Removal of Pb(II) and Cu(II) from aqueous solution using multiwalled carbon nanotubes/iron oxide magnetic composites
Jun Hu, Donglin Zhao and Xiangke Wang

ABSTRACT

Multiwalled carbon nanotubes (MWCNTs)/iron oxide magnetic composites (named as MCs) were prepared by co-precipitation method, and were characterised by scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) in detail. The prepared MCs were employed as an adsorbent for the removal of Pb(II) and Cu(II) ions from wastewater in heavy metal ion pollution cleanup. The results demonstrated that the sorption of Pb(II) and Cu(II) ions was strongly dependent on pH and temperature. The experimental data were well described by Langmuir model, and the monolayer sorption capacity of MCs was found to vary from 10.02 to 31.25 mg/g for Pb(II) and from 3.11 to 8.92 mg/g for Cu(II) at temperature increasing from 293.15 to 353.15 K at pH 5.50. The sorption capacity of Pb(II) on MCs was higher than that of Cu(II), which was attributed to their ionic radius, hydration energies and hydrolysis of their hydroxides. The thermodynamic parameters (i.e., $\Delta H^0$, $\Delta S^0$ and $\Delta G^0$) were calculated from temperature dependent sorption isotherms, and the results indicated that the sorption of Pb(II) and Cu(II) ions on MCs were spontaneous and endothermic processes.

Key words | Cu(II), magnetic composites, magnetic separation, Pb(II), sorption

INTRODUCTION

Contamination of heavy metals in wastewater and drinking water has attracted considerable attention because of their adverse effect on human health and environment. The greatest characteristic of these heavy metal ions is that they are not degradable by microorganisms and have persistent pollution. Lead can diffuse to the water and environment through effluents from lead smelters, battery manufacturers, paper and pulp industries and ammunition industries (Sari et al. 2007). Drinking of lead contaminated water for a long term, even at very low concentration, will cause a series of health problems, such as coma, nausea, cancer, convulsions, renal failure and subtle effects on metabolism and intelligence (Li et al. 2005). The main sources of copper are the industrial waste streams of metal cleaning and plating baths, pulp, paper, paperboard and wood preservative-employing mills, fertiliser industry, etc (Li et al. 2005). Copper is essential to plants, humans, and animals, and the lack of copper in animal diet may cause anaemia, diarrhoea, and nervous disturbances. However, if copper is ingested excessively in the human diet, it may result in vomit, cramps, convulsion, and even death (Zhou et al. 2009). Lead and copper are two representative toxic heavy metals. Therefore, the elimination of Pb(II) and Cu(II) ions from large volume of aqueous solutions is important for the protection of public health and the environment.

Numerous technologies (such as precipitation, reverse osmosis, ion exchange, adsorption, and cementation) have been developed for removing dissolved heavy metals from wastewater (Pohl 2006; Oliveira et al. 2005; Mauchauflée & Meux 2007; Mohsen-Nia et al. 2007). Among these methods, sorption technology has been widely used because it is simple, economical and cost-effective. However, the material with high sorption capacity and easy separation from solution is crucial for the application of material in pollution management. Carbon nanotubes (CNTs) have been studied extensively in multidisciplinary area since their discovery in 1991...
(Iijima 1991). Due to their small size, unique hollow and layered structures and large specific surface area, CNTs have been found as efficient adsorbents for organic and inorganic contaminants, such as dioxin (Long & Yang 2001), 1,2-dichlorobenzene (Peng et al. 2005), nickel (Chen & Wang 2006) and americium (Wang et al. 2005). However, CNTs are notoriously difficult to be separated from solution. To overcome this problem, magnetic composite materials have been considered to treat heavy metal ions and organic compounds because these materials can be separated from solution easily using the external magnetic field. The main advantage of this technology consists of its capability in treating large volumes of wastewater within a short time and producing no secondary pollutants. For the above-mentioned reasons, the magnetic composites have aroused widespread attention as a new type of adsorbent. Banerjee & Chen (2007) studied a gum Arabic modified magnetic adsorbent for the removal of copper ions. Ma et al. (2007) developed magnetic-chitosan particles for the sorption of fluoride. In our previous studies, magnetic materials have been applied in the removal of Ni(II) and Sr(II) (Chen et al. 2009) from large volumes of aqueous solutions, and the results showed that magnetic materials are promising materials in the removal of heavy metal ions from large volumes of aqueous solutions. Although Peng et al. (2005) have studied the removal of Pb(II) and Cu(II) from water by using carbon nanotube-iron oxide magnetic composites (MCs), the effect of environmental parameters on removal of Pb(II) and Cu(II) by using MCs is not available and it is necessary to investigate the sorption property and sorption mechanism of Pb(II) and Cu(II) ions on MCs.

