Activated mineral adsorbent for the efficient removal of Pb(II) and Cd(II) from aqueous solution: adsorption performance and mechanism studies

Tao Zheng, Xiaohui Zhou, Jing Guo, Chubin Zhong and Yaochi Liu

ABSTRACT

Activated mineral adsorbent (AMA) was prepared via double salts (Na₂SO₄ and CaCO₃) heat treatment activation of solid-state potassium feldspar. Adsorption performance of AMA for Cd(II) and Pb(II) was investigated by batch mode and factors affecting adsorption including pH value, initial concentration of adsorbate, contact time, adsorbent dosage and temperature on adsorption performance for Cd(II) and Pb(II) were studied. The results indicated that the adsorption process was pH dependent, endothermic and spontaneous. When the adsorption process of Cd(II) and Pb(II) on AMA reached equilibrium, the maximum saturated adsorption capacities were 263.16 and 303.03 mg/g for Cd(II) and Pb(II) ions, respectively, showing higher adsorption removal efficiency. The Langmuir adsorption isotherm and pseudo second kinetic equation could well fit the adsorption process of Cd(II) and Pb(II) by AMA. Besides, Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques were also performed to further reveal the adsorption mechanism. The results indicated that ion exchange, precipitation and adsorption played an important role in adsorption process. From the investigation, it was concluded that AMA was an excellent adsorbent with the advantages of environment-friendly, inexpensive, facile preparation and higher adsorption capacity of toxic Cd(II) and Pb(II) ions.

Key words | activated mineral adsorbent, adsorption mechanism, Cd(II), Pb(II)

HIGHLIGHTS

- An activated mineral adsorbent (AMA) was prepared via double salts heat treatment activation of a solid-state potassium feldspar.
- The maximum saturated adsorption capacities were 263.16 and 303.03 mg/g for Cd(II) and Pb(II) ions, respectively.

GRAPHICAL ABSTRACT
INTRODUCTION

With the rapid development of modern industry, heavy metals have caught extensive attention due to their toxicity, carcinogenicity, and non-biocompatibility in aqueous solution (Tan et al. 2012). Unfortunately, they can be accumulated in organisms through the food chain and eventually cause a tremendous threat to human health (Ozay et al. 2009; Hu et al. 2011; Yan et al. 2012). Among the heavy metals, Pb and Cd are nonessential elements for living organisms and could lead to a long-term risk to ecological and human health even in parts per billion (ppb or μg/L) (Agrafioti et al. 2014; Christou et al. 2017; Xiao et al. 2017). They are usually found in wastewater from industrial activities including mining, metal smelting, leather tanning, electroplating, and petrochemical production (Parab et al. 2010). A survey of the concentration of heavy metals in wastewater, which is the majority of industrial wastewater and groundwater pollution, indicated that the concentration of Pb and Cd was approximately 50–200 mg/L (Yang et al. 2014). The World Health Organization (WHO) recommended guidelines for drinking water are 0.05 mg/L for Pb and 0.005 mg/L for Cd, respectively. The urgent problem motivates the scientific community to study various methods to remove Pb and Cd from wastewater in efficient and economically practicable approaches.

So far, various methods, such as ion exchange (Mahmoud & Hoadley 2012), chemical precipitation (Ali et al. 2013), filtration (Cotte et al. 2015), electrochemical deposition (Venkatasubramanian et al. 2011), membrane separation (Cheng et al. 2010; Gao et al. 2014), and flotation (Mahmoud et al. 2015; Taseidifar et al. 2017) have been investigated for heavy metals removal from wastewater. However, many of these strategies present several disadvantages, such as high cost, high reagent and energy requirements, generation of a large amount of sludge and secondary pollution (Fu & Wang 2011; Purkayastha et al. 2014). Compared with other methods, adsorption, particularly using low-cost absorbents, has been considered to be the promising one because of its simple operation, economic efficiency and low cost (He et al. 2016a, 2016b, 2017a). That being the case, an adsorbent with excellent adsorption performance has a significant role in the adsorption method. Moreover, as the environmental safety of new materials has been paid more and more attention, environmentally friendly adsorbent has become the mainstream (Zhao et al. 2015; Lessa et al. 2018).

Clay minerals have been recognized as the materials of ‘greening the 21st century material world’ owing to possessing excellent physicochemical properties such as environmental friendliness, biocompatibility, biodegradability and lamellar structure (Zarghami et al. 2016). Many publications have focused on the adsorption performance of secondary clay minerals, such as bentonite, biotite, chlorite, montmorillonite, leenilite and kaolinite, which are mainly the transitional weathering product of the primary clay minerals (Soratto & Cruscio 2008; Al-Jabri 2010; Khan et al. 2012; Mangwandi et al. 2014; Abad-Valle et al. 2016; Harja et al. 2016), while primary clay minerals have seldom been studied. Due to the primary clay minerals being rich in reserves and cheap, they are naturally more available than secondary clay minerals. Besides, China is abundant in primary clay mineral resources, which can provide vast mineral materials for the remediation of heavy metal pollution. Potassium feldspar, a primary clay mineral, has a curved double chain structure connected by Si-O tetrahedron and Al-O tetrahedron, which is extremely stable (Guo et al. 2015). The application of potassium feldspar is limited due to its inherent structure. Therefore, some modification methods should be taken to improve the porous structure and adsorption capacity of potassium feldspar. It is reported that common modification methods including heat treatment, hydrothermal method, organic modification, inorganic pillared, acid treatment, polymer intercalation and complex modification have been applied to modify the primary clay minerals. Cao et al. (2004) modified the sepiolite by heat treatment and acid treatment. It was found that the specific surface area, ion exchange capacity and adsorption performance of modified sepiolite were highly improved.

