



Potential of Magnetic Nanoferrites in Removal of Heavy Metals from Contaminated Water: Mini Review

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Abstract

Water, being an essential element for the survival of living organisms, requires to be free from contaminants and pollutants. These contaminants are generally of organic, biological, microbial or inorganic nature, and all these contaminants pose severe hazards to human health upon consumption through the water. The high concentration of heavy metal ions is being found in water resources owing to the ever-increasing anthropogenic as well as industrial activities. Some of the heavy metals are crucial for the development and functioning of the human body, whereas some are toxic. In any case, consumption of any heavy metal beyond the accepted guideline values can lead to the rise of health complications. Researchers are effectively using magnetic nanoferrites as nanoadsorbents for water treatment. Specially designed magnetic nanoferrites have been found to provide as high as 99% elimination of selective heavy metal ions from the contaminated water. The present study reviews the recent researches conducted in the last two decades in the area of health hazards posed by prolonged consumption of heavy metal ions through consumable water and about using magnetic nanoferrites, their composites and derivatives for efficient removal of different kinds of heavy metal ions.

Keywords Heavy metal ions · Magnetic nanoferrites · Nanoadsorbents · Contaminated water · Adsorption · Health hazards

1 Introduction

1.1 Water Pollution

Water is, undoubtedly, the foundation of human civilization as in the absence of water the life on earth will cease to exist. Water is one of the most vital elements essential for the existence and survival of humans and animals as well as plants. Water acts as the building material for cells, tissues and organs. Water accounts for 70% of the human's body weight and is the

critical constituent of blood and other bodily fluids. Water maintains the balance of bodily fluids in the human body as these fluids assist in numerous biological processes such as digestion, circulation, transportation and absorption of nutrients, along with maintaining the body temperature. Water also contributes to the production of lubricating fluid for joints and acts as a shock absorber due to its tendency to combine with viscous molecules and maintain its cellular shape [1, 2]. According to The National Academies of Sciences, Engineering, and Medicine, US, the adequate daily fluid intake for men and women is around 3.7 l and 2.7 l, respectively [3]. Out of all of the water present on earth, merely 0.014% is fresh and easily accessible for consumption. Humanity is currently using only around 36% of the total 14,000 km³ of available freshwater. Such a considerable availability of consumable water is significant enough to meet the requirements of the world's total population [4]. But due to uneven geographical distribution and unequal conditions, some parts of the world and people living in them face moderate to severe consumable water scarcity. Factors such as exponential increase in human population, spontaneous urbanization and fast industrialisation have also contributed to the escalation of the problem of water scarcity. The ever-increasing anthropogenic activities have resulted in a

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considerable increase in the demand of consumable water in recent decades [5].

Along with the present scarcity of consumable water, the issue of water pollution is an area of grave concern. The augmented anthropogenic activities and industrial growth have not only resulted in a heightened demand for consumable water, but these also contribute majorly to water pollution. Surface runoff water from agricultural and domestic activities and wastewater discharge from industrial establishments lead to the contamination of neighbouring water resources as well as groundwater [6].

Various types of contaminants, i.e. heavy metals, pathogens, dyes, surfactants and radiological substances, are known to severely pollute the water bodies, and consumption of contaminated water is proven to be harmful to the health of living organisms. Many underdeveloped and developing countries have observed that around 70–80% of problems in women and children are related to the consumption of contaminated water [7].

1.2 Heavy Metals as Water Contaminants

Heavy metal is a general term given to any metal and metalloid whose atomic density is higher than 4000 kg/m^3 [8]. Some of the heavy metals such as iron, zinc, nickel and molybdenum are essential for the growth of plants and animals but within permissible limits. Few of the heavy metals such as arsenic, mercury, lead and cadmium are not crucial for plants and animals, and their consumption beyond permissible limits tends to cause severe health problems [9–12]. Most of these heavy metals do not biodegrade and therefore are difficult to eliminate through conventional techniques.

The concentration of heavy metals in the water bodies can increase through natural processes along with anthropogenic activities [13]. Industrial wastewater discharge containing heavy metals by chemical-based industries producing pharmaceuticals, paints, fertilizers, pesticides and speciality chemicals are known to contaminate groundwater and water bodies [14]. Modern manufacturing processes such as electroplating, metal smelting, printed circuit board manufacturing and battery recycling are few of the major industrial activities that contribute largely in the release of heavy metals in the surroundings [15, 16]. Also, combustion exhaust from automobiles as well as various industries can lead to the deposit of few heavy metals such as lead, arsenic, chromium and mercury in the soil that can then reach water bodies and groundwater through surface runoff of water [17]. In a given area, an increase in agricultural and/or industrial activities can significantly pollute the neighbouring water sources. It is seen that the corrosion of plumbing pipes and the various components of water distribution systems can also lead to the addition of heavy metals in the water supply. The degree of heavy metal contamination in such cases is generally governed by

the water source, treatment technology employed, length, pipe coating and material of the supply pipes and water tanks [18, 19]. Geogenic contamination and natural anoxic conditions in the aquifers are also significant sources of heavy metal contamination in water sources in some areas of the world [20].

1.3 Health Hazards of Consumption of Heavy Metals

Out of the thirty-five metals that are defined by regulatory authorities and are known to pose dangers and threats to human health upon exposure, twenty-three of them are heavy metals [21]. Heavy metals can reach in the human body through oral ingestion, inhalation and dermal exposure. Use of heavy metals contaminated water is one of the most common sources through which these toxic heavy metals can be orally consumed by humans [22]. Though consumption of few heavy metals within a permissible limit has been declared essential for the development of human body, excess consumption of any one or multiple of the heavy metals through drinking water can lead to severe consequences to the human health [23]. It has been observed that prolonged consumption of few of the heavy metals can cause severe complications such as cancer, heart diseases, liver and kidney problems, lung and bladder disorders, gastrointestinal disorders, changes in blood composition and damage to fundamental organs [24–26]. The unchecked consumption of heavy metals has also been found detrimental to the cognitive development and central nervous system growth in children along with the improper brain and bone development [27, 28]. These heavy metals are also found to bioaccumulate in lipids or the gastrointestinal system of the human body and are known to give rise to fatal problems like cancer [29, 30]. In pregnant women, over-consumption of heavy metals contaminated water has been observed to increase the risk of stillbirth and congenital disabilities [31, 32]. Table 1 represents the guideline values, various health hazards and contamination sources of various common heavy metal contaminants.