In this paper, the following works are carried out: (1) to synthesise multiwalled carbon nanotubes (MWCNTs)/iron oxide magnetic composites (MCs) and to characterise them using SEM, XRD and XPS in detail; (2) to investigate the effect of pH, ionic strength and temperature on the sorption of Pb(II) and Cu(II) to MCs; (3) to compare the sorption property and thermodynamic parameters of Pb(II) and Cu(II) ions on MCs. The sorption mechanism of Pb(II) and Cu(II) on MCs are discussed in detail. The results are crucial for the application of MCs in the separation of heavy metal ions from large volumes of aqueous solutions in real work.

**MATERIALS AND METHODS**

The synthesis of MCs

MWCNTs were prepared by using chemical vapour deposition method, then oxidised by using 3 mol/L HNO₃ to remove the hemispherical caps of the nanotubes, and washed with Milli-Q water and dried overnight in the oven at 90 °C, and at last calcined at 450 °C for 4 h to get oxidised MWCNTs (Wang et al. 2005). The MCs were prepared by adding 2.0 g oxidised MWCNTs in 200 mL solution of 2.98 g FeCl₃·6 H₂O and 1.53 g FeSO₄·7 H₂O (molar ratio of Fe³⁺: Fe²⁺ = 2:1) at 70 °C under N₂ condition. NaOH solution (50 mL, 1.0 mol/L) was added drop-wise to precipitate iron oxides. After the addition of NaOH solution, the pH of the final mixture was controlled to 10.5, and the reaction was allowed to continue for 1 h. Then the mixture was washed with Milli-Q water and dried in the oven at 100 °C for 10 h. The final product was denoted as MCs.

**Chemical materials**

Pb(NO₃)₂ and Cu(NO₃)₂ (Sinopharm Chemical Reagent Co. Ltd) were purchased in analytical purity. The standard stock solutions (1,000 mg/L) of Pb(II) and Cu(II) were prepared by dissolving the salt in Milli-Q water. All the chemicals used in the experiments were purchased in analytical purity and used without any further purification.

**Batch experiments**

The sorption of Pb(II) and Cu(II) was performed by using batch technique in 10 mL polyethylene centrifuge tubes. The stock suspension of MCs and NaClO₄ solution was pre-equilibrated for 24 h and then Pb(II) or Cu(II) stock solution was added to achieve the desired concentrations of different components, and finally the pH was adjusted using negligible volume of HClO₄ or NaOH. After contact time of 40 h, the MCs were separated from solution by magnetic process using a permanent magnet. The concentration of Pb(II) in supernatant was analysed by spectrophotometry at 616 nm by using Pb(II)-Chlorophosphonazo-III complex and Cu(II) concentration was analysed at 560 nm by applying Cu-Biscyclohexanone oxalyldihydrazone complex.

**Characterisation**

The morphologies of oxidised MWCNTs and prepared MCs were examined by using SEM (JEOL, JSM-6320F). XRD analysis was performed by D/Max 2400 Rigaku X-ray powder diffractometer operated in the reflection mode with Cu Kα (λ = 0.1548 nm) radiation. XPS measurement was recorded on powder with a thermo ESCALAB 250 spectrometer using an Al Kα monochromator source. Surface charging effects
were corrected with C 1 s peak at 284.4 eV to compensate for the surface charging effects.

**RESULTS AND DISCUSSION**

**Characterisation of MCs**

Figure 1A, B shows the SEM images of the oxidised MWCNTs and MCs. In contrast to the oxidised MWCNTs, the MCs depict the clusters of iron oxides coated on the surface of oxidised MWCNTs. In order to validate the MCs and the oxidised MWCNTs, the XRD technique was applied to characterise the structures of the samples. As demonstrated in Figure 1C, the two peaks corresponding to the structure of MWCNTs exist in the XRD pattern of the MCs, which indicates that the MWCNT structures are not destroyed after the chemical coprecipitation of iron oxides. Under the reaction conditions employed, three types of iron oxides are commonly formed, including magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and goethite (α-FeO(OH)). The XRD pattern of the MCs displays the main diffraction peaks at 2θ = 30.25°, 35.56°, 53.41°, 57.26°, and 62.91°, which are assigned to maghemite or magnetite. The peak at 2θ = 45.13° corresponds to the MWCNTs merged with maghemite or magnetite. The other peaks at 2θ = 21.10°, 33.31°, 41.21° and 59.06° can be assigned to goethite (Chen et al. 2009).

