Review

Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: A review

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HIGHLIGHTS

- The review outlined heavy metals' removal from water by nanomaterials affected by HA/FA.
- Potential mechanisms involved in the interactions were discussed.
- Environmental implications of HA/FA to nanomaterials and heavy metals were evaluated.
- Outlook for further challenges and potential development was also offered.

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ABSTRACT

Nowadays nanomaterials have been widely used to remove heavy metals from water/wastewater due to their large surface area and high reactivity. Humic acid (HA) and fulvic acid (FA) exist ubiquitously in aquatic environments and have a variety of functional groups which allow them to complex with metal ions and interact with nanomaterials. These interactions can not only alter the environmental behavior of nanomaterials, but also influence the removal and transportation of heavy metals by nanomaterials. Thus, the interactions and the underlying mechanisms involved warrant specific investigations. This review outlined the effects of HA/FA on the removal of heavy metals from aqueous solutions by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials. Moreover, mechanisms involved in the interactions were discussed and potential environmental implications of HA/FA to nanomaterials and heavy metals were evaluated.

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1. Introduction

Water pollution has become a critical issue worldwide. The quality of water resources is deteriorating day by day due to population growth, rapid development of industrialization, agricultural activities, and other geological and environmental changes (Chong et al., 2010; Zeng et al., 2011, 2013a). The continuous release of various contaminants such as heavy metals and organic compounds into the environment is causing growing concern to the whole world (Deng et al., 2013; Zeng et al., 2013b; Chen et al., 2013). Heavy metals are particularly problematic because, unlike most organic contaminants, they are non-biodegradable and can accumulate in living tissues, posing great threat to both human health and ecological environment (Lesmana et al., 2009).

The most common heavy metals mainly include mercury, cadmium, lead, chromium, arsenic, zinc, copper, nickel, cobalt, etc. These metal ions can cause toxicities and serious side effects toward human health. For example, copper has universally been considered to be very toxic at high concentration. It can cause copper poisoning in humans such as gastrointestinal problems, kidney damage, hair loss, nausea, anemia, hypoglycemia, severe headaches and even death (Tang et al., 2012; Rahman and Islam, 2009). Cadmium is a toxic heavy metal of significant environmental and occupational concern. It has been identified as a human carcinogen and teratogen substance severely impacting lungs, kidneys, liver and reproductive organs (Waalkes, 2000; Filipic, 2012). Chromium exists in the environment both as Cr (III) and Cr (VI) forms. However, Cr (VI) is five hundred times more toxic than Cr (III) and toxicity of Cr (VI) includes skin irritation, lung cancer, as well as kidney, liver, and gastric damage (Kumar et al., 2007; Selvi et al., 2001). Consequently, the need for heavy metals' removal has become a must.

To date, various methods have been proposed for efficient heavy metal removal from waters, including but not limited to coagulation, chemical precipitation, membrane filtration, reverse osmosis, solvent extraction, flotation, ion exchange and adsorption (Xu et al., 2012b; Chen et al., 2010; Hua et al., 2012; Fu and Wang, 2011; Wang et al., 2003; Ali, 2012). In the last two decades, nanotechnology has developed with its applications in almost all branches of science and technology (Kaur and Gupta, 2009; Savage and Diallo, 2005). With the rapid development of nanotechnology, there has been a great deal of interest in environmental applications of nanomaterials. Nanomaterials are excellent adsorbents and catalysts (Khin et al., 2012). Since nanomaterials offer significant improvement with extremely high specific surface area, numerous associated sorption sites, low temperature modification, short intraparticle diffusion distance, tunable pore size and surface chemistry compared to other materials (Ju-Nam and Lead, 2008; Qu et al., 2013; Chen et al., 2007), extensive research have been carried out to remove heavy metals from wastewater by developing and using various nanomaterials.

Humic substances typically represent a large portion of natural organic matter (NOM) distributing in soils, sediments and waters (Morales et al., 2012). They are straw-colored, hydrophobic organic acids that are mainly derived from soil humus and plants. However, it has been also reported that 3–28% of the dissolved organic matter in effluents from wastewater treatment plants are humic substances (Moura et al., 2007; Imai et al., 2002). Thus, humic substances are very important compounds often encountered in the environment as a result of their extensive ubiquity (Matilainen et al., 2011). Humic acid (HA) and fulvic acid (FA) are two major components of humic substances. Generally, HA and FA differ in molecular weight, elemental and functional group contents. HA is higher in molecular weight and contains less oxygen-containing functional groups compared with FA (Güngör and Bekbölet, 2010; Weng et al., 2006). Despite the differences, their common functional groups such as carboxyl, phenol, hydroxyl, amine and quinine groups make it possible that HA and FA in waters cause many serious environmental and health problems. HA/FA has strong complexation ability with heavy metals and thus increases their transportation in waters. In addition, HA/FA can react with chlorine during water treatment, thereby producing carcinogenic disinfection byproducts such as trihalomethanes (Zhao et al., 2008; Wang et al., 2008, 2010b). Literature reports some approaches for removal of HA/FA from water including coagulation/flocculation, membrane separation, advanced oxidation, ion exchange, adsorption etc. (Imyim and Prapalimrungsi, 2010; Tao et al., 2010).

In general, HA/FA and heavy metals exist simultaneously in the environment, where they may affect each other's behavior (Li et al., 2012; Yang et al., 2011; Mak and Lo, 2011; Wang et al., 2009a). As nanomaterials are widely used to remove both HA/FA and heavy metals from water/wastewater, the presence of HA/FA may influence the interaction between heavy metals and nanomaterials. Similarly, the presence of heavy metals may also influence the interaction between HA/FA and nanomaterials. Meanwhile, it is also noteworthy that with their large production and widespread application, nanomaterials will inevitably interact with HA/FA once they are released into the environment, which may alter the surface properties, stability and transportation of nanomaterials and then affect the mobility and transportation of heavy metals in the environment, thus possibly enhancing the bioavailability and toxicity of heavy metals (Hyung and Kim, 2008; Zhang et al., 2011b; Yang and Xing, 2009). Therefore, it is of considerable practical interest to study the effects of HA/FA on the removal of heavy metals by different nanomaterials in waters as well as the potential environmental implications of HA/FA. Recently, extensive relevant studies have been done. However, to the best of our knowledge, up to now a review on this topic is still lacking.

This review highlights the removal of heavy metals by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials, as affected by HA/FA in batch and column systems. The phenomena, factors and potential mechanisms involved in the process are also discussed thoroughly. Meanwhile, the potential environmental implications of HA/FA to nanomaterials and heavy metals are evaluated. Finally, future perspectives are offered to inspire more exciting developments in this promising field.

2. Heavy metals' removal affected by HA/FA using various nanomaterials and the underlying mechanisms

Nanomaterials refer to materials on the nanoscale level between approximately 1 nm and 100 nm (Stone et al., 2010). Generally, nanomaterials can be categorized into carbon-based nanomaterials such as carbon nanotubes and graphenes, and inorganic nanomaterials including the ones based on metal oxides and metals. Combinations of different nanomaterials are also developed (Ju-Nam and Lead, 2008). Nanomaterials hold great promise of reducing contamination of heavy metals. Meanwhile, the production, use and disposal of nanomaterials will inevitably lead to discharges to aquatic environment. HA and FA, which are ubiquitous in natural environment, effectively influence the removal and transportation of heavy metals. The strong complex abilities between metal ions and HA/FA could also influence the underlying mechanisms involved in the interaction among the three components (heavy metals, HA/FA and nanomaterials).

Presently, numerous analytical techniques are being applied in determining the physicochemical properties of NOM and nanomaterials to elucidate the reaction process. C, H and N contents of NOM can be determined using an elemental analyzer. Total acidity values of NOM are determined by the $Ba(OH)_2$ titration method. The carboxyl groups are determined by the calcium acetate method. Phenolic alcohol group content is calculated by subtracting the carboxyl content from the total acidity (Tian et al., 2012). Molecular weight distribution of NOM can be obtained with size exclusion chromatography (SEC) (Sun et al., 2012). The redox state changes in NOM can be shown by fluorescence spectroscopy (Mak and Lo, 2011). For nanomaterial characterization, many analytical instruments are used. For example, scanning electron

microscope (SEM) and transmission electron microscope (TEM) are widely used to observe the morphology and size of nanomaterials. Vibrating sample magnetometer (VSM) is utilized to measure the saturation magnetization of magnetic nanomaterials. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) are performed to analyze the possible species of sorbed heavy metals on nanomaterials. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analyzer (TGA), atomic force microscopy (AFM), dynamic light scattering (DLS), Zeta Meter and Raman spectrometer are employed to analyze chemical surface groups, crystalline structure, surface elemental composition, weight composition, particle surface morphology, aggregation condition, zeta potential and binding sites of nanomaterials, respectively (Peralta-Videa et al., 2011).

