Synthesis of kaolinite/iron oxide magnetic composites and their use in the removal of Cd(II) from aqueous solutions

Pengfei Zong, Shoufang Wang and Chaohui He

ABSTRACT

Kaolinite/iron oxide magnetic composites (kaolinite/MCs) were used as adsorbent for the removal of Cd(II) from aqueous solutions. The influences of pH, ionic strength, solid/liquid ratio and temperature on Cd(II) sorption on kaolinite/MCs were evaluated. The results showed that the removal of Cd(II) on kaolinite/MCs was strongly dependent on pH and ionic strength. An optimal kaolinite/MCs concentration mass per volume for removal of Cd(II) from aqueous solutions was 1.4 g L⁻¹. The Langmuir and Freundlich models were used to simulate sorption isotherms of Cd(II) at three different temperatures of 293, 313 and 333 K. The sorption of Cd(II) on kaolinite/MCs increased with increasing temperature, and thermodynamic parameters (standard entropy change, enthalpy change and Gibbs free energy change) illustrated that this sorption process was spontaneous and endothermic. The sorption behaviors of Cd(II) were mainly dependent on surface properties of kaolinite/MCs and solution chemistry conditions. The sorption capacity of Cd(II) on kaolinite/MCs was lower than that on kaolinite, because iron oxide particles decreased surface charge of kaolinite leading to less sorption capacity. Due to high magnetism, kaolinite/MCs could be easily separated with an external magnetic field. Kaolinite/MCs could therefore be used as potential adsorbent for preconcentration and immobilization of Cd(II) ions from large volumes of aqueous solutions.

Key words | Cd(II), kaolinite/MCs, pH, temperature, thermodynamic data

INTRODUCTION

Heavy metal ion contamination of the soil and water environment is of concern due to their toxic impact on human health; they must be removed from aqueous solutions (Lau et al. 2010). Cadmium is a toxic heavy metal and non-biodegradable element, which is found in some surface and subsurface water. The main source of cadmium contamination originates from industrial production processes such as textile printing industries, metallurgical alloying, mining activities, electro-galvanization and alkaline batteries (Mohapatra & Anand 2007). It has been found that chronic exposure via ingestion of cadmium has a detrimental impact on human health including severe kidney damage, bone marrow damage, lung insufficiency, reduction of red blood cells and other pathological symptoms (Lehoczky et al. 1998). For the purpose of protecting public health, it is of primary importance to remove cadmium from aqueous solutions.

Extraction of heavy metal ions by minerals is an accepted procedure for preserving environmental quality in polluted regions. Recently, numerous technologies have been used for removal of hazardous heavy metal ions from wastewater including filtration, sorption, ion exchange, chemical precipitation, surface complexation and membrane processing (Wang et al. 2005a, b). Among these methods, sorption has been widely applied because of its high removal efficiency and simple operation. Many adsorbents such as carbon nanotubes (Chen et al. 2009; Yang et al. 2012a), alumina (Tan et al. 2008), mordenite (Yang et al. 2012b), diatomite (Sheng et al. 2011) and zeolite (Shao et al. 2009) have been studied for their potential use as adsorbents to remove heavy metal ions from aqueous solutions.

Kaolinite [Al₂Si₂O₅(OH)₄] is a typically stratified aluminosilicate mineral comprising SiO₄ tetrahedral and AlO₆...
octahedral structure (Gong et al. 2009). Both layers are held together in a packet by hydrogen bonds formed between hydroxyl groups attached to unsaturated oxygen sites of the octahedral layer and oxygen ions terminating the reversed tetrahedral layer (Shahwan & Erten 1999). Due to its large surface area, layered structure and high cation exchange capacity (Ma & Eggleton 1999), kaolinite has been used as adsorbent to remove inorganic and organic contaminations from wastewater.

Filtration and ultracentrifugation are the primary approaches for separating adsorbents from aqueous solutions. However, these approaches are unsatisfactory due to the fact that filtration is likely to filter blockages and high-speed centrifugation consumes tremendous electric energy. The application of magnetic composite materials in wastewater disposal has therefore attracted widespread interest due to its convenience and efficiency (Gong et al. 2009). Gupta et al. (2003) used bagasse fly ash for the sorption of cadmium, but the sorption capacity is relatively low. Xie et al. (2011) studied the removal of dyes using magnetic halloysite nanotubes from aqueous solutions. However, only a few studies are available on the use of kaolinite together with magnetic composites (kaolinite/MCs) as adsorbent in remediying environment contamination (Guo et al. 2014). It is therefore of primary importance to study the sorption properties of heavy metal ions at kaolinite/MCs and water interfaces.

