Magnetic nanoadsorbents' potential route for heavy metals removal—a review

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Abstract

Due to the rapid growth in the heavy metal-based industries, their effluent and local dumping have created significant environmental issues. In the past, typically, removal of heavy metals was handled by reverse osmosis and ion exchange techniques, but these methods have many disadvantages. Therefore, extensive work into the development of improved techniques has increased, especially for heavy metal removal. Many countries are currently researching new materials and techniques based on nanotechnology for various applications that involve extracting heavy metals from different water sources such as wastewater, groundwater, drinking water and surface water. Nanotechnology provides the possibility of enhancing existing techniques to tackle problems more efficiently. The development in nanotechnology has led to the discovery of many new materials such as magnetic nanoparticles. These nanoparticles demonstrate excellent properties such as surface-volume ratio, higher surface area, low toxicity and easy separation. Besides, magnetic nanoparticles can be easily and efficiently recovered after adsorption compared with other typical adsorbents. This review mainly emphasises on the efficiency of heavy metal removal using magnetic nanoadsorbent from aqueous solution. In addition, an in-depth analysis of the synthesis, characterisation and modification approaches of magnetic nanoparticles is systematically presented. Furthermore, future opportunities and challenges of using magnetic particles as an adsorbent for the removal of heavy metals are also discussed.

Keywords Magnetic nanoparticles · Heavy metal removal · Magnetic nanoadsorbent

Introduction

Lately, the removal of dye and harmful heavy metals from wastewater released from manufacturing industries is getting much attention. Adsorption is one of the most prominent approaches for water and wastewater de-contamination from heavy metals and organic compounds as well as other inorganic pollutants. Due to this fact, wide ranges of adsorbents with different compositions have been synthesised (Gupta et al., 2010). For instance, low-cost adsorbents like agricultural waste (Bhatnagar et al., 2015, Ahmad and Danish 2018) and biomass-based activated carbon (Yagub et al., 2014) have been considered for effective removal of heavy metals from wastewater. The low price and high

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porosity of natural clay make them suitable for water cleaning process (Singh et al. 2018a, b). Furthermore, chitosan has found many applications related to adsorption (Rasoulzadeh et al. 2019). The presence of amino and hydroxyl groups subsidizes to vary promising adsorption interaction among pollutants and chitosan (Kyzas and Bikiaris 2015).

Recently, extensive studies have been carried out for considering nanoadsorbents for the pollutant removal from wastewater/water (Lingamdinne et al. 2019; Ruthiraan et al. 2019). In fact, new era nanoadsorbents are mostly in the form of nanoparticles. These nanoparticles are generally created through spark discharge, low-temperature reaction, pulsed laser ablation, photothermal, spray pyrolysis, inert gas condensation, ion sputtering, thermal plasma, pulsed laser ablation and flame spray pyrolysis (Palkar 1999). Techniques like scanning electron microscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy are used for the characterization of nanoparticles (Basheer 2018). Primarily, sol-gel procedure assists in the production of improvised adsorbent of titanium/nickel oxide, cadmium sulphide, alumina-silica, sulphide, silica and maghemite. Adsorption rate, as well as efficiencies of nano-structured adsorbents, is higher due to significant surface area, compared with conventional materials. Researchers have proposed different types of efficient, economical and environment friendly nanomaterials for applications related to depollution of industrial discharge, surface, ground and drinking water. An ideal absorbent, however, needs to meet certain requirements which include inexpensive, eco-friendly, high adsorption ability and selectivity. As far as water pollutants are concerned, an ideal absorbent is required to adsorb all contaminants conveniently and efficiently as well as reusable (Sadegh et al. 2017).

In this review paper, a summary of techniques and approaches for the removal of heavy metals using magnetic nanoadsorbent was thoroughly discussed. Also, synthesis and characterisation of the magnetic nanoparticle are elaborated. Furthermore, future opportunities and challenges of magnetic particles for the removal of heavy metals are also collated.

Heavy metals

The sources through which metals are released into the atmosphere include volcanic eruptions, soil and rock weathering and human activities such as the use of polluting chemicals from metals, mining, manufacturing, etc. Metals with density more than 5 g/cm^3 are referred to as heavy metals, for instance, lead, mercury, arsenic, zinc and chromium are few of the heavy metals (Barakat 2011). Figure 1 shows the percent of heavy metals present in different fields. Summary of the anthropogenic origin for known heavy metals and maximum contamination levels is standardized by the United Environmental Protection Agency (USEPA) as shown in
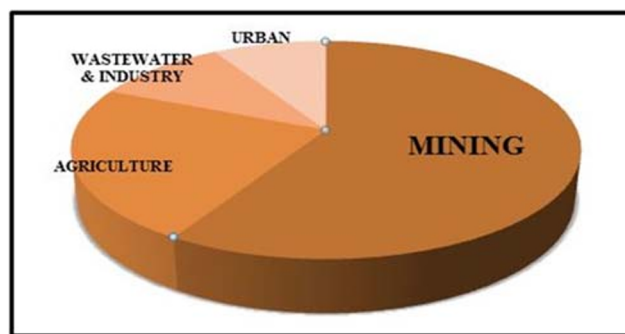

Fig. 1 Percent of heavy metals used in different fields

Table 1. This section comprises of different modified magnetic nanoparticles and their part in heavy metal ions removal. Heavy metals are more often found in rock-forming minerals include those which can conveniently leach because of mineral weathering such as vanadium (V), zinc (Zn), nickel (Ni), copper (Cu) and manganese (Mn), moreover, metals that have intermediate steadiness such as yttrium (Y), scandium (Sc) and many other rare elements, all the way to hafnium (Hf) or uranium (U), which can be found in zircon and are unaffected to weathering. All these heavy metals, later concentrated due to high hydrothermal fluids, permeate the rocks and chemical reactions which lead to precipitation of minerals and ores. These deposits are usually seen inside sedimentary rocks and appropriate for solids storage due to their permeable lattice and extensive permeability (Kobielska et al. 2018).