In this part of review, attempts have been made to discuss heavy metals' removal and transportation in waters affected by HA/FA using various nanomaterials and the underlying mechanisms.

2.1. Carbon-based nanomaterials

2.1.1. Carbon nanotubes

Carbon nanotubes (CNTs), mainly including single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) (Trojanowicz, 2006), have been widely studied regarding their potential environmental application as superior adsorbents for heavy metals (Perez-Aguilar et al., 2011; Lu and Chiu, 2006; Peng et al., 2005) and organic compounds (Yang et al., 2006; Lu and Su, 2007; Cho et al., 2008; Li et al., 2013a) during solid-phase extraction and wastewater treatment. However, most current research is focused on the adsorption of single solute by CNTs in aqueous solution and ignores the potential interactions between mixtures of metal ions and organic substances that may affect adsorption (Chen et al., 2008; Ren et al., 2011; Li et al., 2013b, 2013c). Since humic substances are ubiquitous in the environment, a multiple solute system (HA/FA and heavy metals) may adequately represent the most of mixed contaminant systems commonly encountered in wastewater and natural water systems. Therefore, it is critical to investigate the adsorption behavior and mechanism of heavy metals by CNTs in the absence/presence of HA/FA.

HA/FA is expected to have significant influence on metal ion sorption by CNTs because the hydrophobic parts and aromatic monomers of HA/FA have strong affinity to CNTs through hydrophobic and π–π interactions, and meanwhile the hydrophilic fractions of HA/FA have various functional groups, such as carboxyl, phenol, hydroxyl, amine and quinine groups that can bind heavy metals (Lin et al., 2012). Also, it should be noted that the dissolved HA/FA and CNT-bound HA/FA may have different effects. The surface-bound HA/FA could greatly increase metal ion sorption on CNTs because the surface-bound HA/FA could introduce oxygen-containing functional groups and negative charges to the CNTs, and thus increases the apparent sorption of metal ions through chemical complexation and electrostatic attraction, respectively. For instance, the surface-bound HA significantly promoted Pb (II) sorption on MWCNTs although it would decrease surface areas of the MWCNTs (Lin et al., 2012). The mechanism was that Pb (II) could be electrostatically attracted into outer-sphere of the electric double layer of the HA-coated MWCNTs, while a fraction of the loaded Pb (II) would form coordination complexes with carboxyl groups in the inner-sphere or outer-sphere. Similar results were also observed for Cd (II) sorption onto HA-coated MWCNTs (Tian et al., 2012).

As for the effects of dissolved HA/FA on the sorption of heavy metals on CNTs, the process becomes more complicated. Both HA and FA are negatively charged in the pH range of 3.0–10.0 (Sheng et al., 2010). In acidic and neutral solutions, dissolved HA/FA could enhance the sorption of heavy metals by CNTs because the negatively charged HA/FA could be easily adsorbed on the positively charged surfaces of CNTs due to the electrostatic attraction. Now that most of HA/FA was adsorbed on CNTs, the subsequent interaction was similar to that of

surface-bound HA/FA. The strong complexation ability of surface adsorbed HA/FA with metal ions resulted in the increase of metal ion sorption on CNTs. However, in alkaline solutions, dissolved HA/FA could reduce the sorption of heavy metals by CNTs because of opposite effect of electrostatic repulsion. Most of HA/FA would exist freely in solution and then forms soluble complexes of HA/FA-metal ions, and thus leads to the decrease of metal ion sorption on CNTs. For example, Sheng et al. (2010) found a positive effect of HA/FA on Cu (II) adsorption at pH < 7.5, whereas a negative effect at pH > 7.5 by MWCNTs. In addition, initial HA/FA concentrations played a role in the adsorption of heavy metals on CNTs. The adsorption isotherms of Cu (II) onto MWCNTs at higher initial HA/FA concentrations were higher than those of Cu (II) at lower HA/FA concentrations (Sheng et al., 2010). Moreover, it was found that Cu (II) adsorption by MWCNTs increased with increasing initial NOM concentrations at both low and high pH values (Sun et al., 2012), which was different from the behavior observed for some substances such as aromatic compounds (Wang et al., 2009b). In the meantime, it's noteworthy that there was a higher binding affinity between Cu (II) and FA compared to HA, due to more functional groups (e.g., OH and/or COOH) in FA that could complex with Cu (II) as well as higher polarities.

To improve the adsorption performance and avoid the disadvantage of CNTs in adsorption process (e.g. easy aggregation and inherent insolubility), various CNT-based composites have been synthesized to explore the effectiveness of metal ions' removal under different circumstances. Specifically, combining the magnetic properties of iron oxide with adsorption properties of CNTs is of increasingly environmental concern as a rapid, effective and promising technology for removing hazardous pollutants in water and has been proposed for widespread environmental applications in wastewater treatment and potentially in situ remediation (Tang et al., 2012). Although CNT-based composites have better performances compared with CNTs, the influence of HA/FA on the removal of heavy metals by CNT-based composites might remain similar to that by CNTs (Wang et al., 2011b; Liu et al., 2013; Yang et al., 2011; Hu et al., 2012). For instance, It was found that the presence of HA/FA enhanced Co (II) sorption on magnetic multiwalled carbon nanotube/iron oxide composites (MWCNTs/IO) at low pH values, but suppressed Co (II) sorption at high pH values (Wang et al., 2011b). Similar phenomena were also found in the sorption of Co (II) on MWCNT–hydroxyapatite composites in the presence of HA/FA (Liu et al., 2013) and in the simultaneous removal of Pb (II) and HA by MWCNTs/polyacrylamide composites from aqueous solutions (Yang et al., 2011). In the simultaneous removal of Pb (II) and HA by MWCNTs/polyacrylamide, adsorption mechanisms were indicated based on the fact that different effects of HA/Pb (II) concentrations and addition sequences on Pb (II) and HA adsorption were observed. The proposed mechanisms of Pb (II) and HA adsorption on MWCNTs/polyacrylamide were schematically shown in Fig. 1.

Additionally, combining the excellent adsorption capacity of CNTs with other remarkable properties such as photocatalysis to remove heavy metals affected by HA/FA is also worth studying. In the ternary systems HA/FA–Cr(VI)–TiO₂/MWCNT composites, the increase of HA/FA concentration did not cause any drastic changes in the adsorption capacity of Cr (VI) in the dark, but a minor increasing trend for the photocatalytic reduction of Cr (VI). The presence of HA/FA enhanced the photocatalytic reduction and adsorption of Cr (III) to TiO₂/MWCNT composites (Tan et al., 2008).

