Core@shell Fe_3O_4@SiO_2-NH_2: a convenient reusable adsorbent towards Pb(II)

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Monodisperse and spherical Fe_3O_4@SiO_2-NH_2 nanomaterials have been prepared by co-condensation of TEOS with APTMS employing a green sol-gel process. The Fe_3O_4@SiO_2-NH_2 nanoparticles prepared under optimum conditions possess uniform core-shell structure (~ 200 nm in diameter), relatively high loading of amino-functionality (~ 5.45 wt %), being easily magnetically separated and effective in the removal of Pb(II) (q_m = 243.9 mg/g, 25°C). The adsorption equilibrium data obeyed the Langmuir model reasonably. These results demonstrated that the sol-gel produced Fe_3O_4@SiO_2-NH_2, due to its easy synthesis and recovery and eco-friendliness, can be a potential adsorbent for Pb(II) removal.

1. Introduction

With the increasingly discharged Pb(II)-containing wastewater into the environment, how to efficient remove this heavy metal ions from wastewater has been an extensive research topic worldwide. Currently, several methods, such as chemical precipitation, ion-exchange, membrane filtration, electrochemical treatment technologies and adsorption, have been extensively applied for the removal of Pb(II) from aqueous solutions. Among these, adsorption appears to be one of the most effective way owning to its cost-effective, versatile and simple features to operate for removing lower concentrations levels of ions [1, 2].

Consequently, various adsorbents have been tried for the removal of Pb(II) ions, e.g. activated carbon [3], mesoporous silica [4, 5] and inexpensive naturally-occurring lignocelluloses substrates [6-10]. Noticeably, most of these materials are either poor regeneration inherent or have problems like high cost, generation of secondary wastes and diffusion limitation as well. Most important of all, the separating and recovering of aforementioned adsorbents from the wastewater systems during the large-scale practical wastewater purification application are impractical and energy-inefficient. Considering these drawbacks, recently one such advanced family of multifunctional core@shell structures with magnetically responsive components and functional shells have gained much attention due to their magnetic properties, favorable accessibility and non-toxicity. Such novel adsorbents combining nanotechnology and magnetic separation technique have not only demonstrated high adsorption efficiency due to its large surface area-to-volume, but also shown additional advantages like ease of synthesis, easy recovery and absence of secondary pollutants and environmental-friendliness [11].

However, previous studies on amino-functionalized Fe_3O_4@SiO_2-NH_2 were mainly conducted with post-grafting method, which is tedious and unavoidably using volatile organic solvents [11]. Therefore, this work deals with the one-pot sol-gel synthesis of Fe_3O_4@SiO_2-NH_2 with uniform core@shell structure and relatively high loading of amino-functionality. The potential applicability of Fe_3O_4@SiO_2-NH_2 MNPs were also evaluated towards removal of Pb(II); adsorption experiments revealed that Fe_3O_4@SiO_2-NH_2 gave rise to high adsorption capacities for Pb(II).

2. Experimental

2.1 Materials

Ferric chloride hexahydrate ($FeCl_3·6H_2O$), tetraethyl orthosilicate (TEOS), ethanol (EtOH) and ethylene glycol (EG) were purchased from Tianjin Kermel Chemical Reagent Factory, China. Trisodium citrate dehydrate (Na_3Cit) and lead nitrate ($Pb(NO_3)_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium acetate anhydrous (NaOAc) and ammonia water ($NH_3·H_2O$, 25~28 wt%) were supplied by Shenyang Chemical Plant, China. 3-Aminopropyl trimethoxysilane (APTMS) was purchased from Aladdin Chemistry Co., Ltd, China. All chemical reagents and solvents were analytical grade and used without further purification.

2.2 Preparation

Magnetic Fe_3O_4 MNPs were prepared by a solvothermal method as previously reported [12]. Briefly, $FeCl_3 \cdot 6H_2O$ (1.62 g), NaOAc (4.0 g) and Na_3Cit (1.5 g) were dissolved in EG (60 mL), after vigorous stirring for one hour, the obtained yellow solution was transferred to Teflon-lined stainless-steel autoclave (100 mL), then sealed and heated at 200 °C. After reaction for 12 h, the autoclave was cooled to room temperature. The obtained Fe_3O_4 MNPs were washed several times with water and ethanol. Finally, the products were collected with a magnet and then re-dispersed in 80 mL water for further use.