In this work, the sorption behaviors of Cd(II) on kaolinite/MCs under ambient conditions were investigated. The objectives of this study were: (1) to characterize kaolinite/MCs using Fourier transform infrared (FTIR) spectrum; (2) to study the influence of different experimental parameters on Cd(II) sorption such as ionic strength, pH and temperature; and (3) to apply the sorption mechanism of Cd(II) on kaolinite/MCs and to evaluate the potential application of kaolinite/MCs in disposal of practical wastewater.

MATERIALS AND METHODS

The synthesis of kaolinite/MCs

The kaolinite was purchased from Sinopharm Chemical Reagent Co., Ltd (China) with the primary accessory phase of quartz and muscovite. It was sieved by a 200 mesh sieve to remove impure particles from the sample. The chemical composition of the sample was as follows (wt%): SiO₂ 45.65, Al₂O₃ 39.75, Fe₂O₃ 0.7, SO₃ 0.55, TiO₂ 0.50, MgO 0.40, CaO 0.30, MnO 0.20, humic substance 0.20, K₂O 0.20, Na₂O 0.15 and hydration water 11.42. The kaolinite/MCs were obtained by adding 0.35 g kaolinite to a 500 mL flask of 3.27 g FeCl₃·6H₂O and 1.68 g FeSO₄·7H₂O according to a molar ratio of Fe³⁺:Fe²⁺ = 2:1 under N₂ condition at 80 °C. NH₄OH solution (wt 30%) was added dropwise to form iron oxides precipitates. After adding the NH₄OH solution, the pH of the solution was adjusted to 10.5 and the reaction continued for 5 h. The mixture was finally diluted with Milli-Q water and dried in the oven at 70 °C for 24 h. The final product was expressed as kaolinite/MCs. The N₂-BET (Brunauer, Emmett and Teller) surface area of the kaolinite/MCs was 63.24 m² g⁻¹.

Experimental procedure

The sorption experiments were performed by batch technique in polyethylene test tubes. The cadmium stock solution was prepared by dissolving analytical-grade cadmium chloride and then diluting with Milli-Q water to 60 mg L⁻¹. The stock suspension of kaolinite/MCs and NaClO₄ solution was oscillated for 24 h to reach equilibrium and then Cd(II) stock solution was added to reach desired concentrations of different constituents. The pH values of the suspensions were adjusted by adding negligible volumes of 0.1 or 0.01 mol L⁻¹ NaOH or HClO₄. After the suspensions were oscillated for 2 d, the solid and liquid phases were separated by magnetic process with a permanent magnet. The sorption of Cd(II) on the tube wall was negligible according to the test of Cd(II) sorption in the absence of kaolinite/MCs. The point of zero charge (pHpzc) of kaolinite/MCs was obtained as 5.4 ± 0.1 from acid–base potentiometric titration. The surface charge was positive at pH < pHpzc and was negative at pH > pHpzc. The samples of kaolinite and kaolinite/MCs were characterized using the FTIR spectrum (Perkin Elmer spectrum 100, USA) in the range of 4,000–400 cm⁻¹ pressed KBr pellets. The spectral resolution was set to 1 cm⁻¹, and 150 scans were collected for each spectrum.

RESULTS AND DISCUSSION

Characterization of kaolinite/MCs

The FTIR spectra of kaolinite and kaolinite/MCs are shown in Figure 1. The band at 3,440 cm⁻¹ is attributed to the OH vibration of the hydroxyl molecule and could be observed in nearly all natural hydrated silicates. The band at 2,925 cm⁻¹
has been assigned to a homogeneous stretch of the C–H pattern of the –CH₂ group. The band at 1,637 cm⁻¹ is ascribed to H–O–H bending of water. The peak at 1,097 cm⁻¹ is assigned to the perpendicular mode of Si–O stretching vibration (Vaculíková et al. 2011), and the C–O, C–O–O ring vibration of carbohydrate is considered to be due to involvement of carbohydrates in clay–organo interactions (Spence & Kelleher 2002). The Al–OH sorption band is found at 893 cm⁻¹. The OH deformation band of (AlMgOH) is observed at 836 cm⁻¹, which reflects partial substitution of octahedral Al by Mg (Madejová 2005). The Si–O–Si inter-tetrahedral bridging bond in SiO₂ is observed at 797 cm⁻¹. The peaks between 471 and 635 cm⁻¹ have been attributed to Si–O–Si vibration bending. The Fe–O sorption peak at 576 cm⁻¹ confirms that kaolinite/MCs comprise iron oxide.