2.1.2. Graphenes

As relatively new adsorbents, graphene-based adsorbents have been proven to possess extremely great adsorption capacity for removing organic and inorganic pollutants from water/wastewater (Zhu et al., 2012; Yang et al., 2013b; Wu et al., 2011). Recently, many researchers have been focusing their efforts on investigating the potential application of graphene oxide nanosheets in removing heavy metals from waters because unlike CNTs, which require special oxidation processes
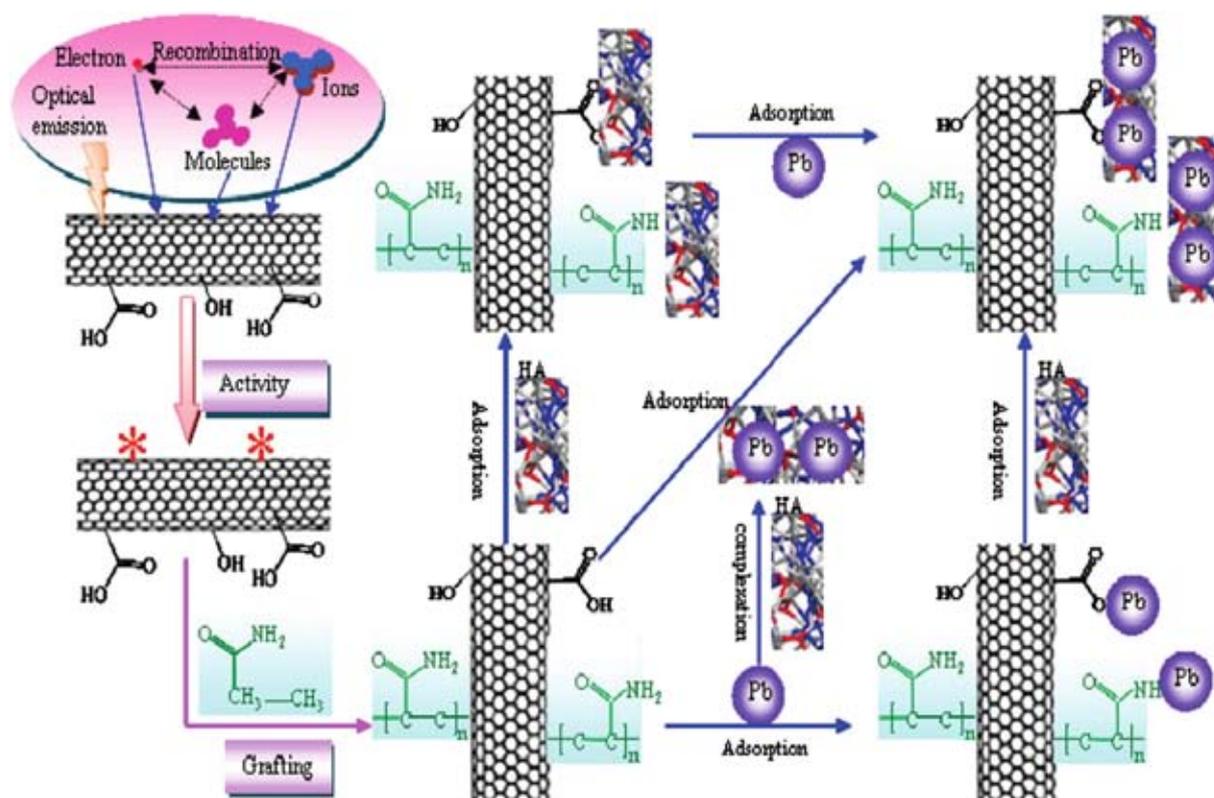
Fig. 1. Proposed schematic mechanisms of Pb (II) and HA adsorption on MWCNTs/polyacrylamide.
Adopted from Yang et al. (2011).

to introduce oxygen-containing functional groups to improve metal ion sorption, graphene oxide nanosheets can contain many oxygen-containing groups such as carboxyl and hydroxyl groups on the surface when they are prepared from graphite using Hummers method (Zhao et al., 2011). However, the application of graphene oxide nanosheets in the removal of heavy metals from aqueous solutions in the presence of HA/FA is still scarce. Only few relevant investigations have been carried out. For example, one type of graphene-based material (few-layered graphene oxide nanosheets) has been synthesized and used as adsorbents for the removal of Cd (II) and Co (II) from aqueous solutions in the presence of HA (Zhao et al., 2011). Results indicated that the presence of HA reduced Cd (II) sorption on few-layered grapheme oxide nanosheets. For Co (II) sorption, the presence of HA reduced Co (II) sorption at pH < 8, while at pH > 8 no obvious difference was found in the presence or absence of HA. The strong surface complexation and high surface site density of graphene oxide nanosheets may result in the decreased adsorption of Cd (II) and Co (II) in the presence of HA at pH < 8. This revealed that the surface properties of adsorbents influenced the effect of HA on the adsorption of heavy metals.

Li et al. (2012) studied the simultaneous removal of FA and Cu (II) from aqueous solution by graphene oxide nanosheets decorated with Fe_3O_4 nanoparticles (GO/Fe_3O_4). Results showed that: 1) the presence of FA led to a strong increase in Cu (II) sorption at low pH and a decrease at high pH; 2) FA concentration greatly influenced Cu (II) sorption and different FA concentrations displayed significantly different trends; and 3) addition sequences had no impact on Cu (II) sorption at pH < 5.5, but differences were observed in the three different addition sequences at pH > 6.0 (Fig. 2). This research confirmed that GO/Fe_3O_4 which combined the high sorption capacity of GO and the separation convenience of Fe_3O_4 can be used as an effective sorbent for the simple and rapid removal of inorganic and organic pollutants from water samples. In addition, the sorption–desorption process indicated excellent regeneration capacity of GO/Fe_3O_4 by using HNO_3 (pH 2.0).

In summary, there is still much room for further exploration in consideration of the widespread application of graphene-based materials and, more importantly, the limited number of experiments about utilizing graphene-based materials to remove heavy metals from aqueous solution in the presence of HA/FA.

2.2. Iron-based nanomaterials

2.2.1. Zero-valent iron nanomaterials

Among the most relevant zero-valent metal nanomaterials to environmental systems, zero-valent iron (ZVI) nanomaterials have received great attention due to their potential applications in the remediation of contaminated groundwater (Elliott and Zhang, 2001; Quinn et al., 2005). Hexavalent chromium and arsenic species are contaminants commonly found in groundwater, caused by various sources, such as wood preservatives and unlined landfills for construction and demolition wastes (Weber et al., 2002). However, Cr (VI) and As (V) contamination has raised much health concern because of their toxic, carcinogenic and mutagenic properties (Smedley and Kinniburgh, 2002). ZVI has been proven to be capable of removing Cr (VI) and As (V) from groundwater effectively. The removal mechanism of Cr (VI) by ZVI mainly involves chemical reduction of Cr (VI) to Cr (III), with subsequent Cr (III) precipitation as Cr (III) hydroxides and mixed Fe (III)/Cr (III) (oxy)hydroxides (Alowitz and Scherer, 2002), while the removal mechanism of As (V) by ZVI is primarily via the adsorption onto or co-precipitation with the iron corrosion products (Lackovic et al., 2000). Humic substances are ubiquitously present in groundwater. It is important to know how they would affect the removal of Cr (VI) and As (V) by ZVI. Unfortunately, to some extent, studies carried out in the presence of HA/FA revealed that the effect of humic substances on ZVI treatment in aqueous solutions was controversial.

In a recent study, HA was found to have an inhibitory effect on Cr (VI) removal by ZVI nanoparticles, especially at low concentrations
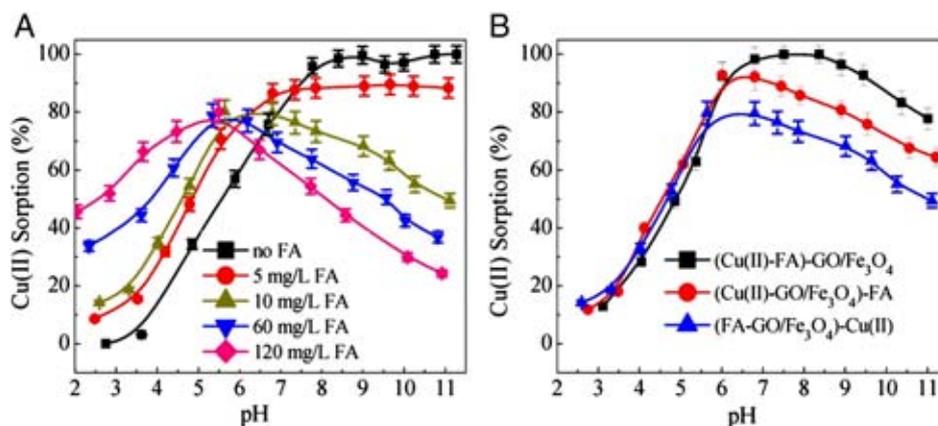
Fig. 2. Effect of FA concentrations on Cu (II) adsorption to GO/Fe$_3$O$_4$, $C_{Cu\ (II)\ initial}$ = 10.0 mg/L, m/V = 0.4 g/L, I = 0.01 M NaNO$_3$, and T = 293 K (A); effect of addition sequences on Cu (II) adsorption to GO/Fe$_3$O$_4$, $C_{Cu\ (II)\ initial}$ = 10.0 mg/L, $C_{FA\ initial}$ = 10.0 mg/L, m/V = 0.4 g/L, I = 0.01 M NaNO$_3$, and T = 293 K (B). Adopted from Li et al. (2012).

