Removal of Cd, Pb and Cu from Water Using Thiol and Humic Acid Functionalized Fe₂O₃ Nanoparticles

Wang Meng, Chen Shibao*

Ministry of Agriculture Key Laboratory of Crop Nutrition and Fertilization, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Zhongguancun South Street 12, Beijing 100081, China

[a] wangmeng19880204@163.com, [*] Corresponding author: sbchen@mail.caas.net.cn

Abstract. Humic acid (HA) and 3-Mercaptopropyltriethoxysilane (MPTES) were successfully coated onto the surface of Fe_2O_3 (α and γ) nano-particles as characterized using IR and BET-N_2 analysis, the potential use of the naked and functionalized nano-Fe_2O_3 particles as novel nano-sorbents for removal of Cd, Pb and Cu ions in solution was investigated in this study. The result indicated that the sorption of Cd, Pb and Cu ions by the nano-particles can be fitted well using langmuir isotherm; all the adsorbents exhibited definitely adsorption ability to Cd, Pb and Cu ions in solution. The sorption maximum and sorption affinity on the nano-particles for Pb (aq) were always higher than Cu (aq) and Cd (aq), the sorption maxima for the Pb, Cd and Cu followed the order Pb>Cu>Cd. Among the nano-sorbents, the Fe_2O_3 (α and γ) nano-particles coated with HA exhibited higher sorption ability to metal ions than the naked and thiolated Fe_2O_3 nano-particles, the sorption maxima of α-Fe_2O_3/HA for Pb(aq) reached 151.5 mg/g, which was significantly higher than the values of 116.3 and 84.0 mg/g observed for the α-Fe_2O_3 and α-Fe_2O_3/MPTES particles. However, no increased sorption maxima was observed for the thiolated Fe_2O_3 nano-particles (Fe_2O_3/MPTES) for the metal ions compared with the naked Fe_2O_3 nano-particles in this study. The greater capability of Fe_2O_3/HA to adsorb Cd(aq), Pb(aq), Cu(aq) indicates its potential use as another promising way to remediate metals-contaminated water.

Introduction

The toxic heavy metals present in wastewater, effluents and soils are becoming a major environmental concern and multi-metal pollution is the usual situation in environmental media [1, 2]. Recently, more and more efforts have been made on remediation of soils and wastewater polluted by toxic metals, several approaches for remediation of aqueous systems contaminated with heavy metals have been reported[3,4]. Among these, adsorption is considered as an effective and economical method for the removal of pollutants from waste-water due to easy handling [1]. With the development of nanoscience and nanotechnology, many of the new nanosorbents are developed for the current water-treatment problems [5,6]. The unique characteristics of enhanced huge planar surfaces of nanosorbents can enable and increase interface reactions with pollutants in environment [7].

Various types of nano-sorbents such as metal oxides, clays, carbonaceous nanomaterials, zero-valent metals have been studied for their usefulness in the water-treatments [1,6]. More recently, iron oxide nanoparticles have been proposed as inexpensive but efficient adsorbents for removal/remediation of metals-contaminated media, the unmodified maghemite (γ-Fe_2O_3) was proved to be very effective for successful capturing of Cr (VI) in solution [8]. Moreover, the addition of small molecule affinity ligands to the surface of the nanoparticles increases the sorbents' affinity for specific heavy metals greatly [9]. Recent research indicated that Cd exposure strongly induced the production of GSH (the thiol (SH)-containing compound) in plant tissues of Sedum alfredii, which has been proven to be a cadmium (Cd) hyperaccumulator [10]. Further, it is a known fact that Humic acid (HA) has a skeleton of alkyl and carboxyl units that attach with phenolic hydroxyl, and quinone functional groups. Due to the high complex capacity of these functional groups with heavy metal ions,

HA was applied to remove heavy metal ions from water extensively [11,12]. The objectives of this study were (1) to examine the feasibility of coating nano- Fe_2O_3 (α and γ) nanoparticles with 3-Mercaptopropyltriethoxysilane(MPTES) and humic acid sodium salt; (2) to evaluate the capability and behavior of naked and Thiol/HA coated nano- Fe_2O_3 (α and γ) for the removal of aqueous heavy metal ions (Pb^{2+}, Cd^{2+} and Cu^{2+}) in solution.

