Removing lead ions from aqueous solutions by the thiosemicarbazide grafted multi-walled carbon nanotubes

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ABSTRACT

A novel multi-walled carbon nanotubes (MWCNTs) material functionalized with thiosemicarbazide was synthesized successfully and used to remove lead ions from aqueous solutions. The technologies of Fourier Transform Infrared Spectroscopy, scanning electron microscopy and thermal gravimetric analysis were used to characterize the structure and properties of thiosemicarbazide grafted MWCNTs. The adsorption conditions, such as pH, contact time and temperature, were investigated. The results showed pH affected the adsorption process greatly, and the adsorption process reached equilibrium within 60 min. The maximum adsorption capacity was 42.01 mg/g. The adsorption process fitted well with the pseudo-second-order kinetic model and the Langmuir model. The thermodynamic parameters indicated the adsorption process was endothermic and spontaneous in nature.

Key words | adsorption, functionalized multi-walled carbon nanotubes, lead ions, thiosemicarbazide

INTRODUCTION

Recently, with the rapid development of the industry, the release of heavy metals into the ecosystem has become more and more serious, which has been causing worldwide concern (Marques et al. 2000). Heavy metals do harm not only to the environment but also to people’s health. Toxic heavy metals may cause high blood pressure, speech disorders, fatigue, sleep disabilities, aggressive behavior, poor concentration, irritability, mood swings, depression, increased allergic reactions, autoimmune diseases, vascular occlusion, and memory loss (Qu et al. 2013). Unlike organic contaminants, heavy metals tend to accumulate in living organisms because they are not biodegradable (Abbas et al. 2016). For example, lead poisoning may cause damage to the central nervous system, and lead is a prior toxic pollutant in industrial wastewater. Thus it’s essential to remove lead ions from wastewater. There have been many conventional treatments used to remove heavy metals in water, such as oxidation (Perić et al. 2004), reverse osmosis (Awual et al. 2015), electrochemical treatment (Liu et al. 2008), precipitation (Khosravi & Alamdari 2009; Rahman & Islam 2009), solvent extraction (Liu et al. 2008; Rahman & Islam 2009), membrane filtration (Al-Rashdi et al. 2011, 2013), ion exchange (Bailey et al. 1999; Fu & Wang 2011) and adsorption (Babel & Kurniawan 2005; Rio et al. 2005). All of these methods have their own limitations. For example, electrochemical treatment has expensive operational costs because of the depletion of energy. For ion exchange, resin regeneration causes serious secondary pollution. The precipitation method needs to treat the hazardous waste production (Abbas et al. 2016). Among these methods, adsorption has proved to be an effective and economic method, owing to its simplicity and flexibility (Ge et al. 2012; Tehrani et al. 2013). So far, many efforts have been made to find new, promising adsorbents.

In recent years, carbon nanotubes (CNTs), a stable and insoluble nanomaterial, have captured increasing attention for the removal of heavy metals in aqueous solutions due to their unique physical and chemical properties, including large surface area, highly porous and hollow structure, and strong interaction with the pollutant molecules (Chen & Wang 2006; Yu et al. 2016). Generally, the raw CNTs have very low adsorption capacity for most heavy metals because of their poor dispersion in aqueous solutions. However, surface functionalized CNTs have been confirmed to be favorable for improving the dispersion and adsorption capacity. And a number of methods have been used to modify CNTs, such as acid treatment (Ihsanullah et al. 2016), impregnation with metal/metal oxides (Gupta et al. 2011) and grafting the functional molecules/group (Chen et al. 2012).
The most simple and effective method to modify CNTs is doping heteroatoms into the carbon framework, such as N, B, P and S, and this will not change the robust framework and properties of the carbon material (Liang et al. 2009; Xia et al. 2012). Especially, the carbon materials containing S and/or N have been proved to be promising for removal of heavy metals (Shin et al. 2007; Gao et al. 2016). Thiosemicarbazide (TSC), containing N and S, is considered as a perfect complexing agent for transition metal ions in aqueous solutions (Leovac et al. 2007). Its simple, elastic and aliphatic structure minimizes steric hindrance (Ahmed 2008). What’s more, according to the hard and soft acids and bases principle, TSC is regarded as a soft base that can interact with soft acids like heavy metals. Therefore, thiosemicarbazide grafted CNTs are hoped to be an effective adsorbent to remove heavy metals.

