Efficient adsorption of Hg(II) from aqueous solution by N, S co-doped MnFe$_2$O$_4$@C magnetic nanoparticles

Hangdao Qin, Hao Cheng, Chenggui Long, Xiaogang Wu, Yanhong Chen, Meng Hu and DingHui Wei

ABSTRACT

N, S co-doped MnFe$_2$O$_4$@C magnetic nanoparticles were successfully synthesized by a simple method involving the preparation of MnFe$_2$O$_4$ nanoparticles and subsequent pyrolysis treatment. The physical and chemical properties of MnFe$_2$O$_4$, MnFe$_2$O$_4$@C and MnFe$_2$O$_4$@C–NS nanoparticles were characterized by X-ray diffraction (XRD), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), N$_2$ adsorption–desorption and the pH at the point of zero charge. Their performances in the adsorption of Hg(II) from water were investigated. The adsorption process followed pseudo-second-order kinetics and the experimental data of equilibrium isotherms fitted well with the Langmuir model. MnFe$_2$O$_4$@C–NS showed the highest adsorption capacity of 108.56 mg/g, increasing more than 1.7 times compared to MnFe$_2$O$_4$. The enhanced adsorption performance was attributed to the larger specific surface area as well as the complexation of N and S ligands on the surface. The thermodynamic parameters of $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ at 30 °C were $-24.39$ kJ/mol, $-0.046$ kJ/mol K and $-10.45$ kJ/mol, respectively, which indicated that the adsorption of Hg(II) on MnFe$_2$O$_4$@C–NS was exothermic and spontaneous in nature. Moreover, MnFe$_2$O$_4$@C–NS showed superior selectivity towards Hg(II) compared with other metal ions generally present in mercury-containing industrial wastewater.

Key words | adsorption, Hg(II), magnetic nanoparticles, MnFe$_2$O$_4$@C, N, S co-doped

HIGHLIGHTS

- Magnetic MnFe$_2$O$_4$ and MnFe$_2$O$_4$@C nanoparticles were synthesized.
- MnFe$_2$O$_4$@C nanoparticles were modified with thiourea to introduce N-containing and S-containing functional groups.
- The modified MnFe$_2$O$_4$@C–NS showed the highest adsorption capacity 108.56 mg/g.
- The enhanced adsorption performance was attributed to the larger specific surface area and the complexation of N and S ligands on carbon surface.
- MnFe$_2$O$_4$@C–NS showed superior selectivity towards Hg(II).
GRAPHICAL ABSTRACT

INTRODUCTION

Mercury (Hg) is a well-known teratogen, which is considered as one of the most hazardous chemicals (Zabihi et al. 2013). The major sources of the highly toxic and harmful Hg-containing wastewater are polyvinyl chloride (PVC), chlorine-alkali, pulp and paper industries (Yardim et al. 2005). Many physicochemical techniques, such as adsorption, chemical precipitation, ion exchange and reverse osmosis have been widely used in the removal of heavy metals from aqueous solution. Among the various water-treatment methods described, adsorption is an attractive approach due to high removal efficiency, easy handling and it does not yield harmful by-products (Eren 2008; Mir et al. 2009).

Recently, there is growing interest in the investigation of different types of low-cost adsorbents especially using iron oxide, manganese oxide and aluminum oxide (Mallikarjuna & Venkataraman 2003; Dong et al. 2010; Wang et al. 2010). Among them, manganese ferrospinel MnFe2O4, a familiar magnetic material, shows outstanding chemical stability and high efficiency for metal ions removal. Magnetic porous MnFe2O4 prepared by a sol-gel method presented high adsorption capacity of Pb(II) and Cu(II) from aqueous solution (Ren et al. 2012). The maximum uptakes were 333.3 and 952.4 μmol/g for Pb(II) and Cu(II) ions, respectively. The adsorbed Pb(II) and Cu(II) ions were in the form of the complex with oxygen in carboxyl and hydroxyl groups binding on the surface of MnFe2O4. Surface-modified MnFe2O4 also showed excellent adsorption performance for the removal of Cr(VI) from synthetic wastewater and the maximum adsorption capacity of 31.5 mg/g was obtained at pH 2 (Hu et al. 2005). A combination of electrostatic interaction and ion exchange were considered as the mechanisms leading to Cr(VI) adsorption by modified MnFe2O4 nanoparticles. Granular activated carbon/MnFe2O4 composite was also reported to be used for removing As(III) and As(VI) (Podder & Majumder 2016).

