Performance of Metal-Based Nanoparticles and Nanocomposites for Water Decontamination

M. K. Mohammad Ziaul Hyder and Sajjad Husain Mir

Abstract Water comprises an integral component of human life and its accessibility is essential for all life in the entire planet. Due to climate changes and other man-made activities, the world is facing shortage of drinking water. There are a number of pollutants present in the water such as gases, chemicals and heavy metals. Therefore, it is imperative to decontaminate water for a healthy planet. There are numerous problems and challenges of wastewater treatment. For better ecological and health issues some measures are required to take in advance to avert possible evil or to secure good results. Metal-based nanomaterials have found exceptional use in the decontamination purpose due to their nature which arises from nanosize, such as better adsorption and catalytic activity. Metal-based nanomaterials can productively remove different contaminants from water and they have been effectively applied in decontamination of water. Due to having larger surface area and having ability to work at low concentration these metal-based nanomaterials are very efficient in wastewater treatment. Nanoengineered nanoparticles impart a promising and effective treatment method to wastewater and thus can be adapted simply. Modern techniques for treatment of wastewater must be cost-effective and accessible for commercial use. In this chapter, we outline the role of metal-based nanoparticles and nanocomposites applied in water decontamination. Moreover, we discuss the advantages, disadvantages, shortcomings and future prospects associated with these nanomaterials.

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1 Introduction

Water is the basic component required for living being on earth. Safe and clean water is vital for direct uses and improved and good health of people. Besides water for drinking and other domestic uses, the second significant application of water is irrigation. The productivity of agriculture largely depends on water and thus indirectly affects food security of the population. There are other precious uses of water apart from human direct consumption and food production. Water for washing, cooking, sanitation and cleaning are essential preconditions for hygiene and health. Hydropower generation and watering of livestock are other prolific applications. Collectively, these principle applications of water infer that the abundance of water in superior quality and smooth supply has a great influence on social development. The change in climate conditions and increasing pollution are making water even scarce, particularly in developing countries. Currently, FAO (Food and Agriculture Organization) published that by 2025, fifty percent of the world will be living in water-scarce area creating more demand to use wastewater directly or indirectly (FAO, United Nations 2020). Table 1 presents types of water contaminants with origins and their impacts on health and environment.

Water sources are diminishing gradually because of overuse and misuse. Most of the normal sources of freshwater such as lakes, rivers, canals, reservoirs and rainwater have been found to be polluted with many types of precarious and poisonous materials or organic waste from different industries, household waste or originated from the

Table 1 Types of water contaminants with origins and their impacts on human health and environment

Water Contaminants	Origin of Contaminants	Impacts of contaminants
Sewage and contaminated water [197]	Domestic wastewater	Diarrhea, cholera, typhoid, etc.
Macroscopic pollutants [93]	Marine debris	Environmental pollution
Organic pollutants (Wang et al. 2019)	Fungicides, detergents, insecticides	Endangering aquatic life, dysgenic
Radioactive contaminants [24]	Different isotopic elements	Carcinogenic, tooth decay, damages bones and skin
Industrial contaminants [131]	Municipal contaminants	Induce air and water Pollution
Pathogens [265]	Germs	Diarrhea, cholera, typhoid, etc.
Suspended solids and sediments [206]	Land demolition, mining, land cultivation, etc.	Endangering aquatic life such as fishes, insects and affecting fish spawning
Inorganic contaminants [234]	Inorganic salts, Heavy metals, Mineral acids, Trace elements	Damage to flora and fauna in aquatic, public health issues
Agricultural contaminants (Tang et al. 2016)	Chemicals used in farming	Freshwater pollution

various point [139, 165]. These contaminants are detrimental to the people and other living beings and devastate the environment with permanent impacts [87, 204, 248].

Present wastewater control frameworks have generally been effectively examined though there are plenty of impediments [42]. For example, there is wide interest in developing advanced technologies to relieve toxicity and to ensure a secure living environment for humans. In this condition, several methods have been utilized such as chemical precipitation [112], electro-dialysis [83], reverse osmosis, ion exchange [58], adsorption [103, 104, 119], solvent extraction [289] and ultrafiltration [6]. The abovementioned technologies are expansive, inadequate and require a large amount of chemicals. These conventional methods of water treatments are no longer productive to eliminate many of the contaminants found in water with a view to attain water quality benchmarks. They regularly depend on a centralized framework, which the distribution and discharge processes are not sustainable for present day's requirements [191]. Upon this issue, nanotechnology could be used as an improved method to treat wastewater due to the size of nanomaterials which have the bigger surface area, high reactivity, fast kinetics; specificity to contaminants and, another advantage is the cost of nanomaterials that are going to decrease [290]. It is assessed that approximately 663 million people don't have access to potable water, mainly in developing countries (World Health Organization 2017). So, it becomes important to ensure basic water treatment to these people, where water treatment often is not available. The removal of pollutants from contaminated water is essential to avoid harm to public health and to the ecosystems [213]. On the aforementioned problems, the present review pointed on the utilization of metal-based nanomaterials to upgrade the standard of water with respect to the removal of metals, pathogens, salinity, oil and discuss the antimicrobial activity and the possible risks that these nanomaterials can affect the environment. Nanofiltration, nanoadsorbent, nano photocatalyst, disinfection and sensing with nanomaterials are the main techniques to treat wastewater by nanotechnology. This chapter emphasizes the method in wastewater control system with metal-based nanoparticle and attempts to point out the modern technology, outlooks, advantages and disadvantages of this emerging field.

The developing field of nanotechnology offers potential advancements to decontaminate water with cost-effective, improved working capability in removing contaminants and recycling capacity. Over the years, nanoparticles are effectively used in several fields such as in medicinal science, photocatalysis, etc. Presently, as the world confronting vital challenges of safe and clean water, scientists discovered that nanomaterial is a way superior choice wastewater treatment since it has some basic characteristics with greater surface area, nanosize, better reactivity [279], tough mechanical criteria, good porousness, hydrophilicity, dispersity. Some organic and inorganic contaminants, heavy metal like Hg, Cr, Pb, etc,. and numerous detrimental pathogens are presented to be effectively removed by utilizing distinctive nanomaterials [64, 153, 265]. Currently, the wastewater decontamination processes are

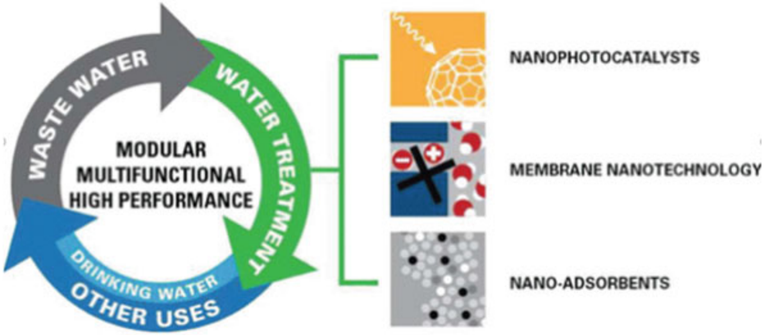

Fig. 1 Different categories of nanomaterials that are used for safe and sustainable water supply (Reproduce with license from American Chemical Society, Copyright (2013))

progressing with the advancement occurring in nanomaterials such as nanoadsorbent, nano photocatalysts and some imprinted polymers. Moreover, we have recently developed range of hybrid nanomaterials based on polymers-metal complexes, which have potential applications in water treatment and pollutant removal [10, 115, 154–160, 219]. In brief, the investigation on using nanomaterial in water treatment is regarded to measure positive viewpoint [23, 160, 221]. Figure 1 presents several types of nanomaterials applied in safe and sustainable water supply [191].

Nanomaterials are generally classified into different groups related to their surface and physical characteristics. Nanomaterials include metallic nanoparticles (Au & Ag nanoparticles), metal oxide nanoparticles (ZnO nanoparticles, Al_2O_3 nanoparticles, CeO_2 nanoparticles and TiO_2 nanoparticles), magnetic nanocomposites, nanocomposite with organic and inorganic supports, carbon nanoadsorbents, polymer nanoadsorbent. These nanomaterials are utilized as nanoadsorbent, nanomembrane, nanocatalyst, disinfectant and nanosensor for waste water treatment. Thus, we have outlined the importance of metal-based nanomaterials for treating wastewater to subdue the crises of fresh water problems in this chapter. A prospective and substantial method with easy accessibility can be obtained by using metal-based nanomaterials but a few flaws still require advanced consideration which is specifically outlined in this chapter. Besides, we also point out the limits, benefits, drawbacks and future prospects with relation to the metal-based nanoparticles. Moreover, merits and demerits of the metal-based nanoparticles with their other diverse uses in treatment of wastewater are shortly explained that can be beneficial to scientists for designing new strategy.

2 Categories of Metal-Based Nanoparticles in Water Treatment

2.1 Nanoadsorbents

One of the important technologies to separate contaminants from water is the notable adsorption method. Nanosorbents exhibit high and efficient adsorption capability with extensive uses in decontamination and purification of wastewater. Here, the nanoparticles absorb the contaminants in the water which can be separated from water after reaching the equilibrium. The method of adsorption of contaminants from wastewater is generally considered as a better process over other methods. Adsorption technology of wastewater control systems is usually a better technique over conventional methods. Due to its inexpensiveness, good performance, easy operation, it has high ability to remediate wide variety of pollutants from water [123]. Nanosorbents possess great properties such as high sorption ability which gives the nanosorbents more capability and more effectiveness for treating wastewater.

Nanoadsorbents have extraordinary ability for unique, more effective and quick decontamination procedures with a view to separation of inorganic and organic contaminants. Scientists are doing a great deal of work to prepare nanosorbents in a bigger amount at commercial level as they are exceptionally uncommon in commercial form. The field of nanotechnology is progressing by doing extensive research in this area to resolve the issues in removing contaminant metals from water with a view to find better nanoparticle combinations. In this method, titanium oxide, iron oxide and aluminum oxide-based nanomaterials have shown promising characteristics with cost-effectiveness and high adsorption property. Besides, nanoadsorbents have high porousness and larger active surface area which make them capable of removing different sizes of pollutants without discharging any toxic elements.

