Adsorption of Tungsten onto Zeolite Fly Ash Produced by Hydrothermally Treating Fly Ash in Alkaline Solution

Fumihiko Ogata,a Yuka Iwata,a and Naohito Kawasaki*a,b

aFaculty of Pharmacy, Kinki University; and bAntiaging Center, Kinki University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan.
Received April 9, 2014; accepted June 21, 2014

Fly ash (FA) was hydrothermally treated in an alkaline solution to produce zeolite fly ash (Z-FA). The properties of the FA and Z-FA were investigated. The amounts of tungsten (W) adsorbed onto the FA and Z-FA surfaces were evaluated. Z-FA was produced by hydrothermally treating FA in an alkaline solution. The specific surface area and pore volume of the Z-FA were greater than those of the FA. More W was adsorbed onto the Z-FA surface than onto the FA surface. The adsorption isotherms for W were fitted using both the Freundlich and Langmuir equations. The equilibrium concentrations of W adsorbed onto the FA and Z-FA surfaces were subsequently reached within 20 h. The pseudo-second-order model more accurately described the data than did the pseudo-first-order model. Sodium hydroxide solutions (1–50 mmol/L) were used to easily recover W from Z-FA, indicating that Z-FA was useful for recovering W from aqueous solutions.

Key words fly ash; hydrothermally treated in an alkaline solution; tungsten; adsorption

High level of tungsten detected in water resources has become a concern for several of the countries in the western United State of America (U.S.A.). The level of tungsten found to be 25 μg/L in the drinking water of Fallon NV. In 2003, the Center of Disease Control and Prevention (CDC) conducted a urine analysis for the residents of Fallon and the tungsten level in the urine of 80% of the sampled residents was found to be about eleven times higher than the level observed for the U.S.A. population. Furthermore, sixteen child leukemia cases have diagnosed in Fallon, NV and three children have died since 1997. Although there is no scientific evidence linking tungsten ingestion to the high rate of leukemia clusters found in children, local residents and some authorities believe that the high tungsten level might be the main reason for it. Therefore, the CDC nominated tungsten to be investigated further by the National Toxicology Program (NTP).1)

Tungsten is element of group BIV in the periodic table having strategic and industrial importance due to their applications in many technological fields.2) Tungsten is valuable resource used to produce cemented carbide tools, and it is wasted during manufacturing processes in Japan. Tungsten is one of the stockpiled in Japan because its supply significantly wasted during manufacturing processes in Japan. Tungsten is used to produce cemented carbide tools, and it is incorporated in molecular sieves, ion-exchangers, adsorbents, catalysts, detergents, and adsorption behavior of metals on zeolites is usually considered from an ion-exchange viewpoint. Many researches have been reported that adsorption behavior of metals onto zeolite.17,18) Despite the great interest in adsorption capability with zeolite, there is very little literature published on the adsorption of rare metals (tungsten) from solution by zeolite.

Thus, we developed an adsorbent by hydrothermally treating FA in an alkaline solution and investigated its efficiency in removing tungsten species from water in a single solution system.

Materials and Methods

Materials FA was obtained from the Tachibana-wan Thermal Power Station (Shikoku Electric Power, Inc., Japan). The main components of FA are SiO2 and Al2O3, which comprise 70–80% of the total weight, and the minor components are Fe2O3, CaO, MgO, Na2O, K2O, and rare earth metals.3) Zeolite X (zeolite fly ash (Z-FA)) was produced by hydrothermally treating FA in an alkaline solution.4,5) FA (0.5 g) was hydrothermally treated in an alkaline solution to produce zeolite fly ash (Z-FA). The properties of the FA and Z-FA were investigated. The amounts of tungsten (W) adsorbed onto the FA and Z-FA surfaces were evaluated. Z-FA was produced by hydrothermally treating FA in an alkaline solution. The specific surface area and pore volume of the Z-FA were greater than those of the FA. More W was adsorbed onto the Z-FA surface than onto the FA surface. The adsorption isotherms for W were fitted using both the Freundlich and Langmuir equations. The equilibrium concentrations of W adsorbed onto the FA and Z-FA surfaces were subsequently reached within 20 h. The pseudo-second-order model more accurately described the data than did the pseudo-first-order model. Sodium hydroxide solutions (1–50 mmol/L) were used to easily recover W from Z-FA, indicating that Z-FA was useful for recovering W from aqueous solutions.