The Fe_3O_4 MNPs were then modified sequentially with TEOS and APTMS to introduce amine groups. Typically, 20 mL magneto-fluid was diluted with 150 mL ethanol, and the mixture was homogenized by ultrasonication for 15 min prior to the addition of 1 mL $NH_3 \cdot H_2O$. After being stirring vigorously for 30 min at 30 °C, 1.0 mL TEOS was dropped into the solution. The reaction was performed for 45 min and then 0.01 ~ 0.08 mL APTMS was introduced and lasted reaction for another 4 h; during the mentioned stages, the amount of APTMS were systematically investigated to correlate the dependence of physicochemical properties of $Fe_3O_4@SiO_2$-NH_2 on the key preparation parameters.

2.3 Characterization

The morphology of as-prepared functionalized MNPs was determined with scanning electron microscopy (SEM, JSM-6460LV, JEOL, Japan) and transmission electron microcopy (TEM, JEM-2000EX, JEOL, Japan). Fourier transform infrared (FT-IR) spectra were recorded with resolution 4 cm^{-1} in the region of 400 ~ 4000 cm^{-1} using a Spectrum One-B FTIR spectrometer with KBr pellets, (Perkin Elmer, USA). The concentration of Pb(II) was analyzed via an ICP-AAS spectrophotometer (Hitachi Limited, Japan). The magnetic property was tested with vibrating specimen magnetometer (Lake Shore 7410, VSM).

2.4 Adsorption experiments

2.4.1 Effect of pH

The effect of pH on Pb(II) adsorption was investigated in pH range from 2.0 ± 0.1 to 6.0 ± 0.1. In a typical procedure, a series of conical flasks containing 50 mg of $Fe_3O_4@SiO_2$-NH_2 and 50 mL Pb(II) solution of 300 mg/L. The required pH was adjusted by HCl (0.1 M) or NaOH (0.1 M), and the pH values were measured by a pH-meter (pH-S-2F, China), then the series of such conical flasks were continuously stirred at 25 °C for 16 h.

2.4.2 Adsorption isotherms

The batch experiments were conducted to evaluate Pb(II) adsorption isotherms over $Fe_3O_4@SiO_2$-NH_2.

Typically, 50 mg of $Fe_3O_4@SiO_2$-NH_2 and 50mL of $Pb(NO_3)_2$ solutions with different initial Pb(II) concentrations (varying from 100 to 400 mg/L) were added to conical flasks and performed at 25, 35 and 45 °C under natural pH conditions (pH = 5.2 ± 0.1) with continuously stirred for 16 h, respectively. The equilibrium adsorption capacity of the $Fe_3O_4@SiO_2$-NH_2 towards Pb(II) was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Where q_e is equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentration of Pb(II) (mg/L), V is the volume of the solution (L) and W was the weight of the $Fe_3O_4@SiO_2$-NH_2 (g).

3. Results and discussion

Fig. 1 (a) shows SEM image of Fe_3O_4 obtained by a solvothermal procedure. It is clear that uniform particles with diameter of about 180 nm are clearly present. The Fe_3O_4 particles were directly used for one-pot amino-functionalization without any other treatment by an optimized sol-gel process under the following conditions; that is, a mixture of 20 mL magneto-fluid, 150 mL EtOH and 1.0 mL of $NH_3 \cdot H_2O$ was homogenized by ultrasonication for 15 min, then 1.0 mL of TEOS as the hydrolysis precursor was added into the mixture. After the mixture was hydrolyzed for 45 min, 0.07 mL APTMS was added to functionalize the MNPs with -NH_2 groups.

The morphology of as-prepared $Fe_3O_4@SiO_2$-NH_2 was firstly examined by SEM and TEM techniques. It can be observed from Fig. 1 (b) and (c) that the SiO_2 layers with a thickness of ca. 20 nm were uniformly coated on Fe_3O_4 cores through all particles.
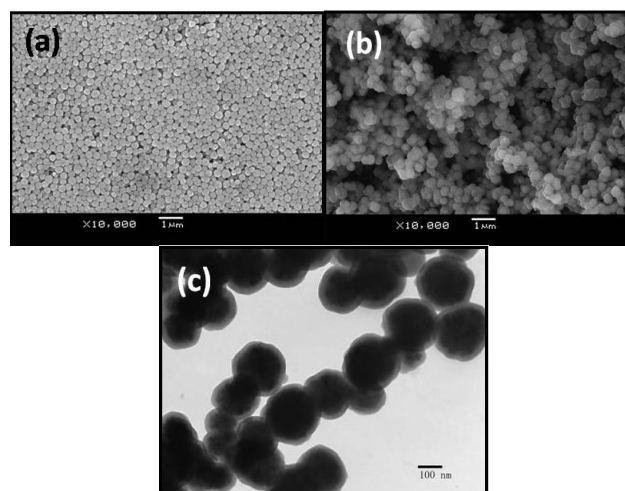