Activated carbon (AC) and surface-modified AC have been widely utilized to remove heavy metals. It was considered that the coordination of functional groups on AC surface was one of the main factors in the adsorption of metal ions by AC (Natale et al. 2006; Hassan et al. 2008; Shang et al. 2014). In the previous work (Qin et al. 2018), AC was modified with thiourea to obtain nitrogen and sulfur co-doped activated carbon (ACNS) which showed the highest Hg(II) adsorption capacity, increasing more than 2.5 times compared to the original AC. The surface N and S ligands were favoured to the adsorption of Hg(II) ions. Moreover, ACNS could be applied over a wide pH range. However, the micro-sized AC powders were difficult to remove and recycle from treated water.
Accordingly, in this work, magnetic MnFe$_2$O$_4$ nanoparticles were prepared by hydrothermal synthesis and MnFe$_2$O$_4$@C composites were successfully fabricated using glucose as carbon source. Magnetic MnFe$_2$O$_4$@C particles can not only take full advantage of the adsorption ability of MnFe$_2$O$_4$ and C, but can also be separated from the solution by a simple magnetic process after the adsorption was completed. The composites were then modified with thiourea to introduce sulfur-containing functional and nitrogen-containing groups. The modified composites were labelled as MnFe$_2$O$_4$@C–NS. MnFe$_2$O$_4$, MnFe$_2$O$_4$@C, MnFe$_2$O$_4$@C–NS samples were characterized by X-ray diffraction (XRD), vibrating sample magnetometry (VSM), transmission electron microscopy (TEM), N$_2$ adsorption–desorption and the pH at the point of zero charge (pH$_{PZC}$). The removal and recovery of Hg(II) using these three nanoparticles was investigated. The adsorption kinetics, adsorption isotherms, adsorption thermodynamics and the effects of pH and coexisting ions were examined.

**EXPERIMENTAL**

**Preparation of MnFe$_2$O$_4$@C–NS nanoparticles**

Ferric chloride (FeCl$_3$·6H$_2$O), manganese acetate (Mn(AC)$_2$·4H$_2$O), ethylene glycol, polyethylene glycol, NaAc, glucose, thiourea and mercuric nitrate (Hg(NO$_3$)$_2$) were purchased from Sinopharm Chemical Reagent Co. A stock solution of 1,000 mg/L of Hg(II) was prepared by dissolving solid Hg(NO$_3$)$_2$ in distilled water. All chemicals were used without further purification.

MnFe$_2$O$_4$ nanoparticles were prepared by a simple solvothermal synthesis (Jiang et al. 2015). In detail, 5 mmol FeCl$_3$·6H$_2$O and 2.5 mmol Mn(AC)$_2$·4H$_2$O were completely dissolved in 40 mL of ethylene glycol. Then NaAc (2 g) and polyethylene glycol (0.5 g) were added into the mixture and stirred until homogenized. The obtained solution was transferred to a 50 ml Teflon-lined autoclave and sealed. Reaction was run in an oven at 200 °C for 10 h. The solid products were collected through an external magnet, washed separately with distilled water and ethanol for several times, and then dried in an oven at 60 °C for 12 h.