As can be seen from the inset of Figure 1, the particles of the kaolinite/MCs are attracted rapidly toward a magnet. Cd(II) ions are separated from the aqueous solution by a magnet and then the clear supernatant solution could be easily removed by pipette or liquid-transferring gun. The magnetic separation experiment suggests that the kaolinite/MCs are magnetic and could be used as a magnetic adsorbent to remove contaminations from aqueous solutions.

**Influence of pH and ionic strength**

The influences of pH and ionic strength on the sorption of Cd(II) on kaolinite/MCs are shown in Figure 2. The removal proportion of Cd(II) on kaolinite/MCs increases gradually at pH < 6.0, abruptly at pH 6.0–9.0 and then maintains a high level at pH > 9.0. The pHₚₑᵥₑ of kaolinite/MCs is found to be 5.4 ± 0.1 from the acid-base potentiometric titration. At pH < pHₚₑᵥₑ, the surface charge of the kaolinite/MCs becomes positive due to protonation reaction (i.e. SOH + H⁺ ⇌ SOH₂⁺); Yang et al. (2011a). The positive cadmium ions (Cd₂⁺) are hardly adsorbed on the surface of kaolinite/MCs because of electrostatic repulsion; the removal proportion of Cd(II) is therefore very low at pH < 6.0. At pH > pHₚₑᵥₑ, however, the surface of kaolinite/MCs becomes negatively charged due to deprotonation reaction (i.e. SOH⁻ ⇌ SOH₂⁻), which increases the sorption of Cd(II) ions on kaolinite/MCs as a result of electrostatic attraction. With increasing pH of solution, the surface charge of kaolinite/MCs becomes more negative and the electrostatic attraction between Cd(II) ions and kaolinite/MCs becomes stronger, which increases the sorption of Cd(II) on the surface of kaolinite/MCs. Furthermore, the relative distribution of Cd(II) species is calculated from the hydrolyzed constants (pK₁ = 7.9, pK₂ = 10.6, and pK₃ = 8.7) and the results indicate that Cd(II) emerges in the shape of Cd₂⁺, Cd(OH)⁺, Cd(OH)₂ and Cd(OH)₃ at different pH values. At pH < 6.0, the predominant Cd(II) species is Cd₂⁺ and the removal of Cd(II) is mainly completed by sorption process.

The initial concentration of Cd(II) was 8.91 × 10⁻⁵ mol L⁻¹ in our experiments and the precipitation constant of Cd(OH)₂(s) was 2.50 × 10⁻¹⁴ (Zhao et al. 2011a). From Figure 2, it can also be seen that Cd(II) ions start to precipitate at pH 9.0 in the absence of kaolinite/MCs. Nevertheless, more than 90% Cd(II) is adsorbed on kaolinite/MCs at pH 9.0; it is therefore unlikely to form precipitates because of the low concentration of Cd(II) remaining in solution. In other words, the abrupt increase

---

**Figure 1** | FTIR spectrum of kaolinite/MCs sample and the photograph of magnetic separation (insert). Bottle A is kaolinite/MCs, bottle B is kaolinite.

**Figure 2** | Effect of pH on the sorption of Cd(II) to kaolinite/MCs. T = 293 K, C_{OBSERVED} = 8.91 × 10⁻⁵ mol L⁻¹, mV = 0.8 g L⁻¹.
of Cd(II) sorption on the surface of kaolinite/MCs at pH 6.0–9.0 is not attributed to the formation of Cd(OH)$_2$(s).

The influence of ionic strength on Cd(II) sorption on kaolinite/MCs as a function of pH is also illustrated in Figure 2. It is obvious that the removal proportion of Cd(II) is distinctly influenced by ionic strength at pH < 9.0 and no drastic distinction is found at pH > 9.0. This phenomenon can occur because: (1) the activity of Cd(II) in solution is reduced with increase of ionic strength, which limits the transfer of cadmium ions from solution to kaolinite/MCs surface; (2) at high ionic strength, electrostatic repulsion reduces and particle aggregation increases, which decreases the available binding sites to bind the cadmium ions on kaolinite/MCs surface and thereby decreases the sorption of Cd(II) on kaolinite/MCs; and (3) the formed electrically diffused double-layer complexes between cadmium ions and kaolinite/MCs particles inhibit Cd(II) ions sorption when the ionic strength is increased.