Fig. 1. SEM images of (a) Fe_3O_4, (b) $Fe_3O_4@SiO_2$-NH_2 and (c) TEM image of $Fe_3O_4@SiO_2$-NH_2.

Furthermore, the magnetization saturation values were measured to be 63.9 and 29.3 emu/g for Fe_3O_4 and

Fe$_3$O$_4$@SiO$_2$-NH$_2$, respectively (see Fig. 2 (a)); meanwhile, the magnetic separation ability of the sample was also tested in solution by placing a magnet near the glass bottle. Clearly, both observations demonstrated that the magnetic properties of Fe$_3$O$_4$@SiO$_2$-NH$_2$ provided an easy and efficient way of separating the Fe$_3$O$_4$@SiO$_2$-NH$_2$ MNPs from a suspension system (see Fig. 2 (b)).
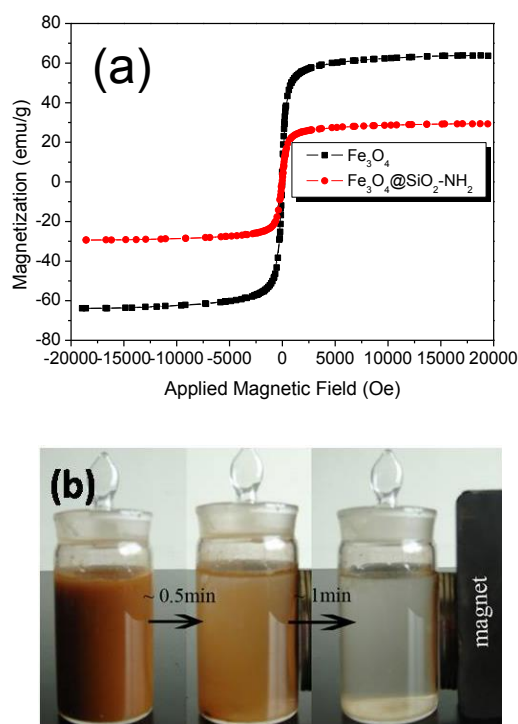

Fig. 2. The magnetic hysteresis loops of Fe$_3$O$_4$ particles and the core-shell Fe$_3$O$_4$@SiO$_2$-NH$_2$ (a), and The photos of aqueous solutions with dispersed Fe$_3$O$_4$@SiO$_2$-NH$_2$ before and after magnetic separation with external magnet.

Meanwhile, successful coating of SiO$_2$ and aminopropyl on the surface of Fe$_3$O$_4$ cores were also supported by FT-IR experiments (see Fig. 3). Both samples show broad bands at around 1630 cm^{-1} and 3430 cm^{-1}, which can be attributed to the adsorbed water molecules. The peak at 598 cm^{-1} is assigned to the stretch of Fe-O bond. In contrast to pure Fe$_3$O$_4$, the characteristic peak of 1057 cm^{-1} can be attributed to the Si-O-Si asymmetric stretching vibration which indicates the formation of silica shells on the surface of Fe$_3$O$_4$. In addition, the typical peak at 2934 and 2870 cm^{-1} corresponding to -CH$_2$- group of aminopropyl from APTMS molecules and 1563 cm^{-1} is the amine groups, indicating that APTMS was successfully introduced onto the surface of Fe$_3$O$_4$@SiO$_2$ particles during the sequential sol-gel process.