In previous studies, researchers commonly chose one kind of additives heat treatment, and the adsorption performance of modified clay mineral is limited. The double salts heat treatment is adopted to modify to activate the K and Si in potassium feldspar, which contributes to improving its structure and adsorption performance. Na₂SO₄ and CaCO₃ are selected as double salts. Na₂SO₄ with a low melting point (884 °C) is used as a co-solvent to lower the melting temperature of the system, which can break the stable structure of Si-Al-O bond in potassium feldspar (Kumar et al. 2018). At the same time, the structure of potassium feldspar is changed from order to disorder. With the goal of enhancing homeomorphism, CaCO₃ is selected to enhance the activity of K, Al and Si in potassium feldspar, which can make it more prone to ion exchange, substitution
and replacement and increase its replacement capacity. Moreover, the melting point of CaCO₃ and potassium feldspar is 1,300 °C. In order to make CaCO₃ fully melt activated potassium feldspar in the melting state and give consideration to energy saving, this paper selected the roasting temperature at 1,300 °C and the roasting time at 1 h (Zhu 2003; Han & Cao 2004).

In this study, an activated mineral adsorbent (AMA) was prepared via double salts (Na₂SO₄ and CaCO₃) heat treatment activation and applied to the Cd(II) and Pb(II) removal. The effect of adsorbent dosage, initial pH value, initial concentration of metal ions, adsorption temperature and contact time on the adsorption efficiency of AMA was investigated by batch experiments. Adsorption kinetics, isotherm and thermodynamics were also studied in detail. In addition, the interaction mechanism of Cd(II) and Pb(II) with AMA was also systematically studied.

MATERIALS AND METHODS

Chemicals and reagents

The potassium feldspar (SiO₂:67wt%) was obtained from Tonghua, Jilin province, China. After grinding and sieving with 100-mesh, the potassium feldspar was oven-dried at 80 °C before use. Na₂SO₄, CaCO₃, Cd(NO₃)₂·4H₂O, Pb(NO₃)₂, HNO₃, HCl, NaOH and other chemicals were purchased from Honghua Reagent Co. Ltd (Changsha, China). All chemicals and reagents were analytical grade except for HNO₃, which was guaranteed grade. The standard stock solutions of Cd(II) and Pb(II) (500 mg/L) were prepared by dissolving Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ in distilled water. Initial concentrations of heavy metals for adsorption were prepared by diluting the standard stock solution. The initial pH of heavy metal solution was adjusted with 0.01M HCl or NaOH as required.

Preparation of AMA

To prepare the AMA with different Ca/Si molar ratios of potassium feldspar, calcium carbonate and sodium sulfate were accurately weighed. Then the mixtures were evenly mixed and calcinated for 1 h at different temperatures in a muffle furnace. Finally, the resultant products were cooled down to room temperature and stored in polyethylene bags. The specific weighing quality of feldspar, calcium carbonate and sodium sulfate and calcination conditions are shown in Table 1.

Characterization of AMA

The surface morphologies of AMA before and after Cd(II) and Pb(II) adsorption were carried out on the scanning electron microscopy (SEM) measurement (JSM-6360LV, Japan). The specific surface area of AMA was determined by N₂ adsorption/desorption isotherm at 77 K on a surface area

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The specific weighing quality of feldspar, calcium carbonate and sodium sulfate and calcination conditions of activated mineral adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Potassium feldspar (g)</td>
</tr>
<tr>
<td>AMA-1</td>
<td>100</td>
</tr>
<tr>
<td>AMA-2</td>
<td>100</td>
</tr>
<tr>
<td>AMA-3</td>
<td>100</td>
</tr>
<tr>
<td>AMA-4</td>
<td>100</td>
</tr>
<tr>
<td>AMA-5</td>
<td>100</td>
</tr>
<tr>
<td>AMA-6</td>
<td>100</td>
</tr>
<tr>
<td>AMA-7</td>
<td>100</td>
</tr>
<tr>
<td>AMA-8</td>
<td>100</td>
</tr>
<tr>
<td>AMA-9</td>
<td>100</td>
</tr>
<tr>
<td>AMA-10</td>
<td>100</td>
</tr>
<tr>
<td>AMA-11</td>
<td>100</td>
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<tr>
<td>AMA-12</td>
<td>100</td>
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<tr>
<td>AMA-13</td>
<td>100</td>
</tr>
<tr>
<td>AMA-14</td>
<td>100</td>
</tr>
<tr>
<td>AMA-15</td>
<td>100</td>
</tr>
</tbody>
</table>

