Equilibrium and kinetics studies of Cd(II) sorption on zeolite NaX synthesized from coal gangue

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ABSTRACT

The adsorption of Cd(II) from aqueous solution by synthesized zeolite NaX from coal gangue was investigated in a batch adsorption system. The studies include both equilibrium adsorption isotherms and kinetics. Different isotherm models were examined and the adsorption isotherm could be best represented with Langmuir. The adsorption kinetic experimental data were found to be better fitted with the pseudo-second-order kinetic model. An intra-particle diffusion model was employed to investigate the adsorption mechanism. The results showed that the intra-particle diffusion step was not the only rate limiting step. According to the Langmuir equation, the maximum adsorption capacity was 38.61 mg/g, suggesting that zeolite NaX synthesized from coal gangue can be used as a potential green alternative for the removal of Cd(II) from aqueous solution.

Key words | cadmium, coal gangue, kinetic, sorption, zeolite NaX

INTRODUCTION

Heavy metals resulting from industrial applications, e.g. battery, textile, and paper industry etc., have caused great damage to water resources. Cadmium, one of the most toxic metals, is attracting much attention due to its harmful effects such as kidney damage, anemia, lung cancer, etc. (Jamali et al. 2009). Hence, the development of an effective way to remove metal from wastewater is urgently required. Among available methods, the most commonly used methods are chemical precipitation, ion exchange, adsorption and reverse osmosis (Hui et al. 2005), while adsorption is viewed as the most effective method. Cadmium adsorption has been widely studied using willow root (Chen et al. 2013), modified sodium alginate (Yang et al. 2013), red mud (Kalkan et al. 2013), activated carbon (Venkatesan & Senthilnathan 2013), and zeolite (Izidoro et al. 2013), etc. According to our knowledge, no attempt was made to remove Cd(II) from aqueous solution using zeolite synthesized from coal gangue.

In this study, coal gangue, a solid waste, was used as an alternative low-cost precursor to synthesize zeolite NaX, aiming to remove Cd(II) from aqueous solution. The detailed synthesis process and method of zeolite NaX using coal gangue will be reported in another paper. The object of the present work was to determine the sorption characteristics of Cd(II) onto zeolite NaX synthesized from coal gangue through the investigation of kinetic and isotherm perspectives.

MATERIALS AND METHODS

Adsorbent and solution

Synthesized zeolite NaX from coal gangue (ZXCG) was used as adsorbent to remove Cd(II) from aqueous solution in the study. The surface area of ZXCG was 557.05 m²/g and its total pore volume and micro-pore volume were 0.217 and 0.198 cm³/g, respectively. ZXCG has a relatively narrow pore distribution within the micro-pore range.
(<2 nm). Its pore size is larger than the hydrated ionic radius of Cd(II) (0.426 nm) (Nightingale 1959), suggesting a possibility to remove Cd(II) from aqueous solution using ZXCG as adsorbent.

Cd(NO₃)₂·4H₂O was purchased from TianJin Chemistry Plant, China. Stock Cd(II) solution (1,000 mg/L) was prepared by dissolving accurate amounts of Cd(NO₃)₂·4H₂O in distilled water. NaOH or HCl was used to adjust the initial pH. All the chemical reagents were of analytic grade.

**Batch equilibrium study**

Adsorbent dose, contact time, initial Cd(II) concentration and initial pH of solution were investigated through batch experiments in a 150 mL volume glass bottle. The mixture was agitated by a magnetic stirrer at a fixed speed of 300 rpm for 120 min. The equilibrium mixture was filtered with a 0.45 μm filter membrane, and the residual Cd(II) concentration in the solution was measured by ICP-AES. The amount of Cd(II) adsorbed at equilibrium, \( q_e \) (mg/g), was determined by the following equation:

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

where \( C_0 \) and \( C_e \) represent the initial and equilibrium Cd(II) concentration in the aqueous solution (mg/L), respectively, \( V \) is the solution volume (L) and \( M \) is the adsorbent dose (g). To ascertain the accuracy of the data, triple experiments were conducted and the average value was employed.

The effect of adsorbent dose on Cd(II) adsorption was investigated by adding different amounts of ZXCG (0.05–0.5 g) into 100 mL 100 mg/L Cd(II) solution. The mixture (at natural pH) was then shaken at room temperature (27 °C) until equilibrium.

The effect of initial pH of solution on Cd(II) removal was investigated by adding 0.2 g ZXCG to 100 mL 100 mg/L initial Cd(II) solution at various pH (2.0–6.0) and then stirred at room temperature, 0.1 M NaOH or 0.1 M HCl was employed to adjust the pH.

The effect of initial Cd(II) concentration on the adsorption result was investigated by adding 0.2 ZXCG to 100 mL solution with different initial Cd(II) concentrations (10, 20, 50, 100, 200 mg/L) which was then stirred at room temperature.