Soil is also an important sink for heavy metal storage. They are found in relocated rock debris, organic matter (solid phases), water and air trapped inside the soil (fluid phases) as well as insoluble minerals. Both phases, i.e. solid and fluid, interact with one another and different ions through the system (Alloway 2013). However, heavy metal concentration in soil is proportional to the rock type from where the soil originated. The B-horizon is termed as soil third layers from where the heavy metals usually found. Due to the significant concentration of iron oxy-hydroxides and clay enabled B-horizon to attract heavy metals (Kobielska et al. 2018).

Furthermore, heavy metal storage is found on significant depth in surface water that followed from streams/springs to lakes/rivers. However, factors that are contributing to heavy metal concentration and identity in surface waters involve chemical, physical and biological aspects. In addition, surface water that contains oxy-hydroxides/aquatic vegetation trap heavy metals results in bio-accumulation inside the living organisms (Siegel 2002). It is important to keep in mind that a biological system requires the intake of heavy metals, but significant tolerable intake on a daily basis may cause toxicity. The sub-section summarized a few of the heavy metals, i.e. arsenic, cadmium and chromium, available in high content in water and soils. Table 2 displays the adsorption performance along with the host substance of various nanomaterials used for heavy metal removal.

Table 1 Anthropogenic origin and MCL of heavy metal pollutant

Heavy metal ion	Anthropogenic origin	Toxicant	Maximum contaminant level (mg/L)	Remarks
Arsenic (As)	Animal supplement, pesticides, ceramics, metallurgy, fireworks, electrical production (geothermal/coal)	Skin disease, vascular complications	0.050	(Barakat 2011); (Kobielska et al. 2018)
Cadmium (Cd)	Ni-Cd batteries, metal coating (anti-corrosive), coal burning, pigments	Kidney injury, renal sickness, carcinogen	0.01	(Barakat 2011)
Chromium (Cr)	Toasting textiles/leather, ferroalloys generation, pigments, data-storage	Migraine, puking, carcinogenic	0.05	(Barakat 2011); (Kobielska et al. 2018); (Babel and Kurniawan 2005)
Copper (Cu)	Water pipelines, chemical/pharmaceutical instruments, roofing, alloys	Liver complications, sleeping disorder	0.25	(Barakat 2011); (Babel and Kurniawan 2005)
Nickel	Computer constituents, moulds of glass/ceramics, Ni-Cd batteries, catalyst	Carcinogen, breathing disorder, skin diseases	0.20	(Barakat 2011); (Kobielska et al. 2018)
Zinc (Zn)	Alloy of zinc, Polyvinylchloride stabilizer, rubber/paint industry	Anxiety, lethargy	0.80	(Barakat 2011); (Babel and Kurniawan 2005)
Mercury (Hg)	Metal extraction process, catalyst, mercury vapour lamps	Kidney failure, circulatory and nervous system disorder	0.00003	(Barakat 2011); (Kobielska et al. 2018)

Arsenic

Arsenic is known as the twentieth furthermost abundant element and traced in most of the environment matrices, for instance, soil, water and air as well as living matters. In water and soil, it generally exists in both organic and inorganic forms. Arsenite, As (III), and Arsenate, As(V), fall under the category of inorganic form, whereas dimethylarsinic acid and monomethylarsonic acid are organic forms (Rahman and Hasegawa 2011). According to the International Agency for Research on Cancer (IARC), compounds containing arsenic contents referred to as group 1-carcinogen. Every year, thousands of people are affected by poisonous arsenic, as the groundwater that has arsenic contaminants is used for daily use as drinking, irrigation, cooking and cleaning. Rice is a well-known staple food, especially in countries like China, Japan, Pakistan, India and Malaysia, where this is grown using ground or river water. Previous studies reported the primary source of arsenic exposure in non-seafood supplements in Europe (Nisticò et al. 2018). In contrast to organic forms, inorganic forms possess higher toxicity. However, organic form in solid-liquid medium is freely mobilized, due to the weak bond with the solid medium. Nevertheless, there is a lack of interest in researching organic arsenic form environmental behaviour, and only limited studies are available on the removal route from wastewater and water (Cheng et al. 2005).

Based on the literature, the predictable adsorbent used for arsenic removal includes activated alumina, oxides, resins and activated carbon, but they have several limitations such as insignificant adsorption strength, high-cost materials, the

Table 2 Adsorption performance of nanomaterials for heavy metal removals

Nanomaterials	Host substance	Adsorption performance	References
Iron oxide	• Bentonite (clay minerals with a significant content of montmorillonite) • Aerated municipal sewage sludge	• The maximum adsorption performance for lead (Pb^{+2}) was 31.86 mg/g • The maximum adsorption performance for heavy metals were as follows: cadmium (Cd^{+2}) 14.7 mg/g; copper (Cu^{+2}) 17.3 mg/g; nickel (Ni^{+2}) 7.8 mg/g; 7.8 mg/g; lead (Pb^{+2}) 42.4 mg/g.	(Hua et al. 2012); (Singh et al. 2018a, b)
Nano-magnesium oxide	Bentonite	Copper (Cu^{+2}) with 58.44 mg/g.	(Hua et al. 2012)
Nano-ferrous ferric oxide (nano-Fe_3O_4)	Cyclodextrin	Copper (Cu^{+2}) with 47.2 mg/g	(Hua et al. 2012); (Singh et al. 2018a, b)

formation of sludge and difficult to separate (Hokkanen et al. 2015). There is strong Fe and As interaction that made magnetic-based iron oxide a suitable candidate as an adsorbent for arsenic species removal, particularly from polluted soil and water. Moreover, magnetic nanoparticles can be stabilized by economic bio-related sources such as biomasses and polysaccharides (Magnacca et al. 2014). Table 3 shows the adsorption capacity of various adsorbents used for the removal of inorganic arsenic form. Therefore, studies on magnetic nanoparticle such as - Fe_2O_3 show excellent results via FTIR and XPS analysis in terms of adsorption strength, particularly for arsenite and arsenate. Moreover, it can be reused for more than five times with the addition of 1 M of sodium hydroxide (Lin et al. 2012). Magnetic nanoparticles have shown positive results for the pollutant removal as well as economic and environmental perspectives (Nisticò et al. 2018).