Where Ca/Si is the molar ratio of calcium in calcium carbonate to silicon in potash feldspar.
and porosity analyzer (Gemini VII 2390, USA). Particle size of AMA was measured by laser particle size analyzer (Mastersizer 3000E, UK). The functional groups of AMA before and after Cd(II) and Pb(II) adsorption were determined by Fourier transform infrared (FT-IR) spectroscopy (Nicolet 6700, USA) in the range of 4,000–400 cm\(^{-1}\) using the KBr pellet technique. The surface chemical composition and binding energy change of AMA before and after Cd(II) and Pb(II) adsorption were determined by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, USA). The crystal structure of AMA before and after Cd(II) and Pb(II) adsorption was analyzed by X-ray diffraction (XRD) analysis using an automated diffractometer (Bruker D8 Venture, Germany) with monochromatic Cu K\(\alpha\) radiation and the wavelength of 1.5406 Å. The Zeta potential of AMA was measured at different pH using a Zeta potential analyzer (JS94H, China).

**Batch adsorption experiments**

Accurately weighed 0.02 g AMA was added into 50 mL Erlenmeyer flask with 40 mL of Cd(II) or Pb(II) solution in batch adsorption experiments. The flasks were shaken in a temperature-controlled shaker (SHA-B, China) with shaking speed of 130 rpm for 16 h until the adsorption equilibrium was reached. The residual concentration of Cd(II) or Pb(II) was determined by the atomic absorption spectrometer (361MC, China).

The effect of adsorbent dosage on the adsorption capacity and removal efficiency of AMA was studied at adsorbent dosage from 0.25 g/L to 2.0 g/L. The effect of initial solution pH was investigated in the range of 2–8 for Cd(II) and Pb(II). The adsorption kinetic experiments were studied from 5 to 120 min for Cd(II) and Pb(II) solutions. The adsorption isotherm experiments of Cd(II) and Pb(II) were conducted with initial Cd(II) and Pb(II) concentrations varying from 25 to 300 mg/L. The adsorption thermodynamic experiments of Cd(II) and Pb(II) were carried out at four different temperatures, including 288, 298, 308 and 318 K. The adsorption capacity and removal efficiency of Cd(II) or Pb(II) on the AMA were calculated by the following equations.

\[
Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)
\]

\[
E\% = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)
\]

where \(C_0\) and \(C_e\) (mg/L) are the initial and equilibrium concentration of metal ions, respectively. \(V\) (L) is the volume of adsorbate solution and \(m\) is the mass of the AMA.

**RESULTS AND DISCUSSION**

Different adsorbents on Cd(II) and Pb(II) removal

0.02 g AMA prepared at different calcination conditions was added to 40 mL Cd(II) or Pb(II) solutions (100 mg/L) to compare with the adsorption capacity of different AMA. The adsorption capacities of Cd(II) or Pb(II) on different AMA are displayed in Figure 1. At the Ca/Si molar ratio of 1.8, the AMA-2, AMA-5 and AMA-8 showed higher adsorption capacity toward Cd(II) than other AMA. It can be obviously observed that the AMA-5 showed the highest adsorption capacity toward both Cd(II) and Pb(II). Therefore, the AMA-5 was chosen for the characterization analysis and adsorption study.

**Characterization of AMA**

The morphological and structural properties of the materials were investigated by SEM. Potassium feldspar (Figure 2) is a complete particle with large particle size and smooth surface. Figure 3 shows the AMA has a porous lamellar structure with a small pore diameter. More channels inside the AMA might be opened due to the double salts heat treatment activation in the preparation process, which increased the specific surface area and pore volume.
of the clay mineral. Besides, with the increase of calcination temperature and Ca/Si molar ratio, the size of the clay mineral was more uniformly distributed.

The physicochemical properties of potassium feldspar and AMA are also listed in Table 2. Potassium feldspar has an average particle size of about 68.3 μm. With the increase of calcination temperature, the average particle size of AMA turns to smaller size. So, the dispersion of AMA was enhanced and it is easier to spread, which is beneficial to adsorption. It was found that Brunauer-Emmett-Teller (BET) surface area and average pore diameter of potassium feldspar was 2.29 m²/g and 11.54 nm, respectively. BET surface area and pore diameter of AMA were all more than that of potassium feldspar. Among them, AMA-5 presented the highest surface area (12.77 m²/g) and biggest pore diameter (14.97 nm). This may be due to the thermal activation of potassium feldspar, which opened up some small closed pores and produced CO₂ from carbonate decomposition, causing AMA to form a porous structure \cite{Murnandari et al. 2017}. High surface area and elevated values of pore diameter for AMA are an excellent indicator that the adsorbent will be efficient for the removal of Cd(II) and Pb(II).