In this work, thiosemicarbazide grafted MWCNTs (TSC-MWCNTs) were synthesized and characterized by the technologies of Fourier transform infrared (FT-IR) spectroscopy, thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). The adsorption performance of lead ions onto TSC-MWCNTs was investigated. The effects of contact time, pH value, initial concentration and temperature were studied in detail. Furthermore, the kinetics and thermodynamics were investigated to understand the adsorption.

**MATERIAL AND METHODS**

**Materials and reagents**

MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd at 20–40 nm in diameter, >5 μm in length, 80–140 m²/g in specific surface area, and >97% purity. TSC was purchased from Sinopharm Chemical Reagent Co., Ltd. N,N′-Dicyclohexylcarbodiimide (DCC) was provided by Shanghai Titan Scientific Co., Ltd. All the reagents used were of analytical grade and used without further purification. Deionized water was used throughout.

**Instruments and apparatus**

FT-IR spectroscopy was conducted by using a Nicolet 6700 FT-IR spectrometer in the range of 400–4,000 cm⁻¹. TGA was carried out using a SDT Q600 V8.0 Build 95 thermal analyzer under argon and in the range of 25–800 °C at a heating rate of 10 °C/min. SEM was performed by MIRA3 TESCAN.

**Preparation of oxide MWCNTs (MWCNTs-COOH)**

Oxide MWCNTs were prepared by oxidation with nitric acid. 500 mg of raw MWCNTs were dispersed in 50 mL of nitric acid by sonication for 10 min. Then the mixture was treated with continuous magnetic stirring at 120 °C for 24 h, which introduced carboxyl groups onto the surface of the raw MWCNTs. After cooling to room temperature, the product was filtered through a 0.45 μm PTFE membrane and then washed several times with deionized water until the pH was neutral. Finally, the obtained oxide MWCNTs were dried under vacuum at 60 °C for 24 h.

**Synthesis of thiosemicarbazide modified MWCNTs (TSC-MWCNTs)**

A mount of 500 mg dried MWCNTs-COOH, 1.6 g of TSC, 1.6 g of DCC, and 40 mL of DMF were added into a 100 mL round bottomed flask in sequence. Then the mixture was stirred at room temperature for 24 h. Afterwards, the resulting solid phase was filtered through a 0.45 μm PTFE membrane, washed with abundant ethanol and water, then dried under vacuum at 60 °C for 24 h. The synthesis procedure for TSC-MWCNTs is shown in Figure 1.

**Adsorption studies**

In the experiment, 5.0 mg of adsorbent and 20.0 mL solution containing 60 mg/L lead ions were added into a series of 50 mL flasks. The pH of the solution was adjusted by using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. A pH range of 2.16–5.23 was investigated to avoid the precipitation of lead ions. The flasks were placed in the thermostat shaker for 2 h. After being filtrated, the concentration of lead ions was determined by atomic absorption spectrophotometer. The adsorption capacity of lead ions was calculated by the following Equation (1) (Bulut 2007):

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]  

(1)

where \(C_0\) and \(C_e\) (mg/L) are the original and equilibrium concentration of the lead ions, respectively; \(V\) (L) is the volume of the solution, \(m\) (mg) is the mass of the absorbent used and \(q_e\) (mg/g) is the equilibrium adsorption capacity.

To study the kinetic adsorption, 5 mg adsorbent was mixed with 20 mL lead ion solution with an initial concentration of 60 mg/L in 50 mL flasks. The flasks were agitated for 2 h in a shaking thermostatic bath. In the whole process,
the pH was kept at the optimum value and the temperature was at 25 °C. The concentration of lead ions was measured at different time intervals up to 120 min. Each data point was obtained from an individual flask.

The equilibrium adsorption experiment was performed by agitating 5.0 mg of adsorbent and 20 mL solution containing different concentrations of lead ions (varying from 10 to 80 mg/L) at the optimum pH for 2 h. The flasks were placed in a thermostat shaker, whose temperature was kept at 25 °C, 35 °C and 45 °C, respectively. After equilibration, the adsorbent was filtered and the residual concentration of lead ions was measured.