Key words fly ash; hydrothermally treated in an alkaline solution; tungsten; adsorption

The authors declare no conflict of interest.
* To whom correspondence should be addressed. e-mail: kawasaki@phar.kindai.ac.jp © 2014 The Pharmaceutical Society of Japan
was added to 40 mL of 3.0 mol/L sodium hydroxide solution, and the mixture was subsequently heated at 93°C for 60 h. The suspension was filtered through a 0.45-µm-pore-diameter membrane filter. The residue was washed with distilled water and dried at 110°C for 24 h.

The characteristics of Z-FA were measured by following method. The crystallinities of the Z-FA was measured using X-ray diffraction (XRD; MiniFlex II; Rigaku, Japan). The specific surface area, pore volume, and mean pore diameter were measured using a specific surface analyzer, NOVA4200e (Yuasa Ioniics, Japan). The pHpzc (point of zero charge) of the samples was measured as follows, as also stated in a previous study.20) Fifty milliliters of a 0.01 mol/L sodium chloride solution was placed in a closed vial. The pH was adjusted to either acid or sodium hydroxide, respectively, and 0.1 g of each solution was placed in a closed vial. The pH was adjusted to either 2 or 12 by adding a 0.1 mol/L solution of either hydrochloric acid or sodium hydroxide, respectively, and 0.1 g of each sample was then added. The solutions were agitated at room temperature for 48 h. The final pH values of the solutions were then measured. The pHpzc is the point where the curve pH final vs. pH initial crosses the line pHfinal = pHinitial.

Adsorption Isotherms FA or Z-FA (0.05 g) was added to 50 mL of solutions initially containing 5–50 mg/L of tungsten (W, Wako Pure Chemical Industries, Ltd., Osaka, Japan) (pH = 2.0). The suspensions were shaken at 100 rpm at 5–45°C for 48 h and were then filtered using a 0.45-µm-pore-diameter membrane filter. The W concentration was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; ICP-7500; Shimadzu Corp., Kyoto, Japan). The pHpzc of Z-FA was measured using Eq. 2.

\[ q = \left( C_0 - C_e \right) V / M \]  
where \( q \) represents the amount of W adsorbed (mg/g), \( C_0 \) represents the concentration of W before adsorption (mg/L), \( C_e \) represents the concentration of W after adsorption (mg/L), \( V \) represents the volume of the solvent (L), and \( M \) represents the mass of the adsorbent (g).

Moreover, the saturated amount of W was measured by following method. FA or Z-FA (0.25 g) was added to 100 mL of solutions initially containing 250 mg/L of W (pH = 2.0). The amounts of W adsorbed onto the FA and Z-FA surfaces were calculated using Eq. 1.

Effects of Contact Time and pH on Adsorption of W onto FA and Z-FA Surfaces FA or Z-FA (0.05 g) was added to 50 mL of the solution containing 50 mg/L of tungsten (pH = 2) in order to determine how contact time affected the adsorption of W onto the FA and Z-FA surfaces. The suspensions were shaken at 100 rpm at 25°C for 0.5–48 h. The amounts of W adsorbed onto the FA and Z-FA surfaces were calculated using Eq. 1.

FA or Z-FA (0.05 g) was added to 50 mL samples of the solution containing 50 mg/L W (pH = 2–10) to determine how pH affected the adsorption of W onto the FA and Z-FA solutions. The suspensions were shaken at 100 rpm at 25°C for 48 h. The amounts of W adsorbed onto the FA and Z-FA surfaces were also calculated using Eq. 1.

Use of Sodium Hydroxide Solutions to Recover W from Z-FA Z-FA (0.25 g) was added to 100 mL of the solution containing 250 mg/L W (pH = 2). The suspensions were shaken at 100 rpm at 25°C for 48 h and were then filtered using a 0.45-µm-pore-diameter membrane filter. The concentrations of W in the suspensions were measured using ICP-AES. The amounts of W adsorbed onto the Z-FA surface were calculated using Eq. 1. The collected adsorbents were dried at 110°C for 24 h and were then added to 200 mL solutions of 5–50 ppm aqueous sodium hydroxide. The suspensions were shaken at 100 rpm at 25°C for 48 h and filtered using a membrane filter with a 0.45-µm-pore-diameter. The amounts of W desorbed from the Z-FA surface were calculated using Eq. 2 as follows:

\[ d = C_e V / W \]  
where \( d \) represents the amount of W desorbed (mg/g), \( C_e \) represents the equilibrium concentration of W (mg/L), \( V \) represents the solvent volume (L), and \( W \) represents the weight of the adsorbent (g).