Table 2 | The physicochemical characteristics of potassium feldspar and AMA

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Average particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium feldspar</td>
<td>2.29</td>
<td>11.54</td>
<td>68.3</td>
</tr>
<tr>
<td>AMA-1</td>
<td>7.12</td>
<td>11.72</td>
<td>19.4</td>
</tr>
<tr>
<td>AMA-2</td>
<td>10.25</td>
<td>12.21</td>
<td>19.8</td>
</tr>
<tr>
<td>AMA-3</td>
<td>7.32</td>
<td>10.33</td>
<td>19.2</td>
</tr>
<tr>
<td>AMA-4</td>
<td>7.23</td>
<td>10.51</td>
<td>18.5</td>
</tr>
<tr>
<td>AMA-5</td>
<td>12.77</td>
<td>14.97</td>
<td>18.8</td>
</tr>
<tr>
<td>AMA-6</td>
<td>8.27</td>
<td>10.89</td>
<td>18.4</td>
</tr>
<tr>
<td>AMA-7</td>
<td>8.25</td>
<td>10.11</td>
<td>17.3</td>
</tr>
<tr>
<td>AMA-8</td>
<td>9.56</td>
<td>11.75</td>
<td>17.7</td>
</tr>
<tr>
<td>AMA-9</td>
<td>7.83</td>
<td>10.88</td>
<td>17.6</td>
</tr>
</tbody>
</table>

Figure 2 | The SEM images of the potassium feldspar.

Figure 3 | The SEM images of (a) AMA-1, (b) AMA-2, (c) AMA-3, (d) AMA-4, (e) AMA-5, (f) AMA-6, (g) AMA-7, (h) AMA-8 and (i) AMA-9.
Adsorption study

The effect of adsorbent dosage on Cd(II) and Pb(II) adsorption

The adsorbent dosage is an important parameter which influences removal of metal ions from aqueous solution; thus, different amounts of AMA-5 were added individually to 40 mL Cd(II) or Pb(II) solutions (100 mg/L). Figure 4 displays the effect of AMA-5 dosage in the range of 0.25 to 2.0 g/L on the adsorption capacity and removal efficiency of Cd(II) or Pb(II). The adsorption capacity diminished with the increase of adsorbent dosage, while the removal efficiency presented the opposite tendency, which might be due to more quantity of the adsorption active sites at higher adsorbent dosage. When the equilibrium state was reached, the removal efficiency would not see any significant change even with the continuously rising adsorbent dosage. Meanwhile, the removal efficiency reached 99.87% and 99.64% for Cd(II) and Pb(II), respectively.

The effect of initial solution pH on Cd(II) and Pb(II) adsorption

The effects of initial pH are on not only the species of heavy metal ions but also the surface charge of the adsorbent. Figure 5(a) shows the adsorption capacity of Cd(II) and Pb(II) on AMA-5 at solution pH of 2–8. It was obvious that the adsorption capacity of Cd(II) and Pb(II) on AMA-5 increased as the pH increased, and eventually reached equilibrium. The influence of pH on Cd(II) and Pb(II) removal was due to the electrostatic interaction and distribution of metal ions species (Yang et al. 2017). At low pH, H⁺ can compete with the positive metal ions on the AMA-5 surface sites resulting in low adsorption efficiency. With the pH value increased, the competitive adsorption was weakened for the decrease of H⁺ and the electrostatic between AMA-5 and Cd(II) and Pb(II) was enhanced, thus improving the adsorption capacity of Cd(II) and Pb(II) in acid conditions (Yan et al. 2014). However, as the pH value increased to weak basic conditions, Cd and Pb species were changed with the pH of the solution. The distribution of Cd and Pb species as a function of pH at 100 mg/L was calculated by Visual MINTED and is depicted in Figure 5(b) and 5(c).

For the distribution of Cd species in Figure 5(b), at pH <6, the predominant species was Cd²⁺. At pH 6–12, the main species were Cd(OH)⁺, Cd₂(OH)₃⁺ and Cd(OH)₂. At pH >12, the main cadmium species that existed were Cd(OH)₃ and Cd(OH)₂⁻. The precipitation constant of Cd(OH)₂(s) was 2.5 × 10⁻¹⁴ (298 K) and Cd began to form precipitation at pH 8.42. For the distribution of Pb species in Figure 5(c), at pH <6, the predominant species was Pb²⁺. The main species at pH 7–12 were Pb(OH)⁺, Pb(OH)₂, Pb₂(OH)₃, Pb₃(OH)₄²⁻ and Pb₄(OH)₄⁴⁻. At pH range of 12–14, the lead species existing was Pb(OH)₃. The precipitation constant of Pb(OH)₂(s) was 1.2 × 10⁻¹⁵ (298 K) and Pb began to form precipitation at pH 8.20 (Xu et al. 2008). The formation of hydroxide complexes of Cd(II) and Pb(II) could affect the adsorbent effectiveness. Therefore, the solution pH was maintained at 7.0 in all the following experiments to ensure the optimum adsorption property as well as to avoid the precipitation of Cd(II) and Pb(II).
The effect of contact time and adsorption kinetics

The effect of contact time was studied to evaluate the adsorption behavior of Cd(II) and Pb(II) on AMA-5 and the results are presented in Figure 6(a). A rapid adsorption rate was observed for Cd(II) and Pb(II) in the first 2 h due to a large number of available adsorption sites on AMA-5 surfaces. The adsorption equilibrium was achieved after reaction for 7 h. The adsorption capacity by AMA-5 was in order of Pb(II) > Cd(II), which indicated that in a single heavy metal system, AMA-5 showed higher removal efficiency of Pb(II) with adsorption capacity of 196.9 mg/g at the initial Pb(II) concentration of 100 mg/L, while a lower removal efficiency of Cd(II) was obtained with adsorption capacity of 186.3 mg/g.