Adsorption method can be employed to extract the metal contaminants from contaminated water of various sources. Pb, Hg, Cr, Cd, Co, Zn, As, Cu, Ni, etc., are the kind of major metal contaminants responsible for water pollution [105]. Current investigations reveal that the nanoparticles are highly efficient for competent removal of abovementioned metal contaminants from wastewater. Nowadays, the nanomaterials of metals and metal oxides are widely utilized in decontamination of water through adsorption process. Nanoadsorbents made from metal nanoparticles are less expensive nanomaterials showing effective sorption quality. They are frequently utilized for the treatment of water containing heavy metals. Among the nanoadsorbents fabricated from metal nanoparticles, TiO_2, Fe_2O_3, MnO_2, MgO_2 and Al_2O_3 are well investigated and were observed to remove the heavy metals from wastewater very effectively. Metal oxide nanomaterials are regarded to be more capable than the normal adsorbent due to their larger active surface area. There are different points of interests related with metal oxide-based nanoadsorbents. The simplicity of synthesis, lesser toxicity, higher active surface area for contact and chemical stability impart the more distinctive properties to these metal oxides-based nanoadsorbents and make them more lucrative than other adsorbents [199].

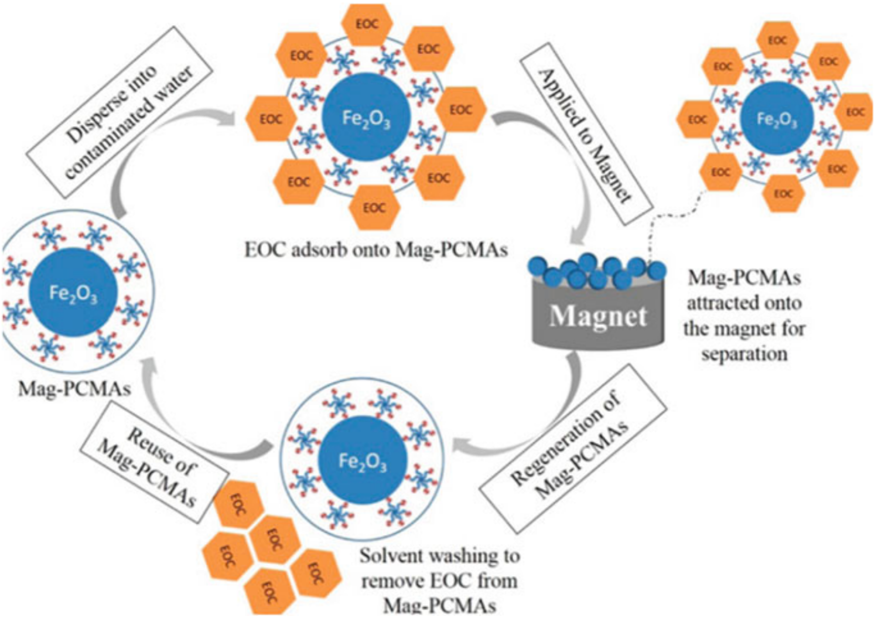

Fig. 2 Magnatic nanoparticle permanently confined micelle arrays adsorbents for complex emerging organic contaminants from wastewater. Reproduce with license from American Chemical Society, Copyright (2013)

The metal-based nanoadsorbents are prominent presently. Huang et al. showed the significant interaction between magnetic nanoparticle permanently confined micelle arrays (Mag-PCMAs) adsorbent and complex emerging organic contaminants (EOCs) which made magnetic nanoparticles efficient to be applied in complex chemical environments, like wastewater treatment (Fig. 2) [100]. The nanocomposite of various materials such as silver/carbon, silver/polyalanine, carbon/titanium oxide, etc., possessing tremendous significance with a view to remove the impact of poisonous properties in the treatment process of wastewater. Metal/metal oxide nanosorbents bear significant adsorption positions and due to their large active surface area they are the efficient materials for the contaminants by adsorbing methods. Likely, organic contaminants and heavy metals from wastewater are effectively removed by the polymeric nanoadsorbents [72]. For instance, with the help of dendrimer-ultrafiltration systems, copper ions can be reduced [226]. They are easily recovered at wide ranges of pH and exhibit biodegradability and non-toxicity. Moreover, dyes and other organic contaminants can be removed with the efficiency of 99% [182]. Zeolite is another vital nanoadsorbent where different nanomaterials such as copper and silver ions could be implanted [76].

The magnetic nanosorbents have a significant and unique capacity in water treatment to eliminate different organic contaminants from water. Nanoadsorbent for magnetic separation with particular affinity to contaminants was synthesized through ligands coating with magnetic nanoparticles [183]. Individual or combined metals can be utilized for the effluent treatment depending on the nature of pollutants. Iron oxides can be simply prepared and modified as the availability of iron is high on earth. The super magnetism and large surface to volume ratio of iron oxide give it the rank of a very good adsorbent with lesser toxicity, chemical inertness. These distinguished criteria of nanoadsorbents create a very fine option for the treatment of wastewater. Magnetic nanosorbents are also conducive in treating wastewater and are tested as very promising tools especially for organic contaminants elimination. Various procedures like cleaning agents, magnetic forces, ion exchangers are applied to eliminate nanoparticles from the system to prevent unwanted perniciousness. Recovered nanosorbents could be a better option for commercialization due to their cost-effectiveness. The surface interaction of magnetic nanoparticles and their aggregation can be restrained by using non-ionic, amphoteric, cationic or anionic surfactants [84]. Different forms of iron oxides that have been studied greatly having the capability to act as nanoadsorbents include maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3) and magnetite (Fe_2O_3), goethite (α-FeOOH), Iron oxide (Fe_xO_y), etc. [17, 39]. The magnetic properties of Fe_2O_3 nano adsorbent cause the separation process to be very simple from the dilute or even from viscous solutions. The removal of heavy metals like Cr^{6+} and Pb^{2+} were carried out efficiently where the protonation or deprotonation of magnetite surface hydroxyl group followed by water loss causes Cr^{6+} and Pb^{2+} adsorption. Likewise, different types of nano-structured wastewater metal adsorbents have been noted with various characteristics such as ZrO_2, TiO_2, CuO, MgO, etc. [109, 241].

2.2 Nanomembranes

Membrane technology is one of the most substantial developed techniques in the water treatment process. There is a broad range of new membrane materials applied to process water for reuse. For example, ceramic and polymeric membranes are familiar in the water treatment process. Presently, the applications of membrane technology are rising due to development of this method that has made them more accessible, flexible and effective. Accordingly, the water treatment industry is witnessing a flourish worldwide for all those factors. The membrane-based on nanofilter is the relatively modern technology in the treatment of wastewater. Nanomembrane removes the ions through ultrafiltration electrical effects following the reverse osmosis ion interaction mechanism as well as combination of ions. Novel properties of nanomembrane make it capable of selectively removing pollutants from the system. The improvement of nanomembrane innovation in recent years makes it for multiple use such as in pharmaceutical industry, demineralization in the dairy industry, bleaching in the textile industry, metal recovery from wastewater. Nanofiltration membrane is one of the suitable methods to treat organic and inorganic contaminants in surface water. Nanofiltration is more credible in treating surface water due to its low pressure activity as

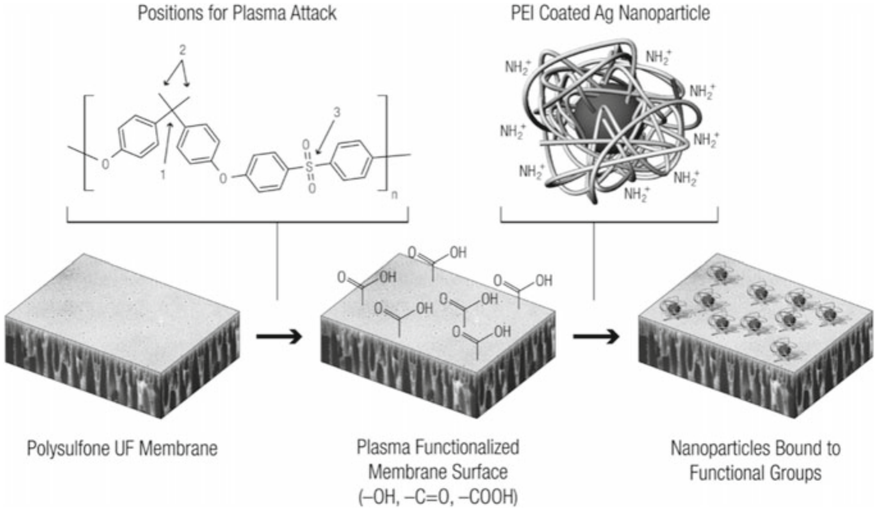

Fig. 3 Silver nanoparticles encapsulated ultrafiltration membranes for water treatment. (Reproduce with license from American Chemical Society, Copyright (2011))

surface water has low osmotic pressure [31]. Application of reverse osmosis methods is a normal procedure to make the water drinkable by filtering process.

Nanometal-based membranes are utilized to eliminate industrial contaminants from wastewater. The merits of nanometal membrane-based wastewater treatment are its easy operation, greater efficacy and low space demands. Moreover, by employing proper chemicals and nanoparticles the filtration capability can be improved [297]. Nanomembranes can be prepared with diversified characteristics of antimicrobial, anti-fouling, improved permeability, photocatalytic activity and selectivity on the basis of applications [168]. Ultrafiltration membrane shows evaluative treatment process in improved wastewater treatment. Figure 3 shows the ultrafiltration membrane where silver nanoparticles are encased in positively charged polyethyleneimine which provides an effective way of water treatment [150].

Multilayered inorganic—organic hybrid membranes using metallic molybdenum disulfide (MoS_2) as two-dimensional transition metal dichalcogenide nanosheets and one-dimensional silk nanofibrils were utilized for water purification [295]. Because of its possessing of negatively charged layers and interaction sites, the hybrid film could adsorb metal ions and dyes from water (Fig. 4). The separation performance can be tuned by changing the component ratios of these two nanomaterials. During filtration, due to the reducing effect of the MoS_2 nanosheets, precious metal ions are reduced to their nanoparticle form without any further thermal or chemical treatments. In addition to the one-step removal and recovery of metal ions, the hybrid membranes exhibit excellent potential for the determination and removal of different dyes from water.

