated with ascorbic acid by hydrothermal method showed effective arsenic removal from the wastewater. Feng et al. (2012) reported that the highest adsorption capacity observed for As (III) was 16.56 mg/g, while 46.06 mg/g for As(V). Recillas (2011) reported that Fe_3O_4 possesses a high adsorption capacity of 83 mg/g in case of lead ions. With the application of the co-precipitation method, metal oxide NPs possess low magnetic behavior which makes it smoothly separable through using a magnetic field. Fe-Ti bimetallic oxide-coated magnetic Fe_3O_4 nanocomposite was able to eliminate fluoride from drinking water. Zhang et al. (2014) prepared nanocomposite by co-precipitation method and observed that these nanocomposites showed a high adsorption capacity of 57.22 mg/g.

11 Copper based nanomaterial in heavy metal removal

Hassan et al. (2009) reported that the optimum adsorbent quantity for removal of cadmium (II) ions as well as nickel (II) ions was 0.1 g, and after this removal, the percentage increased slightly. A study reported that copper nanoflowers act as good adsorbents of Pb (II) in contaminated water, due to the porosity and high-surface area higher removal efficiency was observed (Bhanjana et al. 2017a, b). A study reported that carbon with silver–copper mixed oxides have great removal efficiency for Pb and Fe. It was seen that when the number of copper oxide nanoparticles increased, the efficiency of heavy metal removal was also increased. This is possibly due to the increase in the surface for adsorption (Bazana et al. 2019).

12 Cerium based nanomaterial in heavy metal removal

A study reported that CeO_2-CNTs were able to remove As (V) anions and As (V)-loaded CeO_2-CNTs are easily and effectively regenerated (Peng et al. 2005). CeO_2 nanoparticles can efficiently remove chromium ions from water at a normal pH range. Suspended cerium oxide nanoparticles stabilized with hexamethylenetetramine were applied in chromium (VI) removal from pure water and showed the potential to treat wastewater as well (Recillas 2011). Another study reported that CeO_2 nanoparticles sowed higher Pb (II) elimination proficiency as compared to Fe_3O_4 and TiO_2. The drawback of CeO_2 is its increased phytotoxicity, however, TiO_2 and Fe_3O_4 NPs do not show any such toxicity (Recillas et al. 2011). In a study, cerium oxide nanoparticles are applied in both single as well as multicomponent aqueous systems as nano adsorbents to efficiently eliminate Cd (II), Pb (II), and Cr (VI) from the aqueous solutions. Lead's sorption capacity was unaffected by the pH, whereas cadmium and chromium were affected. The maximum sorption capacities observed were 93.4 mg in the case of cadmium at pH 7, 128.1 mg in the case of lead at pH 5, and 34.4 mg in the case of chromium at pH 5 (Rodríguez et al. 2015).

13 Aluminum based nanomaterial in heavy metal removal

Sheela and Nayaka (2012), suggested that γ-Al_2O_3 NPs adsorbs lead ions more due to their high electronegativity and hydrolysis over cadmium ions. Alumina based nano adsorbent was also studied for the removal of Zn (II) ions. The contact time required for removal was 4.5 h and maximum adsorption capacity of 1047.83 mg/g at pH 7 was observed (Bhargavi et al. 2015). Polyol-y-sineresorcinol wrapped γ-alumina nanotube reported high Cd (II) adsorption capacity (220 mg/g) as compared to γ-alumina nanoparticles (Hossein Beyki et al. 2017). Shokati Poursani et al. (2017) reported that γ-Al_2O_3 nanomembranes showed higher adsorption capacity for chromium. GO infused on mixed matrix membrane highly attracts or supports adsorption of chromium ions (Cr (VI)) besides other heavy metals at a pH range below 7. A study reported that γ- Al_2O_3 nanoparticles can adsorb lead and cadmium and reusability of nanoparticles were up to 3 times (Tabesh 2018).

14 Titanium based nanomaterial in heavy metal removal

TiO_2 is a metal oxide which holds various applications in the industry due to its stable and safe nature, ranging from cosmetic products to heavy metal remediation. It also has good crystallinity with less bandgap and a stable recombination rate, which makes it excellent for heavy metal remediation (Hashimoto et al. 2005). Titanium is used for the elimination of lead, copper, and arsenic in the form of anatase nano adsorbent. A study also reported that TiO_2 can remove lead ions with an adsorption capacity of 159 mg/g (Recillas 2011). In a study, titanium adsorbent showed the highest adsorption for lead (31.25), copper (23.74), and arsenic (16.98 mg/g) where pH increase leads to an increase adsorption capacity in the case of lead and copper (Kocabaş-Ataklı and Yürüm 2013). Application of hybrid material with ZnO and TiO_2, which is mesoporous showed a high surface area between 120–332 m2/L, and the overall cost of the adsorption process was reduced as the nano adsorbent can be reused for up to 3 times due to its microsized-structure (Sharma et al. 2019).