Cadmium

Cadmium (non-degradable) ions mainly hold significant toxicities as well as accessibly developed to organism via food that makes it difficult to rip off and causes biological damage. Cadmium introduces into the environment through gradual erosion and rocks and soil abrasions, such as volcanic eruptions. Furthermore, cadmium is a pollutant that directly affects human health in various ways such as limiting cell growth, bone infections and lung damage. Due to all these health issues, WHO (World Health Organization) has stated that the limit of cadmium in blood should not be more than 0.005 mg/L (Kumar and Chawla 2014).

In this regard, finding efficient material or technique that helps to eliminate/reduce the heavy metal contaminants is getting more attention. Researchers synthesized several materials; however, at present, the most prominent and promising material for the removal of heavy metals, particularly for cadmium removal, is superparamagnetic nanoparticles. Metal contaminants are attracted to the magnetite materials via their exterior active sites. Table 4 shows the different nano-metal

oxides along with their adsorption capability towards cadmium removal from water. Recent studies have proved that several surface coating of magnetite exhibit higher adsorption capability towards cadmium (Huang and Keller 2015). Also, ethylene diamine tetra acetic is toxic that may result in skin rashes up to some extent. The coating of inorganic nanoparticles helps to avoid aggregation and remains its magnetic properties. Moreover, metal oxide-based nanocomposites have been significantly analysed, and shown positive results with higher removal capacity for metal removal. For instance, Al_2O_3-Fe_3O_4 nanocomposite was remarked as the best nanosized metal oxide for the removal of cadmium based on adsorption capacity (El-Latif et al. 2013).

Chromium

Among all heavy metals, chromium is one of the toxic pollutants that are carcinogenic, non-biodegradable and mutagenic to a living organism. The biological and toxicological chromium characteristics vary with their chemical forms. Chromium is introduced to the environment via process industries like metal finishing, electroplating, pigments, dyeing, steel manufacturing and leather tanning. However, in aqueous and soil systems, chromium exists in oxidation states as Cr (III) and Cr (VI) (Shariati et al. 2017). Cr (VI) is more toxic compared with Cr (III) and directly affects human health. Due to high toxicity, chromium presence in drinking water and surface water is limited to 0.05 and 0.1 mg/L, respectively (Gupta et al. 2001). In order to remove chromium pollutants, several techniques like chemical precipitation (Özer et al. 1997), electrocoagulation (Shariati et al. 2017) and membrane separation (Chakravarti et al. 1995) are used in the past. The drawbacks of these techniques include significant energy/chemical quantity, high cost and complicated operations (Ghiaci et al. 2004). However, adsorption does not have these limitations and hence used more commonly.

Several researchers used different adsorbents to remove chromium, but most of them have either limited adsorption

Table 3 Magnetic nanoadsorbents for the removal of arsenic metals

Inorganic arsenic form	Adsorbent	Concentration (mg/L)	Maximum adsorption capacity Q_{max} (mg/g)	Reference
Arsenite (As (III))	Magnetic iron oxide nanoparticles	0.1	46.06	(Lunge et al. 2014);(Feng et al. 2012)
	Haematite	-	31.3	(Giménez et al. 2007)
	Magnetite	-	25.6	(Giménez et al. 2007)
	Magnetic nano-iron oxide	2	188.69	(Lunge et al. 2014)
Arsenate (As(V))	Maghemite nanoparticles	1–11	50	(Tuutijärvi et al. 2009)
	Magnetic nano-iron oxide (MION-Tea)	2	153.8	(Lunge et al. 2014)
	Rice polish	0.1–1	0.14	(Ranjan et al. 2009)

Table 4 Nano-metal oxides for cadmium removal

Adsorbent	pH	Adsorption capability (mg/g)	Other targeted metal ions	References
Gum kondagogu iron oxide	5.0	106.8	Copper, lead, mercury	(Saravanan et al. 2012)
Maghemite	6.0	94.33	Nickel, cobalt	(Roy and Bhattacharya 2013)
Magnetite	5.5	88.93	Iron, lead, zinc, nickel, copper	(Karami 2013)
Haematite	5.0	65.00	Copper, cobalt, nickel	(Kumar and Chawla 2014)
Goethite	5.0	29.15	Copper, cobalt, lead	(Kumar and Chawla 2014)
Aluminium oxide Fe_3O_4	6.0	625	-	(El-Latif et al. 2013)

ability or chromium selectivity, especially for hexavalent form (Sureshkumar et al. 2016). To overcome these limitations, superparamagnetic nanoparticles revealed acceptable results and have advantages like quick separation with higher efficiency, economical cost, reuse and higher surface area (Shariati et al. 2017). Researchers, through experimental studies, noted that the magnetite and maghemite nanoadsorbent adsorption capacity is remarkable. Furthermore, these nanoadsorbents can be easily separated via an external magnetic field. Furthermore, magnetite and maghemite nanoadsorbents holding superparamagnetic characteristics can help to improve its re-dispersion and continual reuse (Singh et al. 2015). However, to enhance the adsorption and surface area, the surface of the magnetic nanoparticles must be coated with significant pore mesoporous such as SiO_2 and amine.

Magnetic nanoparticles

Presently, the unique physical properties of nanomaterials are getting significant attention, especially the salient magnetic properties. There are many factors that determine the magnetic properties of nanomaterials such as chemical composition, type and degree of the crystal lattice, shape and size of particles, and configuration (for non-homogeneous structure). Alteration in the characteristics of nanoparticle such as size, composition, shape and structure can enhance the material's magnetic properties (Khajeh et al. 2013a, b).

Magnetic nanoparticles are highly recyclable, non-toxic, reusable and possess magnetic characteristics that offer advantages of convenient separation upon using an external magnetic field (Lisjak and Mertelj 2018). Magnetic nanoparticles have been also known to have vast potential as catalyst supports. The magnetic characteristics of the support restrict the obligation to let the catalyst separation through centrifugation, filtration or extraction. In addition, the potential of covalent binding among catalyst and magnetic nanoparticles' surface strongly decreases its dispersion thus products' purity (Zhu et al. 2013). However, magnetic nanoparticles as catalyst support have attained significant attention in research society in organic synthesis because of green and sustainable chemistry.