Materials and Methods

1.1 Nano-Fe_2O_3 particles and chemicals.
The nano- Fe_2O_3 (α and γ) for this study were commercially provided by Nanjing Emperor Nano Material Co. (Nanjing, China). 3-Mercaptopropyltriethoxysilane (MPTES) was supplied by Alfa Aesar a Johnson Matthey Co. (Japan); humic acid sodium salt was purchased from Sigma-Aldrich. (Steinheim, Germany); All other chemicals were analytic grade reagents and used as received. The water used throughout this work was the ultrapure water.

1.2 Nanoscale Fe_2O_3 particles preparation and characterization
Functionalized nano- Fe_2O_3 particles were prepared by a solvent diffusion method. Fe_2O_3 (α and γ) seeds were dissolved in 150 mL of ethanol at a concentration of 16.7 g/L, the reaction mixture was sonicated for 30 min after adding 2 mL of ultrapure water. Finally, 8 mL MPTES or 0.4 g HA were added and the reaction mixture was vacuum stirred for 7h. The supernatant and solid residues were separated by ultracentrifugation at 10, 000 r/min for 30 min and washed several times with water and ethanol, and then finally dried in a vacuum oven at 70℃. Surface area of the sample was measured by single point Brunauer, Emmett and Teller N2 sorption procedure (BET-N2: Nova Station C), identification of the functional groups was performed by using infrared spectrum (IR: Spectrum-400) analysis. Total metal concentration in nano- Fe_2O_3 was determined by atomic absorption spectroscopy (AAS: Varian AA 240FS +GTA) following microwave-assisted aqua regia acid digestion described by the method of Lu (1999) [13], the results showed that the nano- Fe_2O_3 material did not contain toxic metals.

1.3 Isotherm adsorption
Adsorption study was conducted in batch experiments: lead (Pb), cadmium (Cd) and copper (Cu) stock solution of 1,000 mg·L^{-1} was prepared from their salts $PbCl_2$, $3CdSO_4·8H_2O$ and $Cu(NO_3)_2·3H_2O$ respectively. 30 mL aliquots of 0.05 mol/L KNO_3 background electrolyte solution, containing a known amount of metal ions concentration ranging from 0 to 120(Cd), to 240 (Pb and Cu) mg·L^{-1} were equilibrated with 0.20 g of naked and functionalized nano- Fe_2O_3 in 50 mL polycarbonate centrifuge tubes. The slurries were shaken on an over-to-over shaker (~50 r/min) at room temperature (25 ± 2°C) for 24 hours according to our preliminary test because no significant adsorption was observed after 24-hours reaction. The supernatant and solid residues were separated by centrifugation at 4, 500 r/min for 30 min. The concentrations of Pb, Cd and Cu in the supernatant solutions, after reactions with NPs, were determined by AAS/FAAS: Varian AA 240FS + GTA. All experiments were performed in triplicate per treatment. The amount of adsorbed Pb, Cd and Cu was calculated as the difference between the amount added initially and that remaining in solution after equilibration. To study and compare the adsorption of aqueous Pb, Cd and Cu on NPs, the adsorption data were analyzed according to the linear form of the Langmuir isotherm to evaluate the parameters directly associated with the sorption process. The linear form of the Langmuir equation is represented by

$$Ce/x/m = 1/kb + Ce/b \qquad (1)$$

Where: Ce is the concentration of metals (Pb^{2+}, Cd^{2+} or Cu^{2+}) in equilibrium in the solution (mg·L^{-1}), x/m is the amount of the metal ions (mg·g^{-1}) adsorbed on the NPs, b and k are Langmuir constants related to maximum sorption capacity (mg·g^{-1}) and energy of sorption, respectively.

Results

2.1 Characterization of Fe_2O_3, Fe_2O_3/MPTES and Fe_2O_3/HA nanoparticles

The surface area for nanoparticles revealed by single-point BET-N_2 sorption procedure is listed in Table 1. The values of surface area of Thiol/HA coated nano- Fe_2O_3 (α and γ) are higher than the naked ones, this might be attributed to the fact that MPTES and HA have highly narrow microporosity which adsorbs no N2 at 77K. Noticeably, the similar surface area of naked and functionalized nano-Fe_2O_3 (α and γ) suggests these materials are likely to have a similar primary size. This reveals that the binding process did not significantly result in the agglomeration and the change in size of the particles. This could be attributed to the reaction occurring only on the particle surface, and thus our attempt to prepare MPTES and HA-bound nano- Fe_2O_3 in this work has been achieved.

