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Review

Use of iron oxide nanomaterials in wastewater treatment: A review

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ABSTRACT

Nowadays there is a continuously increasing worldwide concern for the development of wastewater treatment technologies. The utilization of iron oxide nanomaterials has received much attention due to their unique properties, such as extremely small size, high surface-area-to-volume ratio, surface modifiability, excellent magnetic properties and great biocompatibility. A range of environmental clean-up technologies have been proposed in wastewater treatment which applied iron oxide nanomaterials as nanosorbents and photocatalysts. Moreover, iron oxide based immobilization technology for enhanced removal efficiency tends to be an innovative research point. This review outlined the latest applications of iron oxide nanomaterials in wastewater treatment, and gaps which limited their large-scale field applications. The outlook for potential applications and further challenges, as well as the likely fate of nanomaterials discharged to the environment were discussed.

Contents

1. Introduction

The spread of a wide range of contaminants in surface water and groundwater has become a critical issue worldwide, due to population growth, rapid development of industrialization and long-term droughts (Cundy et al., 2008; Chong et al., 2010; Zeng et al., 2011). It is thus of necessity to control the harmful effects of contaminants and improve the human living environment. Contaminants persisting in wastewater include heavy metals, inorganic compounds, organic pollutants, and many other complex compounds (O'Connor, 1996; Fatta et al., 2011; Li et al., 2011). All of these contaminants releasing into the environment through wastewater are harmful to human beings and ecological environment. Consequently, the need for contaminants removal has become a must (Jiang et al., 2006; Huang et al., 2010; Pang et al., 2011a).

In an effort to combat the problem of water pollution, rapid and significant progresses in wastewater treatment have been made, including photocatalytic oxidation, adsorption/separation processing

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and bioremediation (Huang et al., 2006a; Zelmanov and Semiat, 2008; Long et al., 2011; Pang et al., 2011a, 2011b). However, their applications have been restricted by many factors, such as processing efficiency, operational method, energy requirements, and economic benefit. Recently, nanomaterials (NMs) have been suggested as efficient, cost-effective and environmental friendly alternative to existing treatment materials, from the standpoints of both resource conservation and environmental remediation (Friedrich et al., 1998; Dimitrov, 2006; Dastjerdi and Montazer, 2010).

Nanotechnology holds out the promise of immense improvements in manufacturing technologies, electronics, telecommunications, health and even environmental remediation (Gross, 2001; Kim et al., 2005; Moore, 2006). It involves the production and utilization of a diverse array of NMs, which include structures and devices with the size ranging from 1 to 100 nm and displays unique properties not found in bulk-sized materials (Stone et al., 2010; Wang et al., 2010). Several kinds of nanomaterials, such as carbon-based NMs (Mauter and Elimelech, 2008; Upadhyayula et al., 2009) and TiO_2 NMs (Khan et al., 2002; Shankar et al., 2009), have been widely studied and extensively reviewed. However, iron oxide-based NMs need to be studied in greater detail.

This review evaluates the important properties of iron oxide NMs. It highlights not only recent developments in the application of iron oxide NMs for wastewater treatment, but also gaps which limited their large-scale field application. Primary attention is given to recent development in the utilization of iron oxide NMs as nanosorbents, followed by critical discussion on their application as photocatalysts. Furthermore, the practical potential of iron oxide based immobilization technology for improving pollutant removal efficiency is elaborated. The likely fate of NMs discharged in the environment and associated remediation method are also discussed. A detailed description of synthesis method, properties and characterization of iron oxide NMs is beyond the scope of this article, but can be found in Laurent et al. (2008) and Teja and Koh (2009). The structure of this review is illustrated in Fig. 1.

2. Iron oxide nanomaterials

Iron oxides exist in many forms in nature. Magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) are the most common forms (Cornel and Schwertmann, 1996; Chan and Ellis, 2004). In recent years, the synthesis and utilization of iron oxide NMs with novel properties and functions have been widely studied, due to their size in nano-range, high surface area to volume ratios and superparamagnetism (McHenry and Laughlin, 2000; Afkhami et al., 2010; Pan et al., 2010). Particularly, the easy synthesis, coating or modification, and the ability to control or manipulate matter on an atomic scale could provide unparalleled versatility (Boyer et al., 2010; Dias et al., 2011). Additionally, iron oxide NMs with low toxicity, chemical inertness and biocompatibility show a tremendous potential in combination with biotechnology (Huang et al., 2003; Roco, 2003; Gupta and Gupta, 2005). The unique properties, which account for the application of iron oxide NMs as well as the considerable differences among iron oxide bulk materials, were presented in Fig. 2 (Bystrzejewski et al., 2009; Selvan et al., 2010).

It is reported that preparation methods and surface coating mediums play a key role in determining the size distribution, morphology, magnetic properties and surface chemistry of nanomaterials (Jeong et al., 2007; Machala et al., 2007). Many researchers have been focusing their efforts on developing chemical and physical methods for the synthesis of MNPs (Dias et al., 2011). Recently, a variety of synthesis approaches have been developed to produce high quality nanoparticles (Hassanjani et al., 2011), nano-ovals (Zhong and Cao, 2010), nanobelts (Fan et al., 2011) and nanorings (Gotić et al., 2011) or other nanostructures. Fig. 3 presents the three most important published routes for the synthesis of superparamagnetism iron oxide nanoparticles (SPIONs), summarized by Mahmoudi et al. (2011). Advances in NMs synthesis enable the precise control of surface active sites by manufacturing monodisperse and shape-controlled iron oxide NMs (Bautista et al., 2005; Li and Somorjai, 2010). Some emerging methods, such as fungi/proteins mediated biological method and sonochemical method, necessitate wide development. Future studies should aim to address different challenges to provide new efficient and specific magnetic NMs. In addition, the development of iron oxide NMs into a field scale may provide a productive area of research, and more research is required to explore the application potential of these novel NMs.

