Adsorption of Se(IV) in aqueous solution by zeolites synthesized from fly ashes with different compositions
Xiao Zhang, Xinyuan Li, Fan Zhang, Shaohao Peng, Sadam Hussain Tumrani and Xiaodong Ji

ABSTRACT
Low-calcium fly ash (LC-F) and high-calcium fly ash (HC-F) were used to synthesize corresponding zeolites (LC-Z and HC-Z), then for adsorption of Se(IV) in water. The results showed that zeolites can effectively adsorb Se(IV). The optimal adsorption conditions were set at contact time = 360 min; pH = 2.0; the amount of adsorbent = 5.0 g·L⁻¹; temperature = 25 °C; initial Se(IV) concentration = 10 mg·L⁻¹. The removal efficiency of HC-Z was higher than the LC-Z after it had fully reacted because the specific surface area (SSA) of HC-Z was higher than LC-Z. The adsorption kinetics model of Se(IV) uptake by HC-Z followed the pseudo-second-order model. The Freundlich isotherm model agreed better with the equilibrium data for HC-Z and LC-Z. The maximum Se(IV) adsorption capacity was 4.16 mg/g for the HC-Z and 3.93 mg/g for the LC-Z. For the coexisting anions, SO₄²⁻ barely affected Se(IV) removal, while PO₄³⁻ significantly affected it. Regenerated zeolites still had high capacity for adsorbing Se(IV) from wastewater, and selenium-loaded zeolite has the potential to be used as a Se fertilizer to release selenium in Se-deficient areas.

Key words | high-calcium fly ash, low-calcium fly ash, selenium(IV) removal, synthesized zeolite, wastewater treatment

INTRODUCTION
Selenium is an essential trace element with multiple biological functions in many organisms, including humans. The recommended nutrient intake by the World Health Organization is 40–200 μg/day, depending on gender and life-stage group (Kurniawati et al. 2019). Both an excess and deficiency of selenium can cause serious health problems in humans (Sun et al. 2015). Low Se intakes are associated with considerable health disorders while a toxic dose of Se results in selenosis (Zhu et al. 2017; Kurniawati et al. 2019).

Selenium is also a common and intractable metalloid contamination with high toxicity in water, and the WHO recommends a maximum permissible selenium level in drinking water of 10 μg/L (Hu et al. 2015; Sharp et al. 2016; Tan et al. 2016). Hudak (2004) mapped and statistically analyzed selenium contamination from 112 water wells in south Texas groundwater and found that 21% of selenium observations exceeded the 20 μg/L advisory level for irrigation water, and 5% surpassed the 50 μg/L standard for drinking water. The Lower Arkansas River Valley (LARV) in Colorado is designated as an impaired watershed by the Environmental Protection Agency due to high levels of selenium and uranium, which endangers aquatic life and
impairs domestic water sources (Sharp et al. 2016). The Dorno-Gobi Aimag in Mongolia represents the highest drinking water Se levels ranging from 1.2 to 18.6 μg/L (Golubkina et al. 2018). Aquatic selenium pollution is a universal and chronic global problem (Bailey 2017; He et al. 2018). Selenium exists predominantly as two species, selenite (SeO$_3^{2-}$, Se(IV)) and selenate (SeO$_4^{2-}$, Se(VI)), in the water and both oxyanions could result in health problems (Sun et al. 2015).

Numerous methods for the removal of selenium from aquatic environments have been studied, including coagulation, flocculation, ion exchange, precipitation, bioremediation, membrane filtration, ozone oxidation, electrochemistry treatment, and adsorption (Geoffroy & Demopoulos 2011; Sen 2015; Hamed et al. 2017; He et al. 2018; Jacobson & Fan 2019). Of these, adsorption is one of the most effective and simple methods for point-of-use applications (Awual et al. 2014; Jacobson & Fan 2019). Many materials for adsorption of selenium have been studied, such as metal nanoparticles and metal oxides (Verbinnen et al. 2013; Mafu et al. 2016; Cui et al. 2018; Ma et al. 2018). In recent years, wastewater treatment using zeolite as a low-cost adsorbent has been examined by many researchers. It is found that the zeolite, either natural or synthetic, can improve water quality and wastewater treatment effectiveness by removing substance such as heavy metals, ammonium, phosphorus, chemical oxygen demand (COD), dissolved organic matter, cations, and radioactive elements (Chen & Lu 2016; Kussainova et al. 2016; Kotoulas et al. 2019). Yusof et al. (2009) performed column studies to evaluate the performance of modified zeolite-Y with ion Fe in removing As(III), As(V), Se(IV) and Se(VI) from groundwater and proved that the modified zeolite Y could be an effective adsorbent material.