Spectroscopic analysis shows the successful coating of MPTES and HA on the Fe_2O_3 surface. Infrared spectrum (Fig. 1) shows the -SH stretches were found at ~2900 cm^{-1}, which are typically very weak. The frequency of the thiol-SH stretch is unusual (ca. 2900 cm^{-1}, as opposed to about 2550 cm^{-1} for a normal thiol), but this is presumably due to thiol aggregation within the monolayer and hydrogen bonding effects [14]. In the IR spectrum, the C=O stretches of Fe_2O_3/HA at ~1400 cm^{-1}, The fact that we observed the carboxylate stretches at ~1400 cm^{-1} is consistent with the carboxylate anion interacting with the FeO surface since the free carboxylic acid would have a C=O stretch above 1700 cm^{-1} [15]. For the bare Fe_2O_3 materials, however, no C=O stretches were observed. It is generally believed the binding of HA to Fe_2O_3 surface is mainly through ligand exchange [12].
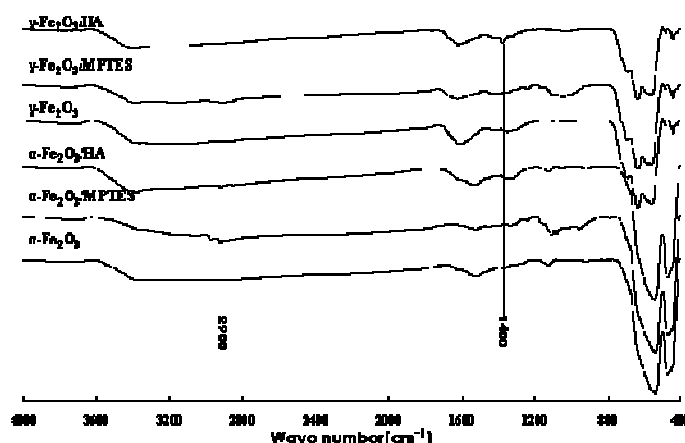

Fig. 1 IR Spectrum of bare and functionalized nano- Fe_2O_3 (α and γ).

2.2 Sorption isotherm

To study and compare the removal efficiency of aqueous Cd, Pb and Cu using the naked and functionalized nano- Fe_2O_3 particles, the sorption data of Cd, Pb and Cu by nano-particles were fitted to the Langmuir isotherm equation (Eq. (1)). The sorption parameters of the adsorbents for the metal ions from solution were listed in Table 2. As shown in Table 2, all the adsorbents exhibited definitely adsorption ability to the metal ions in solution. Figure 2 shows the Ce/x/m as a function of Ce at various adsorbents and metal ions concentrations. As expected, the typical sorption behavior of nano-sorbents occurred with the increasing initial metal ions concentration after 24 h of equilibration. The isotherm constants derived from Eqs. (1) and the correlation coefficients (R^2) were listed in Table 2, which revealed that the adsorption of metal ions on naked and functionalized nano- Fe_2O_3 obey the Langmuir adsorption isotherm well. As shown in Fig.2, a steeper slope of the curve can be observed at lower initial metal ions concentrations (< 30 mg/L) before reaching a plateau at higher concentrations (> 40 mg/L), which means that at lower concentrations, nano-sorbents had sufficient number of adsorption sites to adsorb the metal ions. At higher concentrations, however, adsorption sites of nano-sorbents would be saturated due to the increasing ratio of the number of metal ions to the number of adsorption sites, which is in agreement with results from Kamal et al. (2010) [16].

Table 1 Characteristics of nanoparticles used for the experiments (n=3)

Nanoparticles	Average size (nm)	Surface area (m^2/g)
α-Fe_2O_3	30.21±0.98	82.34±3.88
α-Fe_2O_3/MPTES	29.47±2.13	86.63±5.91
α-Fe_2O_3/HA	31.78±3.24	88.72±8.23
γ-Fe_2O_3	20.52±0.47	92.05±1.39
γ-Fe_2O_3/MPTES	19.67±1.36	94.53±4.86
γ-Fe_2O_3/HA	20.08±3.21	96.71±9.72

Table 2 Parameters of the Langmuir isotherms for the adsorption of Pb(aq), Cd(aq) or Cu(aq) on the adsorbents and the corresponding sum of squares errors (SSE)