The MnFe$_2$O$_4$@C nanoparticles were prepared in accordance with the following procedure: 0.4 g of prepared MnFe$_2$O$_4$ nanoparticles was dispersed in 40 mL of distilled water by ultrasonication. Then 1 g of glucose was put into the solution above. The mixture was transferred to a 50 mL Teflon-lined autoclave and hydrothermal synthesis was carried out in an oven at 200 °C for 12 h. The products were collected, washed, dried and calcined in argon (AR) Ar at 500 °C for 4 h.

Afterwards, 0.2 g of thiourea was dissolved in 30 mL of distilled water, and then 0.4 g of obtained MnFe$_2$O$_4$@C nanoparticles were ultrasonically dispersed in the solution under vigorous stirring. After 2 h, the resulting slurry was filtered, washed several times with distilled water and ethanol and dried at 60 °C overnight. Finally, the resultant samples were heat-treated under a flow of Ar for 4 h at 500 °C. During the heat treatment process, thiourea could react with oxygen-containing functional groups on carbon surface, and nitrogen-containing and sulfur-containing functional groups were introduced on the surface of carbon shell. The obtained samples were labelled as MnFe$_2$O$_4$@C–NS.

**Characterization**

Powder XRD measurements were conducted on a Philips X’Pert MPD diffractometer using Cu Kα radiation from 10° to 80° (2θ). Magnetic properties were analyzed at room temperature using a vibrating sample magnetometer (Digital Measurement System JDM-13). TEM images were obtained with a JEM-2010 transmission electron microscope operated at 200 kV. The specific surface area and pore volume of the nanoparticles were calculated from N$_2$ adsorption and desorption isotherms at –196 °C using a Builder SSA-420 instrument. The zeta potential of the nanoparticles obtained at different pH values was determined using a zeta potential analyzer (ZETA PLUS, Brookhaven Instruments Corporation).

**Adsorption experiments**

The kinetics studies were carried out in 250 mL flasks. The working volume was 100 mL, and the Hg(II) ions concentration was 50 mg/L with the unadjusted initial pH. After the addition of 50 mg nanoparticles each, the flasks were sealed and shaken at 200 rpm in a thermostat shaker maintained at 30 °C. Samples were withdrawn at predetermined time intervals and immediately filtered with 0.45 μm membrane for further analysis.

Adsorption isotherms experiments were carried out in 250 mL flasks at 30 °C, each containing different concentrations (10–200 mg/L) of 50 mL Hg(II) solution. The adsorbent dose was fixed at 50 mg. When reaching equilibrium, the adsorbent was magnetically separated from the aqueous solution, and the residual concentrations of
Hg(II) ions were determined using an atomic fluorescence spectrometer (AFS, A13200, Auror). The amount of uptake capacity at equilibrium was calculated by Equation (1).

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

(1)

where \( q_e \) (mg/L) is the amount of uptake capacity at equilibrium; \( C_0 \) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of the solution, respectively; \( m \) (g) is the mass of adsorbent and \( V \) (L) is the volume of the solution.

The thermodynamics studies were carried out at different temperatures (30, 40, 50 and 60°C) with 50 mg/L Hg(II) ions concentration. Then 50 mg adsorbent was added to 100 mL of Hg(II) solution with the unadjusted pH. The effect of solution initial pH on adsorption was investigated in pH range of 2–10 by adding 0.1 M nitric acid (HNO₃) and 0.1 M sodium hydroxide (NaOH) solution. The adsorbent dose and the Hg(II) concentration were 50 mg and 50 mg L⁻¹, respectively.

To test the selectivity and applicability of synthesized nanoparticles in industries, the effect of coexisting ions (Ca, Mg, Si and Cd) were examined at 30°C and the initial solution pH was not adjusted. Binary selectivity studies for Hg(II) were carried out with individual metal ion concentration of 50 mg/L and adsorbent dose of 50 mg.