(Wang et al., 2011a). HA was adsorbed on the surface of ZVI nanoparticles and occupied the active surface sites, thus leading to the decrease in Cr (VI) reduction rates. The greater the adsorbed HA was, the more obvious the inhibitory effect was. On the contrary, another recent column study (Liu and Lo, 2011) revealed that HA promoted the removal of Cr (VI) by ZVI. The underlying reason might be that HA enhanced the release of dissolved iron in the forms of soluble Fe–HA complexes and stabilized fine Fe hydroxide colloids, which may suppress the precipitation of iron corrosion products on ZVI surfaces. Other studies found that the removal of Cr (VI) by ZVI in the presence of HA/FA was nearly unaffected over the pH range of 6.0–9.5 (Mak and Lo, 2011; Liu et al., 2008c, 2009a, 2009b; Dries et al., 2005). It's important to note that fluorescence spectroscopy showed that HA and FA were not involved in the reduction of Cr (VI) by ZVI, and only Cr (VI) and ZVI were involved in the redox reactions (Mak and Lo, 2011). The insignificant influence of HA/FA on Cr (VI) removal indicated that the extent to which HA/FA was adsorbed did not effectively block the surface or out-compete Cr (VI), or that the majority of HA/FA and Cr (VI) were adsorbed on different types of reactive sites on ZVI surfaces (Liu et al., 2008c, 2009a; Gheju, 2011).

In addition, HA/FA may have dual effects on Cr (VI) reduction by ZVI nanomaterials (Lv et al., 2013). As displayed in Fig. 3A, in the absence of HA, both ZVI and Fe$_3$O$_4$ could reduce Cr (VI) to Cr (III) while Fe^0/Fe^{2+} was oxidized to Fe^{2+}/Fe^{3+}, and then these dissolved iron ions precipitated soluble Cr as mixed Fe/Cr oxy(hydroxides). In Fig. 3B, in the presence of HA for a limited concentration, HA served not only as adsorbent for Cr (VI) removal with precipitation on ZVI–Fe$_3$O$_4$ particles, but also as a bridge to stabilize ZVI–Fe$_3$O$_4$ particles. Therefore, the removal of Cr (VI) was facilitated. However, if HA concentration increased to a certain level, HA could completely surround ZVI–Fe$_3$O$_4$ particles, hindering contacts between ZVI–Fe$_3$O$_4$ and Cr (VI) ions (represented by the dotted line in Fig. 3B) and gradually offsetting the promoted effect.

The combined effects of HA, HCO$_3^-$ and Ca^{2+} on Cr (VI) removal by ZVI appeared to greatly differ from corresponding individual impacts, as reported by Liu et al. (2009a). A schematic diagram of the influencing mechanisms of HA, HCO$_3^-$ and Ca^{2+} in the Cr (VI) removal process by ZVI was presented (Fig. 4). While the impact of HA alone on Cr(VI) reduction was insignificant, addition of HCO$_3^-$ to HA-containing solutions greatly promoted Cr (VI) reduction rates because of the buffering effect of HCO$_3^-$. Instead, further addition of HA into HCO$_3^-$ and Ca^{2+} containing solutions led to an inhibitory effect on Cr (VI) reduction rates, probably because Ca^{2+} enhanced HA adsorption on ZVI surface and thus resulted in greater blockage of the reactive sites. The distinct influences induced by different combinations of geochemical constituents, such as HA, HCO$_3^-$ and Ca^{2+}, cause some difficulties on the design of ZVI based permeable reactive barriers for the remediation of groundwater.

As for the effects of HA/FA on the removal of arsenic by ZVI, HA/FA played a negative role (Mak and Lo, 2011; Tanboonchuy et al., 2012; Mak et al., 2009; Rao et al., 2009; Giasuddin et al., 2007). The removal rate of arsenic by ZVI was inhibited in the presence of HA/FA probably due to the formation of soluble Fe-humate or Fe-fulvate in aqueous solutions which suppressed the production of iron (oxy)hydroxides. The higher initial HA/FA concentration was, the longer reaction time was required for arsenic removal. When the complexation of HA/FA with dissolved Fe was saturated, further corrosion of ZVI would produce iron (oxy)hydroxides. The dissolved Fe-humate or Fe-fulvate underwent bridging to form clusters which would further bridge the colloidal iron (oxy)hydroxides and form complicated iron corrosion product aggregates (Fig. 5). These iron corrosion products could result in the rapid removal of arsenic and Fe-humate/Fe-fulvate from water through adsorption and co-precipitation. Other studies investigating the impact of co-present HA and Cr (VI) indicated that although Cr (VI) removal was not affected by the co-presence of HA and As (V), As (V) removal appeared to be inhibited by the co-presence of HA and Cr (VI) (Liu et al., 2009b).

Also, Dou et al. (2010) investigated the effect of HA on arsenate removal from water by ZVI/activated carbon couples. It was found that HA had negligible effects on As (V) removal. Mak et al. (2011a, 2011b) conducted both batch and column studies using a combination of ZVI and iron oxide-coated sand (IOCS) to remove Cr (VI) and As (V) from HA-rich groundwater. In the batch study, ZVI–IOCS had a better performance on the removal of both Cr (VI) and As (V) than ZVI or IOCS alone. While As (V) was mainly removed by the IOCS and iron corrosion products, Cr (VI) was mainly removed by ZVI and its corrosion products. HA had shown marginal effects on Cr (VI) removal but some effects on As (V) removal. In the column study, a complete mixture of ZVI and IOCS showed the highest removal efficiency of both Cr (VI) and As (V). The impact of HA was negligible. HA could be adsorbed onto IOCS so that the influence of the deposition of HA aggregates on ZVI surface could be reduced, thus enhancing ZVI corrosion. The two studies suggested that ZVI–IOCS mixture could perform well in the removal of Cr (VI) and As (V) in both the absence and presence of HA.

Moreover, the coexistence of Ca^{2+} and HCO$_3^-$ had significant effects on the arsenic removal by ZVI in the HA-deficient and HA-rich groundwater. In the co-presence of Ca^{2+} and HCO$_3^-$, the removal rate of arsenic increased with increasing concentrations of either Ca^{2+} or HCO$_3^-$, whereas in the co-presence of Ca^{2+}, HCO$_3^-$ and HA, HA diminished the positive role of Ca^{2+} because the formation of CaCO$_3$ was delayed, leading to the subsequent delay in the formation of large iron hydroxides (Mak et al., 2009).

Meanwhile, it should be noted that the removal performance of both Cr (VI) and As (V) by ZVI can differ in the presence of HA and FA due to

Fig. 3. Schematic mechanism for HA effects on Cr (VI) removal: (A) in bare ZVI–Fe$_3$O$_4$ system, (B) in the presence of HA. Adopted from Lv et al. (2013).

the structural differences, especially the contents of the carboxylic and phenolic groups (Mak and Lo, 2011). Cr (VI) removal is inhibited in the presence of FA compared to HA. HA has less total binding sites than FA, and thus the adsorption of HA onto the ZVI surface is less than that of FA, as well as the blockage of reactive sites on the ZVI

surface. This results in a higher concentration of free Fe (II) concentration in the presence of HA and thus a faster Cr (VI) reduction rate since Cr (VI) reacts with the free Fe (II). On the contrary, As (V) removal is inhibited in the presence of HA compared to the FA. As (V) removal is mainly attributed to adsorption onto the iron corrosion products. FA,

Fig. 4. Schematic diagram of the influencing mechanisms of HA, HCO_3^- and Ca^{2+} in the Cr (VI) removal process by ZVI. Adopted from Liu et al. (2009a).

with more total binding sites than HA, can promote an earlier bridging of the metal–NOM and thus causes an earlier aggregation of the iron corrosion products. For the above reasons, the composition of NOM is worth consideration when applying ZVI to treat groundwater contaminated by Cr (VI) and As (V).