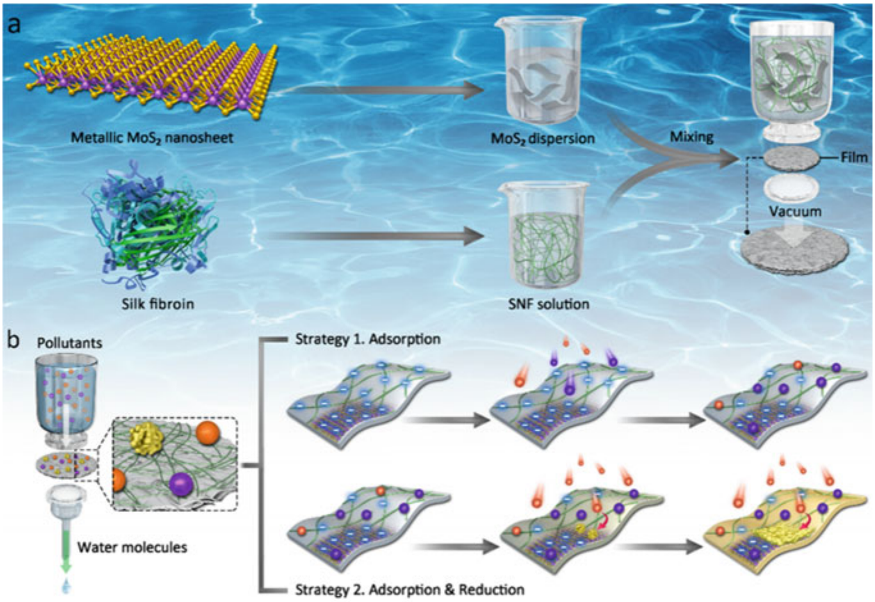

Fig. 4 Fabrication process of the mixed-dimensional MoS_2 silk nanofibrils hybrid membrane and the water purification mechanisms. **a** Scheme of the fabrication steps of the hybrid membrane. **b** Mechanism for the removal of contaminants from water. (Reproduced with license from American Chemical Society, Copyright (2020))

Nanofibers are one of the first species of membrane filters. They are porous and have high surface area with high interlinkage and can be prepared by a simple electrospun method. Nanofibers prepared by electrospinning with the combination of high surface area nanomaterials have shown efficiency in adsorption of pollutants. For instance, trace amounts of arsenite can be effectively removed by chitosan electrospun nanofiber which is manufactured by crosslinking ammonia vapor with the mixtures of Fe^{3+} and chitosan, poly (ethylene oxide) [152].

2.3 Nanophotocatalyst

Photocatalytic technologies have drawn most concentration for water pollution management. Photocatalysis is observed as a more efficient method for the purification of water purification which subdues the environmental pollution. The basic fundamental of photocatalyst is that the catalyst oxidizes the pollutants in water by utilizing radiation from sunlight. Metal oxide-based nanophotocatalysts are the vital candidate for the rectification of environmental pollution through recent application of it in water decontamination. In this method, electron-hole pairs are produced by irradiation of nanophotocatalyst. These photoelectrons create holes by jumping from the valence band to the conduction band.

A good photocatalyst absorbs visible or near ultraviolet more efficiently. For the prevention of the recombination of electron-hole pairs adequate electron vacant states are required. Nanophotocatalysts should be biologically inactive and nonpoisonous due to their ongoing extensive uses in microbiological and agricultural sectors. Nano photocatalysts prepared from semiconductors of metal oxide like TiO_2, WO_3, Zn_2SnO_4, ZnO have shown high efficiency in removing biological and chemical contaminants [21]. Comprehensive studies in the past decades on uses of nanophotocatalysts for the treatment of municipal water were reported in previous literature [145, 214]. A great deal of research work was done to alleviate the detrimental impact of chemical pollutants from wastewater by utilizing nanoparticles photocatalysts such as titanium oxide and zinc oxide [92]. Nanophotocatalysts of activated carbon-supported nano-FeOOH (FeOOH/AC) were synthesized with the help of air oxidation of ferrous hydroxide suspension method [288]. FeOOH/AC heterogeneous nanophotocatalyst owns remarkable adsorption capacity and the oxidation of amaranth happens through the homogeneous and heterogeneous in bulk solution and on catalyst/solution interface, respectively, because of releasing of iron from the nano-FeOOH (Fig. 5).

Ternary oxide zinc stannate is drawing concentration from researchers as viable photocatalyst [97, 195]. Due to improved photocatalytic activity and non-toxicity, TiO_2 nanophotocatalysts are observed to show the effective and prominent activities for photodegradation dyes from contaminated water. The demerits of TiO_2 as

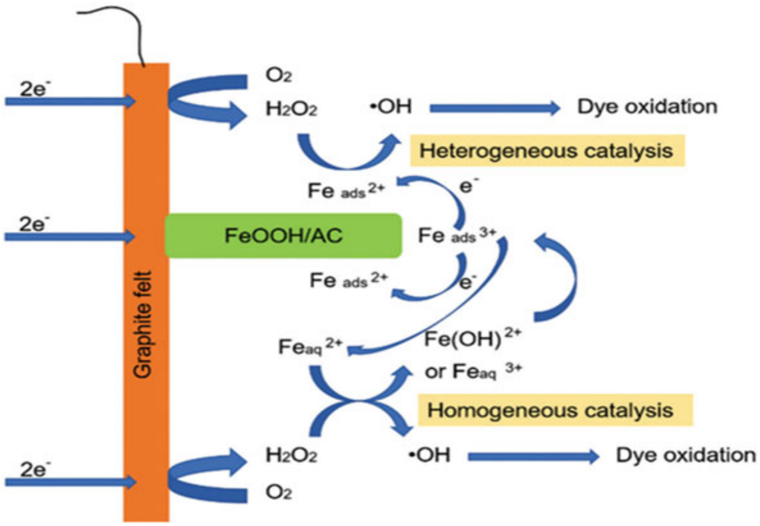

Fig. 5 Effective adsorptibility and Fenton oxidation with the combination heterogeneous/homogeneous process of amaranth utilizing supported nano-FeOOH. Reproduce with license from American Chemical Society, Copyright (2012)

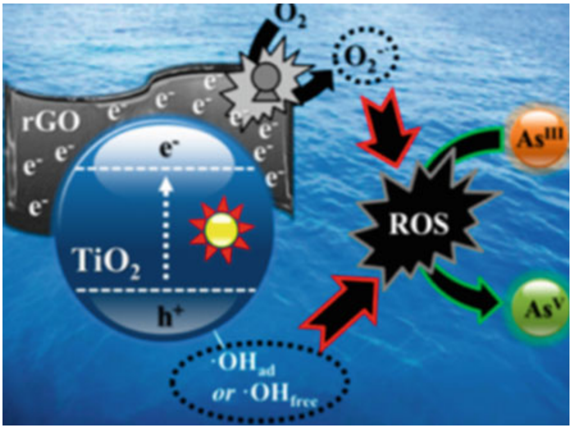

Fig. 6 Reduced Graphene Oxide/TiO_2 for the Effective Photocatalytic Oxidation of Arsenite. Reproduce with license from [163]. American Chemical Society, Copyright (2014)

a photocatalysts is low quantum efficiency in visible regions, decreasing photocatalytic ability on account of wide band gap and quick recombination of charge carriers. Several studies have been noted depicting the antimicrobial activity of TiO_2 nanophotocatalysts against various waterborne pathogens including protozoans and bacteria [86]. Photocatalytic activity of TiO_2 has also been investigated utilizing the TiO_2 mediated photodegradation of Rhodamine B dye and bromoethane [111]. Cyanobacteria have an immense toxic effect on human health. Lawton et al. showed the mechanism of TiO_2 mediated mineralization of cyanobacterial hepatotoxin [124]. The reduced graphene oxide hybridized with TiO_2 was prepared as a cost-effective catalyst compared with Pt/TiO_2 and found to show improved activity for the photocatalytic oxidation of As(III) [163]. The photocatalytic activity and arsenic oxidation mechanism observed with reduced graphene oxide implanted TiO_2 are almost the same activities shown by Pt/TiO_2 (Fig. 6). The nanocomposite of reduced graphene oxide/TiO_2 can be considered as a useful environmental photocatalyst for pretreating the water polluted with As(III).

ZnO nanoparticles also displayed photocatalytic activity by creating hole-electron pair [27]. ZnO-NPs have prominent photocatalytic activity for elimination of different organic contaminants having their high binding energy and broad band energy, powerful oxidation capability and high active surface area [256]. Silver nanoparticles are noted to show antimicrobial activity against waterborne pathogens [71]. Mpenyana-Monyatsi fabricated Ag NPs coated filters and showed the efficiency of the elimination of microbes from water with 100% effectivity [166]. Photocatalytic degradation based on the heterogeneous semiconductors is one of the safest simple and cost-effective techniques for dyes and organic compounds removal from water polluted by industries and residences [68, 118, 152, 169]. Various metal oxides NPs like ZnO, CuO and TiO_2, etc., are being used for photodegradation of organic dyes [232, 233, 239]. This process assists to remove contaminants such as pathogens, organic dyes and micro pollutants, etc. [192, 273]. For instance, a hetero structured nanocomposite $BiVO_4/CH_3COO$ was synthesized for the degradation of the organic contaminations from water by photocatalytic activity [293]. TiO_2 effectively eliminates toxic chemical tartrazine from water utilizing its photocatalytic activity [82]. Polyaniline/ZnO nanocomposites show improved degrading capability toward colored dye through producing enough electrons at the conduction band of zinc oxide semiconductor [215]. Different nanocomposites of zinc oxide or the compounds of zinc oxide with materials have been observed to degrade the contaminants in wastewater very effectively [198]. In a similar way, filtration technology could be developed by integrating photocatalytic characteristics of a photocatalyst[138].

2.4 Disinfection

Nearly all of the sources of potable water have been observed to be polluted with various poisonous materials and pathogenic microorganisms. The World Health Organization (WHO) reported that approximately 12 million people die every year from waterborne illness. 90% of all diseases resulting from impure water were found in developing countries. The global disease infecting people with the use of impure water is nearly 4 billion. The responsible microorganism in water which causes diseases to people is known as pathogen. Different technologies are applied to treat the pathogen in water. Deactivation of pathogens is generally known as disinfection. Presently, the disinfection of drinking water is carried out by chemical or physical method. Various techniques are used to disinfect water such as UV treatment, chlorination and ozonation. The well-accepted method of disinfection by chlorination has some limitations. The excess chlorine beyond the permissible level is toxic and may be responsible for bladder or colorectal cancer. Chemical treatment of water by antibacterial disinfectants like triclosan and triclocarban may cause hormone-disrupting effects. In the presence of natural organic matter, ozone can form non-halogenated organic disinfection by-products such as aldehydes, ketone, carboxylic acids. The effect of UV treatment is temporary and water can be infected by pathogens if the water is stored for a long time. These traditional water disinfection methods have definite limitations to apply at large scale.