Generally, nanomaterials should be stable to avoid aggregation and endow a low deposition rate, in order to assure their reactivity and mobility (Schrick et al., 2004; Kanel et al., 2007; Tiraferri et al.,

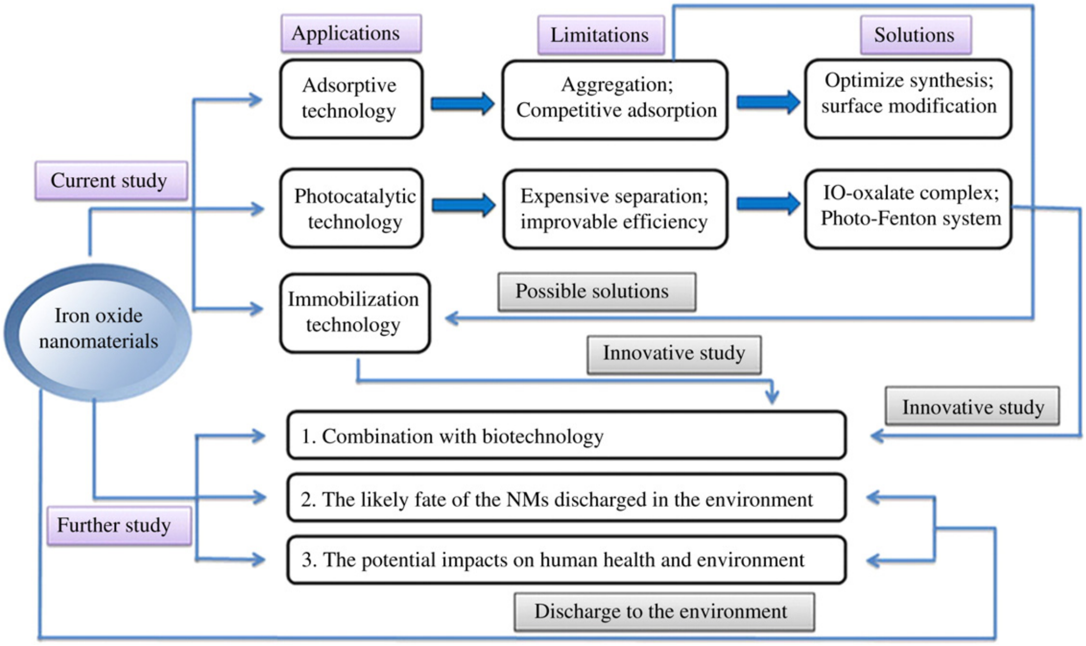

Fig. 1. Overview of the review structure.

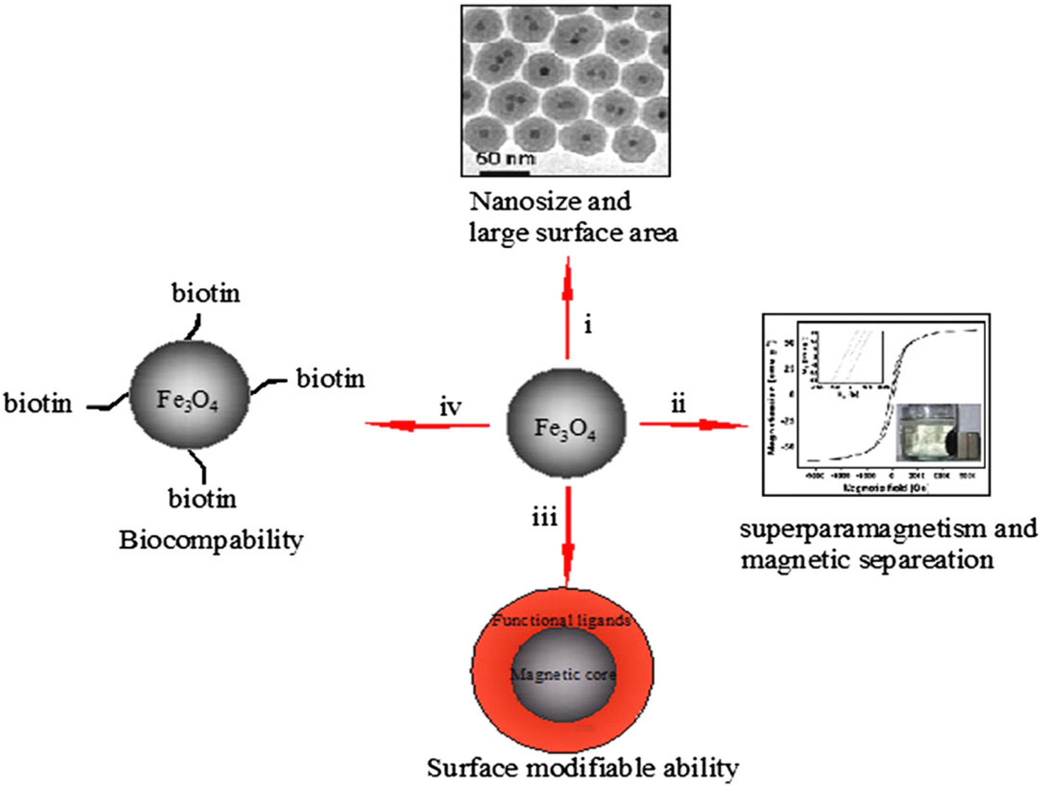

Fig. 2. Important properties of iron oxide magnetic nanoparticles for wastewater treatment applications.