**Batch kinetic study**

The kinetic studies were conducted in a 150 mL volume glass bottle at room temperature, 0.2 g ZXCG was added to different initial Cd(II) solutions (10, 20, 50, 100, 200 mg/L) and the pH of the solution was adjusted to 4.0 with 0.1 M HCl or 0.1 M NaOH. Cd(II) solution was extracted at the given time (0, 5, 10, 20, 40, 60, 80, 100, 120 min) and Cd(II) concentration was measured. The total extraction amount was no more than 5% of the stock ion solution. The extraction solution was filtered with 0.45 μm filter membrane and then diluted into a 25 mL volumetric flask. The amount of Cd(II) adsorbed on ZXCG was determined by the following equation:

\[
q_t = \frac{(C_0 - C_t) \times V}{M}
\]

where \( q_t \) (mg/g) is the amount of Cd(II) adsorbed on ZXCG at the extracting time \( t \) (0, 5, 10, 20, 40, 60, 80, 100, 120 min) and \( C_t \) is the Cd(II) concentration (mg/L) in the aqueous solution at the extracting time \( t \).

**RESULTS AND DISCUSSION**

**Effect of adsorbent dose on Cd(II) removal**

The relationship between the ZXCG dose and Cd(II) uptake indicated that the removal percentage of Cd(II) increases initially with the increasing ZXCG dose and then remains stable when the adsorbent dose was 0.2 g. This shows that the total active sites of 0.2 g ZXCG were completely occupied by Cd(II), and an extra increase of adsorbent would not improve the removal percentage greatly. The optimum ZXCG dose was therefore fixed at 0.2 g.

**Effect of pH on Cd(II) removal**

The effect of initial solution pH on Cd(II) removal was investigated and the results are illustrated in Figure 1. It can be found that the equilibrium amount of Cd(II) adsorbed onto ZXCG increased with an increase in pH value and reached the maximum when pH was 5. Beyond that point, \( q_e \) begins...
to decrease. The calculated precipitation pH of Cd(II) \((C_o = 100 \text{ mg/L})\) is 4.7, therefore, in the subsequent investigations, experiments were performed at a solution pH value of 4 to avoid possible hydroxide precipitation.

**Effect of initial Cd(II) concentration and contact time**

The effects of initial Cd(II) concentration and contact time on Cd(II) removal are displayed in Figure 2. It can be seen clearly that the adsorption rate is quite fast in the higher initial Cd(II) concentration. On the other hand, Cd(II) is absorbed onto ZXCG at the initial adsorption stage more quickly (almost at the beginning of the 30 min for all the concentration cases). This is because the larger difference between the Cd(II) content in the solution and that on the surface of ZXCG, the stronger drive force is achieved; as the adsorption goes on, more Cd(II) is adsorbed onto the ZXCG surface, so the drive force turns to be smaller, resulting in a stable stage.

**Adsorption isotherm**

To predict the adsorption mechanism and determine the maximum adsorption capacity, it is essential to investigate the adsorption isotherm. In the study, three linear isotherm models (Langmuir, Freundlich and Tempkin) were employed. The Langmuir model is suitable to describe the monolayer homogeneous process (Hameed 2009), while the Freundlich model is used to describe multiple adsorption processes that take place on a heterogeneous surface (Allen et al. 2004). The Tempkin model suggests that the adsorption heat of all the molecules in the layer would decrease linearly with coverage due to the interactions between the adsorbents (Thamilarasu & Karunakaran 2013). The linear forms of the Langmuir, Freundlich and Tempkin models are given as follows, respectively:

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

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

\[
q_e = \beta \ln \alpha + \beta \ln C_e
\]

where \(K_L, K_F\) and \(\beta\) are the Langmuir, Freundlich and Tempkin constants, respectively; \(q_m\) is the complete monolayer adsorption value; \(1/n\) is the adsorption intensity and \(\alpha\) is the equilibrium binding constant (L/mg).

Isotherm model parameters and correlation coefficients are shown in Table 1. According to the correlation coefficient values, the fitting outcome is Langmuir \((R^2 = 0.985) > \text{Tempkin} \ (R^2 = 0.937) > \text{Freundlich} \ (R^2 = 0.887)\). The correlation coefficient of the Langmuir model is greater than 0.95, showing that the Cd(II) adsorption process could best be described by this model, which can be clearly proved by
Figure 3. Based on the Langmuir equation, the maximum Cd(II) monolayer adsorption capacity is 38.61 mg/g. Comparisons of the Cd(II) maximum adsorption value reported in the literature (Tangjuank et al. 2003; El-Said et al. 2010; Kannan & Veemaraj 2010; Sen et al. 2010; Chen et al. 2013; Kalkan et al. 2013) are presented in Table 2. It can be found that the ZXCG showed a higher affinity to the cadmium over other adsorbents. This could be ascribed to the larger surface area and its microporous structure. Of course, the interaction between zeolite and water and ions in aqueous solution can cause a change in the crystal structure and porosity of zeolite (Zhu et al. 2010, 2013, 2017), which can influence the adsorption capacity of zeolite.