Nanotechnology in water purification shows huge potential to decontaminate water [20, 22, 22]. This is a viable way to remove the pathogens from wastewater. In the present condition, nanomaterials can be utilized to eliminate microbes more efficiently. The nanomaterials accommodate different processes to kill the organisms. These nanomaterials may connect the organisms specifically through hindering the electron transfer to transmembrane, destroying cell enclosure or by producing reactive oxygen species they can damage cell walls [129]. Various nanoparticles with antimicrobial inherent were reported with action against organisms [129, 246]. A biomass-based renewable film with good mechanical strength and porous network structure was facilely fabricated via Fe (III) crosslinking induced with collagen fibers and gallic acid-protected silver nanoparticles self-assembly (Fig. 7) [132]. This film exhibited both excellent bacterial anti-adhesive and bactericidal activities, which effectively prevented biofouling during the filtration process, due to the anionic

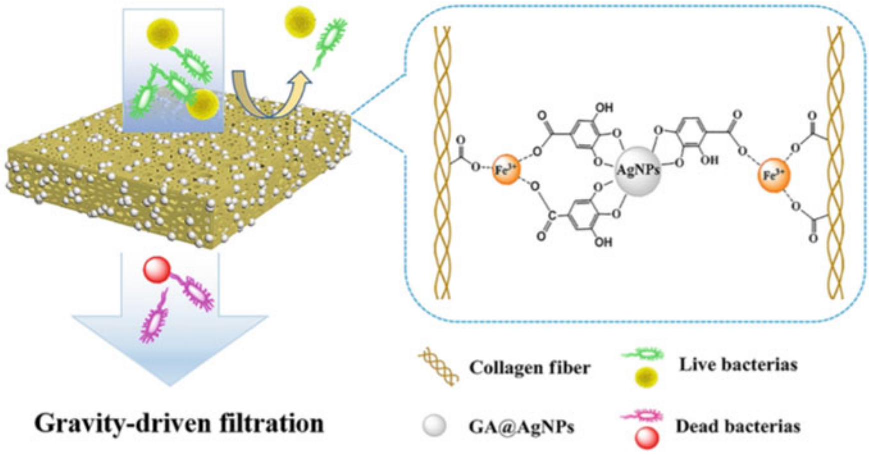

Fig. 7 Point-of-use water disinfection by a cost-effective porous renewable film incorporated with silver nanoparticle. Reproduce with license from American Chemical Society, Copyright (2020)

gallic acid-protected silver nanoparticles. As bactericidal filter driven by gravity, 1 L natural water sample was treated by the film in 20 min, and the water quality is in full compliance with the drinking water guidelines of WHO, demonstrating the potential application of the proposed filter in point-of-use water disinfection.

TiO_2 produces hydroxyl free radicals and forms peroxide with photocatalytic activity which is responsible for antimicrobial properties of its [129]. TiO_2 with the incorporation of other nanomaterials displays enhanced antimicrobial photocatalytic properties [47, 110]. The nanoparticles of zinc oxide exhibit notable antimicrobial properties against waterborne pathogens, and hence they are utilized to purify the wastewater [51]. Salem et al. made a comparison of the antimicrobial properties of Ag nanoparticles and Zn nanoparticles toward *V. cholerae* and enterotoxin *E. coli* [56]. Iron nanoparticles also exhibit antimicrobial activities by eliminating *Entamoeba histolytica* cysts from water [231]. For centuries, silver has been considered a well-known antibacterial material. The release of silver ions efficiently destroys the cell envelope and retards the DNA replication [191]. Nanofiltration techniques are another method to remove the microbes by filtration [218].

As waterborne disease causes serious health effects to humans, the disinfection technology is drawing more attention recently. Titanium dioxide with its environmental friendliness behavior was exhibited to be prepared as antimicrobial agents in more recent studies. The investigations showed that TiO_2 improves the capability of disinfection through the deactivation organisms such as Escherichia coli, Staphylococcus Aureus, etc. Nano-WO_3 synthesized by sol–gel method displayed enhanced capability for the disinfection of E.coli in water [79]. Copper displays high antimicrobial activity with attractive cost and low toxicity. Moreover, it has been reported that Cu_2O showed more activity toward bacteria than silver and CuO [251].

Deng et al. reported that copper graphene sponge can be used for water purification more efficiently through inactivation of bacteria [48]. Bactericidal activity of gold nanoparticles is scarcely reported for gram-negative or gram-positive bacteria [13, 106]. Contrarily, gold NPs display fungicidal activity [7, 106]. Platinum NPs can destroy cell walls and can release cytosolic proteins bacteria and fungi [16]. Palladium NPs show better antimicrobial activity toward gram-positive bacteria than gram-negative bacteria, and exhibit size-dependent antimicrobial properties [2].

2.5 Sensing

The detection of pathogens is essential because of their precarious impact on human health. The traditional sensing methods are steady and incapable of monitoring the existence of harmful viruses and pathogens such as helicobacter, legionella, norwalk viruses, echoviruses, hepatitis A. Most of these microbes are biological operant in the rise of contamination in drinking water. Water sterilization process depends on pathogen recognition. There is great progress in research to develop nanomaterial-enabled nanosensors. Present studies are concentrating on the improvement of three principal parts of nanosensor: (i) nanomaterials (ii) recognition materials and iii) signal transduction mechanism. The recognition materials selectively interact with pathogens. Rapid feedback and selectivity are obtained by using nanomaterials. Nanomaterials intensify the detection speed and sensing capability to perform multiple target identification with their novel optical, electrochemical and magnetic characteristics. Nanosensors may be used for the detection of biomolecules cells.

A numerous research has been done on the appropriate design and application of nanosensors [19, 35, 60, 61, 73, 172, 271]. These nanosensors can be utilized in the central distribution system, at the location of point-of-use or in the water treatment plant. The monitoring of sensing may be online to determine the quality of water during flow through or may be offline by collecting water samples at different points. Nanosensors are more capable than traditional water quality sensors. Nanosensor rapidly and reversibly measures the analyte whereas nanoprobe selectively determines pathogens with great sensing capability in an irreversible way. [207].

A wide variety of nanosensors was reported to show the capability of identification of pathogens, toxin and pH in water [35, 66, 207, 266, 268]. A percolation method was reported to inactivate pathogens through silver nanoparticles containing paper sheets. Here, on blotting paper sheets of cellulose fibers, silver nanoparticles were accumulated [46] (Fig. 8). The silver nanoparticles sheets showed remarkable antimicrobial properties toward enterococcus faecalis and Escherichia coli with high reducing ability. This outcome of deactivation of pathogens through silver nanoparticle sheets is encouraging enough to utilize it in emergency water treatment.

A direct intrinsic signal from the analyte can be acquired by nanosensor or by employing high quality recognition elements that are bound to analyte.

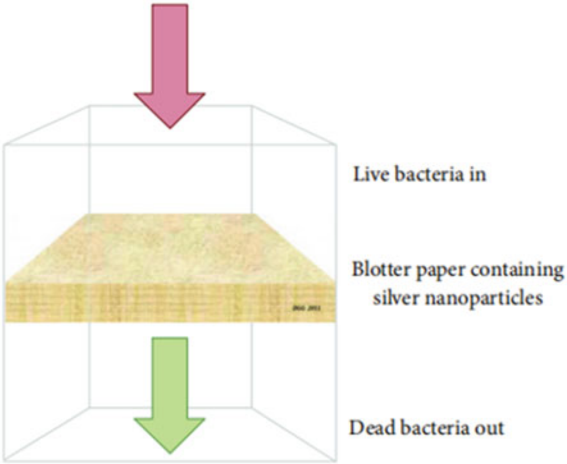

Fig. 8 Blotting paper implanted with Ag nanoparticles for point-of-use treatment of water. Reproduced with license from American Chemical Society, Copyright (2011)

Figure 9 depicts the sensing of environmental analytes by nanosensor architectures. A simple approach to effective detection of bacteria S. aureus through surface-enhanced Raman-scattering with the synthesized gold-coated magnetic nanoparticles core/shell nanocomposites [272].

Ng et al. reported the recent development of fluorescent nanosensors such as metal nanoparticles [174]. Strong electromagnetic field is generated on the nanoparticle surface when silver or gold nanosensors are excited by light [278]. Magnetic nanomaterials are capable of identifying magnetically isolated analytes as they are highly responsive to external magnetic fields [122]. The detection of influenza A and Mycobacterium was carried out through changing the electrical resistance of magnetic nanoparticle-labeled analytes by magnetoresistance sensors [121]. Quantum dots are promising as fluorescent nanosensors which have larger band gaps and narrow fluorescent spectra have been detected through one excitation light source [268]. The Internet of things can be connected to the system of nanosensors used in distribution systems to ensure quality, stability and degrability of nanosensors [151].

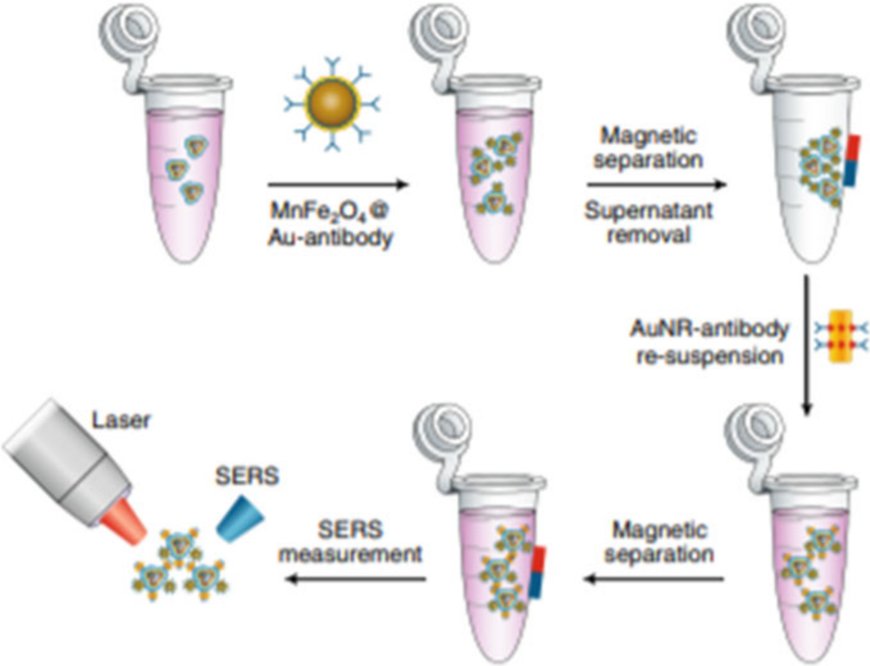

Fig. 9 Schematic illustration of the operating procedures for bacteria detection via a surface-enhanced Raman-Scattering method. Reprinted from with license from American Chemical Society, Copyright (2016)

3 Metal and Metal Oxide Nanoparticles Used in Water Treatment

3.1 Metal Nanoparticles

Nanometals can be used in water purification with high efficiency. There are various forms of nanometals utilized in wastewater treatment for instance nanostructures, cationic forms and inert or active substances supported form. Silver nanoparticles have been reported to be applied to adsorb Cr(II) and Pb(II) as suspended free nanoparticles in the system [12]. Copper nanoparticles were used as antibiofouling, antioxidant and antibacterial agents for wastewater treatment [36]. Those nanoparticles showed efficiency in inactivation of pathogens, inhibition of lipid oxidation and biofilm formation and scavenging free radicals. Citrate-supported silver nanoparticles were used for degradation of organic pesticides chlorpyrifos [30] (Fig. 10). Octahedral palladium nanoparticles were used for reduction of bromate in municipal water treatment [276]. The supported nano metals have various advantages. Support helps to prevent aggregation of nanoparticles and separate nanoparticles from water after treatment which may be responsible for self toxicity [30, 276]. For synthesis