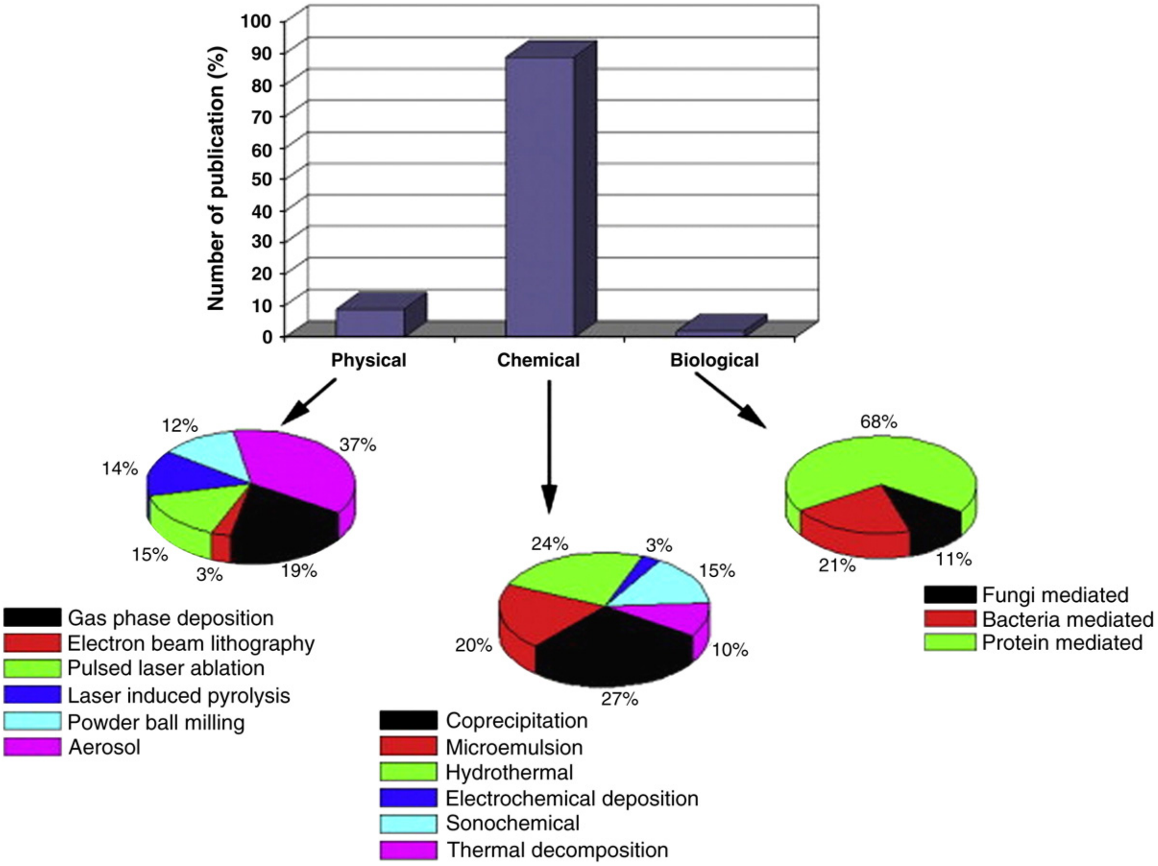

Fig. 3. A comparison of published work (up to date) on the synthesis of SPIONs by three different routes.
Sources: Institute of Scientific Information. (Adopted from (Mahmoudi et al., 2011)).

2008). However, it is reported that NMs tend to aggregate in solution (Lin et al., 2005). Commonly, the stability of colloidal nanoparticles is influenced by the electrostatic and van der Waals interactions (Chen et al., 2007). Much work is still needed to advance knowledge in the enhancement of NMs stability, by reducing their surface energy which limits their large-scale application. One attractive potential approach is the modification of NMs, based on the fact that iron oxide NMs could react with different functional groups. The use of stabilizer, electrostatic surfactant, and steric polymers has been widely proposed for facilitating NMs with non-specific moieties, group specific, or highly specific ligands (Hyeon et al., 2001; Harris et al., 2003; Batalha et al., 2010; Sung et al., 2012).

The stability of iron oxide colloid suspensions could be greatly augmented by surface modification with suitable functional groups, such as phosphonic acids, carboxylic acid, and amine (Fig. 4) (Boyer et al., 2010; Dias et al., 2011). Since the practical application depends on the type of modified medium, it would be critical to functionalize with various mediums (Mohanraj and Chen, 2007). A series of mediums can be tuned to introduce various functional groups to iron oxide NMs, but a robust protocol to achieve this has yet to be developed and demonstrated. Nanomaterials that are sterically stabilized tend to remain well-dispersed even in industrial application (Tiraferri et al., 2008). It should be noted that the application of iron oxide NMs are strongly related to their intrinsic properties, which highly depend on the preparation method and modification mediums (Machala et al., 2007; Girginova et al., 2010).

3. Iron oxide nanomaterials in wastewater treatment

Selection of the best method and material for wastewater treatment is a highly complex task, which should consider a number of factors, such as the quality standards to be met and the efficiency as well as the cost (Huang et al., 2008; Oller et al., 2011). Therefore, the following four conditions must be considered in the decision on wastewater treatment technologies: (1) treatment flexibility and final efficiency, (2) reuse of treatment agents, (3) environmental security and friendliness, and (4) low cost (Zhang and Fang, 2010; Oller et al., 2011).

Magnetism is a unique physical property that independently helps in water purification by influencing the physical properties of contaminants in water. Adsorption procedure combined with magnetic separation has therefore been used extensively in water treatment and environmental cleanup (Ambashta and Sillanpää, 2010; Mahdavian and Mirrahimi, 2010). Iron oxide NMs are promising for industrial scale wastewater treatment, due to their low cost, strong adsorption capacity, easy separation and enhanced stability (Hu et al., 2005; Carabante et al., 2009; Fan et al., 2012). The ability of iron oxide NMs to remove contaminants has been demonstrated at both laboratory and field scale tests (White et al., 2009; Girginova et al., 2010). Current applications of iron oxide NMs in contaminated water treatment can be divided into two groups: (a) technologies which use iron oxide NMs as a kind of nanosorbent or immobilization carrier for removal efficiency enhancement (referred to here as adsorptive/immobilization technologies), and (b) those which use iron oxide NMs as photocatalysts to break down or to convert contaminants into a less toxic form (i.e. photocatalytic technologies). However, it should be noted that many technologies may utilize both processes.