**RESULTS AND DISCUSSION**

**Characterization**

The XRD patterns of MnFe₂O₄, MnFe₂O₄@C and MnFe₂O₄@C-NS nanoparticles are displayed in Figure 1(a). The diffraction peaks for MnFe₂O₄ with a cubic spinel structure can be explicitly observed at 18.07°, 30.62°, 36.05°, 43.72°, 54.12°, 57.72° and 63.32°, which correspond to the crystal planes of (111), (220), (311), (400), (422), (511) and (440), respectively (Chen et al. 2014). The characteristic peaks of MnFe₂O₄@C and MnFe₂O₄@C-NS can also be well indexed as cubic MnFe₂O₄, which implied they maintained a stable spinel structure after the modification.

The room temperature magnetization curves of MnFe₂O₄, MnFe₂O₄@C and MnFe₂O₄@C-NS nanoparticles are presented in Figure 1(b), and the saturation magnetization (Ms) are listed in Table 1. As expected, the Ms decreased from 38.2 to 29.5 emu/g after carbon coating on MnFe₂O₄ surface. Despite the decrease in magnetic properties, MnFe₂O₄@C and MnFe₂O₄@C-NS could be simply and rapidly recovered from the reaction solution under an external magnetic field. The TEM image in Figure 1(c) showed that the MnFe₂O₄@C-NS particles were regular and uniform with a diameter of about 40 nm.

The microstructure parameters of MnFe₂O₄, MnFe₂O₄@C and MnFe₂O₄@C-NS nanoparticles obtained from N₂ adsorption–desorption isotherms are collected in Table 1. As shown in Figure 2, all three nanoparticles showed a type IV isotherm with H3 hysteresis loop, characteristic to

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ms (emu/g)</th>
<th>S(_{BET}) (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
<th>pH(_{ZPC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe₂O₄</td>
<td>38.2</td>
<td>25</td>
<td>0.086</td>
<td>9.18</td>
<td>6.75</td>
</tr>
<tr>
<td>MnFe₂O₄@C</td>
<td>29.5</td>
<td>62</td>
<td>0.17</td>
<td>8.45</td>
<td>6.98</td>
</tr>
<tr>
<td>MnFe₂O₄@C-NS</td>
<td>25.9</td>
<td>61</td>
<td>0.15</td>
<td>8.13</td>
<td>9.01</td>
</tr>
</tbody>
</table>

Table 1 | Physical and chemical properties of MnFe₂O₄, MnFe₂O₄@C and MnFe₂O₄@C-NS nanoparticles

Figure 1 | Characterization of MnFe₂O₄, MnFe₂O₄@C and MnFe₂O₄@C-NS nanoparticles: (a) XRD patterns; (b) magnetic hysteresis loops at room temperature; (c) TEM image of MnFe₂O₄@C-NS.
mesoporous structure. As presented in Figure 2(d), the pore size distribution confirmed that all three nanoparticles were mesoporous materials. The surface area, pore volume and pore size of MnFe₂O₄ were 25 m²/g, 0.086 cm³/g and 9.18 nm, respectively. There was no apparent change in pore volume and pore size. However, the presence of carbon increased the specific surface area from 25 to 62 m²/g for MnFe₂O₄@C and 61 m²/g for MnFe₂O₄@C-NS. Based on these results, it could be concluded that carbon was deposited on the surface of MnFe₂O₄ particles rather than inside the pores.

The pHₚZC of the three nanoparticles are also shown in Table 1. A remarkable enhancement of pHₚZC was observed when N and S elements were introduced onto carbon surface. The pHₚZC of MnFe₂O₄@C-NS was 9.01, implying the surface of MnFe₂O₄@C-NS was positively charged in solution at pH below 9.01. Therefore, the charged surface, as well as the adsorption performance, were highly dependent on the solution pH.

Adsorption kinetics

In the present study, two common adsorption kinetic equations were employed to investigate the adsorption of Hg(II) ions. The pseudo-first-order equation and pseudo-second-order equation were expressed as follows (Ren et al. 2012).

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

where \( k_1 \) (1/min) is the first-order rate constant; \( q_e \) and \( q_t \) (mg/g) are the adsorption capacity of Hg(II) at equilibrium and at time \( t \), respectively. According to the plot of \( \ln(q_e - q_t) \) versus \( t \), the \( k_1 \) and \( q_e \) were calculated by the slope and intercept.