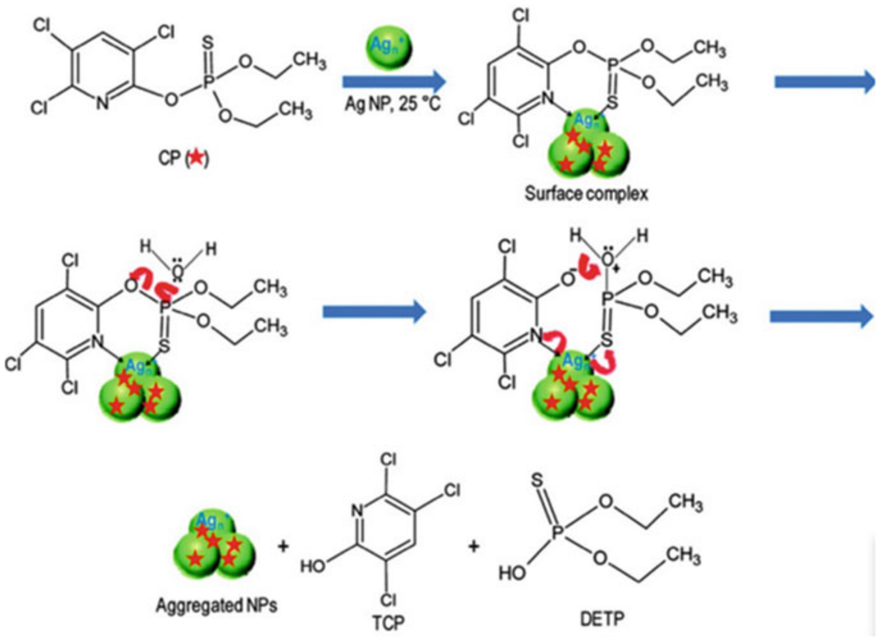

Fig. 10 Representation of degradation of chlorpyrifos on silver nanoparticles. Reprinted with license from American Chemical Society, Copyright (2012)

and stabilization of nano metals, different chemicals are utilized. For instance, to get the reductive and stabilized form of silver nanoparticles, chitosan and polyethylene glycol are used in synthesis [269]. The easiest approach to eliminate harmful contaminants from water is various physicochemical processes such as adsorption, filtration or cuagulation. For instance, silver and iron nanoparticles effectively remove Pb(II), Cr(II) and Cr(VI) ions from aqueous solutions by the physicochemical technique [148].

Ag nanoparticles can effectively remove Hg(III) from aqueous solution [63, 164]. Ag nanoparticles display improved activity due to their decreasing reduction potential with the decrease of particle size [188]. Au nanoparticles with aluminum support could be applied to remove Hg(II) effectively from wastewater. Jiménez et al. reported citrate-coated Au nanoparticles for treating Hg(II) in water [178]. Here, Hg (II) was converted to Hg (0) by weak citrated ions reducing agent without application of $NaBH_4$. The concentration of Hg(II) was reported to decrease from 65 to 5 ppb (Fig. 11). Other noble metal nanoparticles like palladium and ruthenium nanoparticles exhibit effective antimicrobial agents for gram-positive bacteria and display size-dependent antimicrobial activity [2].

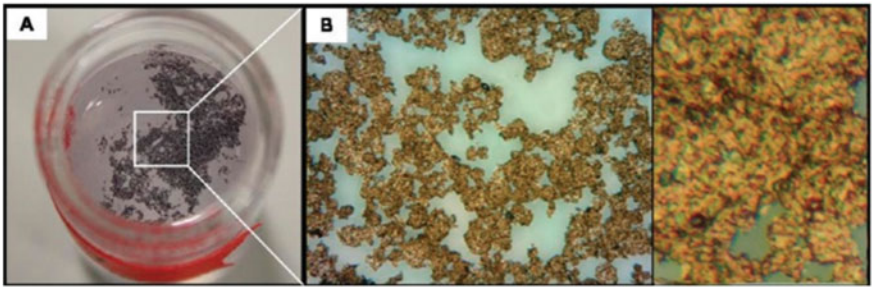

Fig. 11 Hg(II) removal from river water by citrate coated Au nanoparticles. **a** Precipitation image after treatment of Hg(II) with Au nanoparticles (efficiency 40%) **b** Zoomed image of precipitation taken with optical microscope. Reprinted from with license from American Chemical Society, Copyright (2012)

3.2 Zero-Valent Metal Nanoparticles

Wastewater treatment process is greatly advanced through using zero-valent metal nanoparticles. They were found to show excellent antimicrobial ability, degradation ability as well as high removal ability of heavy metal from wastewater. Zero-valent iron was well studied for the elimination of heavy metals and for deactivating pathogens from wastewater. Zero-valent iron (nZVI) nanoparticles consist of Fe (0) and Fe_2O_3 coating [177]. It is applied widely to treat heavy metals like Cr (VI), Hg (II), Cu (II), Ni (II), etc. [133, 222]. Principally, Fe (0) produces the reduction ability whereas the Fe_2O_3 coating creates the active position to attract heavy metals through electrostatic attraction. Moreover, the shape of nZVI could be easily manageable and huge reactive sites could be created on the surface of nZVI [43]. The high reducing ability and high active surface area impart the nZVI higher performance for the removal of heavy metals from contaminated water [98]. Furthermore, nZVI has been displayed to have a promising bactericidal effect and toxicity toward pathogens [49, 125].

The high efficiency and versatility of nZVI have made it perfect technology for practical utilization in wastewater treatment. Nano zero-valent iron can also be applied for improving the quality of groundwater contaminated with perchlorates and chlorinated hydrocarbons. nZVI is more reactive than conventional iron because of its high active surface. On the other hand, the lifetime of nZVI is very low due to its high reactivity characteristic. As a result, more research on surface modification of nZVI is necessary to make it stable [15, 94]. Zhang et al. deposited synthesized nZVI particles on the surface of biomass activated carbon and applied to remove 98% methyl orange from water [287]. nZVI has been efficiently used to treat the wastewater and groundwater with arsenic [173], chlorinated hydrocarbons [53, 247], heavy metals [190, 292], nitroaromatic [285], phenol [220], heavy metals [190, 292], nitrate [102], dyes [229] and phenol [220].

Application of nZVI for the treatment of wastewater has some drawbacks because of its instability, quick aggregating and problematic separation process. To resolve these disadvantages, nZVI could be supported by zeolite, bentonite, resin, etc. Deposition of nZVI nanoparticles on supporting materials for the elimination of contaminants makes the procedure easy and also enhances the reduction ability. The reactivity of ZVI could be improved by depositing a thin film of any other metals like Ni, Pt, or Pd on iron as principal metal which could efficiently remove chlorinated hydrocarbons from wastewater. For instance, Xu et al. synthesized novel Ni–Fe bimetal for effective removal of 4-chlorophenol with enhanced catalytic hydrogenation [280]. Another Pd/Fe bimetallic system shows very effective removal of tetrabromobisphenol A, 2,4-dichlorophenol and polychlorinated biphenyls and displays better dechlorination that than normal nZVI [98]. In addition, deposition of Pd on nZVI decreases the release of toxic intermediate on nZVI's surface [40]. The translocations and transformations of contaminants such as arsenic species at and within the nZVI particle are distinctly depicted in Fig. 12 [283].

Despite a lot of research on decontamination of wastewater by nZVI, zero-valent zinc (nZVZ) has been found as an alternative. nZVZ nanoparticles were shown to degrade dioxin excellently [29]. The reducing ability of Zn is higher than Fe. Thus it is clear that the power of contaminant degradation of nZVZ particles will be higher than nZVI particles. It is reported that degradation of CCl_4 happened more quickly by nZVZ compared to nZVI [261]. Moreover, an investigation was done for the comparison of degradation ability toward halogenated hydrocarbons in water with nZVI, nZVZ, nano zero-valent aluminum (nZVAl), nano zero-valent nickel (nZVN) nanoparticles. The study showed that only nZVZ was capable of degrading octachlorodibenzo-p-dioxin effectively into less chlorine concentrated materials

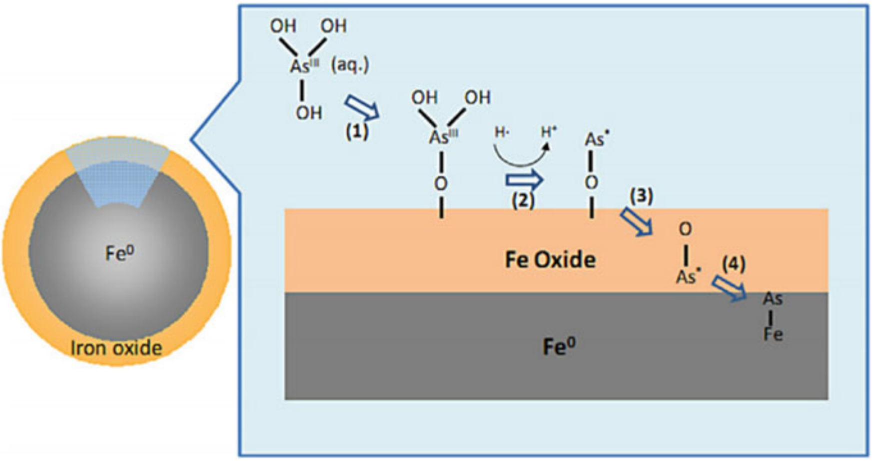

Fig. 12 The translocations and transformations of contaminants such as arsenic species at and within the nZVI particle. Reprinted with permission from American Chemical Society, Copyright (2012)

[29]. Though nZVZ efficiently degrades halogenated hydrocarbons, treatment of other contaminants with nZVZ was not reported a lot yet [261].

3.3 Iron Oxides Nanoparticles

The use of iron oxide nanoparticles in wastewater treatment is remarkably increasing. There has been rising attention on the application of iron oxide-based nanoparticles for the removal of heavy metals and remediation of wastewater in recent years [11, 212]. Due to the higher abundance of iron on earth and simple synthesis method of iron oxide-based nanoparticles, extensive research has been done on it. The challenge of using nanoparticles in water treatment is their recovery and separation from treated water. But, with the help of external magnetic fields, most of the iron nanoparticles can be separated. As a result, iron oxide nanoparticles could be efficiently employed to remove heavy metal from contaminated water and could thus be separated successfully from the systems [127, 175, 257]. Goethite (α-FeOOH) is studied a lot where it is manifested that they are competitive adsorbent of heavy metals owing to their cost-effectiveness, good adsorption capability and environmental friendliness [149]. Goethite was reported to be synthesized from ferrous and ferric salts to remove uranium from water [250].