3.1. Adsorptive technologies

3.1.1. Iron oxide NMs as nanosorbents for heavy metals

Heavy metal contamination is of great concern because of its toxic effect on plants, animals and human beings, and its tendency for bioaccumulation even at relatively low concentration. Therefore, effective removal methods for heavy metal ions are extremely urgent and have attracted considerable research and practical interests (Huang et al., 2006a; Chen et al., 2011; Pang et al., 2011c).

Nowadays, the majority of bench-scale research and field applications of materials for wastewater treatment has focused on magnetic NMs (Iram et al., 2010), carbon nanotubes (Stafiej and Pyrzynska, 2007), activated carbon (Kobya et al., 2005), and zero-valent iron (Ponder et al., 2000). Among these, it seems that iron oxide magnetic NMs, possessing the capability to treat large volume of wastewater and being convenient for magnetic separation, are most promising materials for heavy metal treatment (Hu et al., 2010). The iron oxide NMs could illustrate excellent superiority. In a study performed by Nassar (2010), it was found that the maximum adsorption capacity for Pb(II) ions was 36.0 mg g^{-1} by Fe_3O_4 nanoparticles, which was much higher than that of reported low cost adsorbents. The small size of Fe_3O_4 nanosorbents was favorable for the diffusion of metal ions from solution onto the active sites of the adsorbents surface. It recommended that Fe_3O_4 nanosorbents were effective and economical adsorbents for rapid removal and recovery of metal ions from wastewater effluents.

However, as one of the most important surface-driven phenomena in aquatic environments, aggregation caused by high surface

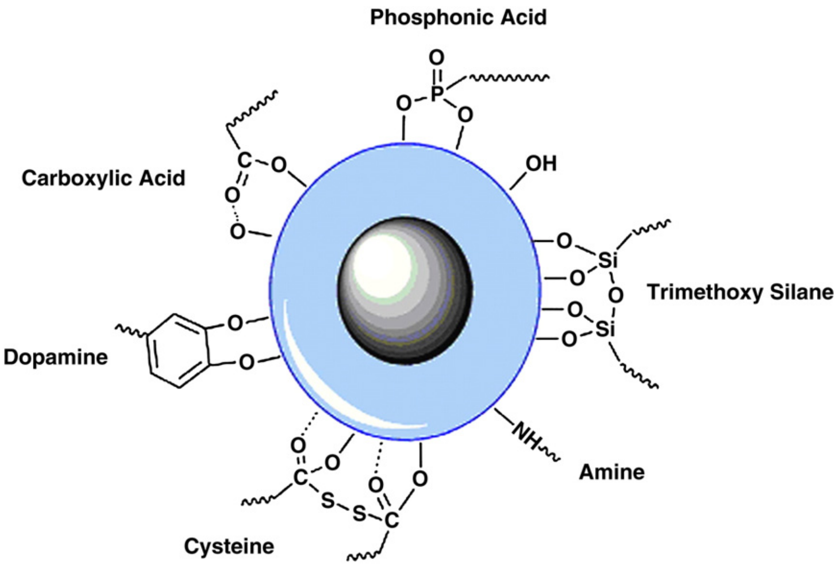

Fig. 4. Common chemical moieties for the anchoring of polymers and functional groups at the surface of iron oxide magnetic nanoparticles (Adopted from (Dias et al., 2011)).

area to volume ratios of NMs could control a number of important environmental processes, including ion uptake (Baalousha, 2009). In addition to aggregation, numerous interactions occurred in wastewater also affect the adsorption of metals. For example, phosphates can be well adsorbed and can out-compete metals for adsorption sites due to their high concentrations in wastewater (Feng et al., 2010). Therefore, the above mentioned factors as well as the types of contaminants may limit the effectiveness of nanosorbents, and the exploration of highly effective modification methods for NMs tends to be a hot research field for enhancing the efficiency of nanosorbents. Surface modification, which can be achieved by the attachment of inorganic shells and/or organic molecules, not only stabilizes the nanoparticles and eventually prevents their oxidation, but also provides specific functionalities that can be selective for ion uptake and thus enhance the capacity for heavy metal uptake in water treatment procedures. Several types of functionalized materials have been utilized by grafting of chelating ligands on the surface of NMs for heavy metal removal (Ambashta and Sillanpää, 2010; Girginova et al., 2010). For example, Bystrzejewski et al. (2009) applied carbon-encapsulated magnetic nanoparticles to remove Cu^{2+} and Cd^{2+}. In their study, the ion uptakes achieved 95% for cadmium and copper, which were considerably higher than the capacities of activated carbons, confirming the prospect of modified iron oxide NMs for efficient heavy metal removal from aqueous solutions.

Mechanisms of contaminant adsorption from wastewater by modified iron oxide NMs include surface sites binding (Hu et al., 2010), magnetic selective adsorption (Ozmen et al., 2010), electrostatic interaction (Zhong et al., 2006), and modified ligands combination (Hao et al., 2010). The addition of novel modification mediums to NMs can achieve high efficiency. For example, a novel magnetic nanosorbent (MNP–NH_2) has been developed by the covalent binding of 1,6-hexadiamine on the surface of Fe_3O_4 nanoparticles for the removal of Cu^{2+} ions from aqueous solution (Hao et al., 2010). The chemisorptions occurred between Cu^{2+} and NH_2 groups on the surface of MNP–NH_2, as shown in Eq. (1). In addition, the prepared nanosorbents had good reusability and stability, and the adsorption capacity of MNP–NH_2 was kept constant (about 25 mg g^{-1}). This further confirmed their application potential, not only considering removal efficiency, but also taking into account the practical application.

$$\mathrm{MNP{-}MH_2} + \mathrm{Cu^{2+}} \rightarrow \mathrm{MNP{-}NH_2Cu^{2+}} \qquad (1)$$

Laboratory studies indicated that iron oxide NMs could effectively remove a range of heavy metals, including Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+} et al. A list of functionalized iron oxide NMs with their sorption capacity values was summarized in Table 1. However, iron oxide-based technology for heavy metal adsorption is still at a relatively early stage for wide application. It is recognized that much work is needed to advance knowledge in the area of NMs, and the transfer of iron oxide NMs from laboratory to field-scale application involves many complexities. With increasing trends in contaminant removal treatment, more data of NMs will become available on performance and cost, which can provide additional information for large-scale industrial application (Otto et al., 2008).