Last but not the least, although most studies have been focused on removing the two types of heavy metals, Cr (VI) and As (V), from groundwater by ZVI in the presence of HA/FA, investigating the effects of HA/FA on the removal of other heavy metals such as Zn (II) and Ni (II) by ZVI is also of great importance (Dries et al., 2005). HA could negatively affect the removal of Zn (II) and Ni (II) by ZVI, both in batch and column experiments. Two mechanisms might be responsible for this: 1) formation of metal–humate complexes in solutions and 2) competition for reactive surface sites between HA and heavy metals.

2.2.2. Iron oxide nanomaterials

Iron oxides exist in the environment with different forms. Hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are the most common species (Chan and Ellis, 2004). Over the past few years, the synthesis and utilization of iron oxide nanomaterials with novel properties and functions have been widely studied, due to their nano-scale size, high surface area to volume ratios and superparamagnetism (Xu et al., 2012a; Pan et al., 2010; Afkhami et al., 2010).

In fact, the removal of heavy metal ions by iron oxide nanomaterials in the presence of HA/FA is a complicated process (Davis and Bhatnagar, 1995; Liu et al., 2008b). On the one hand, if HA/FA and heavy metals occupy the same sites, the binding of HA/FA on the surface of iron oxides might reduce the removal rate of metal ions because of the site blockage and competition. Meanwhile, HA/FA in solutions could prevent a fraction of heavy metals from being adsorbed to the oxides. On the other hand, the binding of HA/FA to iron oxides might promote the removal of heavy metals due to the complexation between HA/FA and metal ions. It is noteworthy that other geochemical constituents also play an important role in the process. Consequently, the numerous interactions indicated above could lead to a comprehensive result.

It was reported that sorption of Cu (II) onto the α-Fe_2O_3 was strongly influenced by FA (Christl and Kretzschmar, 2001). A lower ionic strength resulted in more remarkable effects of FA on Cu (II) sorption to the solid phase (i.e., α-Fe_2O_3 plus surface-bound FA). Below pH 5.8, Cu (II) sorption to the solid phase increased compared to α-Fe_2O_3 without FA in solution. Above pH 5.8, Cu (II) sorption decreased in the presence of FA, which was attributed to formation of dissolved Cu–FA complexes and reduced FA sorption accordingly (Fig. 6). The trends and mechanisms were consistent with the literature studying Cd (II) removal by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles in the presence of HA (Gupta and Nayak, 2012). In addition, the effect of HA/FA on heavy metals' removal by some kinds of
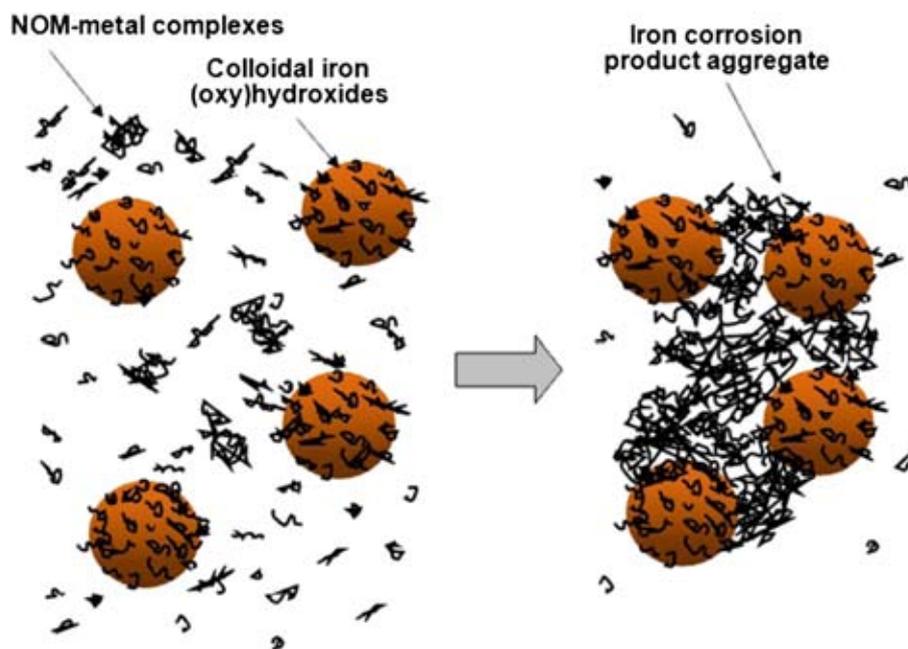
Fig. 5. Illustration of gel-bridging induced aggregation of iron corrosion products. The illustrations are not drawn to scale. Adopted from Mak and Lo (2011).

iron oxides was dependent on HA/FA concentrations (Liu et al., 2008b; Dong et al., 2010). For instance, while increasing of HA concentration from 0 to 1.1 mg/L contributed to the effective removal of Cu (II), Cd (II), Hg (II) and Pb (II) by Fe_3O_4, especially for Hg (II), further addition of HA reduced the metal ions' removal. When HA concentration was up to 50 mg/L, no further effect occurred. Also, there was remarkable variation of metal removal as pH values changed. However, in contrast with Fe_3O_4, HA coated Fe_3O_4 nanoparticles (Fe_3O_4/HA) had high and al-most constant removal efficiencies for metal ions in the entire studied range of HA concentration and pH values (Liu et al., 2008b). Hence, compared with Fe_3O_4, Fe_3O_4/HA exhibited remarkable enhancement of material stability and high heavy metal removal efficiency. It is expected that Fe_3O_4/HA will have wide applicability in the removal of heavy metals from various waters. Similar to Fe_3O_4/HA, no apparent effects of HA on adsorption of Cu (II), Pb (II), and Cd (II) ions were observed by a novel amino-functionalized $Fe_3O_4@SiO_2$ core–shell mag-netic nanomaterial under the tested conditions in the literature (Wang et al., 2010a). Additionally, the desorption studies showed that the novel adsorbent could be effectively regenerated with acid treatment.

A number of studies have demonstrated that iron oxides can effec-tively adsorb arsenate (As (V)), arsenite (As (III)) and Cr (VI), and HA/FA played an important role in regulating arsenic species and chromium removal by iron oxides. Obvious inhibitory effects were observed in the removal of both As (V) and As (III) by α-Fe_2O_3 (Redman et al., 2002), Fe_3O_4 (Yean et al., 2005; Shipley et al., 2010) and goethite (α-FeOOH) (Grafe et al., 2001) in the presence of HA/FA, As (V) by polysaccharide-stabilized Fe_3O_4 nanoparticles in the presence of HA (Liang et al.,

2012), As (III) by ferrihydrite in the presence of FA (Grafe et al., 2002), and Cr (VI) by γ-Fe_2O_3 in the presence of HA (Jiang et al., 2013). Com-petition between humic substances and As or Cr suggested that HA/FA might play a greater role in arsenic and chromium speciation and mobility in geochemical environments than previously recognized. Thus, when geochemical models are used in contaminant transportation prediction and remediation design with respect to groundwater, the influence of NOM must be seriously taken into consideration. Moreover, As (III) removal affected by HA or FA may decrease to a greater extent than As (V), which could partially explain the generally greater mobility of As (III) in natural environments. However, insignificant effects were observed in the removal of As (III) by Fe–Mn binary oxide (Zhang et al., 2007), γ-Fe_2O_3 modified with Fe–Mn binary oxide (Shan and Tong, 2013) and ferrihydrite (Grafe et al., 2002) in the presence of HA, As (V) by cetyltrimethylammonium bromide (CTAB) modified Fe_3O_4 (Jin et al., 2012) and iron-oxide coated sands (Hsu et al., 2008) in the presence of HA, and As (V) by ferrihydrite (Grafe et al., 2002) in the pres-ence of HA/FA. The marginal influence indicated that the above materials could be good candidates for arsenic removal regardless of the absence or presence of HA or FA in solutions. Among them, γ-Fe_2O_3 modified with Fe–Mn binary oxide showed very promising applications. As (III), predominant chemical state of arsenic in groundwater and much more toxic than As (V), could be oxidized by Mn oxides to As (V), which was then tightly bonded with ferric (hydr)oxide on the surface. Containing a magnetic core, the composite could be conveniently separated from water with magnet after treatment. Meanwhile, the hybrid material could be easily regenerated by using a solution comprised of 0.5 M NaOH, 0.1 M NaCl and 0.01 M NaClO, and could remain stable during cyclic runs without significant component loss.