Adsorbents	Pb			Cd			Cu		
	b	k	SSE	b	k	SSE	b	k	SSE
α-Fe_2O_3	116.3	0.46	2.38×10^{-2}	61.0	0.33	5.76×10^{-3}	41.7	0.50	1.84×10^{-2}
α-Fe_2O_3/MPTES	84.0	0.48	6.12×10^{-2}	60.2	0.32	8.07×10^{-3}	25.9	0.16	4.32×10^{-2}
α-Fe_2O_3/HA	151.5	0.17	6.1×10^{-2}	91.7	0.66	4.98×10^{-3}	126.6	0.39	2.13×10^{-2}
γ-Fe_2O_3	98.1	0.13	4.22×10^{-2}	39.2	0.29	7.32×10^{-3}	34.1	0.06	3.77×10^{-2}
γ-Fe_2O_3/MPTES	96.2	0.60	8.41×10^{-2}	48.1	0.34	6.16×10^{-3}	45.5	0.06	3.88×10^{-2}
γ-Fe_2O_3/HA	144.9	0.18	4.39×10^{-2}	78.7	0.39	2.79×10^{-3}	117.6	0.12	1.39×10^{-2}

Table 2 shows that the adsorption of bare α- Fe_2O_3 nano-particles for Pb(aq) is always higher than that for Cd (aq) and Cu (aq); i.e., the sorption maxima (b value) of α- Fe_2O_3 for Pb(aq) could be calculated to be 116.3 mg/g, which was significantly higher than the values 61.0 and 41.7 mg/g observed for the adsorption of Cd(aq) and Cu(aq). A similar phenomenon has also been found by Chen et al. (2010a) [1], who investigated the ability of nano-hydroxyapatite to adsorb aqueous Cd, Pb and Cu ions and explained that the sorption maxima seems to be significant negative correlation with the hydrated ionic radii of the metals. The b values indicated a descending series of affinity to the Fe_2O_3 and Fe_2O_3/MPTES as follows: Pb(aq) > Cd(aq) > Cu(aq), however, the b of Fe_2O_3/HA followed the order Pb(aq) > Cu(aq) > Cd(aq), this might be reasonably referred to the chelate stability constant, being HA-Cu^{2+} (4.863) > HA-Cd^{2+} (3.03). Accordingly, metal ions adsorption capacity of Fe_2O_3/HA was compared favorably with bare Fe_2O_3 and Fe_2O_3/MPTES. This might be attributed to the fact that HA has good chemical stability and high affinity to form complex on the surface of iron oxide, which insure almost all surface adsorption sites available; On the other hand, HA can prevent the coagulation of iron oxide particles and create negatively charged patches on the oxide surface, which is important to the adsorption of positively charged metal ions [17]. More recently, Yantasee et al. [14] found that Fe_3O_4 nanoparticles with a surface thiol-functionalization of dimercaptosuccinic acid (DMSA) are an effective sorbent material for toxic soft metals such as Hg, Ag, Pb and Ti, however, Fe_2O_3/MPTES experimentally showed lower affinity for Pb(aq) and Cu(aq) compared with the naked α- Fe_2O_3 nano-particles in this study, the mechanism remains unclear and need to be further studied.