Results and Discussion

Properties of FA and Z-FA The XRD patterns for the FA and Z-FA show that the FA mainly consisted of mullite crystal (3Al2O3·2SiO2). Moreover, zeolite X (Z-FA) had been produced by hydrothermally treating FA in an alkaline solution.419) These results indicate that hydrothermally treating the mullite FA in an alkaline solution transformed the FA into Z-FA. The specific surface areas and total pore volumes of the FA and Z-FA were 2.7 m3/g and 12.7 µL/g and 23.3 m3/g and 57.6 µL/g, respectively. The mean pore diameters of the FA and Z-FA, on the other hand, were 189.8 and 98.9 Å, respectively. These results suggest that hydrothermally treating the FA in an alkaline solution had significantly developed the Z-FA pores, resulting in a novel adsorbent. The pHpzc of Z-FA was 9.81. The pHpzc value, equal to 9.81, indicates that Z-FA has a zero charge for pH = 9.81; therefore, it shows a positive charge density on its surface for a solution pH < 9.81 and a negative one for a solution pH > 9.81.419

Effect of Contact Time on Adsorption of W onto FA and Z-FA Surfaces Figure 1 shows the effect of contact time on the adsorption of W onto the FA and Z-FA surfaces. The equilibrium adsorption concentrations were reached within 20 h. The amount of W adsorbed onto the Z-FA surface was 41.46 mg/g. The removal of W using Z-FA was >82%, on the other hand, Srivastava et al. reported that the removal of W
using a typical Fe–Mn cake was >92%. Z-FA could be produced from waste FA at low cost, and was useful for adsorption of W.\textsuperscript{21)}

Pseudo-first-order and pseudo-second-order kinetic models were used to study the adsorption of W onto the FA and Z-FA surfaces. The pseudo-first-order kinetic formula is given as:\textsuperscript{22)}

$$\ln(q_t - q_e) = \ln q_e - kt$$

where $q_t$ represents the amount of W adsorbed onto the adsorbent (mg/g) at time $t$, $q_e$ represents the amount of W adsorbed onto the adsorbent (mg/g) at the time the equilibrium adsorption concentration was reached, and $k_1$ is the rate constant of the pseudo-first-order kinetic model (1/h). The pseudo-second-order kinetic model is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2 + t/q_e}$$

where $k_2$ is the rate constant of the pseudo-second-order kinetic adsorption (g/mg/h). The batch kinetic data correlated well with the pseudo-second-order kinetic model. Table 1 shows the fittings obtained using the kinetic parameters of the pseudo-first-order and pseudo-second-order models. From the correlation coefficients, the pseudo-second-order kinetic model ($r$: 0.982–0.996) best describes the adsorption of W onto the FA and Z-FA surfaces. The $q_e$ obtained from the pseudo-second-order model (41.91 mg/g) was similar to that obtained from the batch experiment (41.46 mg/g).

### Amounts of W Adsorbed onto FA and Z-FA Surfaces

Figure 2 shows the amount of W adsorbed onto the FA and Z-FA surface at various temperatures. The amount of W adsorbed increased with increasing temperature.

Many models have previously been proposed to describe the adsorption process; the most common ones are the Langmuir and Freundlich isotherm models.\textsuperscript{23,24)} The Langmuir model is only valid for the adsorption of monolayers onto surfaces that show a finite number of identical sites.

The Langmuir parameters are determined according to the following equation:

$$q = \frac{aW_eC_e}{(1+aW_e)}$$

where $q$ represents the amount of W adsorbed (mg/g), $a$ is a constant related to the affinity between W and the binding sites during adsorption (L/mg), $W_e$ represents the maximum monolayer-adsorption capacity (mg/g), and $C_e$ represents the equilibrium concentration (mg/L).