**Adsorption kinetics**

Kinetic adsorption study can explain the mechanism of adsorption process, therefore two kinetic models, the pseudo-first-order and pseudo-second-order models (Robati 2013), were used in this study to fit the adsorption kinetic data. The pseudo-first-order kinetic Equation (2) and the pseudo-second-order kinetic Equation (3) are expressed as:

\[
\log\left(\frac{q_e - q_t}{q_t}\right) = \log k_1 + \frac{k_1 q_e}{2.303 t}
\]

\[
t = \frac{1}{q_t} \left(\frac{1}{k_2 q_e^2} + \frac{1}{q_e}\right) t
\]

where \(q_e (mg/g)\) is the adsorption capacity at equilibrium; \(q_t (mg/g)\) is the amount of metal ions adsorbed by the adsorbent at time \(t\) (min); \(k_1 \text{ (min}^{-1}\) and \(k_2 \text{ (g mg}^{-1}\text{min}^{-1}\) represent the rate constant of the pseudo-first-order adsorption and pseudo second-order adsorption, respectively.

**Adsorption isotherm**

In this study, the Langmuir and Freundlich isotherm models (Li et al. 2003; Sekar et al. 2004) were used to express the distribution of lead ions between the liquid and solid phase. The Langmuir isotherm model is used to describe the monolayer distribution of adsorbate on the surface of the adsorbent, while the Freundlich isotherm model is used to express the multilayer adsorption on the heterogeneous surface.

The linear equations of the Langmuir model (4) and Freundlich model (5) are expressed as:

\[
\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{b q_m C_e}
\]

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]

where \(C_e\) and \(q_e (mg/g)\) are the concentration of lead ions in solution and the amount of metal ions adsorbed at equilibrium, respectively, \(q_m (mg/g)\) is the maximum adsorption capacity of the adsorbent, and \(b\) is the constant of the Langmuir model related to the energy of sorption; \(k_f (mg/g)\text{-(mg/L)}^n\) and \(n\) are the Freundlich constants, the former correlates to the adsorption capacity while the latter reflects the degree of adsorption. In addition, the values of \(n\) also give an indication of the favorability of adsorption. When the \(n\) values are less than 1 and between 1 and 10, the adsorption is poor and favorable, respectively.

In the Langmuir model, the equilibrium parameter or separation factor \((R_L)\) is used to describe how favorable the adsorption process is. \(R_L\) is defined as:

\[
R_L = \frac{1}{1 + b C_0}
\]

where \(b\) is the Langmuir constant and \(C_0\) is the initial concentration of the adsorbate in solution. The value of \(R_L\) indicates the type of the isotherm to be unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\).

**Adsorption thermodynamics**

In order to evaluate the thermodynamic nature, thermodynamic parameters, standard Gibbs free energy changes (\(\Delta G^\theta\)),
standard enthalpy changes ($\Delta H^\theta$) and standard entropy changes ($\Delta S^\theta$) were calculated using the following equations (Van Brederode et al. 1996):

$$k_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m}$$  \hspace{1cm} (7)

$$\ln k_d = -\frac{\Delta G^\theta}{RT} = -\frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT}$$  \hspace{1cm} (8)

$$\Delta G^\theta = \Delta H^\theta - T \Delta S^\theta$$  \hspace{1cm} (9)

where $C_0$ (mg/L) is the initial concentration of metal ions; $C_e$ (mg/L) is the equilibrium concentration of metal ions; $V$ (L) is the volume of the solution and $m$ (g) is the dosage of the adsorbent; $k_d$ is the distribution coefficient for the adsorption, $T$ (K) is the absolute temperature and $R$ (8.314 J/mol K) is the ideal gas constant. The values of $\Delta S^\theta$ and $\Delta H^\theta$ can be calculated from the intercept and slope of the plots of $\ln k_d$ versus $1/T$, respectively.

RESULTS AND DISCUSSION

Characterization of absorbent

The FT-IR spectra of MWCNTs, MWCNTs-COOH and TSC-MWCNTs are shown in Figure 2 in the range of 500–4,000 cm$^{-1}$. As shown in the spectrum of MWCNTs-COOH, the peaks at 3,443 cm$^{-1}$ and 1,630 cm$^{-1}$ were attributed to the stretching vibrations of O–H and C=O, respectively. In addition, the peak at 1,101 cm$^{-1}$ is assigned to the C-O stretching vibration. These peaks proved that the carboxyl group (COOH) was introduced onto the surface of the MWCNTs. Compared with the spectrum of MWCNTs-COOH, some new peaks were observed in the spectrum of TSC-MWCNTs. The new peaks at 1,400 cm$^{-1}$ and 1,160 cm$^{-1}$ were assigned to C-N and C=S stretching vibrations, respectively (Li 2014). What’s more, the characteristic peak at 1,535 cm was corresponding to the angular deformation of the N–H bond of the amide group (Karnitz et al. 2007). These data verified that TSC was grafted on the MWCNTs successfully.