Fly ash is an industrial solid waste material generated by coal-fired thermal power plants. Currently, over 750 million tonnes of fly ash are produced annually throughout the world, with global average utilization estimated to be only approximately 25% (Blissett & Rowson 2012; Cardoso et al. 2015; Wang et al. 2016). As a resource utilization method, the synthesis of zeolites from fly ash has been widely studied (Zhang et al. 2012a; Jin et al. 2015; Koshy & Singh 2016). Synthetic zeolite from fly ash with different calcium content had been used to remove heavy metals, ammonium, and phosphorus (Zhang et al. 2011b; Ji et al. 2015, 2017). However, there are few studies on the adsorption of Se(IV) from aqueous solution by synthetic zeolites with different calcium content.

In this study, we chose synthetic zeolite from fly ash with different calcium content as an adsorbent to remove Se(IV) from aqueous solutions. The zeolites were synthesized by an alkali fusion-assisted hydrothermal treatment. The impacts of contact time, pH value, adsorbent dosage, initial concentration of Se(IV), and coexisting anions on the adsorption of Se(IV) were investigated to determine the optimal adsorption conditions. The adsorption kinetic and equilibrium were also investigated. Further, adsorbent regeneration and feasibility of slow release of selenium by the selenium-loaded zeolite were studied in order to develop recycling applications.

**MATERIALS AND METHODS**

**Zeolite synthesis**

The low-calcium and high-calcium fly ash samples (LC-F and HC-F) used in this study were obtained from a power plant located in Hebei Province in China. An alkaline fusion method followed by a hydrothermal treatment was adopted for the synthesis of zeolites (Wang et al. 2009; Zhang et al. 2011a). In brief, 10 g of fly ash was mixed with 12 g of NaOH powder (analytical reagent grade) to obtain a homogeneous mixture. The mass ratio of the fly ash to NaOH powder was 1:1.2 (w/w). The homogeneous mixture was then heated in a nickel crucible in 600 °C for 180 min. The fusion products were ground and poured into a flask, to which distilled water was then added to form a mixture. The mass ratio of the fusion products to water was 0.1725 (w/w). The mixture was stirred intensely at 80 °C for 2 h to form aluminosilicate gel and was subsequently poured into a stainless alloy autoclave and kept in an oven at 100 °C for 9 h. After hydrothermal treatment, solid samples were extracted and then washed thoroughly with distilled water until their pH was less than 10. The resultant solid products were dried at 100 °C for 12 h and ground to pass through a 100-mesh sieve for further use.
Characterization

The chemical compositions of fly ash and synthesized zeolites were determined by X-ray fluorescence (XRF) (Philips PW2404, Philips Co., Holland). The percentage and oxide contents of each element were determined by the chemical analysis method of silicate rock in GB/T14506.28-93. The mineralogical compositions of the fly ashes and synthesized zeolites were determined using a powder X-ray diffraction (XRD) instrument (Rikaku D/max-RB, Rikaku, Japan), as shown in Figure 1. Scattering patterns were collected from 5° to 70° with a scan time of 1 min per two steps. Photomicrographs of the two aforementioned materials were obtained using a scanning electron microscope (SEM) (S-3000N, Hitachi, Japan). The results are shown in Figure 2. Before the experiment, about 3 g of fly ash and 0.1 g of synthesized zeolite were degassed in a vacuum at 200 °C for 2 h, then the specific surface area (SSA) of the materials was calculated by using the BET equation. The SSA of the fly ashes and synthesized zeolites was determined using the nitrogen adsorption method. Nitrogen adsorption experiments were conducted at 77 K using QuadraSorb SI (Cantata Instruments Co., USA).

Batch experiments

Stock solutions of Se(IV) (1,000 mg/L) were prepared from anhydrous Na₂SeO₃ (analytical grade), which was diluted to the desired experimental concentrations by adding distilled water. All adsorption experiments were conducted in 150-mL stoppered conical flasks on a temperature-controlled shaker (HZQ-F160) with continuous stirring at 150 rpm.