The Freundlich model assumes a heterogeneous surface and a nonuniform distribution of heat adsorption over the surface, wherein the binding sites are not equivalent and/or independent. The Freundlich parameters are determined using the following equation:

$$\log q = \log K + \frac{1}{n}\log C_e$$

where $K$ and $1/n$ are constants that represent the Freundlich capacity factor and Freundlich intensity parameter, respectively. Table 2 lists the Freundlich and Langmuir constants pertaining to W adsorption onto FA and Z-FA. The experimental data were fitted using both the Freundlich and Langmuir models. The correlation coefficients for the Freundlich and Langmuir models were in the ranges 0.777–0.991 and 0.765–0.996, respectively. Therefore, W had been adsorbed probably through monomolecular adsorption onto the FA and Z-FA surfaces. Moreover, W was easily adsorbed onto the FA and Z-FA surfaces when $1/n$ was in the range 0.23–0.66. Z-FA was useful for adsorption of W, compared to chitosan ($\alpha$:...
0.91 L/mg, (Langmuir constant) or natural clay (W: 5.45 mg/g (Freundlich constant), 1/n: >0.71 (Langmuir constant)).

Saturated amount of W adsorbed onto FA and Z-FA was 1.2 mg/g and 72.5 mg/g, respectively. On the other hand, saturated amount of W adsorbed onto the biopolymer-coated clay particles was 23.9 mg/g. More W was adsorbed onto the Z-FA surface in this study than was adsorbed onto the surfaces of the biopolymer-coated clay particles used in the previous study, indicating that the Z-FA was useful for adsorbing W from aqueous solutions. Moreover, Geol et al. also reported that the surface charge of adsorbent was related to adsorption of W. The pH of the solution decreased (<9.81), and the Z-FA surfaces were positively charged (pH pzc of Z-FA: 9.81). The solution pH after adsorption of W onto Z-FA is <9.81 (data are not shown). These results suggest that the W had been adsorbed onto the Z-FA surfaces through interactions between the electrons of the positively charged Z-FA surfaces and the W anions in solution.

Effect of Temperature on Adsorption of W onto Z-FA Surface
The thermodynamic properties, i.e., the change in enthalpy (ΔH), the change in Gibbs free energy (ΔG), and the change in entropy (ΔS) for the adsorption of W onto the Z-FA surface are calculated from the following set of equations:

\[
\Delta G = -RT \ln K_a
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]

The adsorption equilibrium constant, K_a, is calculated first. ΔH is then determined from the slope of the regression line after plotting K_a against 1/T. ΔG and ΔS are then determined from Eqs. 8 and 9. The thermodynamic parameters for the adsorption of W onto the FA and Z-FA surfaces are shown in Table 3. The change in the Gibbs free energy decreases with increasing temperature for both adsorbents, indicating that more W was adsorbed onto both adsorbents at higher temperatures. The positive ΔH indicates that the adsorption was endothermic, meaning that the reaction had consumed energy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Initial concentration (mg/L)</th>
<th>ΔH (kJ/mol)</th>
<th>ΔS (J/mol/K)</th>
<th>ΔG (kJ/mol) at temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>278K</td>
</tr>
<tr>
<td>FA</td>
<td>5</td>
<td>20.44</td>
<td>71.11</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11.61</td>
<td>35.22</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>17.03</td>
<td>49.13</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>13.69</td>
<td>33.49</td>
<td>4.34</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>9.11</td>
<td>15.79</td>
<td>4.77</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>12.42</td>
<td>26.39</td>
<td>5.04</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>14.05</td>
<td>38.52</td>
<td>3.30</td>
</tr>
<tr>
<td>Z-FA</td>
<td>5</td>
<td>63.24</td>
<td>232.48</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>34.02</td>
<td>122.21</td>
<td>-5.63</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>7.87</td>
<td>41.74</td>
<td>-3.91</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>19.78</td>
<td>76.75</td>
<td>-1.78</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>22.49</td>
<td>80.27</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>21.99</td>
<td>75.82</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>28.23</td>
<td>104.88</td>
<td>-1.53</td>
</tr>
</tbody>
</table>