XPS technique was performed to characterise the functional groups on the surfaces of MCs. Figures 1D, E show the wide scan and O 1 s spectra of the MCs, respectively. The relative C, O, Fe atomic contents (At. %) in the MCs evaluated by XPS analysis are 66.4%, 20.44% and 13.16%, respectively. The wide scan spectrum (Figure 1D) comprises mainly carbon, oxygen and iron, with the atomic ratio of C:O:Fe at 5.05:1.55:1. The XPS spectrum of O 1 s is shown in Figure 1E. The spectrum can be fitted by convoluting three peaks, which represent carbonyl groups (-C=O), ether groups (C-O-C), and hydroxyl groups (-C-OH), respectively.

Figure 1F shows the magnetic separation process of the MCs from aqueous solution using the permanent magnet after adsorption. The result indicates that MCs can be easily separated from the aqueous solution within few minutes, which means that the magnetic separation is simple method to separate the MCs from aqueous solution. The most important is that this separation method can be applied easily and simply on a large scale in real work. After Cu(II) or Pb(II) sorption on MCs, MCs can be removed from water by magnetic separation process using a permanent magnet with the large scale applicability.

**Effect of environmental parameters**

Figure 2A shows the effect of pH and ionic strength on Pb(II) and Cu(II) sorption to the MCs. From Figure 2A, it is obvious that the sorption of Pb(II) and Cu(II) from aqueous solution to MCs is dependent on pH values but independent of ionic strength. The strong pH dependence and ionic strength independence of Pb(II) and Cu(II) sorption on MCs suggest that the sorption of Pb(II) and Cu(II) are mainly dominated by inner-sphere surface complexation rather than ion exchange. The sorption of Pb(II) increases gradually from 0 to 95% with pH increasing from 3 to 6.7 and the sorption of Cu(II) increases from 0 to 92% with pH increasing from 3 to 7.6. Then the sorption of Pb(II) and Cu(II) maintains a high level with increasing pH values. Solution pH is a key factor affecting the sorption of metal ions as it not only influences metal ion species in solution, but also affects the surface properties of the adsorbents according to dissociation of functional groups and surface charge (Deng & Ting 2005). At low pH values, as the protonation reactions of functional groups occur on MCs (i.e., CₓOH + H⁺ CₓOHCₓOH₂⁺), the surface becomes positively charged and dissolved metal ions are hardly adsorbed on the surface of MCs. Meanwhile, sorption of protons has apparent preponderance over that of metal ions on the sorption sites. At high pH values, the surface groups of the MCs become negatively charged because of the deprotonation reaction (i.e., CₓOHCₓOH₂⁻ + H⁺), and dissolved metal ions are easily adsorbed on the surface of MCs; meanwhile, sorption of metal ions would have preponderance over that of protons on the sorption sites.

The precipitation constants of Pb(OH)₂(α) and Cu(OH)₂ are 1.2 × 10⁻¹⁵ and 5.0 × 10⁻²⁰, respectively (Peng et al. 2005). In our experiments, the initial concentration of Pb(II) and Cu(II) are 10 mg/L. Pb(II) and Cu(II) begin to form precipitation at pH about 8.5 and 6.1; respectively. Therefore, within the pH range studied, the precipitation is negligible for the removal of Pb(II) from solution to MCs. Cu(OH)₂ precipitation may form when pH > 6.1; the removal of Cu(II) may be due to the adsorption and precipitation at high pH values.

It is interesting to note that the sorption curve of Pb(II) on the MCs shifts to the left as compared to that of Cu(II), indicating that the sorption of Pb(II) on the MCs is much easier than that of Cu(II). The sorption properties of heavy metals on the MCs are very complicated, which are influenced by their ionic radius, hydration energies and hydrolysis of their hydroxides. In general, the larger the ionic radius, the greater the affinity of the metal ions to the MCs (Lv et al. 2004). Because Pb(II) (0.133 nm) has a larger radius, the greater the affinity of the metal ions to the MCs (Lv et al. 2004).
ionic radius than Cu(II) (0.071 nm), Pb(II) is more easily adsorbed on MCs than Cu(II). This is compatible with our experimental results. The partial dehydration of the hydrated heavy metal ions occurs in order to adsorb on the surfaces of the MCs. The hydration energy of Pb(II) (−1,481 kJ/mol) is lower than that of Cu(II) (−2,100 kJ/mol); thus Pb(II) shows higher sorption capacity than that of Cu(II) on MCs (Lv et al. 2004). The calculation based on equilibrium...
pH values and equilibrium metal concentrations as well as on solubility products of hydroxides (pK$_{sp}$Pb = 16.7, pK$_{sp}$Cu = 18.8) reveals a high probability of copper hydroxide precipitation (Álvarez-Ayuso et al. 2003; Lv et al. 2004), which is consistent with our interpretation mentioned above. Thereby, the precipitation of Cu(II) contributes to the sorption of Cu(II) to MCs at pH $>6.1$.