The effect of contact time on Se(IV) adsorption by the two synthesized zeolites was investigated under different contact times ranging from 0 to 600 min at 25 °C and the adsorbent dosage was 0.5 g. The initial concentration of Se(IV) was 10 mg/L, and the initial pH of the solutions was adjusted to 2.0 ± 0.05.

The effect of pH was investigated in the pH range from 1 to 10 at 25 °C; 0.5 g of the synthesized zeolite was put into 150-mL conical flasks containing 100 mL of a 10 mg/L...
Figure 2  |  SEM images of (a) low-calcium fly ash, (b) high-calcium fly ash, (c) low-calcium zeolite and (d) high-calcium zeolite.
Se(IV) solution. Each solution’s pH was adjusted via the addition of the appropriate volume of 0.1 M HNO₃ or NaOH, and the pH was measured using a pH meter (PHS-3C).

The effect of the synthesized zeolite dosage on the Se(IV) removal was studied in the range from 1 to 20 g/L at 25 °C. The initial concentration of Se(IV) was 10 mg/L. The initial pH of the solutions was adjusted to 2.0 ± 0.05.

The effect of the initial concentration of Se(IV) was studied in the range of 5–30 mg/L at 25 °C. The adsorbent dosage was 5.0 g/L. The pH of the solutions was adjusted to 2.0 ± 0.05.

To investigate the effects of coexisting anions on Se(IV) removal by synthesized zeolites, two types of oxyanion (SO₄²⁻ and PO₄³⁻) of similar molecular structures were tested individually. Stock solutions of two oxyanions were prepared by dissolving anhydrous Na₂SO₄ and Na₂PO₄ (analytical grade) into distilled water. Again, 0.5 g synthesized zeolite was added into each Se(IV) solution (10 mg/L) at 25 °C, with initial pH set to 2.0 ± 0.05. The two oxyanions were fixed at three concentrations (0.1, 1, and 10 mM).

The adsorption isotherm experiments were conducted at different anion concentrations ranging from 5 to 30 mg/L. A total of 0.5 g of adsorbent was added to the different Se(IV) solutions at 25 °C. The initial pH of the solutions was adjusted to 2.0 ± 0.05.

All of the aforementioned batch adsorption experiments were performed in duplicate. After the experiment, the suspensions of the batch experiments were centrifuged and then filtered with a 0.45-μm cellulose acetate membrane. The concentrations of Se(IV) in equilibrium supernatants were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000, PerkinElmer Co., USA). The amount of Se(IV) adsorption by the synthesized zeolites (q (mg/g)) and the removal efficiency was calculated using Equations (1) and (2), respectively:

\[
\text{Adsorption capacity} = \frac{C_0 - C_e}{W} \times V \\
\text{Removal efficiency} (%) = \frac{C_0 - C_e}{C_0} \times 100 \%
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium Se(IV) concentrations of the test solution (mg/L), respectively. \(V\) is the testing solution volume (L), and \(W\) is the mass of the adsorbent (g).

**Adsorbent regeneration**

To investigate the practical reusability of the synthesized zeolites as a potential adsorbent, a regeneration experiment was carried out using 0.1 M NaOH (Bleiman & Mishael 2010). In this experiment 50 mL of the NaOH solution was blended with 5 g of Se(IV)-saturated zeolite, and the mixture was stirred at 150 rpm and 25 °C for 90 min in a temperature-controlled shaker (HZQ-F160). The aforementioned regeneration process was repeated three times. The solid precipitant was then washed with distilled water about 10 times until neutral. The obtained solid samples were dried at 100 °C for 12 h and sieved through a 100 mesh for further study. After regeneration, the adsorbent was reused for Se(IV) removal at doses ranging from 1 to 20 g/L via batch experiments with the same reaction conditions as those above. The results were compared with those from the original zeolites.

**RESULTS AND DISCUSSION**

**Characterization of fly ashes and synthesized zeolites**

The composition (XRF), XRD patterns and SEM images of fly ashes and synthesized zeolites are shown in Table 1, Figures 1 and 2, respectively. The detailed description of the above indicators was consistent with the research done by Ji et al. (2017) and is not discussed in detail here.