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \]
where $k_2$ (g/mg min) is the second-order rate constant; $q_e$ and $q_t$ (mg/g) are the adsorption capacity of Hg(II) at equilibrium and at time $t$, respectively. The values of $k_2$ and $q_e$ were calculated from the slope and intercept of the linear plot of $t/q_t$ versus $t$.

As shown in Figure 3, the adsorption of Hg(II) on MnFe$_2$O$_4$, MnFe$_2$O$_4$@C and MnFe$_2$O$_4$@C–NS was quite quick in the first 30 min, and 3.0 h was enough to achieve equilibrium under the experimental conditions. The parameters of the pseudo-first-order and pseudo-second-order kinetic models for the three nanoparticles are listed in Table 2. It could be concluded that the pseudo-first-order equation might not be sufficient to describe the adsorption process due to the quite low correlation coefficients $R^2$. However, the $R^2$ values derived from the second-order kinetic model were greater than 0.985, which indicated that the pseudo-second-order kinetic model was more likely to explain the adsorption behaviour of the three nanoparticles.

The fact that the adsorption of Hg(II) followed the pseudo-second-order kinetic model implied that the rate limiting step might be the chemical adsorption between adsorbent and adsorbate (Ren et al. 2012).

### Adsorption isotherms

In this work, the experimental data for Hg(II) adsorption on MnFe$_2$O$_4$, MnFe$_2$O$_4$@C and MnFe$_2$O$_4$@C–NS nanoparticles were fitted using the two most widely used models: Langmuir equation (Equation (4)) and Freundlich equation (Equation (5)) (Deb et al. 2017).

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{(4)}
\]

\[
q_e = K_F C_e^{1/n} \quad \text{(5)}
\]

where $q_e$ (mg/g) and $C_e$ (mg/L) are the same as in Equation (1); $q_m$ (mg/g) and $K_L$ (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the affinity of the binding sites, respectively; and $K_F$ ((mg/g)(L/mg)$^{1/n}$) and $n$ are Freundlich constants related to adsorption capacity and intensity of the adsorbent.

The results drawn from Figure 4 and Table 3 indicated that the Langmuir model fitted well to the data because all correlation coefficients ($R^2$) were greater than 0.99 in the Langmuir model. Similar results were reported in the adsorption of Hg(II) by carbon materials (Hadavifar et al. 2014; Deb et al. 2017; Qin et al. 2018). Moreover, the Langmuir model showed reasonable application for Hg(II) adsorption, which signified that this adsorption process acted as a monolayer adsorption on the surface of the three nanoparticles under the applied experimental conditions (Ren et al. 2012).

It can be seen from Table 3 that the adsorption capacity of MnFe$_2$O$_4$ enhanced after carbon coating on the surface, and MnFe$_2$O$_4$@C–NS showed the highest adsorption capacity of 108.56 mg/g. The reasons can be explained as: first, carbon materials showed certain adsorption ability of...
Hg(II) (Hadavifar et al. 2014; Deb et al. 2017; Qin et al. 2018), and therefore the coated carbon could enhance the adsorption capacity. On the other hand, the specific surface areas of MnFe₂O₄@C and MnFe₂O₄@C–NS were much higher than that of MnFe₂O₄ (Table 1). The adsorbent with a larger specific surface area could expose more active sites for the adsorption of Hg(II). As a result, MnFe₂O₄@C and MnFe₂O₄@C–NS showed higher adsorption capacity than MnFe₂O₄. Compared to MnFe₂O₄@C, the introduction of N-containing and S-containing functional groups onto carbon surface enhanced the performance in the adsorption of Hg(II). This result could be explained by the Hard-Soft-Acid-Base theory. Hg(II) was considered as a soft acid that forms strong covalent bonds to soft bases such as −NH₂, −CN, −SH and −RS groups (Sinner et al. 1988; Namavivayam & Kadirvelu 1999; Reddy & Francis 2001). As a result, the interactions of Hg(II) with surface N and S ligands were favoured. Although MnFe₂O₄@C–NS showed a lower adsorption activity than the previous reported ACNS (Qin et al. 2018), the adsorbent had the advantage of easy separation from the reaction mixture due to its magnetic MnFe₂O₄ core.