Certainly, the fabrication of materials can be conducted in environmentally benign solvents that have a good atom economy and produce less environmental contamination (Dalpozzo 2015). Besides, magnetic nanoparticles with controlled size, shape, surface chemistry and magnetic features have been fabricated through chemical synthesis for applications like magnetic energy storage and bio-imaging (Frey et al. 2009).

Recently, metal oxide nanostructures are also broadly considered as magnetic nanoparticles. Metal oxide nanostructures exhibit properties like semi-conductor, insulator or metallic because of its electronic morphology. Convenient and cost-effective approaches have been designed to produce magnetic metal oxides such as Co_3O_4, NiO_2 and Fe_2O_3 (Sahu et al. 2010). Magnetic metal oxides and magnetic iron oxide nanoparticles have been recommended for an extensive number of applications such as biomedical, supercapacitor, heavy metals and dyes removal, and anti-bacterial agents (Akrami and Niazi 2016),(Prabhu et al. 2015), (Mamani et al. 2014). The magnetic iron oxide nanoparticles that hold superparamagnetic strength include magnetite and maghemite, chemically represents as Fe_3O_4 and Fe_2O_3, respectively. Superparamagnetic acts as a huge paramagnetic atom due to significant magnetic moments and it responses faster to the external magnetic field with limited coercivity and remanence (Sonti and Bose 1995). The nanoparticles are conveniently attracted to the magnetic field but lost their magnetic characteristics after their removal. These features and a limited chance of agglomeration make them a suitable candidate for a wide range of applications (Di Marco et al. 2007).

At present, magnetic nanoparticles such as ferrite colloids, maghemite, haematite and magnetite (Roy et al. 2017) hold extensive attention, particularly for water purification. Magnetic nanoparticles like magnetite and maghemite are considered unique nano-sized materials, applicable in biotech and biomedicine fields as well as competent adsorbent. For instance, magnetite with magnetic properties like significant surface area and adsorption capability is eligible for the removal of heavy metals from aqueous solutions and can be extracted and reuse conveniently through the external magnetic field. Nevertheless, bare magnetite nanoparticles oxidize easily and get rusted in the acidic atmosphere, Furthermore, they dispose of aggregation by

magnetic force, thus reduce the magnetic strength as well as adsorption capability. Hence, surface protection of magnetic nanoparticles is a must to avoid aggregation. Therefore, oxide/polymeric compounds (biocompatible polymers) and surfactants have been widely used to improvised the stability of magnetic nanoparticles (Stanicki et al. 2015). Recently, modification of magnetic nanoparticles using organic molecules has been used widely in several applications, for example in the biomedical field for cell separation, drug delivery, gene targeting, hyperthermia, etc. (Osaka et al. 2006). Nevertheless, the modification of magnetic nanoparticles with appropriate coating has verified to be one of the utmost effective ways. Wang et al. (2010) fabricated hybrid magnetic nanoparticles based on poly-methyl meth-acrylate and superparamagnetic iron oxide nanoparticles with surface modification for heavy metals (Cu (II), Pb (II), Co (II) and Hg (II)) removal through external magnetic fields. The removal efficiency of heavy metals depends on the capture of metal ions via the amine group (Wanna et al. 2016). In a method that combined magnetic separation and biosorption techniques, metal ions' adsorption was demonstrated effectively with advantages of eco-friendly, inexpensively low operation cost and flexibility (Li et al. 2008; Mohammed et al. 2017). The advantages of support magnetic nanoparticles, as well as modified magnetic nanoparticles as a suitable candidate for adsorption, are listed as follows: (1) a large number of particles produced using easy and convenient methods. (2) The capacity of adsorption is significant due to the large surface area. (3) Toxicity is lower and offers unique magnetic strength, and (4) metal-laden sorbents conveniently separate from processed wastewater through an external magnetic field (Wu et al. 2016). However, water pollutants are mostly non-magnetic. Therefore, it is preferable that the magnetic nanoparticles mix along with the pollutants competently, and captured carefully with pollutants owing to their maximum ferromagnetism.

Magnetic nanoparticles synthesis

Due to their remarkable strength, several production methods are designed to synthesize these magnetic nanoparticles. Among all synthesis approaches, coprecipitation method is most widely used. The performance of magnetic nanoparticles depends on characteristics like shape, size and composition as well as process factors like ratio of Fe^{2+}/Fe^{3+}, the temperature of the reaction, pH, iron salt and ionic property of the media. An important aspect of the synthesis of magnetic nanoparticles is the production of particles of definite shape and size (Khajeh et al. 2013a, b). The shape and possibilities to produce anisotropic magnetic lattices are exclusively necessary. In order to decrease the interparticle interactions, magnetic nanoparticles mostly require being isolated from others with a coating adjacent to the particle (Bhateria and Singh 2019) (Fig. 2).
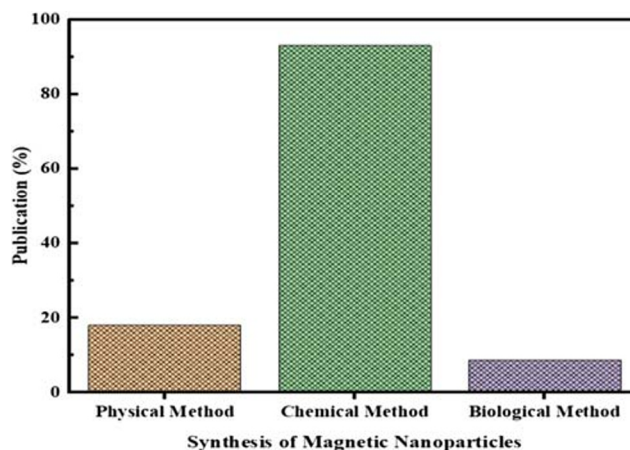
Fig. 2 Comparison of published work on synthesis of magnetic nanoparticles using three different routes (Mahmoudi et al. 2011)

Table 5 shows the advantages and disadvantages of different methods to synthesize magnetic nanoparticles using a chemical approach. The main aspect in the procedure for the synthesis of magnetic nanoparticles is to keep it comparatively easy, economical and reproducible. The methods to produce magnetic nanoparticles is categorised into physical (electron beam lithography, gas-phase deposition, high energy ball milling, aerosols, laser-induced pyrolysis and pulsed laser ablation), chemical (sol-gel, hydrothermal, electrochemical, aerosol/vapour-phase, chemical coprecipitation, flow injection and sonochemical decomposition reactions) and biological (microbial) methods (Chen et al. 2008), (Ali et al. 2016), (Mahdavi et al. 2013), (Roy et al. 2017), (Tapeinos 2018). All these methods are further classified into two classes, i.e. aqueous and non-aqueous. In aqueous class, producing controlled size water-soluble mono-disperse magnetic iron oxide nanoparticles is a challenging task, whereas magnetic iron oxide nanoparticles that are produced through non-aqueous class can only be dissolved in non-polar solvents. The aqueous route is most preferable than non-aqueous, in terms of sustainability and economy (Abdullah et al. 2019).