**Effect of contact time**

Figure 3 shows the effect of contact time on the Se(IV) removal efficiencies by HC-Z and LC-Z. The results indicate that adsorption of Se(IV) by the two synthesized zeolites was a very fast process. HC-Z had better removal efficiency than LC-Z at the end. At 10 min, the removal efficiency of LC-Z was 80.67% while that of HC-Z was 41.62%. After 60 minutes, the removal efficiency of Se(IV) by synthetic zeolites exceeded 80%. Both synthetic zeolites displayed a rapid initial remove rate (<60 min), and afterward the
removal efficiency of LC-Z slightly increased but basically remained steady, whereas the removal efficiency of HC-Z slowly rose. Such a quick initial removal rate could be due to a considerable amount of surface sites and a large area of the zeolites that retains the ions compared with the Se(IV) concentration (Awual et al. 2015; Hamed et al. 2017). According to the SEM and SSA results of synthetic zeolites in Ji et al. (2017) and this study, LF-Z was smoother than HC-Z, whereas HC-Z had a larger SSA. These two pieces of evidence explain why the removal efficiency and removal rate of LC-Z was higher than HC-Z in the first 60 min but lower after 240 min. Adequate contact time allows the zeolite with a larger SSA to have a higher removal efficiency. The highest removal efficiency of HC-Z and LC-Z was 97.4% and 88.49%, respectively.

**Effect of initial pH**

Figure 4 shows the effect of initial pH on the adsorption of Se(IV) at a pH of 1 to 10 at 25 °C. pH played a significant role in Se(IV) removal. When the initial pH of the solution increased from 1.0 to 2.0, the removal efficiency by HC-Z and LC-Z increased dramatically and reached the maximum value at a pH of 2. The biggest removal efficiency of the synthetic zeolites was 96.54% and 87.53%, respectively. However, as pH increased above 3.0, the removal efficiency by HC-Z and LC-Z decreased, and gradually leveled off above a pH of 10.0.

These behaviors could be explained by the change in the density of hydrogen and NO₃⁻. The dominant ionic species of Se(IV) and the surface charge of the synthetic zeolite was a function of solvent pH. The initial solution pH was adjusted by HNO₃ or NaOH. As shown in Figure 4, the point of zero charge (pHpzc) of the HC-Z and LC-Z was at a pH ~ 2.4 and 2.1, respectively, as characterized by zeta potential measurements. At this pH, synthetic zeolites are electrically neutral. Below those pH values, the adsorbent surface sites carried a positive charge, while above those pH values negatively charged sites dominated (Szlachta et al. 2012). In an aqueous solution, Se(IV) species

### Table 1 | Chemical compositions of fly ashes and synthesized zeolites (wt.%)

<table>
<thead>
<tr>
<th>Component</th>
<th>LC-F</th>
<th>LC-Z</th>
<th>HC-F</th>
<th>HC-Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>53.30</td>
<td>43.55</td>
<td>37.95</td>
<td>33.65</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.98</td>
<td>16.27</td>
<td>14.52</td>
<td>12.62</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.57</td>
<td>10.07</td>
<td>16.73</td>
<td>11.70</td>
</tr>
<tr>
<td>CaO</td>
<td>3.14</td>
<td>5.69</td>
<td>17.86</td>
<td>15.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.60</td>
<td>2.96</td>
<td>1.09</td>
<td>0.79</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.97</td>
<td>0.71</td>
<td>1.44</td>
<td>0.46</td>
</tr>
<tr>
<td>MgO</td>
<td>0.91</td>
<td>0.99</td>
<td>1.09</td>
<td>0.70</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
<td>0.12</td>
<td>0.44</td>
<td>0.31</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.08</td>
<td>21.10</td>
<td>1.24</td>
<td>23.16</td>
</tr>
</tbody>
</table>

Figure 3 | Effect of contact time on Se(IV) removal by synthesized zeolites (C₀ = 10 mg/L; adsorbent dosage = 5 g/L; pH = 2.0 ± 0.05; temperature = 25 °C).

Figure 4 | Effect of pH on Se(IV) removal by synthesized zeolites and Zeta potential of synthesized zeolites (C₀ = 10 mg/L; adsorbent dosage = 5 g/L; contact time = 360 minutes; temperature = 25 °C).
generally contained selenious acid ($H_2SeO_3$), biselenite ($HSeO_3^-/C0_3$), and selenite ($SeO_2^-/C0_3$) according to the relationship between $Se(IV)$ dissociation and pH (Sun et al. 2015). The $H_2SeO_3$ is the dominant species below a pH of 3.5, the $HSeO_3^-/C0_3$ is the dominant species at a pH of 3.5 to 9, and the $SeO_2^-/C0_3$ species is dominant above a pH of 9 (Awual et al. 2015; Dorraji et al. 2017).