As described by Sheng et al. (2009), Fan et al. (2011) and Yang et al. (2012a), outer-sphere surface complexation or cation exchange is mainly attributed to Cd(II) sorption on kaolinite/MCs at pH < 9.0; inner-sphere surface complexation is the main sorption mechanism of Cd(II) on kaolinite/MCs at pH > 9.0 (Yang et al. 2012b).

**Effect of solid/liquid ratio**

The removal proportion of Cd(II) on kaolinite/MCs as a function of solid/liquid ratio is shown at pH = 6.5 ± 0.1. As can be seen from Figure 3, the removal proportion of Cd(II) increases rapidly with increasing solid/liquid ratio at m/V < 1.4 g L$^{-1}$ and then maintains a high level with increasing solid/liquid ratio at m/V > 1.4 g L$^{-1}$. With increasing solid/liquid ratio, the number of functional groups on the kaolinite/MCs surfaces increases; more exchangeable surface sites are therefore available for binding Cd(II) ions. From Figure 3, it can also be seen that the sorption capacity ($C_s$) of Cd(II) on kaolinite/MCs decreases gradually with increasing solid/liquid ratio (Zhao et al. 2012; Njoku et al. 2012).

The kaolinite/MCs surfaces are composed of sites with a series of binding energies. At low adsorbent concentration, all kinds of surface sites are totally exposed for sorption, and the surfaces achieve saturation rapidly, resulting in high removal efficiency. However, at higher adsorbent concentration, the higher-energy sites decrease with a larger portion of lower-energy sites becoming occupied, thus leading to lower removal efficiency. In addition, higher adsorbent concentration increases the probability of particle collision and promotes aggregation of kaolinite/MCs particles. This results in an increase in diffusional path length and a decrease in the entire surface area, both of which lead to a reduction in removal capacity of Cd(II) on the surface of kaolinite/MCs. For the above-mentioned reasons, we reach a conclusion that a solid/liquid ratio of 1.4 g L$^{-1}$ is the optimal kaolinite/MCs concentration for removing Cd(II) from aqueous solutions.

**Sorption isotherms**

The sorption isotherms of Cd(II) on kaolinite/MCs at 293, 313 and 333 K are illustrated in Figure 4. It is obvious that
the sorption isotherm is highest at 333 K and lowest at 293 K, which indicates that high temperature is beneficial for Cd(II) sorption. In order to further optimize sorption parameters and predict sorption behaviors, Langmuir and Freundlich models are applied to simulate the sorption data of Cd(II) on the surface of kaolinite/MCs. The equations of the Langmuir and Freundlich models are defined (Zhao et al. 2011b)

\[
C_s = \frac{b_{s, \text{max}} C_{\text{eq}}}{1 + b_{s, \text{max}} C_{\text{eq}}}
\]

(1)

\[
C_s = k_F C_{\text{eq}}^n
\]

(2)

respectively, where \(C_s\) is the amount of Cd(II) ions adsorbed per unit weight of solid after equilibrium (mol g\(^{-1}\)); \(C_{\text{eq}}\) is the equilibrium concentration of Cd(II) ions in solution (mol L\(^{-1}\)); \(C_{s, \text{max}}\) is the maximum sorption capacity (mol g\(^{-1}\)); \(b\) is a constant that relates to the heat of sorption (L mol\(^{-1}\)); \(k_F\) (mol\(^{1-n}\) L\(^n\) g\(^{-1}\)) and \(n\) are the Freundlich parameters referred to as the sorption capacity and sorption intensity, respectively. The similar sorption isothermal experiments of Cd(II) on kaolinite at 293, 313 and 333 K are carried out under ambient conditions.

The relative parameters fitting the isotherm model are listed in Table 1. Although no obvious distinction can be seen from Figure 4, it can be concluded from the correlative parameters (\(R^2\)) that the Langmuir model simulates the experimental data better than the Freundlich model (see Table 1); this indicates that the binding energy on the whole surface of kaolinite/MCs is uniform. In other words, the whole surface has identical sorption activity (therefore adsorbed Cd(II) ions do not interact with each other) and they are adsorbed by forming an almost complete monolayer coverage of the kaolinite/MCs particles (Kamei-Ishikawa et al. 2008). The values of \(C_{s, \text{max}}\) calculated from the Langmuir model are the highest at \(T = 333\) K and the lowest at \(T = 293\) K, which indicates that the sorption of Cd(II) is favored at high temperature.