Characterization of magnetic nanoparticles

To understand the physicochemical feature and the structural character of magnetic nanoparticles as well as pollutant removal mechanisms using magnetic nanoparticles, it is important to characterize magnetic nanoparticles (Fig. 3). These nanoparticles are characterized through various analytical techniques which include X-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray spectroscopy (EDS), scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FE-SEM), X-ray adsorption near-edge structure (XANES), vibrating sample magnetometer (VSM), Brunauer Emmett Teller (BET), confocal micro X-ray fluorescence (μ-

Table 5 Advantages and disadvantages of different methods for the synthesis of magnetic nanoparticles

	Synthesis method	Advantages	Disadvantages	References
Chemical route	Coprecipitation method	• Efficient and easy approach for generating magnetic nanoparticles at gram scale • The mean diameter of particles via this process ranges from inferior up to 50 nm. • Reaction process is faster, significant yield and economical cost of precursor.	• Size-sorting method required due to the poor crystalline particles produced. • Polymeric matrix comprises of particle clusters due to the use of polymers for the stability of magnetite collides.	(Mahdavi et al. 2013); (Laurent et al. 2008); (Zhang and Nan 2015)
	Hydrothermal/solvothermal	• The process can produce crystalline iron oxide nanoparticles, such as alpha-Fe$_2$O$_3$, gamma-Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles. • Compared with other crystal growth types, hydrothermal synthesis can form crystalline phases that are not steady at the melting point. • Shape and size of the iron oxide nanoparticles can be control.	• The process required to maintained pressure > 2000 psi, however, temperature > 200 °C.	(Wu et al. 2015); (Hernández-Hernández et al. 2018)
	Aerosol/vapour-phase	• Manufacture high quality product that can further purified by lowering down the gas contaminants and maintaining the heating time as well as gas concentration.	• Produce larger aggregates. • Low yield	(Ali et al. 2016); (Laurent et al. 2008); (Tombácz et al. 2015)
	Sol-gel synthesis	• Compared with other synthesis processes like coprecipitation, magnetic nanoparticles produced by sol-gel can conveniently disperse in aqueous as well in polar solvents due to the hydrophilic ligands. • Sol-gel synthesis produced magnetic nanoparticles that hold extensive crystallinity and saturation magnetization due to higher process temperature.	• Comparatively, higher cost of metal alkoxides • The process discharges higher content of alcohol at the time of calcination. • Weak bonding. • High permeability • High safety measures required for the process.	(Wu et al. 2015); (Laurent et al. 2008); (Hao et al. 2010)
	Flow injection	• Extensive reproducibility because of laminar and plug-flow conditions • Extensive mixing homogeneity • Magnetite nanoparticles produced via flow injection method ranged from 2 to 7 nm.	• Require continuous/segmented mixing of reagents under laminar flow regime in capillary reactor.	(Laurent et al. 2008)
	Electrochemical	• Fe$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles are produced via electrochemical decomposition under oxidizing environment.	• Inadequate reproducibility	(Laurent et al. 2008); (Mazarío et al. 2016)
	Sonochemical decomposition	• Mixing uniformity and crystal growth reduction result in acceleration effects in chemical dynamics and reactions rates • Growth of particles can be controlled using polymers, organic agents, etc.	• The method is not valuable to realize the production of iron oxide nanoparticles with manageable dispersity and shape. • Cavitation causes in aqueous phase due to the use of ultrasonic irradiation.	(Wu et al. 2015); (Aliramaji et al. 2015)
	Template-assisted fabrication	• Size and morphology of the nanoparticles determine by the template used in fabrication process. • Complex magnetic nanostructure can easily fabricate, and the size and morphology can control too.	• It is a process with more than one step. • Initially, production of base template following magnetic material deposition inside the template	(Khan et al. n.d.)
Physical routes	Electron beam lithography	• Well-maintained interparticle spacing	• Expensive • Extremely complex machines requiring.	(Rishton et al. 1997); (Ghosh Chaudhuri and Paria 2012)
	Gas-phase deposition	• Convenient operation	• Particle size is difficult to maintain.	(Xu et al. 2014b); (Xu et al. 2014a)
	High energy ball milling	• Facile approach • Cost-effective • Time-saving approach • Maintain particle size.	• Highly complex machines requiring	(De Carvalho et al. 2013)

Table 5 (continued)

	Synthesis method	Advantages	Disadvantages	References
		• No residues	• Optimization of several parameters is a must to attain the desired phase.	
	Laser-induced pyrolysis	• Time-saving approach • Uniform-shaped products • Continuous, direct and high production	• High cost • Requirement of reagent/ laser resonance • Specific installation requires	(Cruz et al. 2018)
	Pulsed laser ablation	• Simple approach • Free of surfactants • Synthesized nanoparticles are extremely pure and stable • Time-saving approach	• High-power laser is required	(Mohapatra et al. 2018)
Biological route	Microbial	• Eco-friendly approach • Satisfactory reproducibility and scalability • Cost-effective • High yield • Low temperature and energy requirement	• Require more time to attain the desired product	(Xu et al. 2014a); (Tapeinos 2018)

XRF) and extended X-ray absorption fine structure (EXAFS) (Yu et al. 2016).