Various types of physical, biological and chemical water treatment techniques are employed globally to obtain water that is fit for consumption. Different techniques like adsorption, electrochemical treatments, ion exchange, flotation, reverse osmosis, oxidation precipitation, membrane filtration, evaporation and biosorption processes are extensively used for wastewater treatment [52–56]. The efficacy of a technique to successfully remove the heavy metal contaminants depends on the type of the method. Some of these techniques are highly effective in eliminating pathogens but are not similarly effective in reducing heavy metal contaminants and vice versa. The use of nanomaterials is one such technique which has drawn extensive attention in the area of water treatment. The nanoscale size of these materials provides exclusive properties such as availability of large surface areas, more active sites for sorption process, high reactivity and strong adsorptions

Table 1 Guideline values, impacts and contamination sources of heavy metals

S. no.	Heavy metal	Heavy metal ion	Guideline value	Impacts on human health	Contamination sources	Ref.
1	Aluminium	Al(III)	0.9 mg/l	<ul style="list-style-type: none"> • Anaemia • Cardiac arrest • Nervous system disorders • Osteomalacia • Glucose intolerance 	<ul style="list-style-type: none"> • Water treatment processes • Water purification chemicals 	[33]
2	Antimony	Sb(III)	0.02 mg/l	<ul style="list-style-type: none"> • High cholesterol • High glucose in the blood 	<ul style="list-style-type: none"> • Occurs naturally in ground • Manufacturing of Flame retardants • Manufacturing processes • Natural weathering of rocks • Industrial and municipal waste 	[11, 34]
3	Arsenic	As(III) and As(V)	0.01 mg/l	<ul style="list-style-type: none"> • Arsenicosis • Thickening of the skin • Stomachache • Numbness of hands and feet, partial paralysis • Nausea, vomiting and diarrhoea • Blindness • Skin, lungs, kidney, bladder, liver, nasal passages, or prostate cancer 	<ul style="list-style-type: none"> • Natural deposits • Agricultural activities • Industrial practices • Volcanic emissions 	[10, 11, 35]
4	Barium	Ba(II)	1.3 mg/l	<ul style="list-style-type: none"> • Vasoconstriction • Peristalsis • Convulsions • Paralysis • Atherosclerotic heart disease • Total cardiovascular disease 	<ul style="list-style-type: none"> • Natural sources • Industrial emissions • Anthropogenic activities 	[36]
5	Cadmium	Cd(II)	0.003 mg/l	<ul style="list-style-type: none"> • Chronic renal failure • Kidney failure • Anaemia • Anosmia • Cardiovascular diseases • Osteoporosis • Hypertension • Acute and chronic intoxications 	<ul style="list-style-type: none"> • Naturally present in the soil • Atmospheric deposition • Industrial or agricultural activities • From leaching, erosion and harvested crops 	[9, 12, 37, 38]
6	Chromium	Cr(VI)	0.05 mg/l	<ul style="list-style-type: none"> • Liver and kidney disorders • Dermatitis • Respiratory issues 	<ul style="list-style-type: none"> • Occurs naturally in ground • Old mining operations • Industrial waste disposal 	[11, 39, 40]
7	Cobalt	Co(II)	0.05 mg/l	<ul style="list-style-type: none"> • Trouble in breathing • Asthma • Respiratory issues • Pneumonia • Wheezing 	<ul style="list-style-type: none"> • Natural occurrences • Anthropogenic activities 	[41]
8	Copper	Cu(II)	2.0 mg/l	<ul style="list-style-type: none"> • Mild gastrointestinal distress • Permanent liver or kidney damage 	<ul style="list-style-type: none"> • Natural deposits in rock and soil • Corrosion in household plumbing 	[12, 42]
9	Iron	Fe(III)	0.2 mg/l	<ul style="list-style-type: none"> • Dizziness • Low blood pressure • Headache and fever • Shortness of breath • Fluid in the lungs • Jaundice • Seizures 	<ul style="list-style-type: none"> • Iron coagulants • Corrosion of steel and cast iron pipes 	[43]
10	Lead	Pb(II)	0.01 mg/l	<ul style="list-style-type: none"> • Neurodevelopmental effects • Renal disorders • Cardiovascular diseases • Hypertension • Adverse pregnancy outcomes and infertility 	<ul style="list-style-type: none"> • Corrosion of household plumbing and water distribution systems 	[12, 44]
11	Manganese	Mn(II)	0.1 mg/l	<ul style="list-style-type: none"> • Neurological, cognitive and neuropsychological effects 	<ul style="list-style-type: none"> • Occurs naturally • Under low oxygen conditions in the depth of water bodies 	[45, 46]
12	Mercury	Hg(II)	0.006 mg/l	<ul style="list-style-type: none"> • Impaired brain functions and neurological disorders 	<ul style="list-style-type: none"> • Agricultural runoff • From seepage from landfills 	[47, 48]

Table 1 (continued)

S. no.	Heavy metal	Heavy metal ion	Guideline value	Impacts on human health	Contamination sources	Ref.
13	Nickel	Ni(II)	0.07 mg/l	<ul style="list-style-type: none"> • Growth retardation in infants • Complications in pregnancy • Endocrine system disruption • Nausea, vomiting and diarrhoea • Giddiness and physical tiredness • Headache and exhaustion • Improper breathing 	<ul style="list-style-type: none"> • Industrial activities • From fittings such as chromium-plated taps • From stainless steel well materials 	[49]
14	Silver	Ag(I)	0.05 mg/l	<ul style="list-style-type: none"> • Potential to damage DNA • Lowered blood pressure • Vomiting and diarrhoea • Stomach problems • Respiration issues 	<ul style="list-style-type: none"> • Through natural processes • Weathering of rocks • Erosion of soils 	[50, 51]
15	Zinc	Zn(II)	5.00 mg/l	<ul style="list-style-type: none"> • Stomach cramps • Nausea and vomiting 	<ul style="list-style-type: none"> • Corrosion of piping and fittings 	[12]

capabilities [57]. Owing to their strong adsorption characteristics and inherent anti-microbial tendencies, some of the nanomaterials have known to eliminate a range of contaminants from the polluted water. Numerous types of nanomaterials and their derivatives have been explored to treat contaminated water [58]. One such class of these nanomaterials is magnetic nanoferrites which, along with other crucial characteristics, also exhibit magnetic properties. The separation and recovery of nanomaterials from the treated water after the treatment process are generally the significant challenges involved. This magnetic property of magnetic nanoferrites makes this special class of nanoparticles a preferred choice as the separation and recovery of these nanoparticles can be easily and quickly achieved just by the application of external magnetic field [59, 60]. In the best knowledge of the authors, it is understood that a detailed report on the application of usual and innovative magnetic nanoferrites and their derivatives in the treatment of heavy metal contaminated water is not available. The present study thus aims to provide a comprehensive review of the research published, particularly in the last two decades, about the application and potential of conventional magnetic nanoferrites and their standard as well as novel derivatives for the elimination of toxic heavy metal pollutants from the contaminated or wastewater.