Nanoscale α-FeOOH shows photocatalytic activity and good adsorption quality toward heavy metals [39]. For the present, nanoscale α-FeOOH has shown high adsorption capability toward heavy metals [70, 128]**.** The most stable and corrosion resistance form of iron oxide is hematite (α-Fe_2O_3) [255]. Hematite nanoparticles have been shown very effective to adsorb heavy metals such as Cr (VI) [3, 7, 50]. The high adsorption capacity of nanoscale α-Fe_2O_3 toward heavy metals has been reported [228]. Very recent, superparamagnetic α-Fe_2O_3 nanoparticles were prepared and shown 100% removal efficiency of Mg (II), Al (III), and Mn (II) and 80% of Ni (II) and Zn (II) from acid mine drainage [113]. It proves α-Fe_2O as an excellent nanoparticle to treat wastewater for its low toxicity, high stability and high adsorption capability.

Maghemite (γ-Fe_2O_3) nanoparticles have been widely studied to remove heavy metals from wastewater [59]. There are many advantages to utilize γ-Fe_2O_3 nanoparticles in wastewater treatment. γ-Fe_2O_3 nanoparticles have a high active surface and high adsorption capacity toward heavy metal and it can be separated from the system just by applying an external magnetic field. Furthermore, the preparation of γ-Fe_2O_3 nanoparticles is easy and they behave environmentally [263]. γ-Fe_2O_3 nanoparticles of particle size 14 nm synthesized by single-step method were applied to heavy metals from wastewater [9]. Superparamagnetic γ-Fe_2O_3 nanoparticles with tunable morphology were prepared by utilizing a flame spray pyrolysis approach and applied to remove Cu(II) and Pb(II) from wastewater [200]. Magnetite-based nanoparticles are extensively applied as nanoadsorbent because of their simple preparation, easy use, cost-effectiveness, friendly behavior to the environment and easy separation from systems [146, 223, 277]. Fe_3O_4 nanoparticles are generally altered on surface by –SH [179], $–NH_2$ [258], –COOH [227]. Pan et al. studied adsorption of Cr(IV) on engineered iron oxide nanoparticles [180] (Fig. 13). Damino activated Fe_3O_4 nanoparticles were prepared through utilizing one-pot synthesis method and applied to test the adsorption capacity toward Cr (VI) and Ni (II) [176].

Core–shell structure of Fe_3O_4 nanoparticles have been prepared by utilizing various coating materials such as sodium dodecyl sulfate [4], tannic acid [18], silica [141], oleate [143], p-nitro aniline [140], polyethylene glycol [210], chitosan[194], etc., and used for the treatment of heavy metals in wastewater. For instance, a core–shell structure magnetite NPs was prepared by spraying the polymer of organo disulfifide polymer onto the $–NH_2$ activated Fe_3O_4 nanoparticles and exhibited efficient adsorption capacity toward heavy metals in a high concentration solution [99]. Figure 14 represents the core–shell structure of amphiphilic polyisopreneblock-

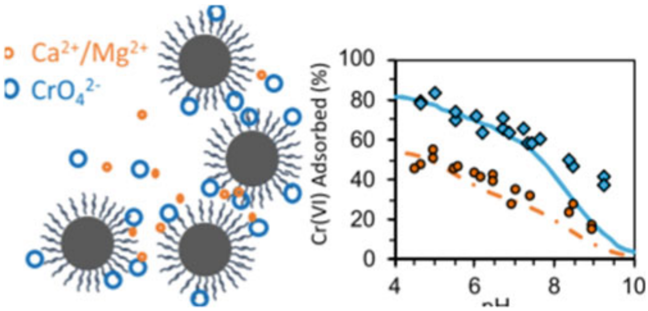

Fig. 13 Cr(VI) Adsorption on engineered iron oxide nanoparticles. Reprinted with license from American Chemical Society, Copyright (2019)

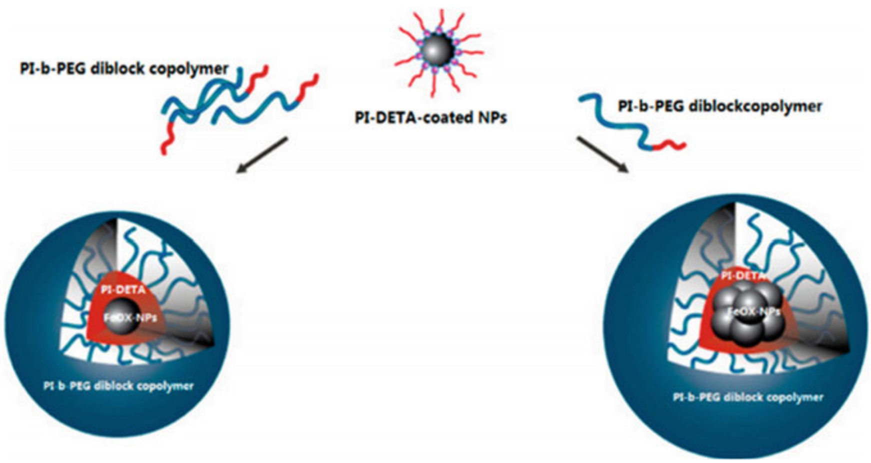

Fig. 14 Encapsulation of single or multiple nanoparticles by polyisopreneblock-poly(ethylene glycol) diblock copolymer. Reprinted with license from American Chemical Society, Copyright (2014)

poly(ethylene glycol) (PI-b-PEG) copolymer which encaged the Fe_3O_4 nanoparticles [217]. These core–shell structure magnetite nanoparticles were found to remove heavy metal with high efficiency and were easily separated from wastewater.

3.4 Titanium Oxide Nanoparticles

Titanium dioxide (TiO_2) nanoparticles with high chemical stability, lower toxicity and low cost are employed as competitive materials in disinfection and decontamination of wastewater. Thus, TiO_2 nanoparticles have drawn more concentration among researchers because of their extensive properties [117, 170, 216, 259]. TiO_2 nanoparticles do not change for a long time during degradation of pathogens and organic compounds. TiO_2 nanoparticles were widely investigated on degradation of organic contaminants with high effectiveness [14]. It was also represented with the effective removal of heavy metals from contaminated water [235]. Nanowires with diameter of 30–50 nm were synthesized from TiO_2 and were applied to eliminate Cu (II), Pb (II), Fe (III), Zn (II) and Cd (II) from contaminated water with high efficiency [286]. Iron-doped TiO_2 nanoparticles were prepared and utilized to remove arsenic with higher effectiveness than pure TiO_2 nanoparticles [171]. TiO_2 NPs coating with starch- were synthesized to eliminate 90% of Ni (II), Cd (II), Pb (II), Co (II) and Cu (II) from tap-water [25]. Microwave-synthesized TiO_2-chitosan nanoparticles were synthesized and were used for the removal of heavy metals applying the microwave-enforced sorption approach. This approach was observed as environmentally friendly and fast removal efficiency. TiO_2 nanoparticles displayed promising adsorption capacity toward organic and inorganic contaminants [252]. TiO_2, the semiconductor photocatalyst exhibits a variety in the case of mineralization or decontamination of harmful substance in water [253]. It is evident that TiO_2 nanoparticles in anatase phase possess strong catalytic activities for having high active surface and redox properties. Magnetic TiO_2 nanoparticles were prepared for the treatment of wastewater and this nanowire could easily be separated from the system with external magnetic fields showing suitability to commercial applications [147]. The demerits of TiO_2 nanoparticles are complex production processes and difficulty in removal from the system after use [137]. It is generally not easy to separate TiO_2 nanoparticles NPs when it is used to treat a slurry suspension of contaminated water [54].

3.5 Other Metal Oxide Nanoparticles

ZnO nanoparticles have come out as a promising material in decontamination of water because of their distinctive characteristics with large band gap in the near-UV electromagnetic spectrum spectral, powerful oxidation capability, enhanced photocatalytic ability [38, 201]. Moreover, having the almost identical band energy gap, the ZnO nanoparticles show similar photocatalytic activity as displayed by TiO_2 nanoparticles. Besides, ZnO nanoparticles are advantageous in the case of cost-effectiveness compared to TiO_2 nanoparticles [45]. ZnO nanoparticles posses the higher adsorption capability of light from the electromagnetic spectrum in a wide range in comparison with some other metal oxides nanoparticles [26]. Rapid reunification of photogenerated charges causes low photocatalytic efficiency of ZnO nanoparticles [78]. Photocatalytic efficiency of ZnO nanoparticles could be enhanced by doping metal. Different kinds of dopants mainly of metals such as inner transition elements dopants, codopants, anionic or cationic dopants, etc., were utilized for improving the photocatalytic efficiency of ZnO nanoparticles [126]. ZnO nanoparticles could be employed as a good nanoadsorbent for its non-toxicity, well antimicrobial activity, chemical, thermal and mechanical stability and overall efficient adsorption quality. ZnO nanoparticles exhibit higher adsorption efficiency toward heavy metals than TiO_2 nanoparticles [193]. ZnO nanoparticles were reported to show enhanced sorption capacity toward inorganic and organic contaminants [41]. ZnO nanoparticles have significant photocatalytic potential for exclusion of various organic compounds and contaminants due to their wide band gap energy, i.e., 3.37 eV, high exciton binding energy, i.e., 60 meV, strong oxidation ability and larger surface to volume ratio [240].

Manganese oxides (MnO_2) nanoparticles have been reported to show good sorption performance toward metal ions [167]. It has also been noted that MnO_2 nanoparticles and hydrous manganese oxide showed good removal efficiency of heavy metals from wastewater [134]. MnO_2/gelatin was prepared to remove Cd (II) and Pb (II) from wastewater through adsorption [274]. Guo et al. reported the effective removal of arsenite from water with synthesized paper-like, free-standing membrane of Mn_3O_4/CeO_2 hybrid nanotubes (Fig. 15) [81]. MnO_2 nanoparticles were noted to adsorb Tl (I) in wastewater [101]. MnO_2 nanoparticles were reported to show high capability to remove Cu(II), Hg(II), Pb(II), U, Cd(II), etc., from wastewater [1, 116, 130]. HMO is reported to exhibit advantageous characteristic in adsorption of heavy metals because of its porosity, ample active sites and high surface area [62].