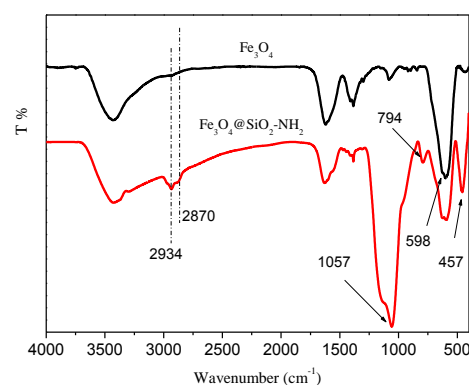*Fig. 3. FT-IR spectra of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$-NH$_2$.*

3.3 Adsorption studies

Commonly, the pH range that determining the form of the metallic species may be the most important factor in the adsorption process because of its impact on the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbent [13]. Fig. 4 displays the effect of solution pH on the adsorption of Pb(II) over Fe$_3$O$_4$@SiO$_2$-NH$_2$ MNPs. Although the adsorption capacity was low at lower pH values, when the pH increased from 2 to 4, the Pb(II) adsorption amount was significantly increased; and when the pH value is about 6, the adsorption capacity of the adsorbent almost reaches a maximum. These results indicated that the solution pH had remarkable impact on the adsorption of Pb(II) onto the Fe$_3$O$_4$@SiO$_2$-NH$_2$ MNPs; the adsorption capability of the material for Pb(II) is favorable under near-neutral conditions while relatively poor in strongly acidic media.
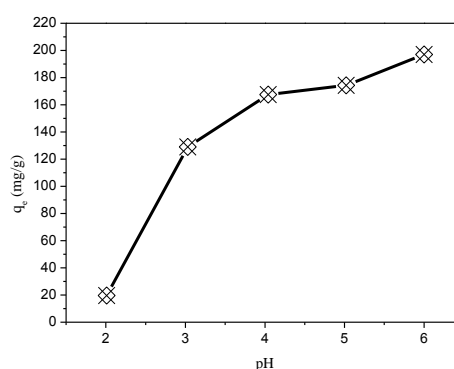

Fig. 4. Effect of the solution pH on the adsorption of Fe$_3$O$_4$@SiO$_2$-NH$_2$ towards Pb(II) from aqueous solution.

In order to evaluate the efficiency of the prepared adsorbents, as-prepared Fe$_3$O$_4$@SiO$_2$-NH$_2$ nanoparticles were employed to adsorb Pb(II) from an aqueous solutions at pH = 5.2 ± 0.1 and T = 25, 35, 45°C for 16 h. As shown in the adsorption isotherms (Fig. 5), Fe$_3$O$_4$@SiO$_2$-NH$_2$ MNPs exhibited very strong adsorption affinity for the tested metal ions; all the isotherms show a sharp initial slope, clearly indicating that Fe$_3$O$_4$@SiO$_2$-NH$_2$ MNPs acted as high-efficacy adsorbents at low Pb(II) concentration. The adsorption of Pb(II) and the equilibrium adsorption capacity is measured to be about

215 mg/g at the equilibrium concentration of 100 mg/L at 25 $^{\circ}$C. Possibly, the high homogeneous surface coverage of organosilane functionalities on the surface of $Fe_3O_4@SiO_2$-NH_2 MNPs is responsible for the ultra high adsorption capacity. Besides, it is interesting to see that the adsorption is enhanced with increasing of temperature and a higher temperature leads to a considerably enhanced adsorption, suggesting the endothermic nature of the adsorption processes. On the other hand, increasing temperature is known to increase the diffusion rate of adsorbate molecules to the external layer of the adsorbent particle, due to the viscosity decrease of the solution [14], and this is also favorable for the adsorption process.
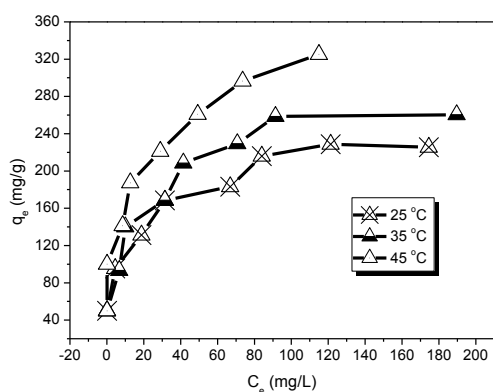

Fig. 5. Equilibrium adsorption isotherms of $Fe_3O_4@SiO_2$-NH_2 towards Pb(II) from aqueous solution.