The sorption isotherm reveals the specific relationship between the concentration of adsorbate in solution and on the surface of adsorbent. The sorption isotherms of Pb(II) and Cu(II) on the MCs at three different temperatures are shown in Figure 2B. One can see that the sorption isotherm is the highest at T = 353.15 K and the lowest at T = 293.15 K for both Pb(II) and Cu(II) ions. The results indicate that the sorption of Pb(II) and Cu(II) on the MCs is favoured at high temperature. Several factors may account for this phenomenon, such as increasing diffusion rate of metal ions into the MCs pores, the increasing pore sizes and sorption sites of MCs due to the breaking of some internal bonds near the edge of the particle are expected at higher temperatures, and an increase in proportion and activity of metal ions in solution. The sorption isotherm data can be simulated by the classical Langmuir model, which is valid for monolayer sorption on the surfaces, assuming that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical.

The Langmuir isotherm model is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m}$$

where $Q_m$ is the maximum sorption capacity at monolayer coverage (mg/g) and $K$ is the Langmuir sorption constant related to bond energy (L/mg). The values of $Q_m$ and $K$ are evaluated from the slope and intercept of the linear plots of $C_e/Q_e$ vs. $C_e$, respectively.

The relative values calculated from the Langmuir model are tabulated in Table 1. It is obvious that the correlation coefficients ($R^2$) of the Langmuir model for Pb(II) and Cu(II) sorption at three different temperatures are higher than 0.99, indicating that the Langmuir model can describe the sorption data well. From the results of Langmuir model simulation, the maximum sorption capacity ($Q_{max}$) of Pb(II) and Cu(II) increases with increasing temperature, which suggests that the sorption of Pb(II) and Cu(II) on the MCs is promoted at high temperature. The $K$ values increase from 0.790 L/mg at 293.15 K to 1.306 L/mg at 353.15 K for Pb(II) sorption and from 1.136 L/mg at 293.15 K to 3.593 L/mg at 353.15 K for Cu(II) sorption, which indicates that there is a chemical interaction between adsorbent and adsorbate (Güzel et al. 2008). The Langmuir sorption constant ($K$) is an indicator of an isotherm rise in the region of lower metal concentrations, which indicates the strength and affinity of the adsorbent for the adsorbate (Gupta et al. 2005). The values of $K$ increase

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>T (K)</th>
<th>$Q_m$ (mg/g)</th>
<th>$K$ (L/mg)</th>
<th>$R^2$</th>
<th>$C_e$ (mg/L)</th>
<th>6</th>
<th>10</th>
<th>14</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>293.15</td>
<td>10.02</td>
<td>0.790</td>
<td>0.999</td>
<td>$\Delta G^\circ$ (kJ/mol)</td>
<td>$-19.75$</td>
<td>$-17.93$</td>
<td>$-16.94$</td>
<td>$-16.13$</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>24.27</td>
<td>0.813</td>
<td>0.999</td>
<td>$-24.61$</td>
<td>$-23.16$</td>
<td>$-21.49$</td>
<td>$-20.61$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>31.25</td>
<td>1.306</td>
<td>0.992</td>
<td>$-29.49$</td>
<td>$-28.39$</td>
<td>$-26.05$</td>
<td>$-25.08$</td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>293.15</td>
<td>3.11</td>
<td>1.136</td>
<td>0.998</td>
<td>$\Delta H^\circ$ (kJ/mol)</td>
<td>$162.63$</td>
<td>$174.35$</td>
<td>$151.76$</td>
<td>$149.17$</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>6.42</td>
<td>1.394</td>
<td>0.985</td>
<td>$-15.22$</td>
<td>$-14.01$</td>
<td>$-13.41$</td>
<td>$-12.76$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>8.92</td>
<td>3.593</td>
<td>0.999</td>
<td>$-19.35$</td>
<td>$-17.55$</td>
<td>$-16.64$</td>
<td>$-15.89$</td>
<td></td>
</tr>
</tbody>
</table>