15 Manganese based nanomaterial in heavy metal removal

Nanomaterial made up of Fe–Mn binary oxide is efficient for removal of both As (V) and As (III) and completely oxidized As (III) to As (V). Manganese-iron oxide ($MnFe_2O_4$) nanoparticles require very short contact time and report the highest chromium adsorption capacity due to the electrostatic attraction (Hu et al. 2005). Fe–Mn binary oxide consists of an increased number of surfaces OH groups leading to twice as higher adsorption than $MnFe_2O_4$ and $CoFe_2O_4$. 0.1 M of NaOH can regenerate 80–90% this nanomaterial within a contact period of 24 h, the long contact time required for regeneration was one of its drawbacks (Zhang et al. 2010). MnO has also shown efficiency in the elimination of arsenic from wastewater (Wang et al. 2011). In a study, to understand the removal of heavy metals, $MnFe_2O_4$ magnetic nanoparticles were synthesized with a coating of amorphous oxide shells of Mn-Co and the adsorption rates were 386.2 mg/g for Cu (II), 481.2 mg/g for Pb (II), and 345.5 mg/g for Cd (II) (Ma et al. 2013). A study reported that GO- $MnFe_2O_4$

magnetic nanohybrids able to remove Pb(II) from water very efficiently (673 mg/g) (Kumar et al. 2014).

16 Other nanomaterials for heavy metal removal

Zirconium titanium oxide microspheres were studied for Cr (VI) anions removal. These nanoadsorbents vary in compositions of Zr content ranging from 0% Zr to 100% Zr. It was found that these binary oxides showed elevated adsorption capacities, i.e., more than 25.40 mg/g. Microspheres containing 30% Zr showed highest adsorption capacity of 29.46 mg/g (Chen et al. 2012). Wei et al. (2018) used hollow hydrous Zirconium (IV) oxide (HHZO) nanoparticle beads for heavy metal removal and highest adsorption capacity of 104 mg/g was observed. HHZO beads showed various advantages like enhancement in stability, easy phase separation and low energy consumption in flow-through systems (Wei et al. 2018).

Effective adsorption of Pb (II) and Cd (II) was observed using MgO (Li et al. 2003). In a study, magnesium ferrite nanocrystallites were used for the elimination of arsenic from contaminated bodies. In a study, it was reported that MgO nanoparticles showed great potential as an adsorbent in the elimination of lead and chromium where maximum absorption was observed at pH more than 7 (Cai et al. 2016). Nano-plates and porous nanosheets made out of ZnO have been extensively applied in the elimination of Cu (II) from contaminated water bodies (Wang et al. 2010). These possess exclusive nanostructure of altered ZnO nano-adsorbent resulting in increased elimination proficiency of copper ions owing to its unique micro/nanostructure. ZnO nano-rods which are mesoporous possess high elimination efficiency of lead and cadmium (Kumar et al. 2013). Chromium metal can also be removed from wastewater using zinc oxide nanomaterial and the removal percentage can be increased by increasing the contact period. The effect of contact time on ZnO sorbent was measured over a range of 45 to 240 min. Equilibrium is observed at 210 min in which the highest removal percentage of 53.1% was observed. The removal efficiency is because of the high surface area of the sorbent available for Cr (VI) ion adsorption.

A study reported that nickel oxide and zinc oxide are efficient in the removal of cadmium and lead from contaminated water. NiO nanoparticles show a higher affinity for lead ions than cadmium ions (Sheela and Nayaka 2012). Synthesis methods also influence the adsorption and removal efficiency. Out of the two methods used to prepare NiO nanoparticles, the organic solvent method was more preferred than precipitation for the elimination of lead ions from wastewater. The contact time required to achieve the equilibrium was nearly 2 h. NiO is also acting as a potential catalyst in wastewater treatment (Mahmoud et al. 2015).

17 Nanotubes for heavy metal remediation

Graphene sheets are used to develop single-walled or multi-walled carbon nanotubes (CNT) (Jiang et al. 2015). These nanotubes varying in their composition due to the difference in the procedure of synthesis and purification. They usually have functional groups like the hydroxyl group, ketone group, and carboxyl group. Other such functional groups can be attached by oxidation of carbon nanotubes with catalysts such as Pd, Ni, or Pt. The functional groups can be eliminated by heat treatment at a temperature as high as 2200 °C.