Therefore, the fact that the adsorption of $Se(IV)$ reached the maximum point at a pH of 2 can be attributed to the decrease of $NO_3^-/C0_3$ ions in solution, leading to a decrease of the competition of the $H_2SeO_3$ and $NO_3^-/C0_3$ ions for adsorption sites onto zeolite particles. At a studied pH from 3.5 to 10, biselenite and selenite were the dominant ionization state of $Se(IV)$ which had a similar negative charge, so the surface charge of adsorbent is the determinative factor in the removal efficiency. So we choose 2.0 as the optimized pH value. Similar trends in selenium anion adsorption were reported in the other literature (Hu et al. 2015; Sun et al. 2015). For some biological materials, such as sulfuric acid-treatment peanut shell and modified rice husk, optimum adsorption was obtained at pH 1.5 (El-Shafey 2011; Soda et al. 2014).

At initial pH range from 1 to 2, the removal efficiency of LC-Z was smaller than HC-Z, but from pH = 3 and above, the removal efficiency of LC-Z was higher than HC-Z. This can be attributed to the impact of SSA. The SSA of HC-Z was larger than LC-Z. When the pH ranges from 1 to 2, HC-Z could provide more contact sites than LC-Z, but when the pH was equal to or higher than 3, contact sites carried negative charges. The larger the SSA of zeolite, the more negative charges it carries, leading to stronger competition with anions and lower removal efficiency.

**Effect of adsorbent dosage**

The effect of synthesized zeolite quantity on the $Se(IV)$ removal efficiency and adsorption capacity ($q$) was investigated to determine the optimal adsorbent dosage, as shown in Figure 5. With the increase of the dosage of the HC-Z from 1.0 to 8.0 g/L, the removal efficiency of $Se(IV)$ increased from 80.83% to 99.9% whereas the adsorption capacity of the HC-Z decreased from 8.08 to 1.25 mg/g. The maximum removal efficiency was achieved with an HC-Z dosage of 8.0 g/L. The removal efficiency of $Se(IV)$ by the LC-Z increased from 80.40% to 88.74% with an increase in the adsorbent dosage from 1.0 to 5.0 g/L; however, the adsorption capacity of the LC-Z decreased from 8.04 to 1.77 mg/g. Removal efficiency peaked at an LC-Z dosage of 5.0 g/L. With higher dosage, more active sites were available for rapid $Se(IV)$ adsorption, resulting in greater removal efficiency. The decrease in adsorption capacity in conjunction with increased zeolite dosage may result from a decrease in the $Se(IV)$ concentration gradient per mass unit of adsorbent (Zhang et al. 2011).

The removal efficiency of $Se(IV)$ decreased when the adsorbent dosage started from 8 g/L of LC-Z and 10 g/L of HC-Z. At an adsorbent dosage of 20 g/L, the removal efficiency of $Se(IV)$ decreased to 72.50% and 31.30% for the HC-Z and LC-Z, respectively. The adsorption capacity also decreased to 0.36 and 0.16 mg/g, respectively. According to Figure 6, these changes related to the change of the solution pH. The pH of the solution rose rapidly and exceeded 3 as the reaction progressed and reached a plateau at 180 min. The higher the adsorbent dosage, the higher the solution pH. As discussed in the previous section, pH is an important parameter in the removal of $Se(IV)$ by synthesized zeolites, contributing to reduced adsorption efficiency. When the pH of the solution was higher than 3, the removal efficiency of zeolites was lower. Therefore, the adsorbent dosage of 5 g/L was the most appropriate amount.
Effect of the initial concentration of Se(IV)

The adsorption of Se(IV) by synthesized zeolites was studied under different initial concentrations of Se(IV) within the range from 5 to 30 mg/L. As shown in Figure 7, the initial Se(IV) concentration was a significant parameter in the adsorption of Se(IV). With an increase in initial Se(IV) concentration from 5 to 30 mg/L, the removal efficiency decreased from 100% to 65.55% for the LC-Z and from 100% to 69.36% for the HC-Z. However, the adsorption capacity \( q \) of the two adsorbents increased with an increase in initial Se(IV) concentration, peaking at 4.16 mg/g for the HC-Z and 3.93 mg/g for the LC-Z. The decrease in removal efficiency can be explained by limited sorption sites on the adsorbents (Perego et al. 2015; Ivanova et al. 2014). The increase in \( q \) was probably due to the greater driving force because of the increasing concentration gradient with greater initial Se(IV) concentrations.