The morphology of raw MWCNTs and functionalized MWCNTs was explored by SEM. As shown in Figure 3, these materials had the morphology of curve and cylindrical shapes and there was no significant change between the original and modified MWCNTs. However, the outer wall of TSC-MWCNTs was rougher than that of MWCNTs, which may be caused by the modification process.

The information about the functional group on the MWCNTs can also be obtained from the TGA curves shown in Figure 4. All materials were treated under argon atmosphere up to 800 °C with a heating rate of 10 °C/min. The weight loss below 200 °C in all samples was due to the evaporation of water adsorbed on the external surface and internal pores or cavities. Above 200 °C, the weight loss of MWCNTs-COOH and TSC-MWCNTs could be owing to the thermal decomposition of the organic functional groups. Compared with the TGA curve of MWCNTs-COOH, the TSC-MWCNTs exhibited a weight loss of about 10% above 200 °C, which indicated the amount of TSC covalently bonded to the MWCNTs was about 10%.

Effect of pH

The pH of the aqueous solutions is an important factor in the heavy metal ion adsorption process due to its effect on the surface charge and the degree of protonation of adsorbent. The effect of pH on the adsorption of Pb(II) by TSC-MWCNTs is shown in Figure 5. It indicated that the removal of Pb(II) increased when the pH increased from 2.16 to 5.23. Also, as shown in Figure 5, the maximum adsorption capacity appeared when pH was about 5.00. At low pH, the competitive adsorption between positively charged protons and lead ions was stronger, which made a low adsorption capacity of lead ions. In addition, the greater protonation of TSC-MWCNTs at low pH would decrease the electrostatic adsorption between lead ions and TSC-MWCNTs, also resulting in a low adsorption capacity.
Figure 3 | SEM images of (a) MWCNTs, (b) MWCNTs-COOH, (c) TSC-MWCNTs.

Figure 4 | The TGA curves of MWCNTs, MWCNTs-COOH, TSC-MWCNTs.

Figure 5 | Effect of pH on the adsorption of Pb(II) by TSC-MWCNTs at 25°C.
Furthermore, as can be seen from Figure 5, when pH > 4.93, the adsorption capacity was near the maximum capacity. Therefore, pH 5.23, the original value of the lead ion solution, was chosen as the optimum pH value for further studies.

**Adsorption kinetics**

The effect of contact time on the adsorption process is shown in Figure 6. As can be seen from Figure 6(a), the maximum adsorption capacity was 40.81 mg/g, and it occurred at 60 min, after which the adsorption reached equilibrium. Thus, in the subsequent experiments, a contact time of 120 min was chosen. Adsorption kinetic parameters were shown in Table 1. According to Table 1, the correlation coefficients ($R^2$) of the pseudo-first-order kinetic equation and pseudo-second-order kinetic equation were 0.3396 and 0.9987, respectively, which indicated the experiment data fitted the pseudo-second-order kinetic equation better. And for the pseudo-second-order model, the experiment adsorption capacity of 40.81 mg/g was close to the calculated adsorption capacity of 39.28 mg/g, while the experiment adsorption capacity in the pseudo-first-order model was only 5.177 mg/g. The fitting line of the adsorption of lead ions by the pseudo-second-order kinetic equation was shown in Figure 6(b).

**Adsorption isotherm**

The adsorption isotherm is shown in Figure 7 and the related parameters are shown in Table 2. As shown in Figure 7(a), the adsorption capacity increased with the increasing
temperature, which indicated the adsorption process was endothermic. From Table 2, the correlation coefficients in the Langmuir equation \( R^2 = 0.9992-0.9994 \) were greater than those in the Freundlich equation \( R^2 = 0.7921-0.8507 \), which meant the adsorption of lead ions agreed well with the Langmuir model. Therefore, the adsorption of lead ions was mainly in the monolayer form. Meanwhile, the theoretical capacities \( q_m \) at different temperature in the Langmuir equation were close to the experiment adsorption capacity, which further verified that the adsorption process obeyed the Langmuir model. In addition, the values of \( R_L \) were about 0.0267–0.2017, which indicated the adsorption towards lead ions was a favorable process.