Recently, hydrous manganese oxide-biochar nanocomposites were synthesized by implanting the hydrous manganese oxide nanoparticles into the biochar [270]. This composite material was applied to remove Pb (II) and Cd (II) in a broad pH range with high efficiency. Hence, hydrous manganese oxide-biochar could be a thriving candidate for the removal of heavy metals from contaminated water.

Aluminum oxides (Al_2O_3)-based nanoparticles are extensively utilized as adsorbent for removal of heavy metals. The major advantages of Al_2O_3 nanoparticles are low preparation cost and efficient decontamination capability [75, 187]. γ-Al_2O_3 nanoparticles were prepared through a sol–gel process and showed the removal capacity of 97% for Pb (II) and 87% for Cd (II) [254]. The effect of phosphate, humic acid and citrate on Al_2O_3 nanoparticles' adsorption behavior toward Cd (II) and Zn (II) has also been investigated and phosphate and humic acid were observed to show improved adsorption capacity toward Cd (II) and Zn (II) while citrate could reduce the capacity of adsorption toward Zn (II) [244]. Beside the abovementioned heavy metals, Al_2O_3 nanoparticles exhibit efficient removal capabilities toward Hg (II), As (III), Cu (II), Ni (II), Cr (VI), etc. [144, 181, 230, 275].

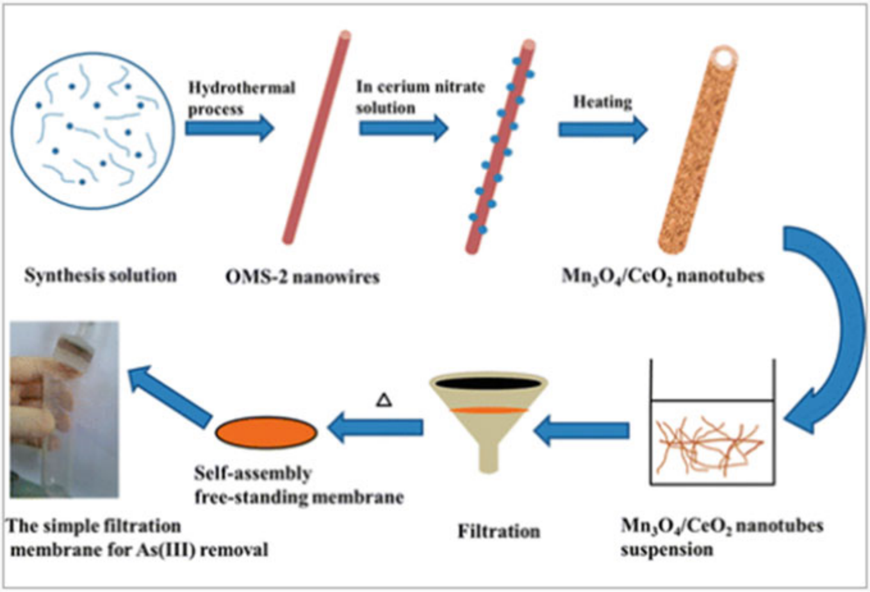

Fig. 15 Removal of arsenite from water by paper-like membrane of Mn_3O_4/CeO_2 Hybrid Nanotubes. Reprinted with license from American Chemical Society, Copyright (2015)

Magnesium oxide (MgO) nanoparticles are promising sorption materials for the removal of heavy metals due to their abundance, non-toxicity, environmental friendliness and overall cost-effectiveness. It was reported that MgO nanoparticles effectively remove Pb (II), Cd (II) and *Escherichia coli* from wastewater [34]. Furthermore, MgO nanoparticles showed extraordinary antibacterial properties toward gram-positive and gram-negative bacteria [245]. In another investigation, mesoporous MgO nanosheets were synthesized and were displayed to be excellently removed 1684.25 $mg{\cdot}g^{-1}$ Ni (II) from aqueous solution [67]. MgO nanoparticles were synthesized through the incineration process and were found to remove 96% Cu(II) from 10 ppm aqueous copper solution with high adsorption capability.

Cerium oxide (CeO_2) nanoparticles are non-toxic substances which have been utilized as photocatalysis and sensing [264], water treatment, etc. [203]. CeO_2 nanoparticles exhibit superior performance in heavy metal removals due to their active surface area, stability, selectivity and dispersion behavior. The sorption criteria of CeO_2 nanoparticles were investigated for the removal of Cr (VI) from aqueous solution [202]. The maximum adsorption capacity for Cr (VI) was reported as 121.95 $mg{\cdot}g^{-1}$. CeO_2 nanoparticles were reported to be prepared and were applied to remove As (V) and As (III) from aqueous solution [162]. The adsorption efficiency toward these two ions were observed as 36.8 and 71.9 $mg{\cdot}g^{-1}$, respectively,

Zirconium oxides (ZrO) nanoparticles are excellent metallic oxide adsorbent for the treatment of wastewater containing heavy metals. The merit of ZrO nanoparticles is the abundance of functional hydroxyl groups and high active surface areas.

Furthermore, ZrO nanoparticles have the chemical stability and show extraordinary sorption capability toward Pb (II), Zn (II) and Cd (II) [108]. A novel e ZrO_2/B_2O_3 nanocomposites were reported to be synthesized and were used to remove Cu (II), Co (II) and Cd (II) [282]. The removal efficiency for Cu (II), Co (II) and Cd (II) were found as 46.5, 32.2 and 109.9 $mg \cdot g^{-1}$, respectively. Polystyrene-supported $Zr(OH)_4$ nanoparticles were fabricated and were applied to remove Cd (II) from aqueous solution in varying pH [291]. The experimental outcome manifested that Cd (II) could be removed effectively in a wide pH range.

4 Nanocomposite in Water Treatment

Applications of nanoparticles in wastewater treatment have some issues regarding aggregation, intensive pressure drop during flow process, difficulties in separation from systems [95]. Though the types of metal nanoparticles discussed above have their own merits, they have often some problems in practical applications. For instance, nZVI aggregate and oxidized rapidly. TiO_2 nanoparticles and ZnO nanoparticles absorb electromagnetic spectrum only in the UV region because of their wide band gap. Carbon nanotube has difficulty in uniform suspension in various solvents and nZVI are easily oxidizable [89]. In order to overcome these problems, a general approach is adopted by synthesizing hybrid nanocomposites for wastewater treatment. For these reasons, the preparation of different nanocomposites has been gaining much attention to the researchers. Qian et al. briefly review the nanocomposite used in water treatment [189]. Figure 16 presents the nanoconfinement mediated water treatment by nanocomposite.

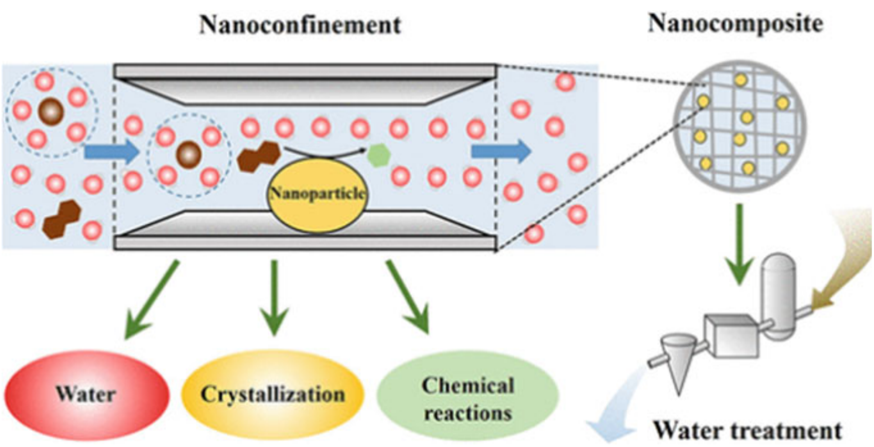

Fig. 16 Nanoconfinement mediated water treatment with nanocomposite. Reprinted with license from American Chemical Society, Copyright (2020)

Accordingly, many investigations have been done to fabricate useful nanocomposite for wastewater treatment throughout the world. For instance, a novel nanocomposite material was synthesized using nano zero-valent iron and carbon nanotubes where chemical deposition of nano zero-valent iron was done on the surface of carbon nanotubes. This nanocomposite adsorbent showed efficient capability to remove nitrate from water and it can easily be separated from the system by external magnetic fields [85]. Nanofiltration membranes of thin film nanocomposite have been synthesized through in situ implantation of TiO_2 nanoparticles on a polyimide support where TiO_2 nanoparticles were functionalized with both amine and chloride compounds to improve its compatibility. Nanofiltration membranes thus prepared displayed effective dye degradation and methanol flux [185]. Perfect nanocomposites for practical uses should be reactive as nanomaterials and continuous [260]. The more important thing is that treatment of wastewater requires non-toxic, cost-effective and log-time stable nanocomposites. To find suitable nanocomposites, further research in this field is still under way. In this section, various types of nanocomposite synthesized and applied for water treatment have been extensively discussed.

4.1 Nanocomposites with Inorganic Support

Nanocomposites are materials of multiple substances where one of the materials must be nanostructured. The combination of materials during preparation of nanocomposites offers suitable characteristics to it for the practical application in water treatment. Combination of TiO_2 and SiO_2 for the preparation of nanocomposites offers advantages of both materials by adsorbing virus on SiO_2 and showing enhanced antimicrobial activity with TiO_2 [107]. Ag_2S@Ag nanocomposite was fabricated which displayed enhanced sorption capability toward methyl orange and methyl blue in contaminated water [211]. In a review, Yin and Deng discussed about different nanocomposites with polymer-matrix for wastewater treatment [284]. Nanofiber membranes synthesized from polymer and metal or metal oxide nanoparticles were reported to show improved adsorption quality to heavy metals and enhanced antimicrobial activity. For example, Polyaniline/FeO composite nanofibers were reported for effective removal of carcinogenic arsenic from the water [28]. Similarly, from drinking water, the arsenic was effectively eliminated using bio-nanocomposite beads fabricated from chitosan goethite [91]. Many investigations on the use of hybrid nanomaterials for the removal of heavy metal from contaminated water were reported. As nanoadsorbent, the discarded parts of Zn-Mn dry batteries have been utilized to remove As, Cd and Pb [262]. Selenium nanoparticles containing polyurethane sponge have been reported for the efficient removal of Hg (II) from very rapidly because of the better affinity of selenium toward mercury [8]. Novel Fe_3O_4@diaminophenol-formaldehyde core–shell ferromagnetic nanorods for the elimination of Pb(II) from water was noted [267]. The nanorods displayed magnificent recovery time (25 s) due to the ferromagnetic properties with a high saturation magnetization value of the nanorod and hence possess better reusability among reported materials. So, the