Effect of coexisting anions

The effect of coexisting ions on the adsorption of Se(IV) by synthesized zeolites is shown in Figure 8. The two oxyanions had a negative impact on the adsorption of Se(IV) that was generally more pronounced with the HC-Z than with the LC-Z. With the HC-Z, the presence of \( \text{SO}_4^{2-} \) did not significantly affect adsorption of Se(IV). \( \text{PO}_4^{3-} \) had the most significant effect on Se(IV) removal, even at low concentrations, and the result is similar to previous findings with AlCl\(_3\) (AC) and FeCl\(_3\) (FC) adsorbents (Hu et al. 2015). With the LC-Z, \( \text{SO}_4^{2-} \) did not significantly affect Se(IV) removal even at concentrations of 10 mM, but \( \text{PO}_4^{3-} \) did lead to a large decrease in Se(IV) removal at this concentration. These results can be explained by the triple-layer model, which is widely applied to solid–liquid interface adsorption (Stumm & Morgan 1996). \( \text{PO}_4^{3-} \) can bind strongly to surface sites of metal hydroxides, forming inner-sphere (o-plane) surface complexes that are barely affected by ionic strength. However, anions such as sulfate...
bind relatively weakly to surface sites. Complexes often form in the outer sphere (β-plane), which is significantly affected by ionic strength. As mentioned above, the negative effect of coexisting anions on Se(IV) removal by the HC-Z was greater than that by LC-Z. Since PO₃SO₄ is usually present in wastewater, its effect should not be ignored.

Adsorption kinetics

The following pseudo-first-order (Equation (3)) and pseudo-second-order (Equation (4)) kinetic models were applied to simulate the experimental data (Lagergren 1898; Ho & McKay 1999):

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

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

where \(Q_e\) and \(Q_t\) are the amounts of Se(IV) adsorbed on the synthesized zeolites (mg/g) at equilibrium and at time \(t\), respectively. The values of \(k_1\) (min⁻¹) and \(k_2\) (g·mg⁻¹·min⁻¹) are the sorption rate constants of the pseudo-first- and pseudo-second-order kinetic models, respectively. The figures are shown in Figure 9. The constants are summarized in Table 2.

In the sorption of Se(IV) by both the HC-Z and LC-Z, the coefficients of determination for the pseudo-second-order kinetic model \(R^2 = 0.9351\) and \(0.7876\), respectively) were higher than that for the pseudo-first-order kinetic model \(R^2 = 0.8729\) and \(0.3291\), respectively). Hence, the pseudo-second-order kinetic model better explained the kinetic process of HC-Z, suggesting an effect of chemisorption. Nevertheless, neither the pseudo-first-order kinetic model nor the pseudo-second-order kinetic model explain the adsorption kinetics of LC-Z well. The differences in the adsorption kinetics of the HC-Z and LC-Z may relate to their composition and structure. The predicted values of \(Q_e\) using the pseudo-second-order kinetic model were 1.95 mg/g by the HC-Z and 1.75 mg/g by LC-Z, closely modeling the experimental data (1.95 mg/g by the HC-Z and 1.77 mg/g by the LC-Z).

Adsorption isotherm

The mechanism of interaction between adsorbent and adsorbate can be described by adsorption isotherms. Of the many models that describe this process, the commonly used Langmuir and Freundlich isotherms were applied in this study to fit the adsorption isotherm data (Herbert 1907; Langmuir 1918).

Table 2 | Rate constants and correlation coefficients for the studied kinetic models

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(Q_e) (mg/g)</th>
<th>(k_1)</th>
<th>(R^2)</th>
<th>(Q_e) (mg/g)</th>
<th>(k_2)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC-Z</td>
<td>1.80</td>
<td>0.0376</td>
<td>0.8729</td>
<td>1.95</td>
<td>0.0276</td>
<td>0.9351</td>
</tr>
<tr>
<td>LC-Z</td>
<td>1.72</td>
<td>0.2668</td>
<td>0.3291</td>
<td>1.75</td>
<td>0.5657</td>
<td>0.7876</td>
</tr>
</tbody>
</table>

Note: \(C_0 = 10\) mg/L; adsorbent dosage = 5 g/L; pH = 2.0 ± 0.05; temperature = 25 °C.
Langmuir isotherm

The Langmuir isotherm assumes that monolayer adsorption occurs on an adsorbent surface, and there is no interaction between the adsorbate molecules. The Langmuir equation is as follows:

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

(5)

where \(K_L\) is the Langmuir coefficient (L/mg), \(Q_m\) is the maximum monolayer adsorption capacity, and \(Q_e\) is the amount of adsorbed Se(IV) on a mass unit of the adsorbent at equilibrium (mg/g). \(C_e\) is the equilibrium Se(IV) concentration (mg/L).