2 Magnetic Nanoferrites and their Properties

Nanotechnology is the study and research of matter at dimensions of nearly 1–100 nm, where extraordinary phenomena allow novel applications [61]. Ferrite is a ceramic material and falls within the group of compounds that have iron oxide as its vital component [62, 63]. Nanoscale ferrites, also called as nanoferrites, exhibit superior magnetic properties when compared to the bulk and pure metal [64]. Ferrites can be

categorized into three categories depending on their chemical structure, namely (a) Spinel Ferrite (MFe_2O_4) (where M stands for divalent metal ions, i.e. Co, Ni, Cu, Mn, Zn, Cd and Mg, with an ionic radius approximately between 0.6 to 1 Å), (b) garnet ferrites ($R_3Fe_5O_{12}$) (where R stands for trivalent ion, i.e. rare earth (Nd, Pr, Dy, Gd, etc.) and (c) hexagonal ferrites ($MeFe_{12}O_{19}$) (where Me stands for the divalent ion of a large ionic radius, such as Ba^{2+} , Sr^{2+} or Pb^{2+} or the trivalent ion such as La^{3+} , Al^{3+} , Ga^{3+} and Cr^{3+}). The ferrites under these categories show exclusive characteristics and distinctive magnetic properties [65, 66]. Magnetic nanoferrites can be synthesized through various synthesis routes, and the features of the prepared nanoferrites depend upon multiple factors and reaction conditions such as annealing temperature, composition, purity of the ingredients and pH of the solution [67, 68]. Nanoferrites offer several specific and exclusive advantages that facilitate them with the close attention of the researchers from the domain of water purification and treatment. Spinel ferrites, also called as soft ferrites, exhibit superparamagnetic properties and thus have been under extensive research for assessing their potential and applications in different domains of science and technology [69, 70].

Chemically speaking, a single unit cell of ferrite comprises a total of 64 tetrahedral and 32 octahedral locations which are available for cations [71, 72]. Ferrites are prepared by systematically mixing iron oxide Fe_2O_3 and the given divalent or trivalent ion, depending on the class of ferrite being synthesized. The mixture is then annealed and sintered at a high temperature. The temperature is generally less than that of the melting point of any of the ingredients of the mixture. In the process of heating, the elements fuse and form a spinel, garnet or hexagonal crystal structure [73]. The atoms of oxygen disperse in parallel layers, whereas the metallic atoms get scattered at the octahedral and the tetrahedral locations in between the layers. Figure 1 represents the crystal structure of an

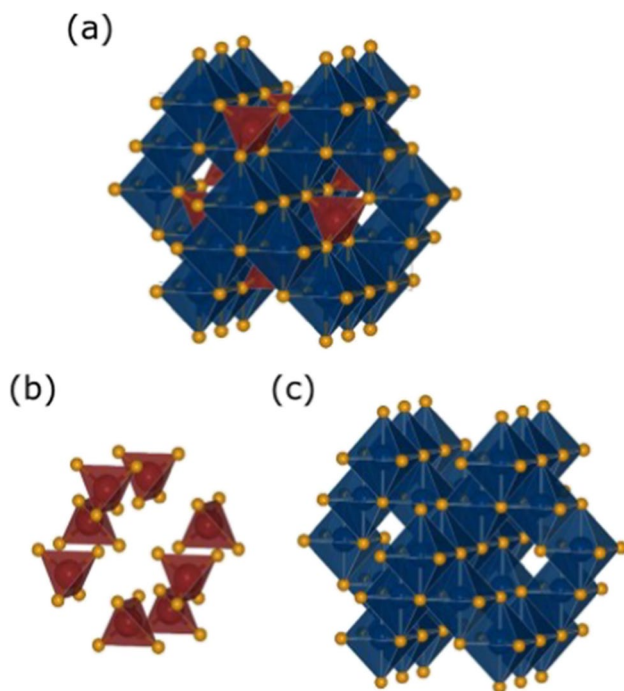


Fig. 1 Crystal structure of a single-cell unit of ideal spinel-type (a) full unit, (b) isolated tetrahedral (A-side) segment and (c) isolated octahedral (B-side) segment (reproduced by permission from Ref. [74], License Number 4861770977901, Copyright 2019, Elsevier)

ideal spinel-type unit cell as a whole as well as the view of tetrahedral and octahedral segments [74].

2.1 Critical Properties of Magnetic Nanoferrites for Contaminated Water Treatment

Magnetic nanoferrites, their derivatives and composites find extensive applications in contaminated water treatment owing to a few of the vital properties, i.e. (a) adsorbent for contaminant removal, (b) extraction of the adsorbate and adsorbent and (c) sensing and detection of heavy metal ions present in the contaminated water. These properties are briefly summarized as follows:

2.1.1 Adsorbent for Contaminant Removal

Numerous types of nanoparticles have been considered and researched for their potential as adsorbents. The nano-sized adsorbents have been highlighted because of the two principal properties, i.e. elemental surface and extrinsic functionalisation [75]. The capability of magnetic nanoferrites to eliminate several contaminants has been established in both laboratories and on-site field testing [76]. Along with dyes, phenols, pesticides, detergents and an extensive range of aromatic compounds, heavy metal ions are the most common pollutants existing in the contaminated water. Treatment of contaminated water to eliminate or significantly reduce the concentration

of the heavy metal contaminants by utilising a ferrite-based magnetic nanoadsorbent is considered as one of the most efficient and cost-effective approaches. The simplicity of synthesising and application make ferrous oxides an inexpensive alternative for heavy and toxic metals adsorption from its liquid form [77]. The metallic ions have been regarded as the contaminants causing pollution due to their harmful influence on humans. Magnetic nanoferrites are particularly suitable for the adsorption of the metallic ions because of their innate characteristic enabling the elimination of metals.

Moreover, their suitability is enhanced by the non-toxicity, recyclability and easiness in the dissolution of magnetic nanoferrites [61]. They are favoured for contaminated water treatment since they have higher adsorption capability and better dynamic locations for an interface with the contaminants [78, 79]. Their superparamagnetic behaviour dramatically assists them in dissolution from the solution by the peripheral magnetic field. Most of the existing applications of magnetic nanoferrites in contaminated water treatment depend upon the adsorptive technologies or photocatalytic technologies. The adsorptive technologies use magnetic nanoferrites either as a type of immobilisation bearer or as a nanoadsorbent for improving the efficiency in the removal of contaminants. While on the other hand, photocatalytic technologies utilize magnetic nanoferrites as semi-conductor photocatalysts for transforming the pollutants into a lesser toxic compound [80]. It is evident that magnetic nanoferrites are very useful in the removal of heavy metal contaminants because of (i) the ability to remove contaminants even at low concentration of the adsorbent, (ii) excellent adsorption characteristics, (iii) the ability to reduce the toxicity of various harmful metal contaminants by changing their oxidation state, (iv) the tendency to furnish adjustable reactive surface, (v) the more facile desorption of the adsorbed contaminants from the adsorbent's surface and (vi) cost-effectiveness and reusability [81, 82].

2.1.2 Extraction of the Adsorbate and Adsorbent

When other stable compounds are used as adsorbents for the adsorption process of heavy metal pollutants, the easiness and cost-effectiveness of the process are always the major challenges [83, 84]. The use of magnetic nanoferrite provides the most recent, most accessible and cost-effective way for the extraction of the adsorbate as well as of the adsorbent via the magnetic solid-phase extraction [85]. This extraction technique is dependent on various properties of magnetic nanoferrites such as high adsorption capacity and superparamagnetic properties. In this technique, a slight amount of magnetic nanoferrites is added in contaminated water holding the contaminants so that the adsorbate gets adsorbed onto the surface of the magnetic adsorbent. Then, the magnetic adsorbent and the object adsorbate are generally isolated by utilising appropriate eluent such as acids, base or

alcohols. The obtained magnetic adsorbent could be reutilized, which makes the use of magnetic solid-phase extraction technique as one of the most profitable and efficient sample preparation techniques. The extraction time is very swift, highly sensitive and efficient [86, 87]. One of such examples is the soft ferrite nanoparticles which are often utilized in the development of magnetic-based solid-phase extraction adsorbents, which are quite easy to synthesize and possess non-toxicity.