3.1.2. Iron oxide NMs as nanosorbents for organic contaminants

As a well-known separation process, adsorption has been widely applied to remove chemical pollutants from water. It has numerous advantages in terms of cost, flexibility and simplicity of design/operation, and insensitivity to toxic pollutants (Zeng et al., 2007; Ahmad et al., 2009; Rafatullah et al., 2010). Therefore, an effective and low-cost adsorbent with high adsorption capacity for organic pollutants removal is desirable. Iron oxide NMs are currently being explored for organic contaminant adsorption, particularly for the efficient treatment of large-volume water samples and fast separation via employing a strong external magnetic field. A lot of experiments have been undertaken to examine the removal efficiency of organic pollutants by using iron oxide NMs for organic pollutants (Zhang et al., 2010; Zhao et al., 2010; Luo et al., 2011). For example, Fe_3O_4 hollow nanospheres were shown to be an effective sorbent for red dye (with the maximum adsorption capacity of 90 mg g^{-1}) (Iram et al., 2010). The saturation magnetization of prepared nanospheres was observed to be 42 emu g^{-1}, which was sufficient for magnetic separation with a magnet (critical value at 16.3 emu g^{-1}) (Ma et al., 2005). These proved that magnetic NMs technology was a novel, promising and desirable alternative for organic contaminant adsorption.

Similar to heavy metal adsorption, the adsorption of organic contaminants took place via surface exchange reactions until the surface functional sites are fully occupied, and thereafter contaminants could diffuse into adsorbent for further interactions with functional groups (Ma et al., 2005; Zhao et al., 2010; Hu et al., 2011). Based on this mechanism, the development of NMs for organic contaminant removal requires an extension of surface modification. The modification and chemical treatment of NMs are essential to enhance the target adsorption capability. One example in this area is the use of carbon coated Fe_3O_4 nanoparticles (Fe_3O_4/C) to extract trace PAHs (Zhang et al., 2010). The recoveries of experimental PAHs on Fe_3O_4/C nanosorbents were significantly increased compared with those pure Fe_3O_4 nanoparticles, and the removal efficiencies of target compounds were above 90% for PhA, FluA, Pyr, BaA, and BbF, as shown in Fig. 5. In addition, through this method, the presence of carboxyl and hydroxyl groups could modify Fe_3O_4/C nanoparticles with hydrophilic surface. The modified nanoparticles can then not only be dispersed stably in solution for practical applications, but also decrease the irreversible

Table 1
Functionalized iron oxide magnetic nanomaterials in heavy metal adsorption.

Nanosorbents	Ligands	Heavy metals	Adsorption capacity	Reference
Mesostructured silica magnetite	–NH_2	Cu(II)	The adsorbents showed a capacity of 0.5 mmol/g for Cu(II).	(Kim et al., 2003)
Magnetic iron–nickel oxide	–	Cr(VI)	The prepared adsorbent showed a maximum of 30 mg/g uptake capability for Cr(VI).	(Wei et al., 2009)
Montmorillonite-supported MNPs	–AlO; –SiO	Cr(VI)	The adsorption capacity was 15.3 mg/g for Cr(VI).	(Yuan et al., 2009)
PEI-coated Fe_3O_4 MNPs	–NH_2	Cr(VI)	The maximum adsorption capacity for Cr(VI) was 83.3 mg/g.	(Pang et al., 2011b)
δ-FeOOH-coated γ-Fe_2O_3 MNPs	–	Cr(VI)	The Cr(VI) adsorption capacity determined to be 25.8 mg/g.	(Hu et al., 2007)
Flower-like iron oxides	–	As(V), Cr(VI)	The As(V) adsorption capacity was 5.3 mg/g.	(Li and Zhang, 2006)
Hydrous iron oxide MNPs	–	As(V), Cr(VI)	8 mg of arsenic per g of adsorbent.	(Pradeep, 2009)
Fe_3O_4–silica	Si–OH	Pb(II), Hg(II)	The removal efficiency was 97.34% and 90% for Pb(II) and Hg(II), respectively.	(Ambashta and Sillanpää, 2010)
Amino-modified Fe_3O_4 MNPs	–NH_2	Cu(II), Cr(VI)	The maximum adsorption capacity was 12.43 mg/g for Cu(II) ions and 11.24 mg/g for Cr(VI) ions, respectively.	(Huang and Chen, 2009)
m-PAA-Na-coated MNPs	–COO	Cu(II), Pb(II) et al.	Adsorption capacity: Cd(II) (5.0 mg g^{-1}); Pb(II) (40.0 mg g^{-1}); Ni(II) (27.0 mg g^{-1}) and Cu(II) (30.0 mg g^{-1}).	(Mahdavian and Mirrahimi, 2010)
Poly-L-cysteine coated Fe_2O_3 MNPs	–Si–O; –NH_2	Ni(II), Pb(II) et al.	The recovery of the tested metals were almost all above 50%, even the removal efficiency of Ni(II) reached 89%.	(White et al., 2009)

adsorption of analytes to overcome the desorption problem of carbon materials.