In addition, there is a difference between hematite (α- Fe_2O_3), the antiferromagnetic rhombohedral form, and maghemite (γ- Fe_2O_3), the ferrimagnetic cubic form [18], however, they experimentally exhibit similar adsorption affinity for metal ions. Thus the magnetic might not be a controlling parameter for the sorption of Cd, Pb and Cu ions in solution.
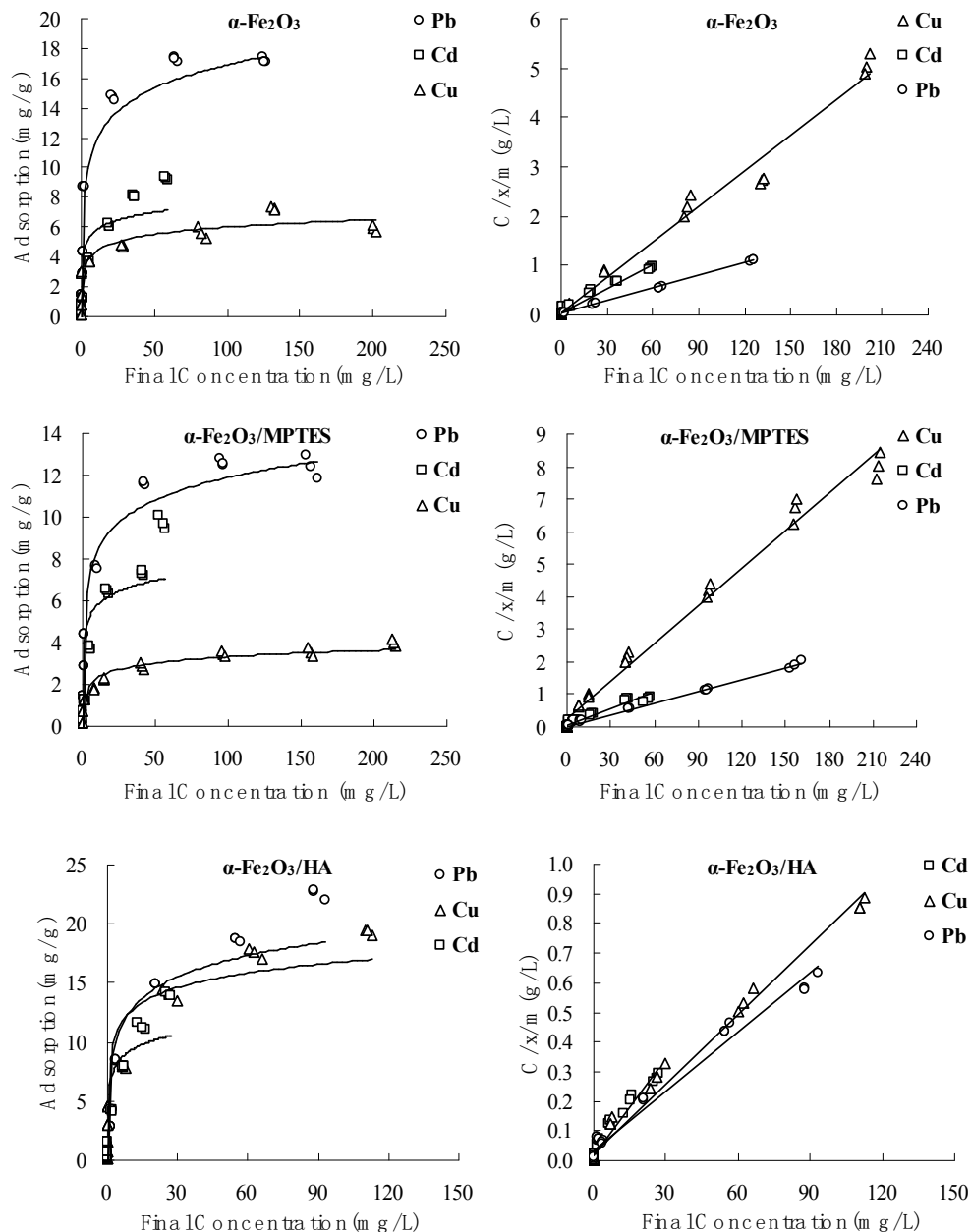
Fig. 2 Langmuir sorption isotherms of Pb(aq), Cd(aq), Cu(aq) onto naked and functionalized nano-α- Fe$_2$O$_3$ and their linear fittings after the transformation by the Langmuir Eq. The data are from 24 hr sorption experiment.