2.3. Photocatalytic nanomaterials

2.3.1. Titania nanomaterials

In general, titania (TiO_2) requires the use of near UV light in order to be photoactivated (Bellardita et al., 2007; Reijnders, 2008). Thus, photocatalysis using TiO_2 nanomaterials has recently become very important. Also, TiO_2 is an ideal adsorbent because its solubility is negligible and the point of zero charge at neutral pH makes it possible to study the sorption of metal ions on TiO_2 over a broad range of pH (Zhang et al., 2011c). As a consequence, TiO_2-based nanomaterials have been focused on the bi-functional properties of great photocatalyt-ic ability and high adsorption capacity. Among NOM commonly existing in waters, HA and FA have significant influence on removal of metal ions via photocatalyzed oxidation/reduction or adsorption by TiO_2-based nanomaterials.

Attempts have been made to remove As (III) by TiO_2-based nanomaterials in the presence of HA/FA. As (III) is more toxic than As (V) and is difficult to remove from water by most techniques (Pena et al., 2005). So As (III) is typically removed by being oxidized to As (V) initially and then As (V) is removed by using adsorption, preci-pitation and so on (Guan et al., 2009, 2012). Lee and Choi (2002) inves-tigated the effect of HA on As (III) oxidation in UV-illuminated TiO_2 suspension. Results indicated that HA was beneficial to the photocata-lytic oxidation of As (III) at pH 3 but had little influence at pH 9. The presence of HA significantly promoted As (III) photooxidation mainly through enhancing superoxide production by sensitization. Tsimas et al. (2009) studied simultaneous photocatalytic oxidation of As (III) and HA in aqueous TiO_2 suspension. It was found that both As (III) and HA oxidation were reduced in the ternary system (As (III)/HA/TiO_2) compared to corresponding binary systems (As (III)/TiO_2 and HA/TiO_2), possibly due to the competition between As (III) and HA for the available photogenerated oxidizing species. The different effects of HA on As (III) photooxidation reported by different researchers may be attributed to the different properties of reactors and different experimental conditions employed in individual studies. However, it should be noted that all the above studies were conducted under
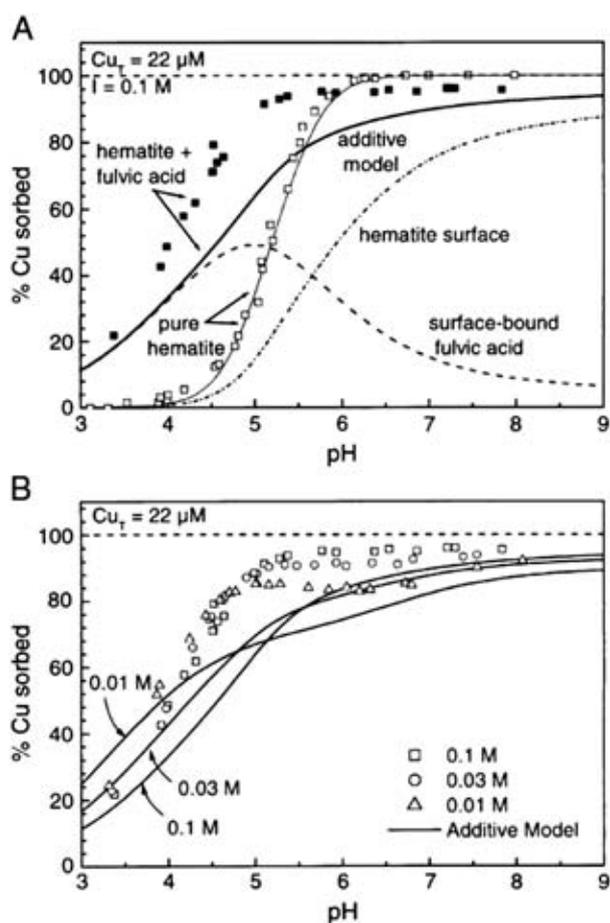
Fig. 6. (A) Cu (II) sorption in ternary systems containing 2 g/L α-Fe_2O_3 and 38 mg/L FA in $NaNO_3$ background electrolyte solutions. The total Cu (II) concentration was 22 M. (B) Cu (II) sorption to the solid phase in ternary systems at three different ionic strengths and corresponding model calculations based on the additivity assumption.
Adopted from Christl and Kretzschmar (2001).

O_2-saturated conditions and in the presence of light. In contrast, Liu et al. (2008a) examined the effects of NOM including HA and FA on arsenic adsorption by TiO_2 in simulated As (III)-contaminated raw waters under anaerobic conditions and in the absence of light. It was reported that NOM could suppress the sorption of arsenic by TiO_2, but could accelerate As (III) oxidation to As (V) at TiO_2 surface under alkaline conditions and in the absence of O_2 and light. The possible mechanism for this phenomenon was illustrated in Fig. 7. Under the above conditions, some As (III) could be still oxidized to As (V) due to the vacancies of bridging oxygen atoms on TiO_2 surface, and the presence of NOM greatly promoted this oxidation process.

Photocatalytic reduction of Cr (VI) has been studied in the presence of HA/FA (Uyguner and Bekbolet, 2004; Yang and Lee, 2006; Cid et al., 2012; Yang et al., 2012). Most of the studies indicated that the reduction of Cr (VI) proceeded more quickly in the presence of HA/FA than that in the absence of HA/FA. HA and FA can cause environmental problems by increasing mobility of toxic heavy metals. TiO_2 photocatalysis is a promising alternative treatment method for such systems because it can oxidize NOM and reduce Cr (VI) simultaneously (Cid et al., 2012). When HA/FA is added to the photoreduction system, the direct oxidation of HA/FA by positive holes and then the elimination of holes cause a reduced recombination between positive holes in the valence band and the electrons in the conduction band of TiO_2 and thus an increased photocatalytic efficiency despite the possible competition of HA/FA and Cr (VI) for the active sites of TiO_2. Hence, illuminated TiO_2 may be more effective when being applied to treat wastewaters containing both organic compounds and Cr (VI) than those containing a single species.

Removal of other heavy metals by TiO_2-based nanomaterials affected by HA/FA has been focused on utilizing the high adsorption capacity of TiO_2-based nanomaterials. Compared with original TiO_2, HA coated TiO_2 had increased adsorption of heavy metals such as Cd (II) (Chen et al., 2012), implying that adsorption of HA onto TiO_2 could alter its surface properties and HA coating might modify bioavailability and toxicity of heavy metals in real aquatic environment. However, HA had little

effect on the surface properties of titanate nanotubes although HA concentration tended to significantly affect competitive adsorption of Pb (II), Cd (II) and Cr (III) ions due to the formation and stability of HA–metal molecular (Wang et al., 2013). It is worth mentioning that FA may have a stronger effect on the adsorption of heavy metal ions onto titanate nanotubes than HA (Sheng et al., 2011). Additionally, efforts have been made to improve the adsorption performance of TiO_2 by combining TiO_2 with other materials. A novel adsorbent, TiO_2/eggshell composite, was developed by sol–gel method and used to remove Co (II) from aqueous solutions. It was reported that HA/FA enhanced Co (II) sorption on TiO_2/eggshell at low pH values, while inhibited Co (II) sorption at high pH values (Zhang et al., 2011c).

2.3.2. Zinc oxide nanomaterials

Photocatalysis technology is considered as an alternative approach of removing heavy metals from waters. Previous studies (Li and Qu, 2009; Sun et al., 2005; Xu et al., 2007) have suggested that TiO_2 could efficiently remove various heavy metal ions such as As (III) and Cr (VI). Although TiO_2 appears to be the most effective photocatalytic nanoparticle for environmental pollution treatment, zinc oxide (ZnO) nanoparticle has been demonstrated to be a suitable alternative to TiO_2 for the removal of heavy metals because it can be excited at room temperature under low excitation energy and it absorbs over a larger fraction of the solar spectrum than TiO_2 (Chakrabarti et al., 2009; Siboni et al., 2011). Moreover, ZnO nanomaterials are believed to be non-toxic, biosafe and biocompatible (Zhou et al., 2006), which makes ZnO an ideal photocatalyst with additional attractive advantage.