Adsorption kinetics is commonly applied to estimate the adsorption rate and offer some valuable information about the adsorption process. Hence, the experimental adsorption kinetic data were analyzed by using the pseudo-first-order and pseudo-second-order model. The equation of the pseudo-first-order model is given as follows (Lagergren 1898):

\[ \ln\left(\frac{Q_e}{Q_t} - \frac{Q_e}{Q_e}\right) = \ln Q_e - k_1t \]  

(3)

By contrast, the pseudo-second-order model is represented by the following (Ho & McKay 1999):

\[ \frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t \]  

(4)

where \( Q_t \) (mg/g) is the adsorption capacity at time t(min), \( Q_e \) is the adsorption capacity at equilibrium and \( k_1 \) (1/min) and \( k_2 \) (g/(mg·min)) are the pseudo-first-order and pseudo-second-order kinetic constant, respectively. The linear fitting curves are displayed in Figure 6(b) and 6(c) and the relevant fitting parameters are listed in Table 3.
pseudo-second-order were 0.9983 and 0.9982, respectively, which were much higher than those of pseudo-first-order. Moreover, the $Q_e$ calculated from pseudo-second-order showed a good agreement with the experimental $Q_e$ values, which illustrated that the adsorption process favored a pseudo-second-order process.

To better understand the adsorption rate controlling steps, the Weber Morris intraparticle diffusion model was used to fit the experimental data (Chabani et al. 2017; Chaari et al. 2015). The intra-particle diffusion model is expressed by the following equation.

$$Q_t = k_{pi}t^{1/2} + C_i$$  \hspace{1cm} (5)

where $k_{pi}$ is the rate constant and $C_i$ is the constant obtained from the intercept and reflects the thickness of the boundary layer. In general, the larger the intercept, the thicker the boundary layer effect.

The fitting curves of intra-particle diffusion model are depicted in Figure 6(d) and the relevant fitting parameters are listed in Table 4. The plots obtained from the adsorption kinetic data did not yield a straight line, which suggested that the intra-particle diffusion was not the only rate-controlling step. The fitting curves exhibited three distinct regions. The first linear region could be attributed to the transport of the heavy metals from the solution to the surface of AMA-5, which was related to boundary layer diffusion. The second linear region was the gradual adsorption

**Table 3** | Constant and correlation coefficients for the kinetic model of Cd(II) and Pb(II) on AMA-5

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>$Q_e,exp$ (mg/g)</th>
<th>$k_1$ (1/min)</th>
<th>$Q_e,cal$ (mg/g)</th>
<th>$R^2$</th>
<th>$k_2 \times 10^{-4}$ (g/mg·min)</th>
<th>$Q_e,cal$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>186.37</td>
<td>0.0069</td>
<td>115.32</td>
<td>0.9890</td>
<td>1.4003</td>
<td>192.31</td>
<td>0.9983</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>196.97</td>
<td>0.0096</td>
<td>144.07</td>
<td>0.9843</td>
<td>1.5610</td>
<td>200.00</td>
<td>0.9982</td>
</tr>
</tbody>
</table>
step and the intra-particle diffusion was the rate-control step. The third linear region was ascribed to the final adsorption equilibrium where a very low concentration of heavy metals remained in the solution. Therefore, the adsorption of Cd(II)/Pb(II) on AMA-5 was controlled by both boundary layer diffusion and intra-particle diffusion.

**The effect of initial adsorbate concentration and adsorption isotherm**

The effect of initial concentration on Cd(II) and Pb(II) on AMA-5 is depicted in Figure 7. It can be observed that in the same adsorption temperature, the adsorbent capacity of AMA-5 for Cd(II) and Pb(II) increases with increasing initial concentration as the concentrations of heavy metal ions were less than 100 mg/L. Once beyond 100 mg/L, the increase of equilibrium adsorption capacity slowed down. The adsorption capacity of AMA-5 for Cd(II) and Pb(II) also increased with adsorption temperature, implying the adsorption was an endothermic reaction and higher adsorption temperature would benefit the adsorption process.

In order to understand the adsorption mechanism, two commonly used adsorption isotherm models named Langmuir and Freundlich were used in this study for adsorption isotherm data analysis. The Langmuir isotherm model proposes monolayer adsorption on a homogeneous surface and the adsorbates have no interaction with each other, which can be expressed as follows (Farghali et al. 2013):

\[
\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}
\]

(6)

The Freundlich isotherm model assumes multilayer adsorption with a heterogeneous distribution of active sites, which could be represented as follows (Ho & McKay 1999):

\[
\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

(7)

where \(Q_e\) (mg/g) and \(Q_m\) (mg/g) are the equilibrium adsorption ability and the maximum adsorption capacity, respectively, \(K_L\) is the Langmuir constant and \(K_F\) and \(n\) are the Freundlich constant related to the adsorption capacity and intensity, respectively.