In summary, combination of the superior adsorption performance and magnetic properties of iron oxide NMs tend to be a promising approach to deal with a variety of environmental problems. Advances in iron oxide NMs could provide opportunities for developing next-generation adsorption systems with high capacity, easy separation, and extended lifecycles. The novel physical, chemical and magnetic properties of iron oxide NMs can facilitate many advanced applications in the development of adsorptive technologies, and thus generate more efficient and cost-effective remediation approaches as compared with conventional technologies (Babel and Kurniawan, 2003; Cundy et al., 2008; Brar et al., 2010).

3.2. Photocatalytic technology

Photocatalysis, one of the advanced physico-chemical technology applicable in photodegradation of organic pollutants (Akhavan and Azimirad, 2009), has attracted much attention in recent years. However, some obstacles hinder the wide application of iron oxide NMs for the photocatalysis of toxic compounds: (a) the separation of materials after the treatment process tends to be expensive owing to manpower, time and chemicals used for precipitation followed by centrifugation or decantation at the end of treatment process, and (b) the low quantum-yield of treatment process restricts the kinetics and efficiency (Bandara et al., 2007). These limitations should be taken into account for the development of NMs based technologies. Considerable efforts have been made to enhance photocatalytic activity, such as decreasing photocatalyst size to increase surface area, combining photocatalyst with some novel metal nanoparticles, and increasing hole concentration through doping (Zhang and Fang, 2010). On the other hand, improved charge separation and inhibition of charge carrier recombination are essential in improving the overall quantum efficiency for interfacial charge transfer (Beydoun et al., 1999; Watson et al., 2002; Hu et al., 2009).

Iron oxide NM can be a good photocatalyst absorbing visible light. Compared with commonly applied TiO_2, which mainly absorbs UV light with wavelengths of <380 nm (covering only 5% of the solar spectrum) due to its wide band-gap of 3.2 eV, Fe_2O_3 with band-gap of 2.2 eV (Akhavan and Azimirad, 2009) is an interesting n-type semiconducting material and a suitable candidate for photodegradation under visible light condition. The better photocatalytic performance of iron oxide NMs than TiO_2 can be attributed to considerable generation of electron–hole pairs through the narrow band-gap illumination (Eq. (2)) (Bandara et al., 2007).

$$Fe_2O_3 + hv \rightarrow Fe_2O_3(e^-_{cb}, h^+_{vb}) \tag{2}$$

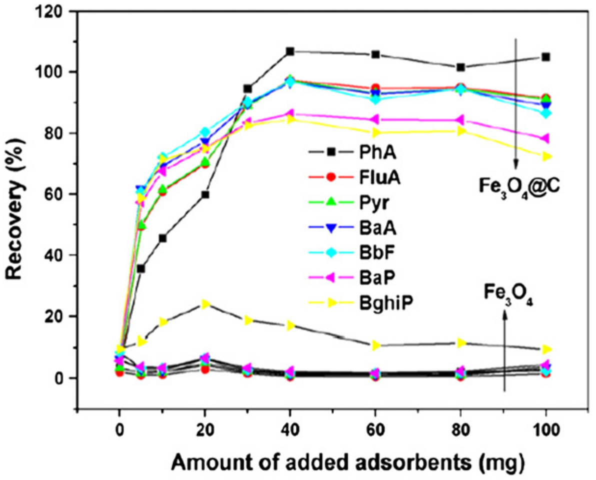

Fig. 5. Removal efficiencies of PAHs by Fe3O4 and Fe3O4/C nanosorbents (Adopted from (Zhang et al., 2010)).

Many species of Fe(III) oxides have been proposed, such as α-Fe_2O_3, γ-Fe_2O_3, α-FeOOH, β-FeOOH and γ-FeOOH, to degrade organic pollutants and reduce their toxicity due to enhanced photocatalysis effect (Wu et al., 2000). These NMs are illustrative of a new way to manipulate the catalytic properties of iron oxide for photocatalysis, towards a safe and effective wastewater treatment nanotechnology. An example is the photodegradation of Congo red (CR) dye ($C_{32}H_{24}N_6O_6S_2$) by iron oxide nanoparticles which were synthesized by thermal evaporation and co-precipitation approach (Khedr et al., 2009). The maximum removal efficiency was 96% at a size of 100 nm. Further, irradiation was found to have no pronounced effect on the catalytic decomposition capacity, but the rate of degradation was fast in the presence of light.

Iron oxide NMs have been widely applied as photocatalysts, but their activity decline is frequently encountered because of the electron–hole charge recombination on the oxide surface, as fast as within nanoseconds (Rothenberger et al., 1985). Deposition of a noble metal on a metal oxide support can be employed to address this problem. For example, gold/iron oxide aerogels were used as photocatalysts to degrade disperse Blue 79 azo dye in water under ultraviolet light illumination (Wang, 2007). In the photocatalysis system, metallic gold particles, which were considered to function as the sites for electron accumulation under UV light irradiation, could facilitate the transfer of surface electrons. The better separation between electrons and holes would allow a better efficiency for oxidation and reduction reactions (Liu et al., 2004), thus enhancing the photocatalytic activity. Meanwhile, hydroxyl radicals near the catalyst surface, acting as the main oxidative species to attack dye molecules, were efficient to improve dye degradation. The combination of metals with iron oxide nanomaterials can increase the kinetics of oxidation–reduction reaction, and tend to be an effective approach for photocatalytic improvement (Otto et al., 2008).

In addition, due to its narrow band-gap, Fe_2O_3 can be applied as a sensitizer of TiO_2 photocatalyst (Zhang and Lei, 2008; Akhavan and Azimirad, 2009). Electrons in the valence bands of TiO_2 are driven into Fe_2O_3 due to formation of the built-in field in Fe_2O_3–TiO_2 heterojunction. The charge transport between the valance bands of Fe_2O_3 and TiO_2 is regarded as an effective process to promote photocatalytic activity of the composition, since it results in an increase in the electron–hole recombination time (Peng et al., 2010a; Shinde et al., 2011).