### Adsorption thermodynamics

MnFe₂O₄@C–NS showed the highest adsorption capacity, and so the adsorption thermodynamic of MnFe₂O₄@C–NS was systematically investigated for better industrial application. The enthalpy change (ΔH°) and entropy change (ΔS°) for Hg(II) adsorption by MnFe₂O₄@C–NS were determined using Equations (6) and (7) (Bessbousse et al. 2010). When lnKd was plotted against temperature 1/T, data fitted a straight line and ΔH° and ΔS° corresponded to the slope and intercept of the line, respectively. The ΔG° is the change in Gibbs free energy, calculated according to Equation (8) (Bessbousse et al. 2010).

\[
\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

\[
K_d = \frac{(C_0 - C_1)}{C_0} \times \frac{V}{m}
\]

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]

where \(K_d\) (mL/g) is the distribution coefficient; \(R\) (8.314 \times 10^{-3} \text{ kJ/mol K}) is the universal gas constant; and \(T\) (K) is the absolute temperature.

The effect of temperature on the adsorption of Hg(II) on MnFe₂O₄@C–NS was illustrated by a linear plot of lnKd versus 1/T in Figure 5. The evaluated thermodynamic parameters and correlation coefficient are summarized in Table 4. The negative value of ΔH° with a decreasing trend of Kd with increasing temperature revealed that the adsorption process was exothermic in nature. The negative value of ΔS° indicated that no ion replacement reactions occurred in the adsorption process because the increase of entropy of the system could have happened due to release of the ion from the solid surface to the solution (Dujardin et al. 2000). On the other hand, the release of water molecule produced by the interaction of Hg(II) with functional groups and surface sites of the adsorbent resulted in the positive ΔS° value (Deb et al. 2017). In addition, the negative value of ΔG° indicated that the adsorption of Hg(II) on MnFe₂O₄@C–NS was spontaneous. The value of ΔG° increased from −10.45 to −9.07 kJ/mol for the temperature
range 30–60 °C, which implied that the adsorption was more favourable at lower temperatures.

Effect of solution pH

Solution pH played a significant role in determining the adsorption of metal ions from it aqueous solution because it could affect the surface property of adsorbent as well as the dominating form of adsorbate. As shown in Figure 6, the uptake of Hg(II) on MnFe₂O₄@C-NS was strongly dependent on solution pH. The adsorption capacity increased with the increase in pH from 2 to 7, and then decreased at higher initial pH. In the first zone (between 2 and 4), the adsorption capacity of MnFe₂O₄@C-NS enhanced sharply from 22.56 to 48.88 mg/g, which could be explained by the competition between H⁺ and Hg(II) for the same donating atoms that caused the adsorption to be strongly pH-dependent (Bessbousse et al. 2010). Under the pH range of 4–7, Hg²⁺ and Hg(OH)⁺ were the predominant species. They were considered to be soft acids and had more affinity for binding with N-containing and S-containing functional groups on MnFe₂O₄@C-NS surface according to the Hard-Soft-Acid-Base theory (Sinner et al. 1988; Namasiyavam & Kadirvelu 1999; Reddy & Francis 2001). At the pH range of 7–10, the predominant species Hg(OH)³⁻ were negatively charged and showed less affinity with surface N and S ligands. On the other hand, as shown from Table 1, the pHPZC of MnFe₂O₄@C-NS was 9.01, revealing the surface of MnFe₂O₄@C-NS was positively or negatively charged in solution at pH below or above 9.01. Therefore, the adsorption capacity slightly decreased due to electrostatic attraction between adsorbent and adsorbate at the pH range of 7–9, whereas it decreased sharply at pH 10 due to the electrostatic repulsion.