The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites with no transmigrates of adsorbate in the plane of the surface [19]. Figure 2 showed the adsorption isotherms of Cd(aq), Pb(aq) and Cu(aq) on naked and functionalized nano- Fe$_2$O$_3$ against the final metal concentration in solution. These isotherms reach a well-defined plateau and are typical L-shape type based on the classification of Giles et al. [20]. They are characterized by decreasing slopes as equilibrium metals concentration increases, indicating high affinity of the sorbent for low concentrations of metals in solution [21]. The mechanism for the adsorption of the metal contaminants was proposed to involve surface complexation, the highly porous structure and ion exchange between the iron oxide surface and the aqueous toxic ions [4]. On the other hand, the large surface area of nanosorbents afforded a high number of ligands on the materials, which increased the loading capacity of ions.
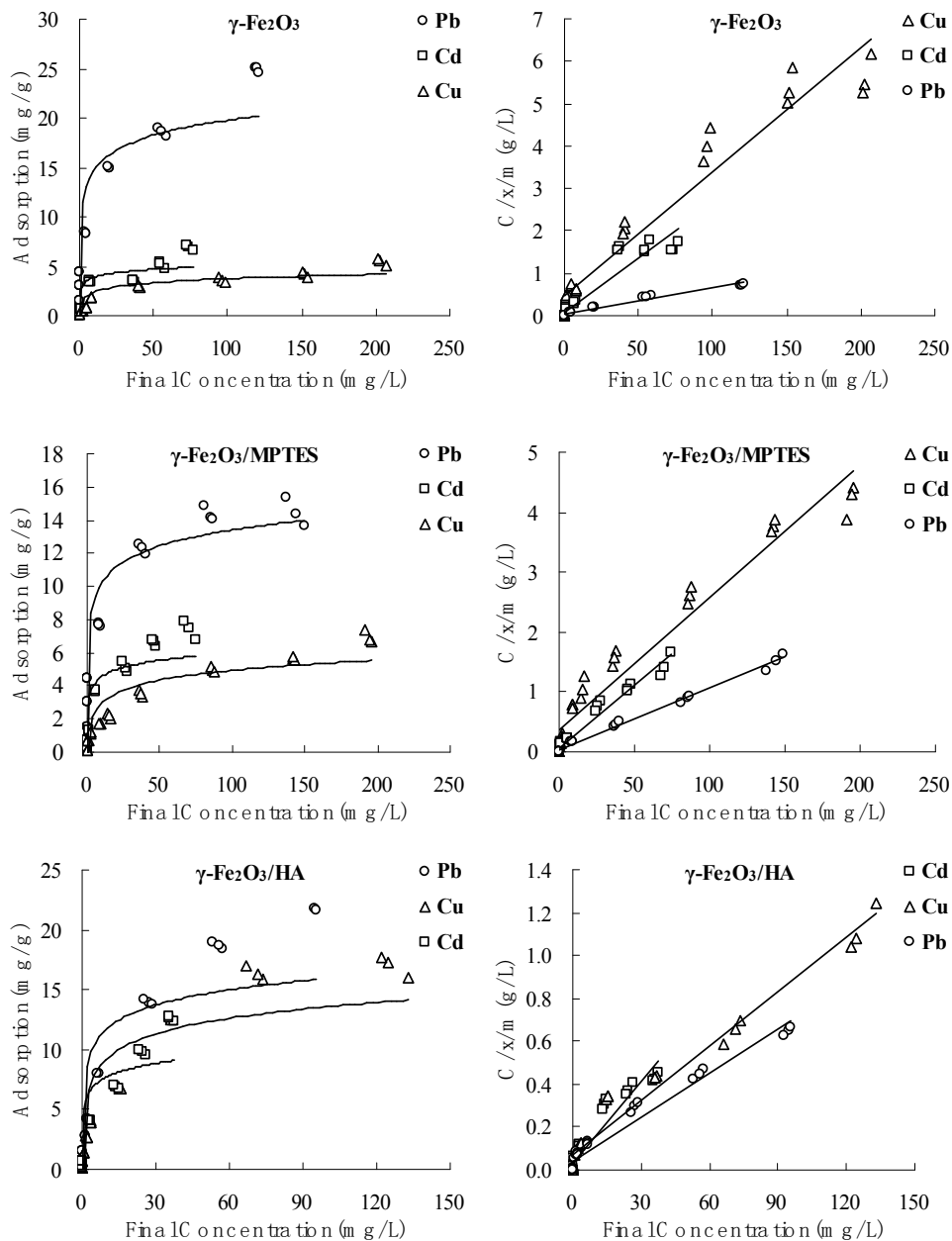
Fig. 3 Langmuir sorption isotherms of Pb(aq), Cd(aq), Cu(aq) onto naked and functionalized nano-γ-Fe_2O_3 and their linear fittings after the transformation by the Langmuir Eq. The data are from 24 hr sorption experiment.

In addition, it was noteworthy that the equilibrium metal ions concentration was almost undetectable (< 0.01 mg/L) when the initial metal ions concentration was less than 30 mg/L. This revealed the naked and functionalized nano- Fe_2O_3 were quite efficient for the adsorption of Pb(aq), Cd(aq), Cu(aq) and could reduce the metal ions to a concentration level less than 0.01 mg/L.