Recently, a novel photo-Fenton-like system has been set up with the existence of iron oxides and oxalate (Lei et al., 2006). Iron oxides were mainly acted as a photocatalyst, while oxalic acid could be excited to generate electron–hole pairs (Leland and Bard, 1987; Siffert and Sulzberger, 1991). The heterogeneous iron oxide–oxalate system could exhibit a strong ligand-to-metal charge transformation ability as described below (Lei et al., 2006):

Firstly, oxalic acid can be adsorbed by iron oxide particles to form iron oxide–oxalate complexes including $[Fe^{III}(C_2O_4)_n]^{(2n-3)-}$ or $[Fe^{II}(C_2O_4)_{n-1}]^{4-2n}$ on the surface in solution, which are much more photoactive than other Fe^{3+} species, with the generation of oxalate radical $C_2O_4^{\bullet -}$.

$$\text{Iron oxide} + nH_2C_2O_4 \leftrightarrow [\equiv Fe(C_2O_4)_n]^{(2n-3)-} \tag{3}$$

$$[\equiv Fe(C_2O_4)_n]^{(2n-3)-} + hv \rightarrow Fe(C_2O_4)_2^{2-} \text{or} (\equiv Fe(C_2O_4)_2^{2-}) + CO_2{\bullet}^- \tag{4}$$

$$[Fe^{III}(C_2O_4)_n]^{(2n-3)-} + hv \rightarrow [Fe^{II}(C_2O_4)_{n-1}]^{4-2n} + C_2O_4{\bullet}^- \tag{5}$$

Then, a rapid de-carboxylation is followed. Oxalate radical is transferred into carbon-centered radical$CO_2^{\bullet -}$, then further transformed into superoxide ion ($O_2^{\bullet -}$).

$$C_2O_4{\bullet}^- \rightarrow CO_2 + CO_2{\bullet}^- \tag{6}$$

$$C_2O_4{\bullet}^- + O_2 \rightarrow CO_2 + O_2{\bullet}^- \tag{7}$$

Finally, $O_2^{\bullet -}$ produces H_2O_2 and O_2 by disproportion. •OH, generated in their redox–oxidize transformation process accompanied with the production and consumption of H_2O_2, as described below, plays a key role in the photodegradation process.

$$Fe^{3+} + O_2{\bullet}^- \rightarrow {\bullet}Fe^{2+} + O_2 \tag{8}$$

$$O_2{\bullet}^- + nH^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 \tag{9}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {\bullet}OH \tag{10}$$

According to above equations, photolysis of Fe(III)–oxalate complexes forms H_2O_2, Fe^{3+} could result in the radical chain mechanism described above, and the Fenton reaction (Eq. (10)) is enhanced by the participation of Fe^{2+}. Therefore, the photochemical reduction of Fe(III)-complex will be coupled to a Fenton reaction, with the production of oxidative species such as superoxide ($O_2^{\bullet -}$), hydroperoxyl (H_2O_2) and OH radicals (Quici et al., 2005) by utilizing natural materials (iron oxides and oxalic acid) to produce •OH without external H_2O_2 and artificial injection of iron (Faust and Zepp, 1993). In short, photo-Fenton-like system can provide a promising and effective method for photocatalysis of organic pollutants, possessing great application potential. It is also important to not only enhance the photocatalyst ability but justify the combination of iron oxide NMs with microbes (or other organisms) secreting oxalic acid or other organic acids on the basis of photocatalyst, therefore expanding the application of iron oxide NMs in removal of organic contaminants.

3.3. Immobilization carriers

Iron oxide NMs have also shown considerable potential in the immobilization of biomass. The biosorption capacity of a variety of macro and microbial biomass has been widely used to remove various pollutants. NMs can offer larger surface areas and multiple sites for interaction or adsorption (Paljevac et al., 2007). In particular, due to the advantage of chemical inertness and favorable biocompatibility, iron oxide NMs have been widely used in immobilization technology (Huang et al., 2003; Sulek et al., 2010).

A great deal of efforts has been made by various researchers (Jolivalt et al., 2000; Jiang et al., 2005; Huang et al., 2006b) to develop effective immobilization technology. Immobilization of biomass onto a more rigid and open support has been extensively studied for fungi and microalgae (Li et al., 2010). In fact, immobilized cells have been attracting great attention since the 1970s, mainly due to their distinct advantages over dispersed cells (McHale and McHale, 1994). First of all, the immobilization of native biomass enhances physical characteristics and offers a higher level of activity (Rodriguez, 2009). In addition, resistance to environmental perturbations such as pH, temperature and toxic chemical concentrations can be enhanced (Shin et al., 2002). Moreover, immobilization is conducive to cyclic biomass utilization, easier liquid–solid separation and minimal clogging in continuous-flow systems. Such advantages could satisfy the engineering needs for application of immobilization technology.

Appropriate techniques must be combined to provide technically sound and economically feasible options (Oller et al., 2011). Recently, *Saccharomyces cerevisiae* immobilized on the surface of chitosan-coated magnetic nanoparticles (SICCM) was applied as a novel magnetic adsorbent for the adsorption of Cu(II) from aqueous solution (Peng et al., 2010b). In the study of Peng et al. (2010b), a series of experiments were performed to examine the removal efficiency of the prepared adsorbents. It was found that SICCM was quite efficient as a magnetic adsorbent for the adsorption of Cu(II). The removal efficiency reached over 90% within 20 min, and the maximum adsorption capacity reached 134 mg g^{-1}. Hopefully this kind of novel adsorbent will have broad applications in the removal of heavy metals from wastewater. It is thus reasonable to presume that immobilization of biomass on suitable support is a precondition for the use of biosorbents in large-scale processing. In addition, more studies should be conducted to optimize the adsorbent, mainly by selecting proper strains which have great adsorption ability to heavy metals and organic compounds.