The fitting plots of Langmuir and Freundlich isotherm models are presented in Figure 9 and the related fitting parameters are listed in Table 5. As shown in Figure 8, the experimental adsorption data of Cd(II) and Pb(II) on AMA-5 fitted well with the Langmuir adsorption model.

**Table 4 | Intra-particle diffusion model parameters of adsorption Cd(II) and Pb(II) on AMA-5**

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Film diffusion</th>
<th></th>
<th>Intra-particle diffusion</th>
<th></th>
<th>Equilibrium stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(k_{p1})</td>
<td>(c_1)</td>
<td>(R^2)</td>
<td>(k_{p2})</td>
<td>(c_2)</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>9.758</td>
<td>35.68</td>
<td>0.9773</td>
<td>5.085</td>
<td>84.34</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>9.846</td>
<td>48.50</td>
<td>0.9793</td>
<td>5.045</td>
<td>98.097</td>
</tr>
</tbody>
</table>

![Figure 7](http://iwaponline.com/wst/article-pdf/82/9/1896/781412/wst082091896.pdf)
and the plots showed quite good linearity. The correlation coefficients \( R^2 \) of Langmuir model were much larger than that of Freundlich model, which indicated that the Langmuir model was more suitable for describing the adsorption of Cd(II) and Pb(II) on AMA-5. The maximum adsorption capacities calculated by Langmuir model were 263.16 mg/g for Cd(II) and 303.03 mg/g for Pb(II) at 318 K.

Based on the Langmuir adsorption isotherm model, a dimensionless separation constant \( R_L \) could be applied to determine the favorability of the adsorption process, which is expressed as the following equation:

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

\( (8) \)
where $C_0$ (mg/L) is the initial concentration of adsorbate and $b$ (L/mg) is the Langmuir constant. The value of $R_L$ ranges from 0 to 1, which indicates the adsorption process is favorable, once the value of $R_L$ is greater than 1, implying the unfavorability of the adsorption process. In this study, the $R_L$ values were calculated to be $0.0232 - 0.2221$, $0.0198 - 0.1948$, $0.0138 - 0.1438$ and $0.0102 - 0.1105$ for Cd(II) and $0.0104 - 0.1115$, $0.0082 - 0.0904$, $0.0059 - 0.0670$ and $0.0045 - 0.0517$ for Pb(II) with initial concentration ranging from 25 - 300 mg/L at 288, 298, 308, and 318 K, demonstrating that favorable process of AMA-5 for Cd(II) and Pb(II).

The removal capacities of AMA-5 for Cd(II) and Pb(II) were compared with other presented adsorbents to illustrate the excellent adsorption performance of AMA-5 (Table 6). It can be seen that AMA-5 could efficiently remove Cd(II) and Pb(II) compared with other adsorbents published in the previous literature.

### The effect of adsorption temperatures and adsorption thermodynamics

The effect of adsorption temperature on the adsorption of Cd(II) and Pb(II) on AMA-5 is shown in Figure 9. It can be obviously observed that the adsorption capacity of Cd(II) and Pb(II) on AMA-5 increased with the increasing of adsorption temperature. To investigate whether the adsorption process of Cd(II) and Pb(II) on AMA-5 was endothermic or exothermic, spontaneous or nonspontaneous, the thermodynamic parameters including standard free energy change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$) and standard entropy change ($\Delta S^0$) were calculated from the following equations (Ghosh & Bhattacharyya 2002):

$$K_d = \frac{Q_e}{C_e}$$  
(9)

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  
(10)

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$  
(11)

where $R$ (8.314 J/mol·K) is the universal gas constant and $T$ is the adsorption temperature in Kelvin; $K_d$ is the distribution coefficient. The linear regression of $\ln K_d$ versus $1/T$ for adsorption of Cd(II) and Pb(II) on AMA-5 at 288, 298, 308, and 318 K are given in Figure 10. By fitting each linear regression, we could calculate the value of $\Delta S^0$ and $\Delta H^0$ as shown in Table 7. The positive $\Delta H^0$ values suggested that the adsorption of Cd(II) and Pb(II) on AMA-5 was endothermic in nature. The negative $\Delta G^0$ values suggested that the adsorption of Cd(II) and Pb(II) on AMA-5 was feasible and spontaneous and higher adsorption temperature was beneficial for adsorption of Cd(II) and Pb(II) (Xie et al. 2015). The $\Delta S^0$ values indicated the increased randomness at the solid–solution interface (Yu et al. 2015).