Conclusions

Water pollution by toxic heavy metals is becoming a major environmental concern, strict environmental regulations on the discharge of heavy metals and the demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal [1,12]. In the present study, a new method combining nano-particles preparation and heavy metals adsorption was developed, i.e. MPTES and HA were successfully immobilized onto nano- Fe_2O_3 particles (α and γ) and the adsorption of Pb(aq), Cd(aq)

and Cu(aq) on the naked and MPTES, HA coated Fe_2O_3 (α and γ) nano-particles in aqueous solutions was also investigated. The equilibrium adsorption data were fitted well using the Langmuir isotherm equation, the result showed that the adsorption maxima for the tested metals on nano- Fe_2O_3 and Fe_2O_3/MPTES was as follows: Pb(aq) > Cd(aq) > Cu(aq); however, the sorption ability on Fe2O3/HA followed the order of Pb(aq) > Cu(aq) > Cd(aq). Compared to the bare Fe_2O_3 and Fe_2O_3/MPTES nanoparticles, the Fe_2O_3/HA exhibited remarkable sorption maxima of the metal ions in solution, the sorption maxima (b-value) of α- Fe_2O_3/HA for Pb(aq) reached 151.5 mg/g; After equilibrium, the metal ions concentration were almost undetectable (<0.01 mg/L) when the initial metal ions concentration was less than 30 mg/L. The adsorption mechanism of the metal ions onto the Fe_2O_3 nanoparticles is most likely that large surface area of nano-sorbents afforded a high number of ligands on the materials, which increased the loading capacity of ions.

Recently, various amendments have been tested for their potential use with the aim to purify wastewater polluted by toxic metals, development of high-efficient and environment-friendly amendments and their application in decontaminating polluted wastewater have received a considerable attention, the unique properties of nanosorbents (such as oxide nanoparticles (NPs) and various kinds of clay materials) in decontaminating polluted media (soils and waters) has gained even more attention in recent times. Although the applications of magnetite nanoparticles in biological field were extensively studied, only few papers on its application in the environmental remediation were reported [22], and some previous studies have been just conducted on a limited number of nanoparticles. In terms of iron nanoparticles, the bare magnetite Fe_2O_3 nanoparticles are very much susceptible to air oxidation. Recent research indicated that humic acid (HA) has high affinity to iron oxides, and coating of HA on the Fe_3O_4 nanoparticles enhanced the stability by preventing their aggregation; in addition, HA has a skeleton of alkyl and aromatic units that attach with carboxylic acid, phenolic hydroxyl, and quinone functional groups [12] and these functional groups have high complex capacity with heavy metal ions. For example, a previous study showed that the Fe_3O_4 nanoparticle was able to remove over 99% of Hg (II) and Pb(II) and over 95% of Cu(II) and Cd(II) in water at optimized pH [12]. This study revealed that, compared to bare Fe_2O_3 nanoparticles, the remarkable enhancement of heavy metal removal efficiency was observed for as prepared Fe_2O_3/HA and Fe_2O_3/MPTES. In particular, by coating with HA the adsorption efficiencies of Fe_2O_3/HA for Pb(II), Cd(II) and Cu(II) in solution significantly increased. The synthesis procedure of Fe_2O_3/HA and Fe_2O_3/MPTES is simple and cost effective. In summary, a simple, flexible method for the preparation of highly effective nano- Fe_2O_3 (α and γ) sorbent materials was shown in this study and their high effiency for the removal of Pb(II), Cd(II) and Cu(II) from solution was demonstrated.

Acknowledgements

References

[1]　S.B.Chen, Y.B. Ma, L. Chen. Adsorption of aqueous Cd^{2+}, Pb^{2+}, Cu^{2+} ions by nano-hydroxyapatite: Single- and multi-metal competitive adsorption study. Geochemical Journal, 44(2010a), 233-239.

[2]　P. Liu, H.J. Zhao, L.L. Wang, Z.H. Liu, J.L. Wei, L.H.Wang. Analysis of Heavy Metal Sources for Vegetable Soils from Shandong Province, China, Agricultural Sciences in China, 10(2010), 109-119.

[3]　L.R. Skubal, N.K. Meshkov, T. Rajh, M. Thurnauer. Cadmium removal from water using thiolactic acid-modified titanium dioxide nanoparticles. Journal of Photochemistry and Photobiology A: Chemistry, 148(2002), 393-397.