From Table 1, it can also be seen that the sorption capacity of Cd(II) on kaolinite is higher than that on kaolinite/MCs. The difference between kaolinite and kaolinite/MCs towards Cd(II) may originate from the changes in the surface properties of kaolinite/MCs. Considering kaolinite/MCs centrifugation and regeneration, the recovery process is easily conducted by external magnetic field. However, the adverse effects of the iron oxide particles on magnetic material surfaces include lower surface charge and sorption area (resulting in lower sorption capacity). The value of \(n\) obtained from the Freundlich model is <1, showing that a non-linear sorption of Cd(II) occurs in kaolinite and kaolinite/MCs surfaces.

### Thermodynamic studies

The thermodynamic parameters of standard entropy change \(\Delta S^0\), enthalpy change \(\Delta H^0\) and Gibbs free energy change \(\Delta G^0\) for Cd(II) sorption on kaolinite/MCs are calculated from the temperature-dependent sorption isotherms. \(\Delta H^0\) and \(\Delta S^0\) of specific sorption are calculated from the slope and intercept of the plot of ln \(K_d\) (distribution coefficient) versus 1/\(T\) from the following equation:

\[
\ln K_d = \frac{-\Delta H^0}{R} \frac{1}{T} + \frac{\Delta S^0}{R}
\]

(3)

where \(R (8.314 \text{ J mol}^{-1} \text{ K}^{-1})\) is the ideal gas constant and \(T\) is the temperature in Kelvin (K). The sorption equilibrium constant \(K^0\) can be calculated by plotting ln \(K_d\) versus \(C_{\text{eq}}\) and extrapolating to zero.

\(\Delta G^0\) is calculated from:

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

(4)

| Table 1 | Sorption isotherm parameters for Langmuir and Freundlich isotherm models of Cd(II) sorption on kaolinite and kaolinite/MCs at different temperatures |
|---------|-----------------|-----------------|-----------------|
|         | Langmuir        |                 | Freundlich      |
|         | \(T\) (K)       | \(C_{\text{max}}\) (mol g\(^{-1}\)) | \(b\) (L mol\(^{-1}\)) | \(R^2\) | \(k_F\) (mol\(^{1-n}\) L\(^n\) g\(^{-1}\)) | \(n\) | \(R^2\) |
| Kaolinite/MCs | 293             | 1.21 \times 10^{-4} | 1.26 \times 10^{4} | 0.994 | 1.59 \times 10^{-2} | 0.592 | 0.976 |
|             | 313             | 1.24 \times 10^{-4} | 1.98 \times 10^{4} | 0.990 | 1.08 \times 10^{-2} | 0.526 | 0.969 |
|             | 333             | 1.27 \times 10^{-4} | 3.96 \times 10^{4} | 0.988 | 5.52 \times 10^{-3} | 0.427 | 0.930 |
| Kaolinite   | 293             | 1.32 \times 10^{-4} | 1.57 \times 10^{4} | 0.994 | 1.33 \times 10^{-2} | 0.551 | 0.982 |
|             | 313             | 1.35 \times 10^{-4} | 2.61 \times 10^{4} | 0.989 | 1.01 \times 10^{-2} | 0.497 | 0.978 |
|             | 333             | 1.40 \times 10^{-4} | 5.66 \times 10^{4} | 0.991 | 5.61 \times 10^{-3} | 0.404 | 0.959 |
In order to evaluate the potential prospects of kaolinite/MCs with other adsorbents is difficult due to the different experimental conditions applied, it has been identified that Cd(II) sorption capacity of kaolinite/MCs is higher than that of cork waste, hazelnut shells, petiolar feel-sheath of palm and GMZ bentonite, but lower than that of Brevundimonas sp. ZF12 and PVA/TEOS/TMPTMS. However, the low cost, simple preparation process and high removal efficiency make kaolinite/MCs a potential adsorbent for the solidification of Cd(II) ions from large volumes of aqueous solutions.