Modification of magnetic nanoparticles

Magnetic nanoparticles are often stable at solid state, and due to this fact, they are applied in many applications, for instance as catalytic and sensing. The only drawback of using magnetic nanoparticles is its inadequate stability especially in the aqueous phase that leads to aggregation. Figure 4 shows the modification approach of a magnetic nanoparticle. Furthermore, pristine magnetic nanoparticles are usually unstable in a strongly acidic medium. This aspect holds magnetic nanoparticles to be considered as long-lasting or reusable material. Moreover, significant surface area to volume ratio results in decreasing surface energy, owing to the durable magnetic attractions along with particles, which lowers their dispersion in aqueous and matrices. The protein or enzyme exposure to such boundaries may result in activity loss (Roy et al. 2017).

Therefore, in order to improve the stability of the magnetic nanoparticles, extensive studies have been conducted and designed various modification approaches, for example surfactants ($C_{18}H_34O_2$, $C_{12}H_{24}O_2$, alkane sulphonic acids, alkyl phosphonic acids, lauric acid and oleic acid), polymers (polyethylene glycol, poly-vinyl-pyrrolidone, poly-vinyl alcohol and poly-acrylic acid)

Fig. 3 Characterization techniques for magnetic nanoparticles
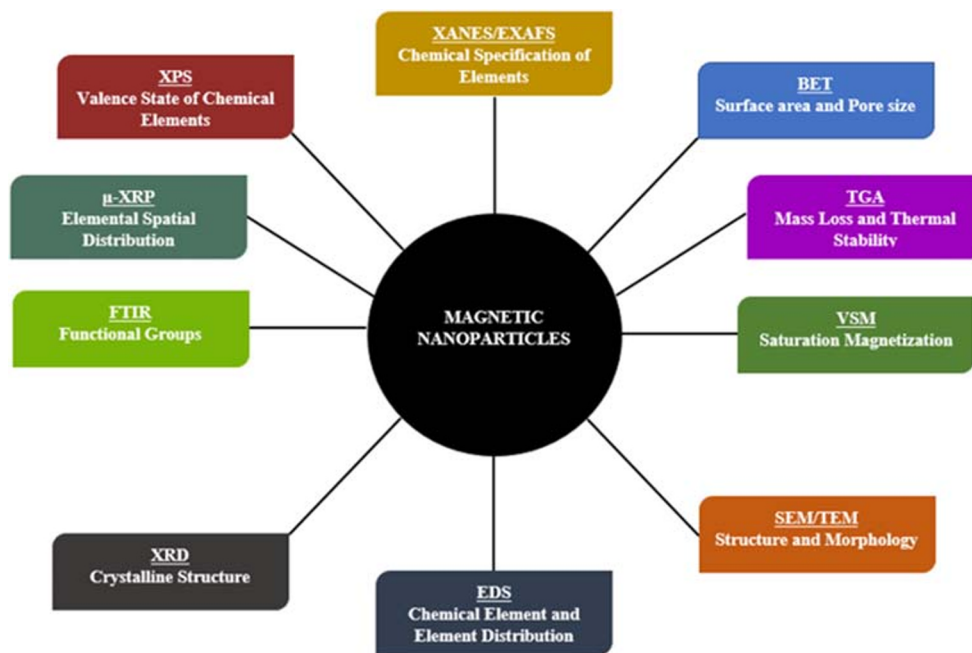
Fig. 4 Magnetic nanoparticle
modification approaches
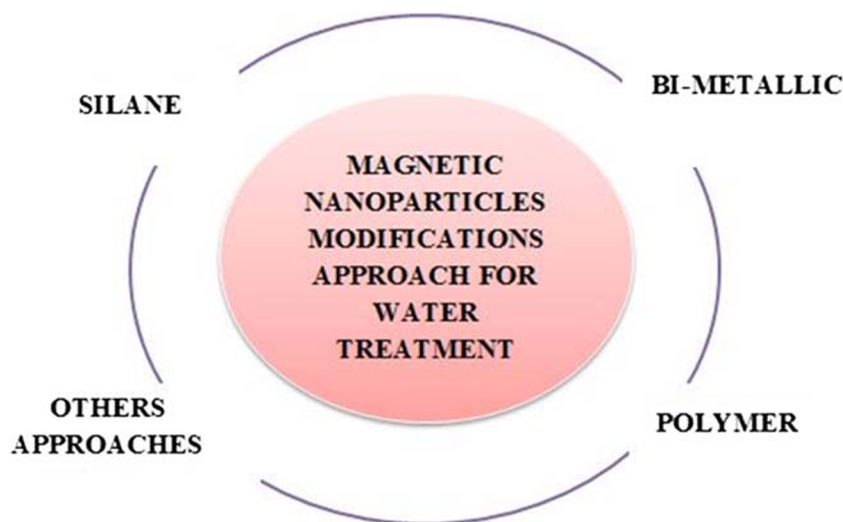
and natural dispersants (starch, chitosan, albumin, ethyl-cellulose, gelatin and dextran) (Roy et al. 2017); (Shete et al. 2015); (Mamani et al. 2013); (Nemati et al. 2012); (Zhang et al. 2010); (Lee, Lee et al. 2006); (Dung et al. 2009); (Fang et al. 2014); (Lüdtke-Buzug et al. 2009); (Lu et al. 2006). Table 6 shows the various modification approaches of iron oxide nanoparticles along with their merits and demerits (Xu et al. 2014b). Moreover, modification approaches enhance biocompatibility, biodegradability and surface strength. It also replaces the iron oxide nanoparticles' hydrophobic nature into hydrophilic (Sadeghi et al. 2012). With suitable modification approach, the dispersibility, biocompatibility and stability of iron oxide nanoparticles can be upgraded; moreover, the oxidation process can also be slowed down significantly (Widder et al. 1981); (Lu et al. 2010). Table 6 shows the various modification approaches of iron oxide nanoparticles along with their merits and demerits (Xu et al. 2014a):

Surface modification of magnetic nanoparticles for heavy metal removal

Surface modification is a path of selective incorporation of the functional group onto nanomaterials' surface without altering or affecting the materials' core. It offers the material a new

surface chemical characteristic such as stability, melting point, electronic morphology and reactivity that vary from that of original material thus building it homogenously in size, providing better shape distribution and maintaining its stability in the aqueous phase (Zhu et al. 2010).