The Langmuir isotherm-fitting results are summarized in Table 3. For the HC-Z and LC-Z, \(Q_m\) was 3.912 and 2.451 mg/g, respectively, both closer to the respective experimental results of 4.161 and 2.831 mg/g. The value of \(K_L\) was 1.664 L/mg for the HC-Z and 3.939 L/mg for the LC-Z. The obtained \(R^2\) value was 0.74214 for HC-Z and 0.61228 for the LC-Z, which confirms that the Langmuir isotherm equation cannot be supposed an accurate model for adsorption of Se(IV) by the synthesized zeolite adsorbent.

Freundlich isotherm

The Freundlich isotherm is an empirical equation, as follows:

\[
\lg Q_e = \lg K_F + n_F \lg C_e
\]

(6)

where \(K_F\) and \(n_F\) are the Freundlich parameter and adsorption intensity, respectively. The \(n_F\) should be in the range of 0.1–1 for beneficial adsorption. The results are shown and listed in Figure 10 and Table 3. For the HC-Z, the obtained \(K_F\) was 2.190 mg/g, and \(n_F\) was 0.276, indicating favorable adsorption. For the LC-Z, the constant \(K_F\) was 1.749 mg/g, and the \(n_F\) was 0.236, also in the range for beneficial adsorption. The coefficient of determination \((R^2 = 0.9654\) for HC-Z and \(R^2 = 0.9578\) for the LC-Z) was higher than those of the Langmuir isotherm model, illustrating that the Freundlich isotherm model is a better fit for the experimental data and that the adsorption of selenium by synthetic zeolite is a spontaneous process.

A comparison of the maximum Se(IV) sorption capacities of different adsorbents is shown in Table 4. The synthesized zeolites in this study showed higher sorption capacity in comparison with various other adsorbents. Within this study, the maximum sorption capacity of the HC-Z was slightly higher than that of LC-Z; this was because the HC-Z has larger SSA, which can provide...
more adsorption sites, which would allow the increased equilibrium maximum Se(IV) sorption capacity.

Adsorbent regeneration

The adsorption ability of regenerative zeolites was evaluated to investigate their reusability. A comparison of Se(IV) adsorption between regenerated zeolites at different dosages and the original zeolites is shown in Figure 11. Under the same adsorbent dosage, the removal efficiency of the initial zeolite was higher than the regenerated zeolite. When the adsorbent dosage was 5 g/L, the removal efficiency of regenerated zeolites reached the maximum and the differences in removal efficiency between initial zeolite and regenerated zeolite reached the minimum (25.02% for HC-Z and 1.2% for LC-Z). Subsequently increasing the regenerated zeolite dosage resulted in decreased removal efficiency, similar to the trend seen with the original zeolites. The reduction of removal efficiency of regenerated zeolite relative to the initial zeolite may be attributable to the incomplete release of Se(IV) adsorbed to the original zeolites during regeneration, leading to a collapse of the structure of zeolites. These preliminary results indicate that regenerated zeolites still had a relatively high capacity for Se(IV) adsorption. Hence, synthesized zeolites can be recycled and utilized for Se(IV) removal from wastewater.

Application prospect

Selenium is an essential trace micronutrient for both human beings and animals. The concentration of selenium in soil influences its concentration in food (Mechora et al. 2011). Se-deficient areas of soils are relatively larger than those with a potentially harmful concentration of Se as China is located in a low Se area (Li et al. 2015). Soil applications of commercial fertilizers enriched with Se appear to be a safe method to increase the selenium uptake in Se-deficient areas (Temmerman et al. 2014). Bañuelos et al. (2015) found that the Se-hyperaccumulator plants such as Stanleya pinnata can be used as organic Se fertilizer. Shang et al. (2018) studied the adsorption of phosphate by the quaternary ammonium-based sugarcane bagasse (QA-SB) and its sustained release of laden phosphate in aqueous solution and soil. The research found that the laden phosphate on