2.1.3 Sensing and Detection of Heavy Metal Ions Present in the Contaminated Water

Easier and accurate sensing and detection of different metal ions present in contaminated water is a significant area of concern [85]. Magnetic nanoferrite-based sensors have proven to be advantageous in many ways due to their faster response rate, high sensitivity and highly efficient in the selection of the detection of various chemical items than single oxides [88]. Since there are many toxic metal ions generally present in the contaminated water in different concentrations where each of these metal ions possesses their specific properties, the enhanced capability of magnetic nanoferrites in sensing and detecting these metal ions is highly appreciated. For example, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles are capable of delivering extremely discriminatory detection for Zn(II) with a detection limit of 10^{-4} M [89]. Sensing and detection of the heavy metal ions present in the contaminated water is an indispensable requirement which could be best fulfilled by the use of magnetic nanoferrites as is seen from the works of various researchers.

3 Heavy Metal Removal by Magnetic Nanoferrites and Their Derivatives

Aluminium is the most extensively utilized non-ferrous inorganic metal and also considered as an extremely toxic metal in the water at high concentrations, especially for drinking purposes. Utilization of aluminium-based coagulants, i.e. $\text{Al}_2(\text{SO}_4)_3$ or poly aluminium chloride (PACL), at times increases the aluminium concentrations in addition to the naturally occurring aluminium content in the water. Acid rain also leads to the rise in the aluminium level in various sources of freshwater [90]. A high concentration of aluminium ranging from 3.6 to 6 mg/L in the water leads to turbidity, decreases efficiency for disinfection and may precipitate as $\text{Al}(\text{OH})_3$ during the distribution time. In very high doses, aluminium causes neurotoxicity, followed by a transformed function of the blood-brain barrier. Several procedures have been extensively used for the removal of aluminium ions such as sedimentation, chemical precipitation, coagulation method, filtration, reverse osmosis, electrodialysis and cation exchange but nanotechnology has the best potential for removal of the

aluminium heavy metal ions from the contaminated water. The aluminium(III) ions present in the contaminated water can be removed using magnetic nanoferrites via the batch procedure. A fast, specific and cost-effective magnetic solid-phase removal of aluminium(III) ions from water has been developed with magnetic nanoferrites, and the whole adsorption process can be completed in just 4 min [91]. In recent times, the removal of antimony(III) contaminant from contaminated water has been of great concern. In nature, the antimony(III) is much less predominant, but its influence on human health as well as the environment is of great importance. The speciation and distribution in freshwater related to antimony(III) have not yet been extensively studied. Different technologies have been used and proposed for the removal of antimony(III) from aqueous media. Not much literature is available related to antimony(III) as it has recently come into the limelight, and the researches are still in the commencement phase [92]. Two magnetic nanoferrite-based adsorbents have been successfully developed to remove antimony(III) from water, i.e. $\text{Fe}_3\text{O}_4@\text{Fe}_2\text{O}_3@\text{CNs}$ and $\text{Fe}_2\text{O}_3@\text{CNs}$, and these have the capability of magnetic separation and high removal capacity for removing antimony(III) [93].

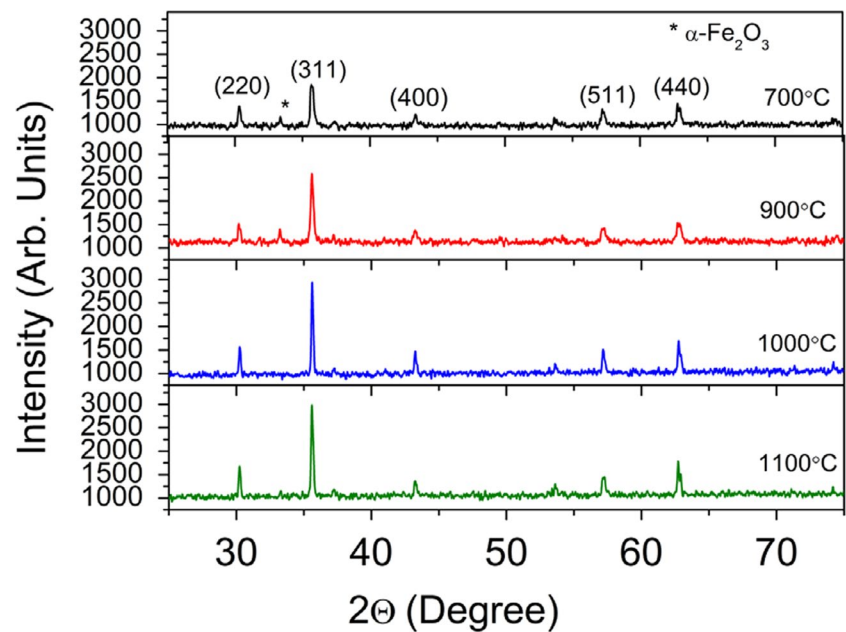
Spinel ferrites such as CoFe_2O_4 , MnFe_2O_4 and Fe_3O_4 , when used as nanoadsorbents, are capable of successfully removing arsenic(V) from contaminated water within a contact time of 48 h even when the arsenic(V) concentration in the water is as high as 1000 $\mu\text{g/L}$. Around 40 mg/L of these adsorbents are sufficient to bring down the concentration of arsenic(V) in the water below the permissible limit of 10 $\mu\text{g/L}$. Figure 2 depicts the XRD patterns of CoFe_2O_4 nanoferrites pre-sintered at 700 °C and sintered at 900 °C, 1000 °C and 1100 °C for 3 h [73].

An innovative magnetic composite comprising of chitosan, clay and nano-magnetite in the mass ratio of 1:1:2 can also be employed as a nanoadsorbent to eliminate arsenic(V) from contaminated water. This novel composite can provide an arsenic(V) removal efficiency of around 26% at nano-magnetite's relative mass ratio of 4, water's pH level of 5, for a contact period of 10 h at 23 ± 2 °C and 150 rpm. Figure 3 represents the FE-SEM images and EDX analysis of chitosan, clay and nano-magnetite particles [94].

Novel synthetic nanoferrite (Fe_3O_4) of size ~ 12 nm, prepared by co-precipitation method, exhibits potential as a nanoadsorbent to eliminate arsenic(V) from the aqueous solution of arsenic(V) ions when maintained at pH value of 5.0. Only 0.2 g of the nanoadsorbent is capable of removing arsenic(V) from the aqueous solution after the contact and stirring time of 24 h. The synthesized magnetite exhibits the maximum adsorption capacity of 66.53 mg/g. Figure 4 shows the SEM images of these synthetic nFe_3O_4 and magnetite samples [95].