In spite of numerous studies on utilizing ZnO nanomaterials to remove heavy metals, only very few studies examined the effects of co-existing humic substances on photocatalytic removal of heavy metal ions by ZnO nanomaterials, and the few studies were focused on photocatalytic reduction of Cr (VI). Selli et al. (1996) confirmed that HA could act as sensitizers in the photoinduced reduction of Cr (VI) to Cr (III) in aqueous suspensions containing ZnO nanoparticles. Adsorption of HA on ZnO facilitated charge transfer reactions driven
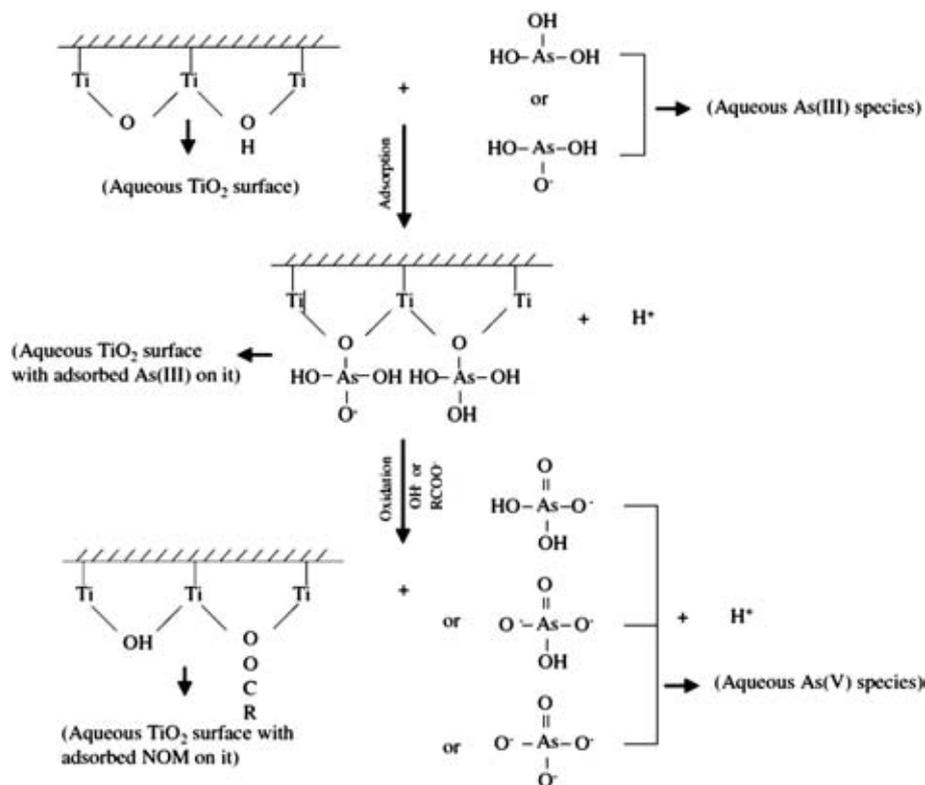
Fig. 7. Illustration of the possible mechanism for As (III) oxidation to As (V) on TiO_2 surface in the presence of NOM and in the absence of O_2 and light. Adopted from Liu et al. (2008c).

by solar irradiation. The reaction was promoted both in the presence of HA and under oxygen-deficient environment. Similar effect has been observed in the literature (Delgado-Balderas et al., 2012) in which photocatalytic reduction of Cr (VI) from agricultural soil column leachates using ZnO under UV light irradiation was evaluated. There was a synergistic effect between photocatalytic reduction of Cr (VI) and degradation of HA both in real samples and in synthetic solutions. The result was in good agreement with that reported by Yang and Lee (2006).

2.4. Other miscellaneous nanomaterials

In addition to carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials, other miscellaneous nanomaterials such as alumina, silica and manganese dioxide have also been investigated for the removal of heavy metals affected by HA/FA. These miscellaneous nanomaterials have been focused on their excellent adsorption properties.

Generally, there are three possible structures for the adsorption of heavy metals in the presence of HA/FA on mineral surfaces (Strathmann and Myneni, 2005). When HA/FA coexists with metal ion, the metal ion is absorbed by forming ligand-bridging ternary surface complexes (M-HA/FA-S) or surface complexes in which the metal ion remains directly bonded to functional groups of the mineral, that is, binary M-S or metal-bridging ternary surface complexes (HA/FA-M-S), where S represents the adsorption site on the solid surface and M is the metal ion. The effects of HA/FA on the removal of heavy metals by adsorbents depend on the relative contribution of the above individual sorption complexes, types of adsorbents and metal ions, and geochemical conditions. In many cases, HA and FA were shown to enhance heavy metals' sorption at low pH, but to reduce heavy metals' sorption at high pH. However, the comparison of the effect of HA/FA on the adsorption of heavy metals by miscellaneous nanomaterials is still necessary. Table 1 lists reports on the effects of HA/FA on the adsorption of heavy metals by miscellaneous nanomaterials.

3. Environmental implications of HA/FA

Humic substances, with high reactivity and strong binding ability, play a significant role in altering surface properties, aggregation, transportation and toxicity of nanoparticles and in controlling removal, mobility and bioavailability of metal ions in the environment. Knowledge of their environmental impact would be highly important and useful.

First of all, with their large production and widespread application, manufactured nanomaterials will inevitably enter environment, which may bring certain health and environmental risks. The ecotoxicity of nanomaterials is increasingly becoming a major concern issue in the world (Handy et al., 2008; Nel et al., 2006). Once released into environment, nanomaterials may acquire a coating of HA/FA due to the pervasiveness of humic substances. As a consequence of HA/FA coating, the surface properties, fate, transportation and toxicity of nanomaterials in the aqueous environment could be altered. Therefore, study of the stability, fate, transportation and toxicity of nanomaterials in the presence of HA/FA is extremely important. With respect to aggregation of nanomaterials, the presence of HA/FA had significant effects. It was reported that with the addition of HA/FA, the negative surface charge of nanomaterials (e.g. ZnO, TiO2, Fe2O3, NiO, Ag) increased greatly and thus their propensity to aggregate decreased (Tiller and O'melia, 1993; Zhang et al., 2009; Adegboyega et al., 2013). It should be noted that SiO2 remained stable no matter whether the solution contained HA/FA or not, because of its low NOM adsorption capacity and small Hamaker constant (Zhang et al., 2009). Understanding aggregation is critical for characterizing transportation of nanomaterials in the environment. Less aggregation yields lower rates of sedimentation and greater mobility (Maurer-Jones et al., 2013). Also, the stability of nanomaterials is of great significance in determining their bioavailability and toxicity. Previous work revealed that HA/FA had different effects on the toxicity

Table 1
Effects of HA/FA on the adsorption of heavy metals by other miscellaneous nanomaterials.

Nanomaterials	Heavy metals	Humic substances	Highlights	Refs
γ-Al2O3	Ni (II), Co (II)	HA, FA	HA/FA enhanced Ni (II) sorption at low pH, but reduced Ni (II) sorption at high pH.	Zhang et al. (2011a) and Li et al. (2009)
	Cd (II), Cu (II)	HA	HA enhanced the interaction of Cu (II) with γ-Al2O3, but had little effect on the interaction of Cd (II) with γ-Al2O3.	Plavšić and Ćosović (1999)
	Zn (II)	FA	No effect of FA on Zn (II) sorption was observed at pH < 7 and concentrations of FA at 4.2 and 21 mg/L, while Zn (II) sorption was dramatically reduced at pH > 8 and concentration of FA at 21 mg/L.	Tao et al. (2000)
	Cu (II), Pb (II)	FA	FA promoted Cu (II) sorption in concentrations greater than 5 mg C/L and the promotive ability of FA was more significant at lower pH. Effect of FA on Pb (II) sorption was similar to that of Cu (II).	Wu et al. (2003)
MnO2	Co (II)	HA, FA	HA/FA enhanced Co (II) sorption at low pH, but reduced Co (II) sorption at high pH.	Mou et al. (2012)
SiO2	Pb (II), Cd (II), Cu (II), Zn (II)	HA, FA	HA/FA significantly enhanced the adsorption of the metal ions on SiO2.	Stathi and Deligiannakis (2010)
	Co (II)	FA	FA enhanced Co (II) sorption at low pH, but reduced Co (II) sorption at high pH. Also, Co (II) sorption on SiO2 was not affected by the addition sequence.	Li et al. (2009)
ZrO2	As (III)	HA	HA didn't notably influence As (III) adsorption.	Zheng et al. (2012)
γ-AlOOH	Ni (II)	FA	FA enhanced Ni (II) sorption at low pH, but reduced Ni (II) sorption at high pH.	Strathmann and Myneni (2005)
Fe and Mn hydroxides	Hg (II)	HA	HA inhibited Hg (II) adsorption in freshwater system, but promoted Hg (II) adsorption in marine system.	Liang et al. (2013)