Recently, there is a renewed attention in magnetic nanoparticle modification as a result of the capability of magnetic nanoparticles to make bonds with various terminal groups of different compounds, specifically ligands. Thus, considerable efforts have been progressed with the pollutant removal from wastewater via magnetic nanoparticles through reinforcing it onto different nanomaterials (Rebuttini 2014). Recently, magnetic nanocomposite materials comprising of two/more different nanomaterials have been considered for water and wastewater purification. This is due to the gain of permitting for enhancement in magnetic nanoparticles' adsorption property, manipulation of purification technologies, prevention of aggregation and cost. Nanocomposite materials support to restrict the challenging task of suitable coating the magnetic core deprived of altering bare magnetic nanoparticle properties as well as avoid leaching of surfactant during separation (Ojemaye et al. 2017a, b). For example, titanium dioxide (TiO$_2$) with extremely strong photo-catalytic characteristic are reinforced into magnetic nanoparticles to enhance the

Table 6 Merits and demerits of different modification approaches of iron oxide nanoparticles

Modification approach	Merits	Demerits
Covalent Conjugation	• Binding method can be rationally structured with certain functional groups	• Non-specificity • Support cannot be capable to be reused.
Biologically mediated specific interaction	• Site-specific	• Site selective attachment is required
Physical	• Conveniently process and recycle • No further coupling reagent and surface treatment is needed.	• Binding strength is directly affected via environmental conditions • Non-specificity

latter photo-catalytic features for their use in pollutant removal from water or wastewater. Typically, nanocomposite materials are renewed to be very active for pollutant removal from wastewater compared with bare magnetic nanoparticles (Koduru et al. 2019; Lingamdinne et al. 2019). Magnetic TiO_2, magnetic carbon nanotubes, graphene magnetic nanocomposites, TiO_2 carbon nanotubes nanocomposites, etc. have all been stated for organic, inorganic and microbial pollutants removal from wastewater (Ojemaye et al. 2017a, b; Sahu et al. 2019). Nonetheless, challenges like lower magnetic and adsorption properties are few of the challenges that come across with these materials.

When modified through ligand exchange, maleimide coupling or covalent linkage, magnetic nanoparticles can be very effective for pollutant removal from wastewater. Synthesized ligands have great adsorbing chelating properties/functional groups that can make bonds via their terminal groups with bare/coated magnetic nanoparticles to remove pollutants, organic and inorganic, from wastewater and with enhanced adsorption efficiency. The prospective of ligands and modification of magnetic nanoparticles improves their adsorption efficiency; also, it helps convenient separation and avoids the nanoparticles' toxicity channelled into the environment (Ojemaye et al. 2017a, b). Modified nanoadsorbents allows several techniques to target pollutants even at low concentration and advances pollutants movement on its exterior surface.

The following four techniques for multi-modification of magnetic nanoparticles for wastewater purification application are possible, and these have brought massive progress in environmental nanotechnology sector:

Covalent bond formation: This technique requires the attachment of amine, carboxylic and hydroxyl group on nanoparticles' surface. For a nanoparticle with the attachment of carboxylic group, the ligand should have amine/hydroxyl group on magnetic nanoparticles' surface. The attachment of carboxylic group on magnetic nanoparticles' surface is activated by using 1-ethyl-3-(dimethyl-amino-propyl)-carbodiimide and N-hydroxy-succinimide. On the other hand, a nanoparticle with amine group attachment can make a covalent bond with a ligand of the carboxylic group. The ligand is initially activated with 1- ethyl-3- (dimethyl-amino-propyl) and N-hydroxy-succinimide led by its coupling with amine containing magnetic nanoparticles attach with an amine group. Both aforementioned compounds, 1-ethyl-3-(dimethyl-amino-propyl)-carbodiimide and N-hydroxy-succinimide, are used for carboxylic activation only if carboxylic acid comprising compound is soluble in water; however, 4-dimethyl-amino-pyridine and N,N-Dicyclo-hexyl-carbodiimide are used for water-insoluble compound (Sun et al. 2015).

Ligand exchange: Ligand molecules on nanoparticles' surface can be exchanged for another to offer an enhancement in magnetic nanoparticles' stability and adsorption capability. Here, novel ligand coming in must have an extremely high affinity for magnetic nanoparticles, therefore, capable of exchanging the molecules that were initially used for magnetic nanoparticle coating. Moreover, ligand joins more strongly on to the inorganic nanoparticles' surface. Based on these techniques, the incoming ligand is a bifunctional, where one of its functional group attaches to the surface of the nanoparticle and other for additional modification. Typically, this technique is usually considered for silver/gold magnetic nanoparticles via tetra-octyl-ammonium bromide (Thanh and Green 2010).

Magnetic nanoparticles coated with oleic acid are replaced with triazolyl fatty acids using the ligand technique. Nonetheless, modified magnetic nanoparticles displayed good superparamagnetic features and provided steady colloidal suspensions. Huang and co-workers developed mercapto-modified magnetic nanoparticles using solvent-assisted ligand exchange techniques (mild conditions) for mercury (Hg^{2+}) removal from water with a removal efficiency of 282 mg/g. In comparison with other available modified techniques, this technique offers high stability and dispersibility in an aqueous medium; moreover, the technique is convenient to operate and efficient (Huang et al. 2016a); (Huang et al. 2016b).

Click reaction: This technique includes cyclo-addition of Cu (I)-catalysed terminal alkyne-azide under a wide range of conditions with significant stereospecificity and efficiency. There are also other known click reactions whereby functional groups and molecules are grafted on magnetic nanoparticles' surface (Tucker-Schwartz et al. 2011). Thus, extensive reactions concerning with click reaction for magnetic nanoparticle modification have been testified, but limited or none has stated for water purification application (Erathodiyil and Ying 2011). This modification technique has been reported and is known as an important technique in terms of magnetic nanoparticles' modification due to the significant number of advantages; however, it is surprisingly underutilized for modification of magnetic nanoparticles for water purification applications.

Maleimide coupling: In comparison with covalent coupling, this technique includes conjugation of thiols with primary amines. This technique for magnetic nanoparticles and ligand coupling is barely employed and acknowledged. Sulfo-succinimidyl-4-(maleimide-methyl)-cyclo-hexane-1- carboxylate is used as a coupling agent for maleimide technique. Huh and co-workers developed cross-linking of magnetic nanocrystal with Herceptin using an abovementioned coupling agent. The developed material was 14 nm in size and Herceptin has been

conjugated successfully to magnetic nanoparticles. Besides, the maleimide technique can also be used for both carboxyl and amino group modification of magnetic nanoparticles (Huh et al. 2005) (Table 7).