Arsenic(III) and arsenic(V) can be removed from the contaminated water by the use of magnetic nanohybrid

Fig. 2 XRD patterns of CoFe_2O_4 nanoferrites at different pre-sintering temperatures (reproduced by permission from Ref. [73], License Number 4861670455830, Copyright 2015, Elsevier)



nanoparticles comprising of graphene oxide and manganese ferrite nanoparticles (GO-MnFN). These magnetic nanohybrid nanoparticles can successfully remove arsenic(III) and arsenic(V) from an aqueous solution of 400 mg/L of arsenic concentration. The usual manganese ferrite nanoparticles (MnFN) exhibit a maximum adsorption capacity of 97 mg/g whereas (GO-MnFN) exhibit the maximum adsorption capacity of 146 mg/g for arsenic(III) under similar conditions. In the case of arsenic(V), the maximum adsorption capacity of 137 mg/g and 207 mg/g can be achieved using MnFN and GO-MnFN, respectively, with pH ranging from 2 to 7 [96].

Magnetic hydroxyapatite nanoparticles can be employed for the removal of cadmium(II) ions from the aqueous solution where it can deliver the maximum adsorption capacity of ~

1.964 mmol/g. A small quantity of 0.002 g of magnetic nano-adsorbent can be used in 20 mL of cadmium(II) solution when the pH value of the solution is around 5 [97]. Chromium(VI) is also carcinogenic and irritates tissues when present, even in small concentrations. The hexavalent chromium is a strong oxidant, behaves like a tissue poison and thus can lead to severe health issues [98]. Chromium(VI)-contaminated water is put to ferrite process where the present chromium(VI) binds with ferric oxide and forms Cr-ferrite [99]. Novel hybrid nanoparticles prepared by combining sodium-rich montmorillonite (MMT) with magnetite and coated with polyethylenimine polymer (PEI 800 g/mol or PEI 25000 g/mol) exhibit potential in removing chromium(VI) from the chromium solution of 12 mg/L at pH value of 3. The adsorption capacity of 8.77 mg/g and

Fig. 3 FE-SEM images and EDX analysis of chitosan, clay and nano-magnetite particles (reproduced by permission from Ref. [94], License Number 4860290781940, Copyright 2012, Elsevier)

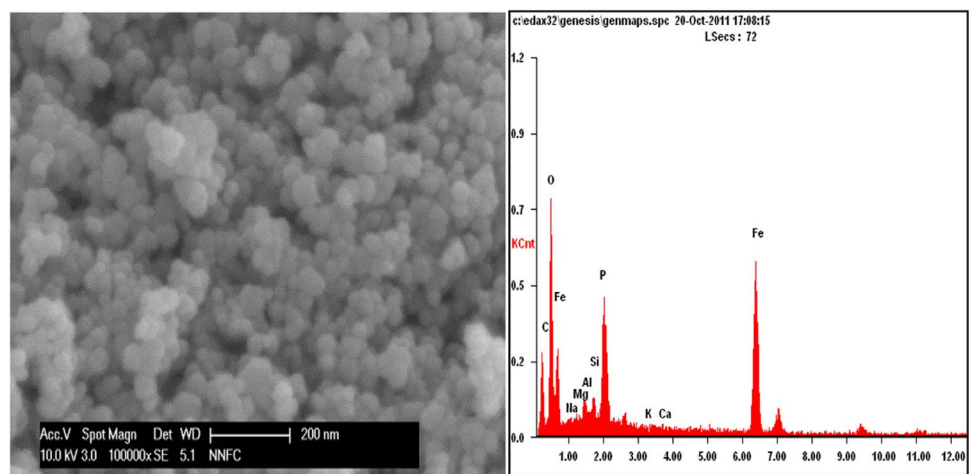
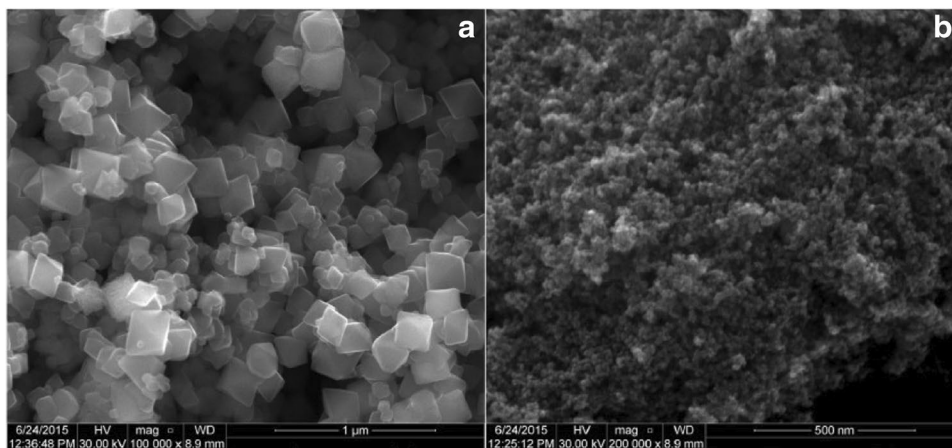


Fig. 4 SEM images of **a** synthetic $n\text{Fe}_3\text{O}_4$ and **b** magnetite samples (reproduced by permission from Ref. [95], License Number 4860290994370, Copyright 2016, Elsevier)



7.69 mg/g can be achieved by using MMT-PEI800-Magnetite and MMT-PEI25000-Magnetite nanoparticles, respectively. Figures 5 and 6 show the TEM images of MMT-PEI800-Magnetite and MMT-PEI25000-Magnetite nanoparticles, respectively. [100].

Tetraethylenepentamine functionalized magnetic polymer nanoadsorbents (TEPA-MPN) deliver the maximum adsorption capacity of 370.4 mg/g when the solution is maintained at 35 °C having a pH value of 2.0. Only 0.05 g of TEPA-MNP

delivers such high adsorption capacities and with a contact time of 3 h [101]. Cobalt-zinc magnetic nanoferrites with chemical composition as $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, when used as nanoadsorbent, deliver a maximum adsorption capacity of ~ 16.0 mg/g when the chromium(VI) solution of the initial concentration of 4.0 mg/mL and pH value of 2.0 is treated. For an acidic aqueous solution of chromium(VI), the equilibrium time ranges between ~3 min and ~ 120 min with the adsorbent dose of 4.0 g/L. In contrast, the concentrations of

Fig. 5 TEM images of MMT-PEI800-Magnetite nanoparticles (reproduced by permission from Ref. [100], License Number 4860280733120, Copyright 2012, Elsevier)