[4] S.Z. Liang, J.S.Hu, H.P. Liang, A.M. Cao W.G. Song, L.J.Wan. Self-Assembled 3D Flowerlike Iron Oxide Nanostructures and Their Application in Water Treatment. Journal of Advanced Materials, 18(2006), 2426-2431.

[5] M.H. Liao, D.H. Chen. Preparation and characterization of a novel magnetic nano-adsorbent. Journal of Materials Chemistry, 12(2002), 3654-3659.

[6] A.F. Ngomsik, A. Bee, M. Draye, G. Cote, V. Cabuil. Magnetic nano- and microparticles for metal removal and environmental applications: a review. Comptes Rendus Chimie, 8(2005), 963-970.

[7] B.R. White, B.T. Stackhouse, J.A. Holcombe. Magnetic γ-Fe_2O_3 nanoparticles coated with poly-l-cysteine for chelation of As(III), Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II). Journal of Hazardous Materials, 261(2009), 848-853.

[8] J. Hu, G. Chen, I.M.C. Lo. Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. Water Research, 39(2005), 4528-4536.

[9] C.L. Warner, R.S. Addleman, A.D. Cinson, T.C.Droubay, M.H. Engelhard, M.A.Nash. High-Performance, Superparamagnetic, Nanoparticle-Based Heavy Metal Sorbents for Removal of Contaminants from Natural Waters. Chem.Sus.Chem, 3(2010), 749-757.

[10] Q. Sun, Z.H.Ye, X.R. Wang, M.H.Wong. Cadmium hyperaccumulation leads to an increase of glutathione rather than phytochelatins in the cadmium hyperaccumulator Sedum alfredii. Journal of Plant Physiology, 164(2007), 1489-1498.

[11] N.P. Hankins, N. Lu N. Hilal. Enhanced removal of heavy metal ions bound to humic acid by polyelectrolyte flocculation. Separation and Purification Technology, 51(2006), 48-56.

[12] J.F. Liu, Z.S. Zhao, G.B. Jiang. Coating Fe_3O_4 Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water. Environmental Science and Technology, 42(2008), 6949-6954.

[13] R.K.Lu. Analytical Methods for Soils and Agricultural Chemistry. China Agricultural Science and Technology Press, Beijing (1999).(in Chinese)

[14] W.Yantasee, C.L. Warner, T. Sangvanich, R.S.Addleman, T.G. Carter, R.J. Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles. Environ. Sci. Technol., 41(2007), 5114-5119.

[15] R.M. Silverstein, G.C. Bassler, T.C. Morrill. Spectroscopic Identification of Organic Compounds. 3rd ed.; John Wiley and Sons: New York.(1974)

[16] M.H.M.A. Kamal, W.M.K.W.K, Azira M. Kasmawati, Z. Haslizaidi, W.N.W.Saime. Sequestration of toxic Pb(II) ions by chemically treated rubber (Hevea brasiliensis) leaf powder. Journal of Environmental Sciences, 22(2010), 248-256.

[17] E. Ills, E. Tombacz. The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. J. Colloid Interface Sci. 295(2006), 115-123.

[18] G. Ennas, G. Marongiu, A. Musinu. Characterization of nanocrystalline γ-Fe2O3 prepared by wet chemical method. Journal of Materials Research, 14(1999), 1570-1575.

[19] J.W. Wang, Y.M. Kuo. Preparation and Adsorption Properties of Chitosan-Poly(acrylic acid) Nanoparticles for the Removal of Nickel Ions. Journal of Applied Polymer Science, 107(2008), 2333-2342.

[20] C.H. Giles, T.H. McEvan, S.N. Nakhawa, S.D. Smith. Studies in adsorption Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface area of solid. Journal of the Chemical Society, 5(1960), 3973-3993.

[21] S.B.Chen, Y.B. Ma, L. Chen. L.Q.Wang. Comparison of Pb(II) Immobilized by Bone Char Meal and Phosphate Rock: Characterization and Kinetic Study. Archives of Environment Contamination and Toxicology, 58(2010b), 24-32.

[22] J.M.Nam, C.S. Thaxton, C.A. Mirkin, Nanoparticle-based bio-bar codes for the ultrasensitive detection of proteins. Science, 301(2003), 1884-1886.

Removal of Cd, Pb and Cu from Water Using Thiol and Humic Acid Functionalized Fe$_2$O$_3$ Nanoparticles