Carbon nanotubes have a few drawbacks like low dispersion ability, separating problems, and low size of the particles. As a solution, researchers altered ordinary CNT into multi-wall carbon nanotubes (MWCNT), which can be applied to eliminate metals such as manganese, lead, and copper (Tarigh and Shemirani 2013). A study reported that coated CNT showed improved elimination efficiency as compared to other CNTs (Gupta et al. 2015). Multi-wall CNT results in elevated Cd (II) adsorption efficiency hence, recommended for cadmium removal from contaminated water (Bhanjana et al. 2017a, b). Copper, zinc, and lead can be eliminated by maghemite nanotubes, and the highest adsorption was recorded as 111.11 mg/g in the case of copper ions, followed by lead ions, i.e., 71.42 mg/g and 84.95 mg/g for zinc ions (Roy and Bhattacharya 2012). Sun et al. (2015) reported the effect of MWCNTs on Cd2 + adsorption from river sediments and found that the presence of MWCNTs in the sediments causes variation in adsorption rate. The application of magnetic multiwalled CNT nanocomposite was reported for the elimination of nickel ions from wastewater (Kaushal and Singh et al. 2017). Regeneration of carbon nanotubes is done by altering the pH nature of the contaminant body. By making the solution acidic, metal adsorption or recovery can be increased by 90% (Qu et al. 2013).

18 Economical aspect of remediation process

Remediation processes are not limited to social costs and procedure details, and it is also based on socio-economic consequences. Nanotechnology is a recent field which is developed in the last few decades, hence assessment of economic aspect of nano-remediation is not fully feasible yet. Using well-defined methods and techniques, nanotechnology will have some impacts on the industrial sector as well as in research sector. Assessing the economic aspect of remediation process will help policymakers and stakeholders in designing the process and materials that are involved (Hussain et al. 2020). Nanotechnology is an eco-friendly, robust and economically viable solution to decontaminate polluted water bodies as well as other remediation techniques (Vardhan et al. 2019). Economic analysis has highlighted that it is not feasible to use activated carbon in a commercial scenario. Instead, we can opt for a similar alternative material to make the process more cost-effective and wider regeneration behavior (Schutyser et al. 2018).

19 Conclusion

Owing to high contamination due to heavy metals, there is a need to improve the efficiency of existing remediation process or establish new ones if required. Heavy metals have stable ionic forms which make them difficult to remove them from wastewater. This pose a huge threat to the environment and health of individuals. Conventional methods are widely adapted and accepted yet they have major drawbacks like low-metal removal efficiencies, high-operational costs, production of waste by-products that are difficult to manage, high-energy requirements, secondary pollution generation, reduction in soil fertility, etc. Similarly, for microbial and plant-based remediation techniques, few drawbacks have been observed. However, recent advances in nanotechnology and application of nanomaterials in remediation processes have shown great improvement and future scope. Nanotechnology can modify and enhance existing technologies being applied in various sectors, including pollution control, wastewater treatment, medicines, etc. It holds great significance in the production and discovery of new materials to exchange already existing production methods, with increased efficiency and better performance. Nanoparticles derived from various sources like plants, fungi, and bacteria are applied in detoxification and bioremediation of highly polluted conditions. In the review both real-time and experimental studies of nanomaterials have been highlighted which poses great potential in heavy metal remediation. The development of nanomaterials and advancements in this field helps us to find new remediation methods. Designing of nanomaterials gives us the chance to alter the properties of the material with increasing affinity, capacity, and selectivity of pollutants. This will lead to reduced releases of toxic substances into the environment. Treatment methods that use nanotechnologies can be safer by eliminating the need to use toxic chemicals such as chlorine and ozone. Productivity and commercial-scale application will increase with the study of nanomaterial's harmful nature and desorptivity for their regeneration, reuse, and extraction of contaminants. Other nanomaterials can be explored for their potential as adsorbents in heavy metal remediation. The focus should also be given on their reuse, regeneration, and recovery to make the processes cost-effective and economically efficient. From the literature survey, it can be concluded that nanomaterials can be applied in existing conventional and bioremediation processes to enhance their efficiency and reduce cost. The integration of nanomaterials in bio-regulated processes will help in better water purification. As we strongly suggest their use in treatment processes, it is necessary to highlight the downsides of them as well. These have to reduce their environmental toxicity and risks, such catalysts have to be developed which poses little or no threat to the environment. The future scope will lead to the development of cost-effective and large-scale efficient nano-catalysts for real-time applications.

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