### Adsorption thermodynamics

The thermodynamic parameters of \( \Delta H^\theta \) and \( \Delta S^\theta \) were separately obtained from the slope and intercept of the curves of \( \ln k_d \) versus \( 1/T \) in Figure 8. The values of the thermodynamic parameters such as \( \Delta G^\theta \), \( \Delta H^\theta \) and \( \Delta S^\theta \) are listed in Table 3. As shown in Table 3, the values of \( \Delta G^\theta \) were negative at different temperatures, indicating the adsorption was feasible and spontaneous. The positive value of \( \Delta S^\theta \) indicated the increasing disorder and randomness at the solid-solution interface during the adsorption process. Moreover, the positive value of \( \Delta H^\theta \) indicated the adsorption process was endothermic, which meant the increase of temperature was favorable for the adsorption. This might be that the effective contact chance between the adsorbent and lead ions went up with the degree of disorder increasing at higher temperature.

### Contrast experiment

In order to further investigate the performance of TSC-MWCNTs, a contrast experiment was conducted. 5 mg adsorbent (MWCNTs, MWCNTs-COOH or TSC-MWCNTs) was mixed with 20 mL lead ion solution, with an initial concentration of 60 mg/L in 50 mL flasks at the optimum pH. Then, the flasks were agitated for 2 h in a shaking thermostatic bath at 25 °C. The adsorption amount of MWCNTs, MWCNTs-COOH and TSC-MWCNTs was 2 mg/g, 30.48 mg/g and 35.44 mg/g, respectively. The adsorption capacity of TSC-MWCNTs was better than MWCNTs and MWCNTs-COOH due to more active sites being introduced. Therefore, the results once again proved that TSC modified MWCNTs can remove lead ions efficiently.

### Table 2: Langmuir and Freundlich isotherm parameters for the adsorption of Pb(II) on TSC-MWCNTs

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>( q_m ) (mg/g)</td>
<td>36.71</td>
</tr>
<tr>
<td></td>
<td>( q_e ) (mg/g)</td>
<td>35.56</td>
</tr>
<tr>
<td></td>
<td>( b ) (L/mg)</td>
<td>0.4398</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9994</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td>( n )</td>
<td>0.2082</td>
</tr>
<tr>
<td></td>
<td>( k_f ) (mg/g)·(mg/L)(^n)</td>
<td>( 1.49 \times 10^{-6} )</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.7921</td>
</tr>
</tbody>
</table>

### Table 3: Thermodynamic parameters for the adsorption of Pb (II) on TSC-MWCNTs

<table>
<thead>
<tr>
<th>( \Delta H^\theta ) (kJ/mol)</th>
<th>( \Delta S^\theta ) (J/K·mol)</th>
<th>( T ) (K)</th>
<th>( \Delta G^\theta ) (kJ/mol)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.997</td>
<td>17.88</td>
<td>298</td>
<td>−2.334</td>
<td>0.9999</td>
</tr>
<tr>
<td>308</td>
<td>−2.513</td>
<td>318</td>
<td>−2.692</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption mechanism

The adsorption capacity of TSC-MWCNTs for lead ions increased with the increasing temperature, indicating a complex adsorption mechanism, which meant the adsorption process was a combination of physisorption and chemisorptions (Vukovic et al. 2011). The functionalized groups played an important role in the process of adsorption. From the FT-IR spectrum of TSC-MWCNTs, there is a remnant carboxyl group and covalently bonded TSC group. The remnant carboxyl group can capture lead ions through ion exchange. And it was confirmed that the electrons presenting on nitrogen in the amino groups and the sulphur in the TSC can establish dative bonds with transitional metal ions, forming stable complexes (Ahmad et al. 2015). Therefore, the adsorption process of lead ions included ion exchange and surface complexation, which was shown in Figure 9.

CONCLUSION

In this work, TSC was introduced successfully onto the surface of MWCNTs, and TSC-MWCNTs were used as an adsorbent for removing lead ions from aqueous solutions. The pH of the aqueous solutions affected the adsorption capacity greatly, and the optimum pH was 5.23. The adsorption data fitted the pseudo-second-order kinetic model well and the adsorption isotherm followed the Langmuir isotherm. From the Langmuir isotherm, the maximum adsorption capacity was 42.01 mg/g. Furthermore, the thermodynamic parameters revealed the adsorption process was endothermic and spontaneous. In summary, TSC-MWCNTs could be used as an efficient adsorbent to remove lead ions from aqueous solutions.

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