In this work, Langmuir and Freundlich adsorption models were used to test the adsorption process of $Fe_3O_4@SiO_2$-NH_2 MNPs. The fitting parameters for Pb(II) adsorption isotherms according to Langmuir and Freundlich equations are listed in Table 1. Clearly, both Langmuir and Freundlich equations are suitable for characterizing the equilibrium adsorption isotherms since $R^2 > 0.90$. Contrary to Freundlich equations, the Langmuir equations yielded R^2 values higher than 0.99 for Pb(II) ions in all testing temperatures, demonstrating that the adequacy of this model can be surely used for comparison purpose and favorable monolayer adsorption of the Pb(II) onto the surface of $Fe_3O_4@SiO_2$-NH_2 MNPs at the concentrations of adsorbent and adsorbate applied. In addition, it is seen that the R_L values in this study were in the range from 0.0304 to 0.123, which indicated the favorable adsorption between Pb(II) and $Fe_3O_4@SiO_2$-NH_2 MNPs. On the other hand, the values of 1/n are all less than 1 for all different test temperatures, indicative of high adsorption intensity.

Table 1. The correlated parameters for the adsorption of Pb(II) on $Fe_3O_4@SiO_2$-NH_2 based on Langmuir and Freundlich isotherm models.

T/$^{\circ}$C	Langmuir isotherm model				Freundlich isotherm model		
	K_L /(L/mg)	q_m /(mg/g)	R_L range	R^2	K_F /[(mg/g)(L/mg)$^{1/n}$]	1/n	R^2
25 $^{\circ}$C	0.0756	243.90	0.0320-0.117	0.9928	6.153	0.253	0.9684
35 $^{\circ}$C	0.0708	281.69	0.0304-0.123	0.9957	6.000	0.300	0.9067
45 $^{\circ}$C	0.0657	361.01	0.0327-0.092	0.9945	6.700	0.302	0.9696

4. Conclusions

$Fe_3O_4@SiO_2$-NH_2 with uniform core@shell structure and relatively high loading of amino-functionality were prepared via a proposed sol-gel process by conformal coating Fe_3O_4 particles with SiO_2 and -NH_2 groups in one-pot sol-gel process, avoiding using toxic organic solvents throughout the preparation procedure. As-prepared $Fe_3O_4@SiO_2$-NH_2 were employed in adsorption of Pb(II) ions from aqueous systems and the maximum Pb (II) adsorption occurred in the range of pH 5~6 with maximum adsorption capacity of 238 mg/g at 25°C. The adsorption isotherm fitted the Langmuir model well. On the basis of observed experimental data, the acceptable adsorption capacity of the synthesized $Fe_3O_4@SiO_2$-NH_2 and the good magnetic features of the adsorbent endow them with a more efficient and convenient separation method so that the time-consuming solid-phase separation procedure can be favorably avoided.

References

[1] A. Bhatnagar, E. Kumar, M. Sillanp, Chemical Engineering Journal **171**, 811 (2011).
[2] S. Chattopadhyay, S.S. Das, Applied Radiation and Isotopes **67**, 1748 (2009).
[3] D. Clifford, S. Subramonian, T. Sorg, Journal Environmental Science and Technology **20**, 1072 (1986).
[4] E. Da'na, A. Sayari, Desalination **285**, 62 (2012).
[5] A. Benhamoua, M. Baudub, Z. Derrichea, J. P. Basly,

Journal of Hazardous Materials **171**, 1001 (2009).

[6] A. Saeed, M. Iqbal, M. W. Waheed, Journal of Hazardous Materials **117**, 65 (2005).

[7] M. Šćiban, M. Klašnja, B. Škrbić, Journal of Hazardous Materials **136**, 266 (2006).

[8] J. H. Suh, D. S. Kim, Journal of Chemical Technology and Biotechnology **75**, 279 (2000).

[9] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Environmental Science and Technology **36**, 2067 (2002).

[10] H. Parab, S. Joshi, N. Shenoy, R. Verma, A. Lali, M. Sudersanan, Bioresource Technology **96**, 1241 (2005).

[11] J. H. Wang, S. R. Zheng, Y. Shao, J. L. Liu, Z. Y. Xu,

D. Q. Zhu, Journal of Colloid and Interface Science, **349**, 293 (2010).

[12] J. Liu, Z. K. Sun, Y. H. Deng, Y. Zou, C. Y. Li, X. H. Guo, L. Q. Xiong, Y. Gao, F. Y. Li, D. Y. Zhao, Angewandte Chemistry International Edition **121**, 5989 (2009).

[13] O. S. Amuda, A. A. Giwa, I. A. Bello, Biochemical Engineering Journal **36**, 174 (2007).

[14] Z. Al-Qodah, Water Research **34**, 4295 (2000).

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