Selectivity

Binary selectivity of Hg(II) over a number of other metal ions (Ca, Mg, Si and Cd) present in typical Hg plant wastewater (Deb et al. 2017) was measured. The adsorption capacity for Hg(II) compared to other metal ions by MnFe₂O₄@C-NS is depicted in Figure 7. Clearly, MnFe₂O₄@C-NS was found to be highly selective for Hg(II) in all the studied pairs. This result was attributed to the soft nature of Hg(II) compared to other metal ions, and the interaction between Hg(II) (soft acid) and N and S ligands (soft base) was favoured (Sinner et al. 1988; Namasiyavam & Kadirvelu 1999; Reddy & Francis 2001). Among the four metal ions, all metal ions except Cd(II) showed no significant adsorption in the binary solution with Hg(II). Approximately 41.2% of Cd(II) was removed compared to 58.6% Hg(II) by MnFe₂O₄@C-NS in the binary mixtures.
The lower selectivity of Hg(II) with Cd(II) could be due to the chemical similarity because both elements are adjacent members in the periodic table.

CONCLUSIONS

Magnetic MnFe$_2$O$_4$, MnFe$_2$O$_4$@C and MnFe$_2$O$_4$@C–NS nanoparticles were successfully synthesized and applied as adsorbing material in the removal of Hg(II) from aqueous solution. The adsorption process was found to follow the pseudo-second-order kinetic equation and Langmuir isotherm model, demonstrating that the chemical monolayer adsorption was involved in the adsorption of Hg(II) on the surface of MnFe$_2$O$_4$@C–NS. MnFe$_2$O$_4$@C–NS showed the highest adsorption capacity of 108.56 mg/g, increasing more than 1.7 times compared to MnFe$_2$O$_4$. The enhanced adsorption performance was attributed to the larger specific surface area and the complexation of N-containing and S-containing functional groups on the surface. The values of thermodynamic parameters Δ$H^\circ$, Δ$S^\circ$ and Δ$G^\circ$ were obtained as −24.39 kJ/mol, −0.046 kJ/mol K and −10.45 kJ/mol, respectively, suggesting an exothermic and spontaneous nature of the adsorption. In addition, MnFe$_2$O$_4$@C–NS presented superior selectivity towards Hg(II) compared to other metal ions generally present in Hg-containing wastewater. Therefore, it may have a prospective application in the treatment of Hg-containing industrial wastewater.

ACKNOWLEDGEMENTS

The authors would like to convey their gratitude for the financial support from Provincial Key Disciplines of Chemical Engineering and Technology in Guizhou Province (No. ZDKX [2017] 8), Guizhou Provincial Department of Education Foundation (No. QJHKYZ2016-107) and Student’s Platform for Innovation and Entrepreneurship Training Program (20195200505).

REFERENCES


Hadavifar, M., Bahramifar, N., Younesi, H. & Li, Q. 2014 Adsorption of mercury ions from synthetic and real wastewater aqueous solution by functionalized multi-walled carbon nanotube with both amino and thiolated groups. Chemical Engineering Journal 237 (2), 217–228.


Mallikarjuna, N. N. & Venkataraman, A. 2005 Adsorption of Pb\textsuperscript{2+} ions on nanosized $\gamma$-Fe\textsubscript{2}O\textsubscript{3}: formation of surface ternary complexes on ligand complexation. *Talanta* 60 (1), 139–147.


Podder, M. S. & Majumder, C. B. 2016 Studies on the removal of As(III) and As(V) through their adsorption onto granular activated carbon/MnFe\textsubscript{2}O\textsubscript{4} composite: isotherm studies and error analysis. *Composite Interfaces* 23 (4), 327–372.


First received 22 January 2020; accepted in revised form 28 April 2020. Available online 11 May 2020