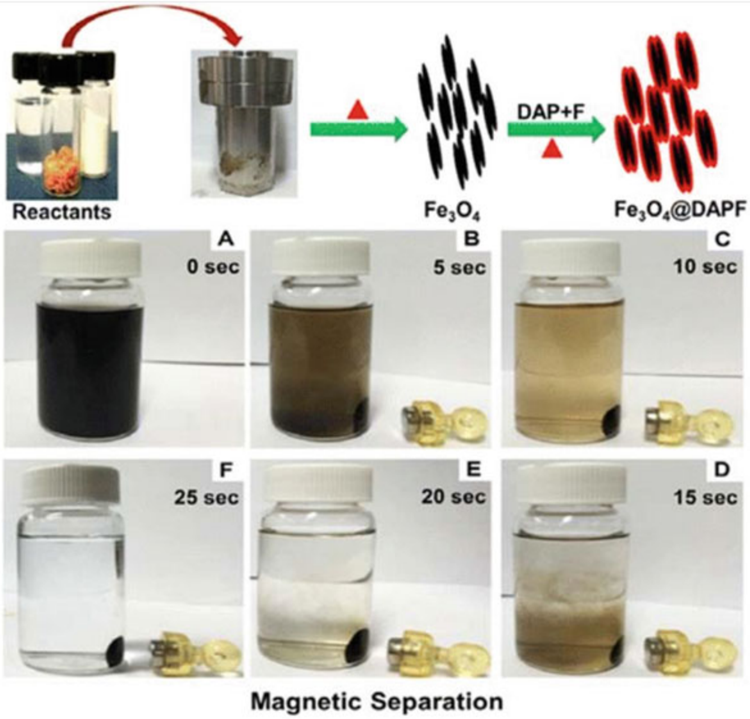

Fig. 17 Polymer composite of Fe_3O_4@diaminophenol-formaldehyde core–shell ferromagnetic nanorods based on core–shell ferromagnetic nanorod for the rapid removal of Pb(II). Reprinted with license from American Chemical Society, Copyright (2015)

Fe_3O_4@diaminophenol-formaldehyde core–shell ferromagnetic nanorods can act as good recyclable adsorbent alternatives to commonly utilized adsorbing materials for the fast removal of heavy metals from aqueous solutions (Fig. 17). Bentonite is excellent competitive material for the treatment of concentrated heavy metal contamination [52]. nZVI were found to be used with bentonite and applied for the removal of heavy metals [5].

4.2 Nanocomposites with Organic Supports

Organic polymer has numerous excellent properties with extraordinary mechanical strength, simple regeneration, easy degradability and modifiable functional group which enable it a promising candidate for being the host of nanocomposites [296]. Generally, there are two types of polymer-supported nanocomposite namely biopolymer-supported nanocomposites and synthetic organic polymer-supported nanocomposites [136]. The common example of the synthetic organic polymer used to support materials for preparing nanocomposites is polyaniline, polystyrene, etc. [196]. For instance, polypyrrole-polyaniline/Fe_3O_4 magnetic nanocomposites were synthesized and were reported to remove 100% of Pb (II) from 20 ppm aqueous solution [5]. Beside the synthetic organic polymers, natural polymers such as chitosan, cellulose, alginate, etc., were also applied as host materials for nanocomposites. The most abundant natural polymer cellulose has ample coordination sites for which make it amazing materials for adsorbent and support for nanoadsorbent [34]. Nanocellulose -Ag nanoparticles embedded pebbles-based nanocomposite was prepared and used to remove heavy metals, microorganisms and dyes from wastewater. Complete removal of Pb (II), 98% removal of Cr (III) and 99% disinfection capability toward microbial agents were displayed by Nanocellulose-Ag nanoparticles embedded pebbles-based nanocomposite [249].

Chitosan is another starting material for fabrication of promising adsorbent for metal contaminants because of the presence of amino and hydroxyl groups. ZnO/chitosan nanocomposite with low cost and lesser toxicity were fabricated and applied to remove Pb (II), Cd (II) and Cu (II) from aqueous solution [208]. The experimental result manifested the efficient sorption capability towards Cd (II), Pb (II) and Cu (II) and the recurring usable capacity of nanocomposites. A review on nanocomposites blend of functional polymers for the removal of metals from water with their preparation method, toxicity, separability and interactivity between nanoparticles and polymer were reported [135]. In another investigation, nanocomposite of hydrous Zr(IV) oxide was fabricated with the combination of a cation exchange resin and hydrous Zr (IV) oxide [96]. The investigated result showed remarkable adsorption capacity of nanocomposite of hydrous Zr(IV) oxide toward Cd (II) and Pb (II) in a column adsorption process. The cyclic column method displayed that the nanocomposites could be applied to practical acid mine wastewater time and again without loss of any capacity.

4.3 Magnetic Nanocomposites

Magnetic nanocomposites are promising candidates for the removal and degradation of contaminants from the polluted systems. The extensive studies of the toxicity of magnetic nanomaterials within or outside of an entire living organism have already been carried out. Hence, the abundant information on the toxicity of magnetic nanoparticles assists improved use of magnetic nanocomposites with less toxicity for treatment of contaminated water. However, there are a limited number of available magnetic nanoparticles such as Fe_2O_3, Fe_3O_4, nZVI, Co_3O_4 and NiO nanoparticles, etc. These are not enough for fabrication of magnetic nanocomposites to apply in the decontamination of water. There are also some issues to use magnetic nanocomposite for commercial purposes. First of all, the magnetic nanocomposite should be cost-effective to the practical application in the environment field. Otherwise, it will not be sustainable for common application for water treatment. Second, the properties of magnetic nanocomposite are essentially needed to improve for avoiding aggregation. The aggregation of the magnetic NPs and composite materials will hinder reusable capacity of the nanocomposite in the practical environmental remediation field. Finally, hazardness to the environment with application of magnetic nanocomposites in wastewater treatment should be minimized.

Studies on the toxicity of magnetic nanocomposites are just at the beginning stage. More research about the toxicity of the magnetic nanocomposites is necessary for the improvement of technology based on magnetic nanocomposite for water purification. Magnetic nanocomposites could be fabricated through surface modification of magnetic nanoparticles by different functional groups, combining magnetic nanoparticles with other organic or inorganic compounds like polyethylenimine, polyrhodanine, humic acid, MnO_2, etc. [116, 136, 161, 238]. Magnetic nanocomposites were synthesized through spraying the magnetic nanoparticles on graphene oxide or carbon nanotubes [57]. A core–shell $Fe_3O_4@SiO_2$ novel magnetic nanocomposite was synthesized and showed high removal ability toward Pb (II) and methylene blue. [99]. Fe@MgO nanocomposite was synthesized with the combination of nZVI MgO [74]. The advantage of strong magnetism of nZVI and efficient adsorption capability of MgO made it superior material for the effective removal of Pb (II) and methyl orange from wastewater. It is proven that magnetic nanocomposites have a high ability to remove heavy metal and to degrade the organic and inorganic pollutant from contaminated water with some limitations.

5 Conclusion and Perspective

Clean water is the key requirement to human health. The world is confronting critical challenges to meet the increasing demands of clean water as the sources of freshwater are declining due to climate change, population growth, increasing food production, increasing competition for fresh water resources in some areas, etc. Moreover, fresh water is polluted by agricultural contaminants, industrial contaminants, sewage contaminants, radioactive contaminants, microbes, organic and inorganic pollutants. There are several traditional ways for the treatment of wastewater. But nanomaterials have a number of important physicochemical properties that enable them especially attractive as a decontaminator wastewater. Nanomaterials can be modified by different functional materials to enhance their attraction toward contaminants. It is proved that they have the higher ability to remove organic and inorganic pollutants, toxic metal and radionuclides from aqueous solutions. Nanomaterials also give outstanding possibilities for the improvement of water purification systems more efficiently due to their high active surface areas and their size-dependent catalytic, optical and electronic characteristics. Nanomaterials are also being applied as active antimicrobial agents to treat pathogens containing water. Nanomaterials are widely applied to remove heavy metals from wastewater or aqueous solution of metal ions due to their excellent adsorption capabilities toward heavy metals.

In this chapter, metal-based nanomaterials are used in decontamination of wastewater which are fabricated from metal and metal oxide nanoparticles such as zero-valent nanoparticles (Fe, Zn, etc.), noble and transition metal nanoparticles (Fe, Cu, Ag, Au, Pd, etc.), metal oxide nanoparticles (iron oxide, titania, zinc oxide, magnesium oxide aluminum oxide, etc.) and overall nanocomposites of metal or metal oxide were discussed in detail. With the recent progress in wastewater treatment technology, nanomaterials-based water treatment methods are considered as extensive promising technology for wastewater decontamination. However, further investigations are still required to solve the issues regarding practical use of nanomaterials.

The drawback of existing nanomaterials will be required to be resolved for better application of these nanomaterials in water decontamination. First, most of the nanomaterials are not stable and easily aggregate. Moreover, it is generally troublesome to separate the nanoparticle from the system after the treatment process due to their nanosize. The development of nanocomposite materials could be an effective tool to solve this separation problem issue. Furthermore, to devise the facile synthesis procedure, to acquire long-time stability and to solve some other problems regarding nanocomposites, it requires more study in this area. Second, the commercial nanomaterials for heavy metal removal are scarce and more research is needed to obtain nanomaterials for commercial use. Finally, the effect and toxicity to the environment and human health due to extensive use of nanomaterials should be paid attention. There has been some research concentrated on the biological behavior and toxicity of nanoparticles toward human health [70, 114, 128, 225, 290]. The standard assessments of the toxicity of nanomaterials are quite inadequate at present. It is noticed from the previous study that most of the nanomaterials are observed as toxic substances after a certain level [32, 205]. Therefore, extensive study on the toxicity of nanomaterials is essential to ensure the safety for practical application.

The introduction of nanomaterials in the water treatment process is becoming a thriving tool. Moreover, the removal efficiency of contaminants with the above-mentioned nanomaterials is mostly studied in laboratory scale. More data of their application in practical wastewater treatment are inadequate and are badly needed. Present nanotechnology approaches for wastewater treatment seem promising. But, more extensive investigation is necessary to prove their safety in practical use. The metal-based nanomaterials should be low cost and superior to the traditional technologies that are applied for the water treatments. It is not easy to figure out the capabilities of different nanomaterials in practical applications and it requires more investigation to find out improved nanomaterials for the real application toward wastewater decontamination. Hence, the assessment of metal-based nanomaterials on the basis of performance in decontamination of wastewater should be perfected in the future. We visualize that metal-based nanomaterials will become excellent candidates for industrial and public water purification systems as more development is done through cost-effective synthesis and utilizing the environmentally acceptable functional materials.

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