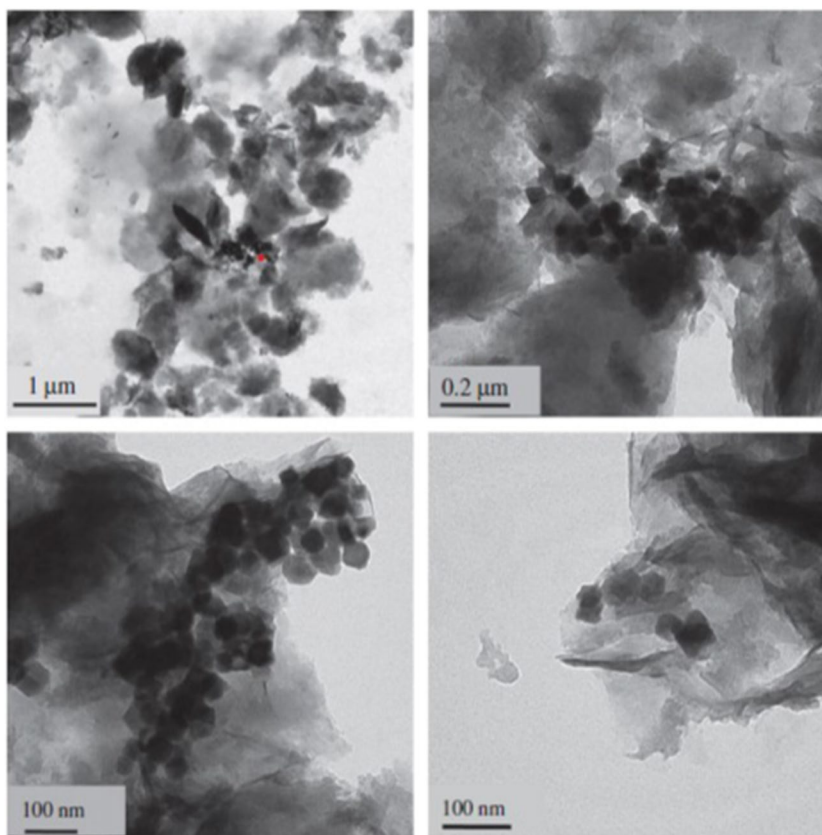
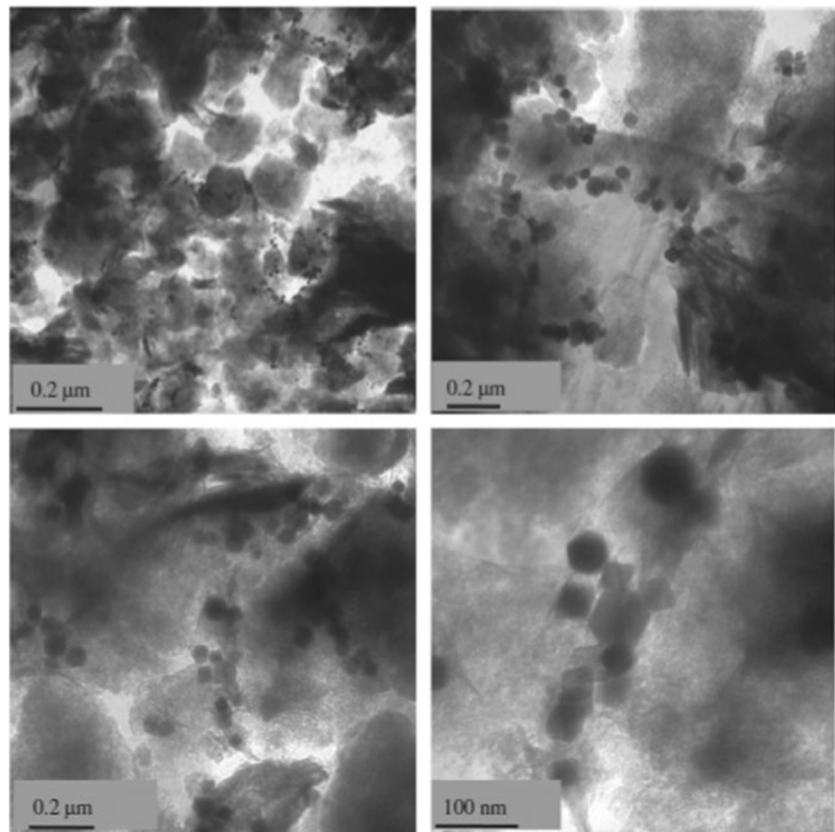


Fig. 6 TEM images of MMT-PEI25000-Magnetite nanoparticles (reproduced by permission from Ref. [100], License Number 4860280733120, Copyright 2012, Elsevier)



chromium(VI) solution varies between 20 and 100 mg/L [102]. Cobalt nanoferrites, synthesized by co-precipitation method, can be successfully employed to remove chromium(VI) from tannery wastewater and ~23.75% of removal efficiency can be achieved with using between 0.1 g and 0.3 g of cobalt ferrite in 50 mL of the Cr(VI) solution [103]. Maghemite nanoparticles of size 10 nm, prepared by the sol-gel method, can effectively remove the chromium(VI) from electroplating wastewater. 1.0 g of maghemite nanoparticles can be added to 40 mL of 100 mg/L concentration of acidic chromium(VI) solution with a pH value of 2.5, and adsorption equilibrium can be achieved within 10 min of duration, and ~17.0 g of chromium(VI) can be removed under given conditions [104].

The magnetic composite of chitosan/clay/nano-magnetite can remove copper(II) from a copper(II) ion solution of 1000 mg/L concentration, maintained at pH 5. It is to note that increase in the mass ratio of nano-magnetite in the composition results in a decrease in the copper(II) removal efficiency since chitosan is the key ingredient that facilitates copper(II) removal [94]. Maghemite nanoparticles can also be used to remove copper(II) from copper(II) ion solution, and adsorption equilibrium can be achieved within 10 min. 0.1 g of maghemite nanoparticles can successfully remove ~26.8 g of copper(II) ion from the 40 mL solution with an initial concentration of 100 mg/L and with a pH value of 6.5 [95].

The maximum adsorption capacity of around 488 mg/g and 673 mg/g can be achieved when an aqueous solution of lead(II) is treated using MnFN and GO-MnFN, respectively. The adsorption of lead(II) ions increases with an increasing pH value of the aqueous solution, i.e. from 2 to 6 and having a lead(II) ion concentration of 100 mg/L [96]. The novel magnetic nanoadsorbent, synthesized by sequential modification of SiO₂-coated Fe₂O₄ with (3-Chloropropyl) trimethoxysilan, polyetherimide, epichlorohydrin and thiourea, shows promising capabilities for the removal of lead(II) from aqueous solutions. The maximum adsorption capacity of ~110.13 mg/g can be achieved with 10 mg of adsorbent in a lead(II) solution of 100 mg/L of concentration with a contact time of 10 min. The synthesized nanoadsorbent retains its reactivity and adsorbing potential even after six cycles. Figure 7 depicts the TEM images of (a) Fe₃O₄@SiO₂ and (b) Fe₃O₄@SiO₂-PEI-SH and XPS spectra of (c) Fe₃O₄@SiO₂ and (d) Fe₃O₄@SiO₂-PEI-SH [105].