### Adsorption mechanism

In order to explore the mechanisms of metal sorption by AMA, FT-IR, XRD and XPS analysis were performed. The FT-IR spectra were recorded and the results are shown

---

**Table 6 | Comparison of the maximum adsorption capacity of Cd(II) and Pb(II) on AMA with various adsorbents published in literature**

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$Q_m$(mg/g) Cd(II)</th>
<th>$Q_m$(mg/g) Pb(II)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan coated cotton fibers</td>
<td>14.14</td>
<td>86.09</td>
<td>Zhang et al. (2008)</td>
</tr>
<tr>
<td>Magnetic graphene oxide/LDH</td>
<td>45.05</td>
<td>192.31</td>
<td>Huang et al. (2008)</td>
</tr>
<tr>
<td>Activated carbon-chitosan complex (2:1)</td>
<td>69.4</td>
<td>125.4</td>
<td>Ge &amp; Fan (2011)</td>
</tr>
<tr>
<td>Fe₃O₄/cyclodextrin</td>
<td>27.7</td>
<td>64.5</td>
<td>Badruddoza et al. (2013)</td>
</tr>
<tr>
<td>P-MCS</td>
<td>71.53</td>
<td>151.06</td>
<td>Zhao et al. (2017)</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>15.70</td>
<td>21.80</td>
<td>Rao et al. (2009)</td>
</tr>
<tr>
<td>β-CD polymer</td>
<td>163.20</td>
<td>215.20</td>
<td>He et al. (2017b)</td>
</tr>
<tr>
<td>potash feldspar</td>
<td>10.56</td>
<td>12.34</td>
<td>Saha et al. (2009)</td>
</tr>
<tr>
<td>AMA-5</td>
<td>243.90</td>
<td>294.18</td>
<td>This study</td>
</tr>
</tbody>
</table>
in Figure 10. The relatively intense and broad peaks at around 3,457 cm$^{-1}$ corresponded to the $\text{-OH}$ stretching bond, whereas the peak at 3,664 cm$^{-1}$ was attributed to the intermolecular hydrogen $\text{-OH}$ stretching bond. The peaks at 1,409 cm$^{-1}$ and 1,460 cm$^{-1}$ were assigned to the symmetric and asymmetric vibrations of carboxylic bonds, respectively. The strong absorbance peak appeared at 1,648 cm$^{-1}$ owing to the stretching vibration of $\text{C=O}$. The peaks at 607 cm$^{-1}$ were the bending vibration of $\text{Si-O}$. The absorbance peaks at 983 cm$^{-1}$ and 507 cm$^{-1}$ were ascribed to the stretching vibration and bending vibration of $\text{Al-O}$, respectively. The carboxylate could donate the $\text{H}^+$ and $\text{OH}^-$ due to the presence of carboxyl and hydroxyl groups, and ligands were formed between metal ions and carboxylic groups by substituting $\text{H}^+$ with metal ions; the bands of carboxyl groups shift when adsorption was over. Moreover, the $\text{-OH}$ bond and $\text{Si-O-Si}$ bond disappeared after adsorption, which indicated the involvement in metal adsorption. These changes revealed that the carboxyl, $\text{-OH}$ and $\text{Si-O-Si}$ are involved in formation of bonds with heavy metal ions.

The XRD patterns of AMA-5 before and after adsorption of Cd(II) or Pb(II) are shown in Figure 11(a) and 11(b). The characteristic peaks of calcium silicate lead occurred, suggesting that it was the predominant lead silicate generated after adsorption of Pb by AMA-5. Cadmium silicate was also found in the residual AMA-5 solids after Cd adsorption. The XPS spectra of AMA-5 and Cd(II) or Pb(II) loaded AMA-5 are shown in Figure 12. The XPS spectra showed that the main peaks corresponding to $\text{O 1s}$, $\text{Ca 2p}$, $\text{C 1s}$, and $\text{Si 2p}$ were around 529.8, 346.3, 285.3, and 102.7 eV, respectively. It can be seen that Cd(II) or Pb(II) loaded AMA-5 showed new strong peaks compared with AMA-5 spectra, thanks to Cd 3d peaks (Figure 12(b)) and Pb 4f (Figure 12(c)). The binding energies of 405.51, 412.03, 138.56 and 143.38 eV were assigned to Cd 3d$_{5/2}$, Cd 3d$_{3/2}$, Pb 4f$_{7/2}$ and Pb 4f$_{5/2}$, respectively, indicating that Cd and Pb had been adsorbed on the AMA-5 surface. Therefore,

| Table 7 | Thermodynamics parameters for adsorption of Cd(II) and Pb(II) on AMA-5 |
|----------------|------------------|------------------|------------------|
| Heavy metal | T (K) | $\Delta G^o$ (kJ/mol) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol) |
| Cd(II) | 288 | −6.67 | 27.36 | 118.15 |
| 298 | −7.85 |
| 308 | −9.03 |
| 318 | −10.21 |
| 288 | −7.81 |
| Pb(II) | 298 | −9.63 | 44.44 | 181.44 |
| 308 | −11.44 |
| 318 | −13.25 |