Although lots of immobilization mediums and methods have been investigated, little information is available on combining iron oxide nanotechnology with other biological technology for environmental application, which may show a great application prospect by combining respective advantages of both NM and biomass. Thus it is of great importance to study not only the large-scale application of adsorption method but also immobilization technology with high capacity and stability. Future studies may need to draw the field of magnetic NMs into biological applications such as nano-biosensors, cells/proteins immobilization for magnetic separation and environmental improvement. There is an emerging need for iron oxide NM immobilization technology to be applied in environmental treatment. As a result, it is of significance to select suitable biomass which possesses favorable adsorption capacity and is well compatible with magnetic NMs. In combined chemical and biological wastewater treatment, it is also very important to keep in mind how the characteristics of each individual treatment process can improve the destruction of a persistent contaminant (Oller et al., 2011). In addition, commercial issues such as scale up of the preparation of a biocatalyst or biosensor by immobilization of enzymes or microbes have to be assessed in competition with existing materials (Wang et al., 2008). It is anticipated that the practical performance will increase significantly after combining with biotechnology and iron oxide-based technology, and large-scale field application will also expand to a great extent.

4. Iron oxide nanomaterials in environment

It is recognized that there are many potentially serious issues concerning the environmental fate of engineered NMs and their potential impacts on human health. Currently, there are very few information on the background concentrations and physical–chemical forms of NMs in the environment due to limitations in separation and analytical methodologies, although some laboratory based studies have been carried out. However, such information is urgently required and a major advance in knowledge would come through the development of accurate and robust methodologies for the measurement of NMs concentration and form in the environment (Ju-Nam and Lead, 2008). A definitive need exists to evaluate the effects that NMs may have on the environment, yet little is known regarding interactions of NMs with environmental matrices, either naturally or in the test environment (Darlington et al., 2009).

First of all, it is imperative to identify the ecotoxicity of NMs in aquatic systems, or focus on transport in a terrestrial environment with an aim of prediction of NM behavior and evaluation of exposure pathways. Nanomaterials, that are near commercialization and are produced in large quantities, will enter the aquatic environment, resulting in direct exposure to humans via skin contact, inhalation of water aerosols and direct ingestion of contaminated drinking water (Nel, 2006). Thus the study of toxicity and pathology is extremely important (Gatti and Rivasi, 2002). Since there is so little data available for the fate of discharged NMs, research is required to test the behavior and particulate binding properties of manufactured NMs with ecosystem and human beings. But it is noted that cells and tissues have effective antioxidant defenses that deal with reactive oxygen species generation by NMs (Bell, 2003). Throughout their uptake and transport through the body, NMs will encounter a number of defenses that can eliminate, sequester, or dissolve NMs.

The unique characteristics of NMs will necessitate new test strategies to delineate the novel mechanisms of injury that may arise from these materials. Risk assessment is of key importance to the regulatory agencies that are responsible for formulating exposure and safety guidelines (Nel, 2006). Predicting the physical behaviors and biological toxicity of NMs is likely to be much more difficult than predicting those of conventional chemical pollutants, which is still often a major problem (Bucheli and Gustafsso, 2000; Moore, 2006). A major challenge for ecological risk identification will be the derivation of toxicity thresholds for NMs, and determining whether or not currently available biomarkers of harmful effect will also be effective for environmental nanotoxicity and nanopathology. It is therefore necessary that effective risk assessment procedures are in place as soon as possible to deal with potential hazards of NMs (Galloway et al., 2002; Galloway et al., 2004; Moore, 2006). It is also important for regulatory agencies to develop positive and negative benchmarks that can be used as reference controls (Nel, 2006).

In general, the attention on this field is still not enough, and additional studies should be conducted to advance knowledge in the area of safety and biocompatibility studies. In particular, for long-term toxicity studies, the potential impacts on human and environmental health should be essentially addressed. More refined methods for NM characterization and toxicological evaluations will be emerging. For example, some of specific nanosensors tend to be an available approach to detect ROS generation by nanoparticles. This could make these evaluations cost effective, facilitating new product development (Nel, 2006).

5. Conclusions

Wastewater treatment and reuse is a practice related not only to a number of benefits in regards to water balances and management but also to a number of question marks. Immediate research must be launched towards this direction so as to safeguard human health and environmental ecosystems. Nanomaterials, with unique physical and chemical properties, have a tremendous potential for contaminants removal. To bring the NMs development a step forward, NMs prioritization and further application prospect have been presented. As a kind of effective photocatalysts, iron oxide NMs would display their dominant superiority even at a source of visible light. In fact, iron oxide NMs are efficient nanosorbents for heavy metals and organic pollutants. Employing iron oxide NMs to adsorb heavy metals and organic pollutants are the most attractive and successful applications. While applications as immobilization carriers are only sparsely addressed, the potential of utilization as support carriers, consisting of biosensors and biosorbents, could not be ignored.

Although many cases of success in NMs were benefited from their unique chemical and physical properties, the applications of NMs in wastewater treatment are still limited in the early stage. As illustrated in this review, a range of iron oxide-based technologies have been proposed or are under active development for wastewater treatment, but many techniques are still at an experimental or pilot stage. Potential difficulties may be encountered in application in vitro and in vivo studies with iron oxide NMs. The field of iron oxide NMs (in a variety of chemical and structural forms) has already exhibited its diversity and potential applications in many frontiers of environmental area.

In conclusion, there is much recent interest in the use of engineered iron oxide NMs as an in-situ, relatively non-invasive tool in wastewater treatment. But it is noted that uncertainties over the health impacts and environmental fate of these nanomaterials need to be addressed before their widespread application. Increasingly, study of their fate and impact in the environment is becoming important due to the discharges already occurring to the environment. The likely further increase in NMs discharges along with the dramatic industry growth, and the immense knowledge gaps in risk assessment and management, would necessitate expanding studies in this area.

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