Table 4 | Comparison of maximum sorption capacity of Se(IV) on different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Maximum sorption capacity (mg/g)</th>
<th>Initial Se(IV) concentration (mg/L)</th>
<th>Dosage of adsorbent (g/L)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural goethite (α-FeOOH)</td>
<td>4</td>
<td>7.74</td>
<td>0.05–0.25</td>
<td>0.01–0.5</td>
<td>Jacobson &amp; Fan (2019)</td>
</tr>
<tr>
<td>Candida utilis ATCC 9950 yeast</td>
<td>5</td>
<td>5.47</td>
<td>60</td>
<td>Slightly lower amount</td>
<td>Kieliszek et al. (2016)</td>
</tr>
<tr>
<td>Hematite</td>
<td>5.5</td>
<td>4.19</td>
<td>8.647</td>
<td>0.8</td>
<td>Jang et al. (2015)</td>
</tr>
<tr>
<td>Hydroxypatite (FHAP)</td>
<td>5</td>
<td>5.51</td>
<td>0.01</td>
<td>4</td>
<td>Kongsri et al. (2015)</td>
</tr>
<tr>
<td>Microwave-assisted Fe3O4</td>
<td>4</td>
<td>2.40</td>
<td>0.1</td>
<td>2.5</td>
<td>Gonzalez et al. (2012)</td>
</tr>
<tr>
<td>Nano-Jacobsite</td>
<td>4</td>
<td>6.573</td>
<td>0.1</td>
<td>2.5</td>
<td>Gonzalez et al. (2010)</td>
</tr>
<tr>
<td>Iron-coated GAC</td>
<td>5</td>
<td>2.50</td>
<td>1–2</td>
<td>1.5–3</td>
<td>Zhang et al. (2008)</td>
</tr>
<tr>
<td>High-calcium zeolite (HC-Z)</td>
<td>2 ± 0.5</td>
<td>4.16</td>
<td>5–30</td>
<td>5</td>
<td>This study</td>
</tr>
<tr>
<td>Low-calcium zeolite (LC-Z)</td>
<td>2 ± 0.5</td>
<td>3.93</td>
<td>5–30</td>
<td>5</td>
<td>This study</td>
</tr>
</tbody>
</table>
the QA-SB could be desorbed efficiently and 27.8% of laden phosphate released in soils after 4 days (Shang et al. 2018). Meanwhile, the use of zeolites as feed supplements for animals and medical applications indicates that zeolites are not harmful to humans (Smedt et al. 2015). Zeolite had been used as both carriers of nutrients and medium for free nutrients (Ramesh & Reddy 2011). Compared with the above research, we could assume that selenium-loaded zeolite can be used as a Se fertilizer to release selenium in Se-deficient areas. Of course, selenium-loaded zeolites may also release other chemical elements while releasing selenium, which needs to be clarified in the next study. In the subsequent studies, we will study the slow release of selenium by the selenium-loaded zeolite and the available potential and risk.

CONCLUSIONS

This study confirms that the zeolites synthesized from different fly ashes can be used to remove Se(IV) from industrial wastewater. Parameters such as contact time, pH value, and adsorbent dosage were investigated in terms of their effects on adsorbent Se(IV) removal. The results show that the optimum adsorption conditions were contact time = 360 min; pH = 2.0; the amount of adsorbent = 5.0 g/L; temperature = 25 °C; initial Se(IV) concentration = 10 mg/L. The removal efficiency of HC-Z was higher than that of the LC-Z after they had fully reacted because the SSA of HC-Z was higher than that of LC-Z. With the increase of adsorbent dosage, the solution pH increased and the removal efficiency of zeolites decreased. The adsorption kinetics of Se(IV) uptake by the HC-Z followed the pseudo-second-order model. The equilibrium data of the two zeolites are fitted better with the Freundlich model. The maximum adsorption capacities of Se(IV) were 4.16 mg/g for the HC-Z and 3.93 mg/g for the LC-Z. Of the coexisting anions, PO₃⁴⁻ caused a large decline in Se(IV) removal at a concentration of 10 mM. Regenerated zeolites still had a relatively high capacity for Se(IV) adsorption. The study shows that zeolites produced from fly ashes are inexpensive alternative adsorbents for the removal of Se(IV) from industrial wastewater. Furthermore, using fly ash to synthesize zeolite achieved the reutilization of the fly ash resources. Selenium-loaded zeolite has the potential to be used as a Se fertilizer to release selenium in Se-deficient areas.

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