in Figure 10. The relatively intense and broad peaks at around 3,457 cm$^{-1}$ corresponded to the $\text{-OH}$ stretching bond, whereas the peak at 3,664 cm$^{-1}$ was attributed to the intermolecular hydrogen $\text{-OH}$ stretching bond. The peaks at 1,409 cm$^{-1}$ and 1,460 cm$^{-1}$ were assigned to the symmetric and asymmetric vibrations of carboxylic bonds, respectively. The strong absorbance peak appeared at 1,648 cm$^{-1}$ owing to the stretching vibration of $\text{C=O}$. The peaks at 607 cm$^{-1}$ were the bending vibration of $\text{Si-O}$. The absorbance peaks at 983 cm$^{-1}$ and 507 cm$^{-1}$ were ascribed to the stretching vibration and bending vibration of $\text{Al-O}$, respectively. The carboxylate could donate the $\text{H}^+$ and $\text{OH}^-$ due to the presence of carboxyl and hydroxyl groups, and ligands were formed between metal ions and carboxylic groups by substituting $\text{H}^+$ with metal ions; the bands of carboxyl groups shift when adsorption was over. Moreover, the $\text{-OH}$ bond and $\text{Si-O-Si}$ bond disappeared after adsorption, which indicated the involvement in metal adsorption. These changes revealed that the carboxyl, $\text{-OH}$ and $\text{Si-O-Si}$ are involved in formation of bonds with heavy metal ions.

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the component elements analyzed by the XPS spectrum were consistent with the XRD survey.

Based on the results obtained in the above investigation, the high adsorption capacity of Cd(II) and Pb(II) on AMA can be summarized as follows:

After activation, a mass of the potassium ions could be removed and replaced by exchangeable calcium ions, meanwhile has a large specific surface area. Therefore, AMA shows strong ion exchange ability to remove Cd^{2+} and Pb^{2+}, which usually occurs in the surface, interlamellar domain and pore channels of AMA, and can be represented by the following equation:

\[(AMA)Ca^{2+} + Me^{2+} \rightarrow (AMA)Me^{2+} + Ca^{2+}\]  (12)

As the main components of AMA, Ca_{2}A1_{2}Si_{7} and 2CaO·SiO_{2} are partially hydrolyzed after entering aqueous solution, and the reactions in Equations (13) and (14) promote the increase of OH\(^{-}\) in aqueous solution. Meanwhile, insoluble compounds such as aluminosilicate of cadmium/lead or hydroxide precipitated.

\[
Ca_{2}Al_{2}Si_{7} + 5H_{2}O \rightarrow SiO_{2} + 2Al(OH)_{3} + 2Ca^{2+} + 4OH^{-} \]  (13)

\[
2CaO \cdot SiO_{2} + 2H_{2}O \rightarrow 2Ca^{2+} + H_{4}SiO_{4} + 4OH^{-} \]  (14)

Me^{2+} + 2OH^{-} \rightarrow Me(OH)_{2}  \]  (15)

2Me^{2+} + SiO_{2}^{2-} \rightarrow Me_{2}SiO_{4}  \]  (16)

Cd^{2+} and Pb^{2+}, on the other hand, cannot exist in the pH < 4.0 (Duan & Su 2014). While the AMA in acidic conditions still showed a greater Cd^{2+} and Pb^{2+} removal ability, suggesting that AMA in acid environment conditions showed strong chemical adsorption, the adsorption process

Figure 12 | XPS wide scan showing surface elemental composition of AMA-5, Cd-AMA-5 and Pb-AMA-5 (a), high-resolution XPS spectra of Cd 3d (b) and Pb 4f (c) of AMA-5 after Cd^{2+} or Pb^{2+} adsorption.
is as follows:

\[ >\text{Si} - \text{OH} \ldots \text{H} - \text{O} - \text{H}[\text{Me}(\text{OH})_2]^{2+} \]
\[ \rightarrow >\text{Si} - \text{O} - \text{Me} + \text{H}_2\text{O}^+ \]  \hspace{1cm} (17)

This process is mainly attributed to the surface of AMA silanol sites (≡Si-OH) and aluminols (≡Al-OH) deionization (Arancibia-Miranda et al. 2014). In a word, removal of metal ions by AMA occurs mainly by cation exchange mechanism, followed by precipitation and adsorption.

**CONCLUSION**

In this work, AMA (at Ca/Si molar ratio of 1.8) was synthesized successfully via heat treatment at 1,300 °C, it contains potassium feldspar, Na2SO4 and CaCO3, which was a new efficient adsorbent for the removal of Cd(II) and Pb(II) from aqueous solution. The dosing quantity of AMA, the initial pH, contact time, and initial metal concentration were found to be important for the removal of Cd(II) and Pb(II). Furthermore, Cd(II) and Pb(II) adsorption thermodynamic parameters ΔG < 0, ΔH > 0 and ΔS > 0 indicated that the removal process was spontaneous with heat adsorption and entropy increase. The adsorption equilibrium was attained at 7 h and the maximum adsorption capacity of Cd(II) and Pb(II) was 303.03 and 263.16 mg/g at 318 K, respectively, showing outstanding removal efficiency. The Langmuir equation could well describe the adsorption isotherm of Cd(II) and Pb(II) solution and the adsorption mechanism obeys the quasi-second-order kinetic equation, and the adsorption rate constants are 0.3220 and 0.7333, respectively. The results of FT-IR, XRD, and XPS analysis showed the precipitation as calcium silicate lead occurred and cadmium silicate. These results showed that AMA was an effective and alternative adsorbent for the removal of Cd(II) and Pb(II) ions from aquatic ecosystems.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

**REFERENCES**


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