$\Delta G^\circ$ (kJ/mol) = $27.94$ $\pm 1.13$ $\Delta H^\circ$ (kJ/mol) = $27.55$ $\pm 0.22$ $\Delta S^\circ$ (J/(mol·K)) = $149.17$ $\pm 3.35$

$\Delta S^\circ$ (J/(mol·K)) = $149.17$ $\pm 3.35$

Table 1 | Relative sorption isotherm parameters and thermodynamic parameters of Pb(II) and Cu(II)
with increasing temperature for Pb(II) and Cu(II), which reflects that the sorption strength and affinity of the MCs for Pb(II) and Cu(II) at high temperature is higher than that at low temperature. $Q_m$ values increase with increasing temperature, showing an endothermic process.

Figure 2C shows that the distribution coefficient, $K_d$ (mL/g), of Pb(II) and Cu(II) increases with a rise in temperature. The thermodynamic parameters ($\Delta H^o$, $\Delta S^o$ and $\Delta G^o$) for Pb(II) and Cu(II) sorption on MCs are calculated from the temperature dependent sorption isotherms. The values of enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) are calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$ (Figure 2C) from the following equations:

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \quad (2)$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (3)$$

where $C_0$ is the initial concentration (mg/L), $C_e$ is the equilibrium concentration (mg/L), $V$ is the volume (mL), $m$ is the mass of MCs (g), $T$ is temperature in Kelvin and $R$ is the ideal gas constant (8.314 J/(mol·K)).

Free energy changes ($\Delta G^o$) are calculated from the relationship:

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (4)$$

Relevant data calculated from Equations (3) and (4) are tabulated in Table 1. The evaluation of thermodynamic parameters provides an insight into the mechanism of Pb(II) and Cu(II) sorption to the MCs. A positive standard enthalpy change suggests that the interactions of Pb(II) and Cu(II) sorption on the MCs are endothermic. The possible interpretation of this phenomenon is that Pb(II) and Cu(II) ions are well hydrated, and the hydration sheath of Pb(II) and Cu(II) has to be denuded before their sorption on the MCs. This dehydration process needs energy, and it is favoured at high temperature. It is assumed that this energy of dehydration exceeds the exothermicity of the ions attaching to the solid surface, so the removal of water molecules from Pb(II) and Cu(II) is an endothermic process in essence. It appears that the endothermicity of the desolvation process exceeds that of the enthalphy of sorption to a considerable extent (Chen & Wang 2006).

The low value of $\Delta H^o$ also suggests that the endothermic process of Pb(II) and Cu(II) sorption on the MCs is weak. The negative $\Delta G^o$ values indicate that the sorption of Pb(II) and Cu(II) on the MCs is thermodynamically feasible and spontaneous. The free energy changes of Pb(II) and Cu(II) sorption are endothermic and the endothermicity of the desolvation process exceeds that of the enthalphy of sorption to a considerable extent. It is assumed that this energy of dehydration exceeds the exothermicity of the ions attaching to the solid surface, so the removal of water molecules from Pb(II) and Cu(II) is an endothermic process in essence. It appears that the endothermicity of the desolvation process exceeds that of the enthalphy of sorption to a considerable extent (Chen & Wang 2006).

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Cu(II) sorption on the MCs are more negative with the increase in temperature, which reflects more energetically favourable sorption at higher temperature. In addition, at higher temperature, ions are readily desolvated, and therefore the sorption becomes more favourable. The positive values of $\Delta S^0$ reflect the affinity of the MCs towards Pb(II) and Cu(II) in aqueous solutions and may suggest the degree of freedom increases at the solid–liquid interface during the sorption of metal ions on the MCs.

**CONCLUSION**

The MCs were prepared easily by co-precipitation method. The surface of the MCs consists of large amounts of hydroxyl and carboxyl groups, which supply enough sorption sites to bind metal ions. Sorption of Pb(II) and Cu(II) are dependent on pH and temperature. Sorption isotherms are better described by Langmuir model than by Freundlich model, and the sorption of Pb(II) and Cu(II) increases with increasing temperature. The thermodynamic parameters calculated from the temperature dependent sorption isotherms indicate that the sorption process is spontaneous and endothermic. From the results, one may conclude that the MWCNTs/iron oxide magnetic composites may be promising materials in the preconcentration and separation of heavy metal ions from large volumes of aqueous solutions through sorption and magnetic separation methods in metal ion pollution cleanup in real work.

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