When single Fe₃O₄ magnetic nanoparticles are employed for the removal of lead(II) through the batch-adsorption process, the equilibrium can be achieved within 30 min. For Fe₃O₄ as magnetic nanoadsorbent, the initial concentration, pH value of the solution and operating temperature are the key factors governing the adsorption capacity. Figure 8 represents the graph showing the effect of pH on lead(II) adsorption onto Fe₃O₄ nanoadsorbents for an initial lead(II) concentration of

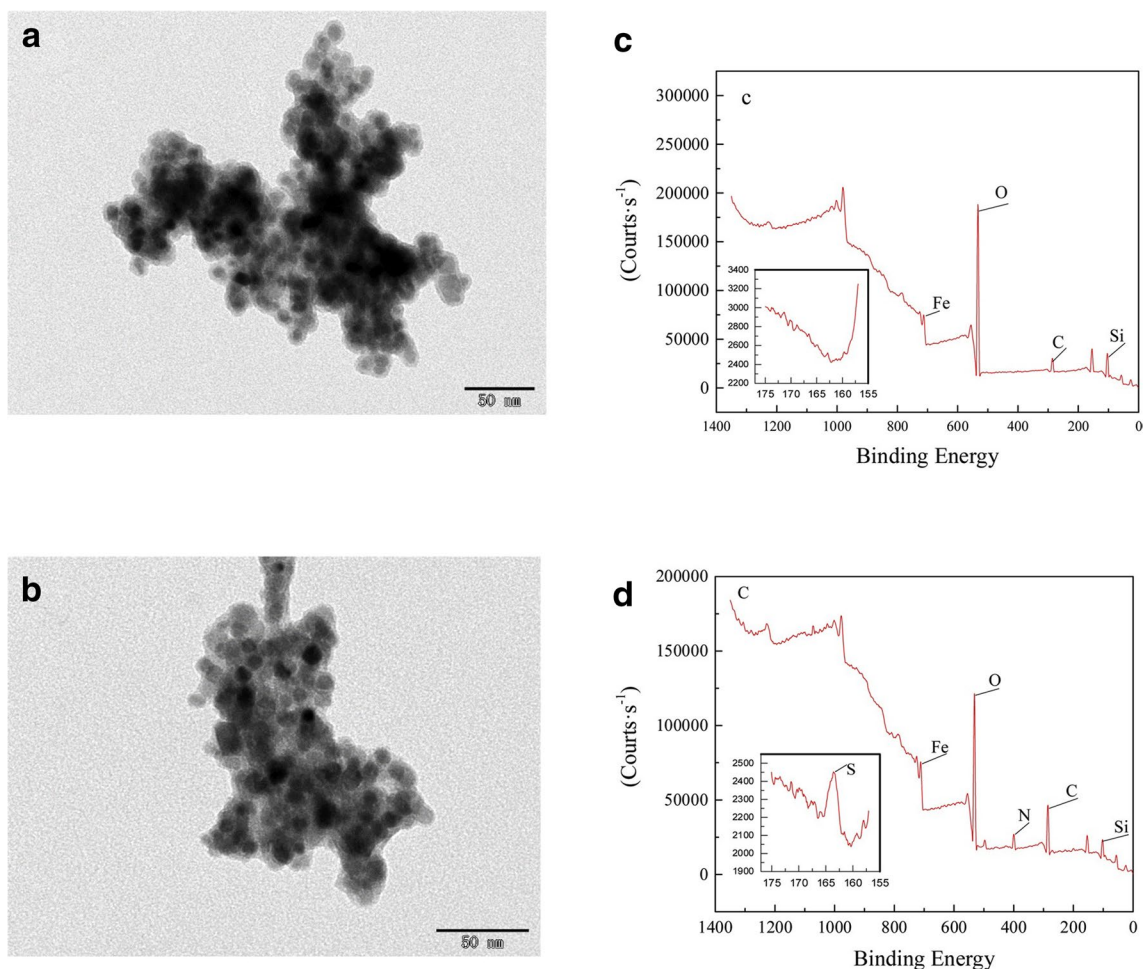


Fig. 7 TEM images of **a** Fe₃O₄@SiO₂ and **b** Fe₃O₄@SiO₂-PEI-SH and XPS spectra of **c** Fe₃O₄@SiO₂ and **d** Fe₃O₄@SiO₂-PEI-SH nanoparticles (reproduced by permission from Ref. [105], License Number 4860660508678, Copyright 2019, Elsevier)

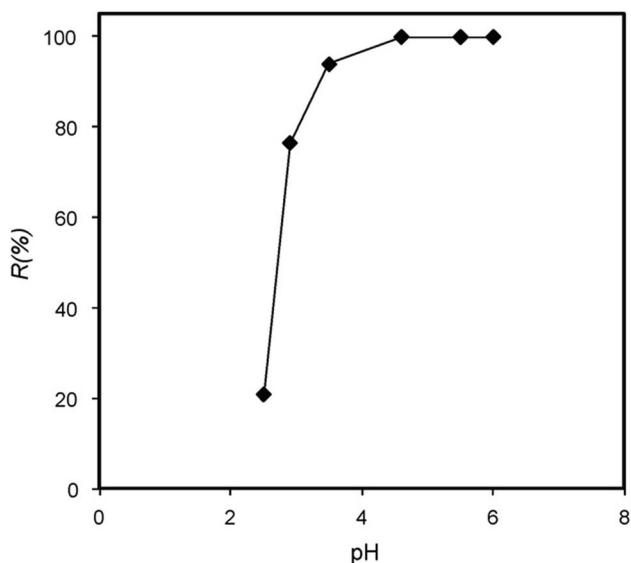


Fig. 8 Effect of pH on lead(II) adsorption onto Fe₃O₄ nanoadsorbents (reproduced by permission from Ref. [106], License Number 4860660941328, Copyright 2010, Elsevier)

220 mg/L while using an adsorbent dose of 10 g/L for a contact time of 24 h and at room temperature [106].

The magnetic Fe@MgO nanocomposites, synthesized by the facile precipitation-calcination method, show maximum adsorption capacity of ~1476.4 mg/g in removing lead(II) from lead(II) ion from aqueous solution. Ten milligrams of magnetic Fe@MgO nanocomposites in 100 mL of the aqueous solution with the initial concentration of 100 mg/L to adsorb lead(II) within 60 min of duration. Figure 9 shows the SEM and TEM (inset) image of Fe@MgO nanocomposites [107].

Surface-functionalized nano-sized Fe₃O₄@SiO₂ core of ~15 nm coated with Zr-based magnetic metal-organic frameworks shows potential in removing lead(II) from contaminated water, and maximum adsorption capacity of 102 mg/g can be achieved. Ten milligrams of the adsorbent can successfully remove lead(II) from 10 mL of lead(II) ion solution with a pH value of 6 and after a contact time of 60 min [108]. Ten milligrams of humic acid-coated Fe₃O₄ nanoparticles of size ~10 nm, prepared by co-precipitation method when added to