### Adsorption kinetics

For the certain Cd(II) concentration (100 mg/L) and ZXCG dose (0.2 g), contact time is essential since it reveals the adsorption kinetic. The Cd(II) adsorption rate was characterized by two different kinetics models (pseudo-first-order, pseudo-second-order) which can be expressed as follows.

The pseudo-first-order model

\[
\log \left( q_e - q_t \right) = \log q_e - \frac{K_1}{2.303} t
\]

The pseudo-second-order model

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} t
\]

where \( K_1 \) (min\(^{-1}\)) and \( K_2 \) (g/(mg min)) represent the pseudo-first order adsorption rate constant and the pseudo-second-order rate constant, respectively.

The values of the adsorption rate constant and correlation coefficient are listed in Table 3. Obviously, the

<table>
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<th>Isotherm model</th>
<th>Parameters</th>
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<tr>
<td>Langmuir</td>
<td>( K_L ) (L/mg)</td>
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<td>( q_m ) (mg/g)</td>
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pseudo-second-order plot seems to cover all the experimental data points while some points do not lie in the pseudo-first-order plot (Figure 4). Moreover, the correlation coefficients for the pseudo-second-order are much higher than that of the pseudo-first-order. Besides, the experimental $q_e$ for the pseudo-second-order model seems to highly agree with the calculated $q_e$, indicating that it is more suitable to describe the adsorption process. It also indicates that such an adsorption is controlled by chemisorption (Hameed 2009).

**Sorption mechanism**

Kinetic studies fail to figure out the diffusion mechanism and rate determining step, and thus the intra-particle diffusion model was chosen to be tested. The intra-particle diffusion model can be expressed as:

$$q_t = K_{id} t^{1/2} + C$$

where $K_{id}$ ((mg/g min$^{-1/2}$)) is the intra-particle diffusion rate constant, $q_t$, the amount of metal ions adsorbed at time $t$ and $C$ (mg/g), a constant proportional to the thickness of boundary layer (Ravichandran & Arivoli 2013).

The amounts of Cd(II) adsorbed versus $t^{1/2}$ for varied Cd(II) concentrations are displayed in Figure 5. It shows that the adsorption involved more than one model. Research (Khaled et al. 2013) found that there are four steps throughout an adsorption process: (1) bulk diffusion; (2) film diffusion; (3) pore diffusion or intra diffusion; and (4) surface adsorption. The first step could be ignored since the Cd(II) is enough and the adsorption rate stays high at the beginning. Figure 5 shows three stages while the second one is the gradual adsorption which controls the rate. Beyond that, in the third stage, namely the equilibrium process, diffusion remains low because of the relatively low Cd(II) concentration.

The values of $K_{id}$ and $C$, calculated from the second portion, are listed in Table 4. As can be seen from Figure 5, there is occasionally a linear region, but in not the whole process. Additionally, the plot does pass through the origin. It demonstrated that the intra diffusion was not the only control step and others may be involved.

**Stability studies**

Stability studies are useful to map out the adsorption nature and its recyclability. After the adsorption process,
ZXCG was separated and dried. Then it was employed to do repeated Cd(II) adsorption experiments three times. The results were then characterized with X-ray diffraction (XRD) and scanning electron microscopy (SEM). From Figure 6 it can be clearly observed that the structure of ZXCG remains undestroyed, even though the surface suffered corrosion (Figure 7) when compared with raw ZXCG. The research shows that coal gangue based zeolite NaX has a high stability, even when used several times.

**CONCLUSIONS**

The zeolite NaX synthesized from coal gangue is proved to be effective for Cd(II) adsorption from aqueous solutions. Batch adsorption data were fitted with Langmuir, Freundlich and Tempkin isotherm models and it turned out that the process could be best described by the Langmuir equation. The kinetic was well determined by a pseudo-second-order...
model which suggests that the adsorption was chemisorption controlled. According to the intra-particle diffusion model fitting result, the rate was not only controlled by the intra-particle diffusion step and some other step may have been involved. The maximum equilibrium adsorption capacity for Cd(II) was found to be 38.61 mg/g, indicating that zeolite NaX synthesized from coal gangue can be a promising green adsorbent for removing Cd(II) from aqueous solutions.

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AUTHOR DISCLOSURE STATEMENT

No competing financial interests exist.

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