**CONCLUSIONS**

In this study, kaolinite/MCs were characterized by FTIR to determine the chemical functional groups. A batch technique was used to investigate the sorption of Cd(II) on kaolinite/MCs as a function of various environmental factors such as pH, ionic strength, solid/liquid ratio and temperature. The removal proportion of Cd(II) increases with increasing pH values at pH > 9.0, and then maintains a high level for pH > 9.0. The removal of Cd(II) is dependent on ionic strength at low pH values and independent

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Thermodynamic data of Cd(II) sorption on kaolinite/MCs at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$ (mol L$^{-1}$)</td>
<td>$\Delta S^0$ (J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>1.78 x 10$^{-5}$</td>
<td>124.58</td>
</tr>
<tr>
<td>5.34 x 10$^{-5}$</td>
<td>123.74</td>
</tr>
<tr>
<td>8.91 x 10$^{-5}$</td>
<td>122.63</td>
</tr>
<tr>
<td>1.25 x 10$^{-4}$</td>
<td>102.21</td>
</tr>
<tr>
<td>1.61 x 10$^{-4}$</td>
<td>93.69</td>
</tr>
<tr>
<td>1.78 x 10$^{-4}$</td>
<td>87.88</td>
</tr>
</tbody>
</table>

The relevant parameters obtained from Equations (3) and (4) are listed in Table 2. A positive value of $\Delta H^0$ for Cd(II) sorption shows that the Cd(II) sorption on kaolinite/MCs is an endothermic process. One reasonable explanation for this phenomenon is that Cd(II) ions are solvated well in solution and the hydration sheath of Cd(II) must be destroyed before its sorption on the surface of kaolinite/MCs. The dehydration process demands energy, so it is favored at high temperature (Tahir & Rauf 2003). Cd(II) ions are easily dissolved at higher temperature; the sorption of Cd(II) on kaolinite/MCs therefore becomes more favorable. The removal proportion of Cd(II) increases with increasing temperature, indicating more favorable sorption at higher temperature. The thermodynamic data derived from temperature-dependent sorption isotherms suggest that the sorption process of Cd(II) on kaolinite/MCs is endothermic and spontaneous.

**Comparison of Cd(II) sorption capacity of kaolinite/MCs with other adsorbents**

In order to evaluate the potential prospects of kaolinite/MCs, the Langmuir parameter ($C_{s,max}$) was used in the present study to compare the removal efficiency of kaolinite/MCs with those of other adsorbents reported in earlier references (see Table 3). Although a direct comparison of kaolinite/MCs with other adsorbents is difficult due to the different experimental conditions applied, it has been identified that Cd(II) sorption capacity of kaolinite/MCs is higher than that of cork waste, hazelnut shells, petiolar feel-sheath of palm and GMZ bentonite, but lower than that of Brevundimonas sp. ZF12 and PVA/TEOS/TMPTMS. However, the low cost, simple preparation process and high removal efficiency make kaolinite/MCs a potential adsorbent for the solidification of Cd(II) ions from large volumes of aqueous solutions.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Comparison of Cd(II) sorption capacities of kaolinite/MCs with other sorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbents</td>
<td>Solution chemistry conditions</td>
</tr>
<tr>
<td>Cork waste</td>
<td>pH = 5.0, $T = 298$ K</td>
</tr>
<tr>
<td>Hazelnut shells</td>
<td>pH = 4.0, $T = 293$ K</td>
</tr>
<tr>
<td>Petiolar felt-sheath of palm</td>
<td>pH = 5.0, $T = 298$ K</td>
</tr>
<tr>
<td>GMZ bentonite</td>
<td>pH = 6.5, $T = 298$ K</td>
</tr>
<tr>
<td>Kaolinite/MCs</td>
<td>pH = 6.5, $T = 293$ K</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>pH = 6.5, $T = 293$ K</td>
</tr>
<tr>
<td>Brevundimonas sp. ZF12</td>
<td>pH = 6.0, $T = 303$ K</td>
</tr>
<tr>
<td>PVA/TEOS/TMPTMS$^*$</td>
<td>pH = 5.0, $T = 298$ K</td>
</tr>
</tbody>
</table>

$^*$ Functionalized poly(vinyl alcohol)/tetraethyl orthosilicate hybrid membranes with 3-mercaptopropyltrimethoxysilane groups.
of ionic strength at high pH values. The outer-sphere surface complexation or cation exchange is the main mechanism for the sorption of Cd(II) on kaolinite/MCs at low pH values, whereas inner-sphere surface complexation is the primary mechanism at high pH values. The thermodynamic data describing temperature-dependent sorption isotherms illustrate that the sorption process of Cd(II) on kaolinite/MCs is endothermic and spontaneous. The sorption capacity of Cd(II) on kaolinite/MCs is lower than that on kaolinite because the presence of the iron oxide particles decreases the surface charge of kaolinite, resulting in less sorption capacity. Further, kaolinite/MCs can be easily separated from aqueous solution with an external magnetic field. Considering the low cost, accessibility and high removal efficiency of kaolinite/MCs, a potential application is the solidification of Cd(II) ions from large volumes of aqueous solutions.

REFERENCES