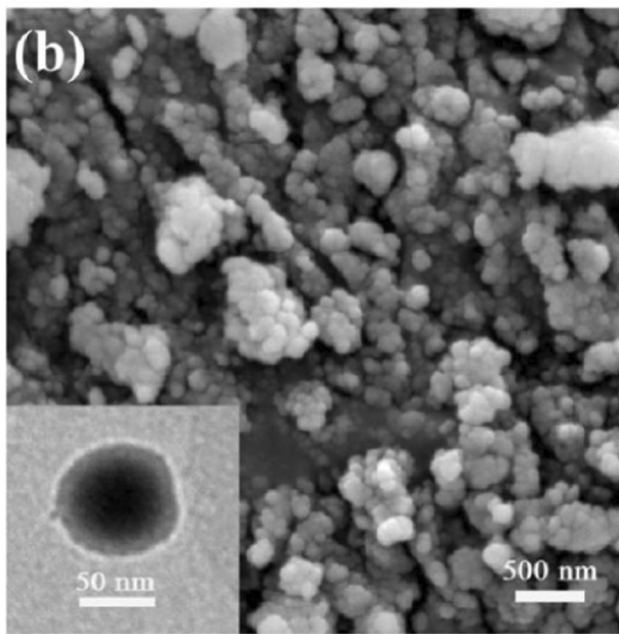


Fig. 9 SEM and TEM (inset) image of Fe@MgO nanocomposites (reproduced by permission from Ref. [107], License Number 4860661418272, Copyright 2018, Elsevier)

a 100 mL metal ion solution of 1 mg/L of initial metal concentration, can successfully remove over 99% of lead(II) from natural and tap water. The adsorption equilibrium is reached within 15 min when the pH value of the mixed solution is kept as 6 [96].

When humic acid is used as a coating for Fe_3O_4 magnetic nanoparticles, 50 mg of these modified nanoparticles can successfully remove 99% of mercury(II) from the 100 mL of real water. The adsorption equilibrium reaches in 15 min and agrees well with the Langmuir adsorption model. The adsorption capacity and metal removal efficiency of these nanoparticles range between 90 and 99% as it gets influenced by the pH of the solution and due to desorption of humic acid by Fe_3O_4 magnetic nanoparticles [109]. Core-shell magnetic $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles can be functionalized with sulfonic and carboxylic acid groups, and these can facilitate easy and complete removal of the mercury(II) ions from the contaminated water. The experimental procedure involving these nanoparticles can achieve equilibrium within 5 min. The maximum adsorption capacity of 83.1 mg/g with the removal efficiency of 98.1% towards mercury(II) heavy metal ions can be achieved by using these $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles [110]. Modified magnetic nanoparticles functionalized with diverse organic ligands, such as aminopropyl silane (MNP-APS), peptone (MNP-P) and yam peel biomass (MNP-YP), and obtained by the process of conventional co-precipitation method show the potential to remove mercury(II) ion from the contaminated water. The adsorption equilibrium can be achieved within 5 h. Mercury adsorption evaluation as a function of the

pH shows that 94% of adsorption for samples of MNP-APS, 87% for MNP-P (both having pH value of 7.0) and 75% for samples of MNP-YP (having pH value of 8.0) can be achieved using these derivatives of magnetic nanoferrites [111].

Polyrhodanine-coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles can be effectively utilized to remove mercury(II) from wastewater, but these nanoparticles follow the Freundlich isotherm model instead of a Langmuir model. Five milligrams of polyrhodanine-coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles are mixed with 10 mL of mercury nitrate solution, and when the mixture is shaken for 2 h, the maximum mercury(II) ion absorptivity of 94.5% can be achieved with the initial mercury(II) ion concentration of around 1.3 mg/L. Figure 10 represents the TEM images of the polyrhodanine-encapsulated magnetic nanoparticles [112].

Nickel(II) is one of the heavy metals that is used extensively in the manufacturing of stainless steel, alloys, coins and batteries. Some nickel compounds are carcinogenic and can prove fatal in the cases of prolonged exposure [49]. The hydrothermal reaction-based ferrite process of wastewater can treat the nickel(II) and chromium(VI) ions present in contaminated water and convert them into Ni-Cr ferrites. The optimum conditions to achieve this conversion include managing the water with the pH value of 9.0 at 70 °C when the mixture is stirred for 40 min at a stirring speed of 120 rpm [99]. 0.1 g of nanoscale maghemite particles exhibit superb adsorption characteristics when allowed to come in contact with 40 mL of 100 mg/L concentration of nickel(II) ion solution. Within 10 min, adsorption equilibrium can be achieved, and ~ 23.6 mg of nickel(II) can be removed from the nickel(II) solution of pH value of 8.5 [104]. In case of the removal of zinc(II) ions from zinc(II) ion solution, the magnetic hydroxyapatite nanoparticles deliver a maximum adsorption capacity of ~2.151 mmol/g with 0.1 g/L of the adsorbent dosage. The adsorption capacity of the magnetic hydroxyapatite

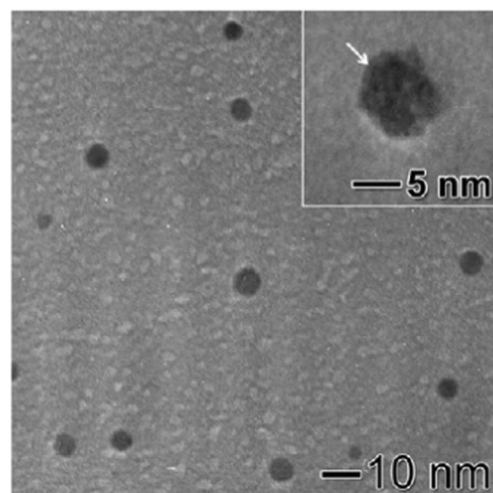


Fig. 10 TEM images of the polyrhodanine-encapsulated magnetic nanoparticles (reproduced by permission from Ref. [112], License Number 4860651418600, Copyright 2011, Elsevier)

nanoparticles, having a high surface area of $\sim 142.5 \text{ m}^2/\text{g}$, increases with an increasing pH value of the solution from 4 to 8 [97].

4 Conclusion and Outlook

Nanotechnology, an emerging field of science, has been finding its applications in almost all branches and domains of technology. The inherent characteristics of the nanomaterials give them added advantages over the bulk materials. The ever-increasing global problem of consumable water scarcity and pollution has motivated the researchers to explore novel and innovative methods and materials that can be utilized to treat contaminated water successfully. The use of nanoferrites and the phenomenon of adsorption has been one of the most effective techniques to treat contaminated water. The presence of heavy metal ions in consumable water poses various types of dangers and severe threats to human health, and thus, the concentration of these toxic and heavy metal ions should be reduced below the set acceptable limits. Various types of nanoferrites, their composites and their derivatives have been synthesized and explored by researchers to evaluate their potential in removing heavy metal contaminants from the contaminated water. The magnetic tendency of magnetic nanoferrites along with their high reactivity and sizeable available surface area makes them the preferred candidates to be used as nanoadsorbents. The properties of the magnetic nanoferrites can be further enhanced by exploring the surface-functionalized, core-shell structure design of magnetic nanoferrites. The present review concludes that the nanoferrites, their composites and their derivatives have been widely used in removing a few of the heavy metals such as arsenic, lead, mercury and cadmium. Still, their use in removal of other heavy metal ions such as antimony, aluminium, barium and thallium have not been much explored. There is a need to extensively examine and evaluate the potential and suitability of different types of nanoferrites and their derivatives in the removal of all kinds of heavy metal ions. There exists an untapped and broad scope of conducting meaningful research in the area of detection and removal of these less-explored heavy metal ions.

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