of nanomaterials to organisms. For example, HA could decrease the antibacterial activity of Ag and CeO2 nanoparticles (Fabrega et al., 2009; Chen et al., 2011), and FA could decrease the antibacterial activity of CuO nanoparticles (Zhao et al., 2013). On the contrary, the presence of HA could increase the toxicity of TiO2 nanoparticle to developing zebrafish (Yang et al., 2013a). However, HA/FA in wastewater decreased the attachment of bacteria on SWCNTs, but didn't reduce the toxicity (Kang et al., 2009). The importance of the state of nanoparticles to subsequent behavior and toxicity, complicated by the interaction between dynamic nanoparticle transformations necessitates careful, time-dependent in situ characterization of nanoparticles under environmentally relevant conditions.

Second, HA/FA will affect the removal and mobility of heavy metals by various nanomaterials and thereby potentially alter the fate, transportation and bioavailability of heavy metals in the environment since HA/FA could change the surface properties, aggregation, transportation and toxicity of nanomaterials, and more importantly, HA/FA could bind metal ions by forming complexes on mineral surfaces or in solutions. For example, when HA and As were incubated together or introduced sequentially with hematite, HA greatly reduced the sorption extent of

both As (III) and As (VI) because As (III) and As (VI) formed aqueous complexes with HA in the presence of bridging metals and negatively charged functional groups in HA competed with arsenic (Redman et al., 2002; Ko et al., 2004). Thus, HA may promote mobility of arsenic in the environment, in the form of free or organically complexed arsenic species. Generally, HA/FA influences metal bioavailability by decreasing the amount of metal ion available for the biotic ligand (Fig. 8A). But in real aquatic environments, HA/FA may react with a continuum of dissolved metals, clusters and nanoparticles (Fig. 8B). In this way, bioavailability of metals depends on the type of organisms, routes of exposure, dissolved metal speciation and mobility, and the characteristics of nanoparticles (Aiken et al., 2011).

Currently, although some relevant lab-based studies have been studied, there is still little information about the environmental implications of HA/FA due to complication in mutual effect among factors and limitations in analytical methodologies. However, such information is urgently needed because it can explain the interactions among dissolved organic matter, metal ions, and nanoparticles. A major advance would come in elucidating the interactions between DOM and nanoparticles and the consequences of these interactions for metal removal, speciation, mobility and bioavailability in waters through development of accurate analytical methodologies and progress of extensive scientific experiments in this field.

4. Conclusions and outlook

The present study indicated that HA/FA has complex effects on the removal and environmental behavior of heavy metal ions by nanomaterials. The effects were controversial, depending on types of nanomaterials and metal ions as well as geochemical conditions (e.g. HA/FA concentration, pH, ionic strength, coexistence of other substances). Furthermore, this work demonstrated that the presence of HA/FA could significantly modify the mechanisms controlling metal ions' removal and transportation by nanomaterials in heterogeneous aquatic environments. These mechanisms involved complexation, adsorption, electrostatic force, oxidation/reduction, catalysis and so on. And further research is needed to carefully investigate the interaction mechanisms between nanomaterials, HA/FA and heavy metals.

In conclusion, there is much interest to study the effects of HA/FA on the removal of heavy metals by different nanomaterials in water/wastewater as well as the potential environmental implications of HA/FA. The rapid growth of nanotechnology along with the potential increase in nanomaterial discharges, the severe pollution caused by heavy metals, the prevalent existence of HA/FA in the aquatic environments and the immense limitations in analytical methodologies would necessitate expanding studies in this field. But it should be noted that uncertainties over the influence and environmental implications do exist and need to
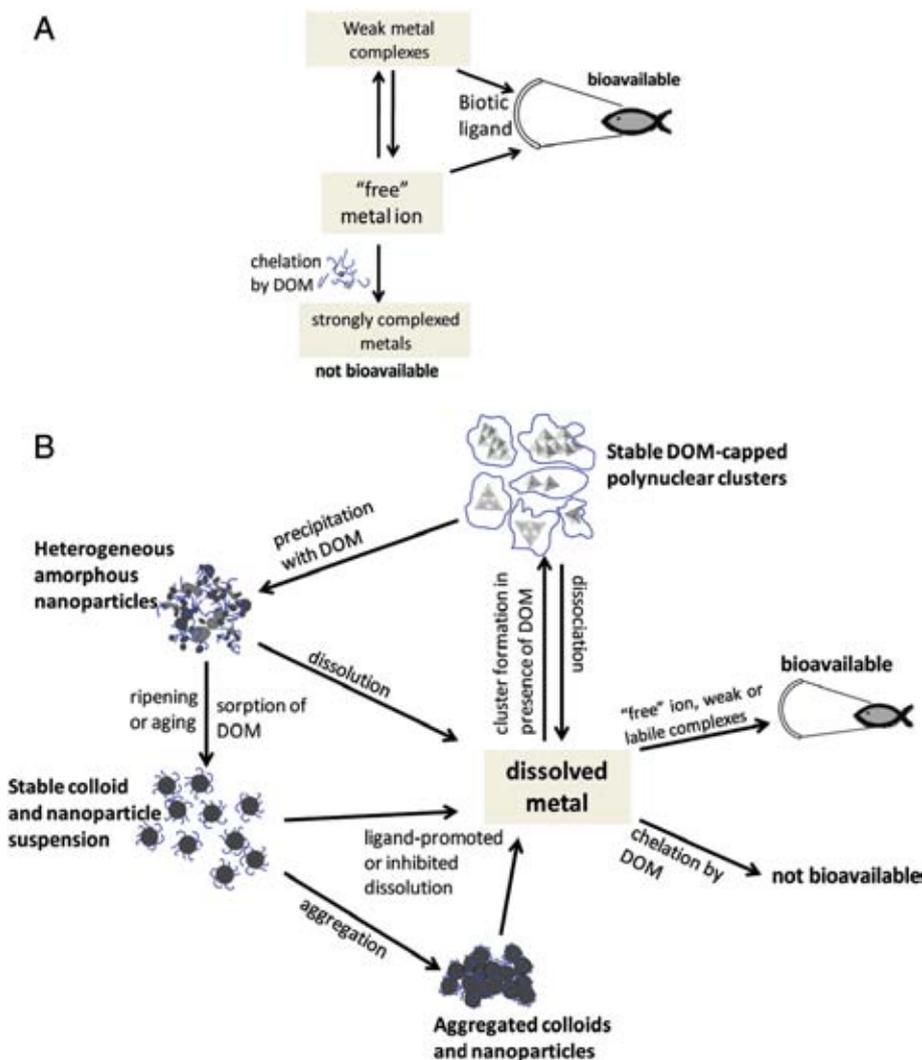
Fig. 8. (A) Generally, DOM influences metal bioavailability by decreasing the amount of metal ion available for the biotic ligand. (B) In real aquatic environments, DOM may react with a continuum of dissolved metals, clusters and nanoparticles. Whereas bioavailability of metals depends on the type of organisms, routes of exposure, dissolved metal speciation and mobility, and the characteristics of nanoparticles.
Adopted from Aiken et al. (2011).

be urgently addressed. Moreover, there are some issues related to developments in the near future. The regeneration/management of the depleted nanomaterials is an important issue and has not been taken care seriously. Only a few relevant studies are available in literature. It would be worthwhile to investigate the reusability of the spent adsorbents (e.g., carbon-based nanomaterials) and the management of the exhausted reducing agents (e.g., ZVI nanomaterials) as well as oxidizing agents (e.g., TiO₂-based nanomaterials). In addition, most of the studies discussed herein were conducted by batch mode instead of at pilot and industrial scales. Therefore, future is seeking for the design and development of effective columns for removing heavy metals by various nanomaterials affected by HA/FA at a large scale.

Acknowledgments

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