Prospective and future challenges of magnetic nanoparticles

Magnetic nanoparticles' development as an effective adsorbent for heavy metals removal has been studied significantly, due to its high adsorption efficiency and chemical stability, good recyclability and convenient separation. A significant number of researches associated with the fabrication of magnetic nanoparticles through various methods are discussed herein. The biocompatibility of iron oxide nanoparticles may confirm the safety of fabricated materials in water treatment as well as to magnetic properties, which help the benefits of convenient separation by an external magnetic field. Based on the literature, the summary of how the fabrication methods can affect the production of iron oxide nanoparticles on the overall matrix also have been discussed. Moreover, it is realized that maghemite and magnetite are two of the primary phases that contributed to the magnetism of nanoparticles. In comparison with maghemite, magnetite nanoparticles displayed great magnetization (Lu et al. 2015). Thus, its production with high saturation magnetization is still a challenging task by researchers as it can be oxidized easily and needed

an oxygen-free environment during production. Additionally, maghemite nanoparticles have good stability as compared with magnetite. Regarding large-scale production, maghemite nanoparticles' fabrication is more economical and facile as compared with magnetite nanoparticles that typically carried out in inert surroundings. While, maghemite displays lower magnetism strength; however, with size-controlled production within the solid matrix and suitable weight ratio, they may offer adequate magnetism for the recovery process and ease of separation. Consequently, considerable studies must be carried out to explore promising materials to produce effective adsorbent in water and wastewater treatment (Fulekar et al. 2009). Nevertheless, there have been significant studies on heavy metal ions' adsorption, but the mechanism of how the reaction happens is not completely understood, therefore, still require to be investigated further (Esakkimuthu et al. 2014). The in-depth understanding of physical and chemical features of adsorbents can offer a good understanding of the nature of chemical interaction/bonding among nanoparticles and composites to develop efficient adsorbent.

Iron oxide nanoparticles incorporation with solid matrices can improve the adsorbent properties with interesting features of ease of separation, high-specific surface area and sage to be used. Parameters like heavy metal ion concentration, pH, temperature, contact time and adsorbent dosage are considered as the utmost significance, as any change in the abovementioned parameters can greatly change the adsorbent' removal efficiency (Zhang et al. 2016). Hereafter, in-depth knowledge of fabrication methods and controlled parameters in adsorption process will help in producing magnetic iron oxide

Table 7 Modified magnetic nanoparticles for heavy metals removal

Modified magnetic nanoparticle	Target metals	Adsorption efficiency (%) or capacity (mg/g)	References
Rhodamine-Fe$_3$O$_4$-SiO$_2$	Mercury (Hg (II))	97.34%	(Sun et al. 2015)
Amino-modified-Fe$_3$O$_4$	Copper (Cu (II)) Chromium (Cr (IV))	12.43 mg/g 11.24 mg/g	(Mahdavian and Mirrahimi 2010)
Fe$_3$O$_4$-SiO$_2$-Graphene oxide	Chromium (Cr (III))	4.3 mg/g	(Li et al. 2014)
Malic acid- Fe$_3$O$_4$-SiO$_2$	Cadmium (Cd (II)) Nickel (Ni (II))	81.63 mg/g 63.96 mg/g	(Ghafoor and Ata 2017)
Dimercaptosuccinic acid- Fe$_3$O$_4$	Mercury (Hg (II)) Lead (Pb (II))	227 mg/g 83%	(Yantasee et al. 2007)
Mercapto-modified- Fe$_3$O$_4$	Mercury (Hg (II))	282 mg/g	(Huang et al. 2016a)
Succinic acid- Fe$_3$O$_4$	Copper (Cu (II)) Cobalt (Co (II))	93.58% 96.87%	(Singh et al. 2011)
Carboxy-methyl-β-cyclodextrin-Fe$_3$O$_4$	Copper (Cu (II))	47.2 mg/g	(Badruddoza et al. 2011)
Multiwalled boron nitride nanotubes Fe$_3$O$_4$	Arsenic (As (V))	32.3 mg/g	(Chen et al. 2011)
Amino-modified Fe$_3$O$_4$- SiO$_2$	Copper (Cu (II))	0.45 mmol/g	(Wang et al. 2010)
Polyethylenimine Fe$_3$O$_4$	Copper (Cu (II))	41.4 mg/g	(Goon et al. 2010)
Dendrimers-modified Fe$_3$O$_4$	Zinc (Zn (II))	24.3 mg/g	(Chou and Lien 2011)

nanoparticles for water purification. Also, limited literature has been reported related to magnetic iron oxide nanoparticle regeneration. Therefore, it is important to have profound studies on the regeneration process of magnetic iron oxide nanoparticles for environmental sustainability. Lastly, it is still a massive challenge for research society to find an appropriate solution for effective water treatment with a reliable and economical approach. Hence, it is noteworthy that all the abovementioned issues must be addressed properly so that for the upcoming generation, clean water can be preserved.

Conclusions

The use of nanotechnology to treat water and wastewater is receiving a lot of attention. Magnetic nanoparticles and incredible strength, as well as their integration with existing treatment technologies, give tremendous opportunities to effectively treat water and wastewater. Whereas in many areas, different magnetic nanoparticle structures can offer alternative applications. Furthermore, magnetic nanoparticles are effectively considered for contamination removal such as heavy metals, dyes, fluoride and chlorinated organic compound, which are commonly found in ground water, drinking and wastewater. Even though several characteristics of magnetic nanoparticles were discussed in this review paper, however, most of the magnetic nanoparticles are still at the laboratory research stage. In addition, the obstacles faced in the remediation of water and wastewater by nanomaterials are essential, but many of these obstacles are only impermanent, such as expensive cost and technical handling. To overcome these issues, co-operation between research societies, government and industries as well as a stakeholder is important. It is expected that evolving nanotechnology by cautious handling to evade unexpected results can continuously offer robust explanations to water and wastewater remediation challenges.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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