Table 4. Recovery of W from Z-FA Using Sodium Hydroxide Solution

<table>
<thead>
<tr>
<th>Cycle (times)</th>
<th>NaOH (mmol/L)</th>
<th>Amount adsorbed (mg/g)</th>
<th>Amount desorbed (mg/g)</th>
<th>Recovery percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>61.8</td>
<td>63.3</td>
<td>102.5</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>58.9</td>
<td>61.1</td>
<td>103.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>63.6</td>
<td>69.2</td>
<td>108.8</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>29.0</td>
<td>16.5</td>
<td>54.7</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>35.3</td>
<td>32.8</td>
<td>88.8</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>37.6</td>
<td>41.0</td>
<td>98.3</td>
</tr>
</tbody>
</table>
was existed in solution. If the pH level is lower than 4, tungstic acid would form. Therefore, \([\text{HW}_6\text{O}_{20}]_3\) tetrameric ions exist. At pH 1, tungstate species precipitate. At pH 4.0, a further increase in pH decreased the adsorption. The maximum value of W adsorption was achieved at pH approximately 1.5 onward, the amount of W adsorption also increased. The positively charged Z-FA surfaces and the W anions in the aqueous solution have a tendency to form condensed iso-paratungstate B occur. When the pH level is 4, \([\text{HW}_6\text{O}_{20}]_3\) species, and the reversible formation of paratungstate A and W in aqueous solution has a tendency to form condensed isopolytungstate ions and the condensation grade increases with decreasing pH. At pH of about 6, the formation of dimeric, tetrameric, hexameric species, and the reversible formation of paratungstate A and paratungstate B occur. When the pH level is 4, \([\text{HW}_6\text{O}_{20}]_3\) was existed in solution. If the pH level is lower than 4, tetrameric ions exist. At pH 1, tungstate species precipitate to form tungstic acid. Therefore, \([\text{HW}_6\text{O}_{20}]_3\) specie would be suitable for adsorption using Z-FA. The pH of the solution decreased (<9.81), and the Z-FA surfaces were positively charged (pH_{pzc} of Z-FA: 9.81). W had been adsorbed onto the Z-FA surfaces through interactions between the electrons of the positively charged Z-FA surfaces and the W anions in solution.

**Conclusion**

Z-FA was produced by hydrothermally treating FA in an alkaline solution. The specific surface area and pore volume of the Z-FA were greater than those of the FA. The W was adsorbed through interactions between the electrons of the positively charged Z-FA surface and the W anions in the bulk solution. Isotherms for the adsorption of W onto the FA and Z-FA surfaces were fitted using both the Freundlich and Langmuir equations. Moreover, the equilibrium concentrations for the adsorption of W onto the FA and Z-FA surfaces were reached within 20h. The pseudo-second-order model more accurately described the data than the pseudo-first-order model did. The amount of W adsorbed onto the Z-FA surface increased with increasing temperature. The change in the Gibbs free energy for the adsorption decreased with increasing temperature for both adsorbents. The positive \(\Delta H\) indicated that the adsorption was endothermic, meaning that the reaction had consumed energy. The positive \(\Delta S\) suggested that the degree of randomness at the solid/solution interface had increased during adsorption.

**Effect of pH on Adsorption of W onto FA and Z-FA Surfaces**

Figure 3 shows amount of W adsorbed onto FA and Z-FA at different pH conditions. W adsorption onto Z-FA was highly dependent. Amount adsorbed onto Z-FA was greater than that on FA at all pH conditions. As pH increases from approximately 1.5 onward, the amount of W adsorption also increases. The maximum value of W adsorption was achieved at pH 4.0. A further increase in pH decreased the adsorption. W in aqueous solution has a tendency to form condensed isopolytungstate ions and the condensation grade increases with decreasing pH. At pH of 6.2 and higher, the dimeric tungstate ions are in equilibrium with \(\text{W(OH)}_2\)\(^{2-}\). Between pH 6.2 and 6.0, thermodynamically unstable species coexist in water. At a pH of about 6, the formation of dimeric, tetrameric, hexameric species, and the reversible formation of paratungstate A and paratungstate B occur. When the pH level is 4, \([\text{HW}_6\text{O}_{20}]_3\) was existed in solution. If the pH level is lower than 4, tetrameric ions exist. At pH 1, tungstate species precipitate to form tungstic acid. Therefore, \([\text{HW}_6\text{O}_{20}]_3\) specie would be suitable for adsorption using Z-FA. The pH of the solution decreased (<9.81), and the Z-FA surfaces were positively charged (pH_{pzc} of Z-FA: 9.81). W had been adsorbed onto the Z-FA surfaces through interactions between the electrons of the positively charged Z-FA surfaces and the W anions in solution.

**Use of Sodium Hydroxide Solutions to Recover W from Z-FA**

Table 4 shows the results of using 1–50 mmol/L solutions of sodium hydroxide to recover W from Z-FA. The percentages of W recovered from the Z-FA the first and second times were in the ranges 102.5–108.8 and 54.7–98.3%, respectively. The results demonstrate that the 50 mmol/L solution of sodium hydroxide was suitable for desorbing W from Z-FA. Moreover, the amount of W adsorbed and desorbed the second time was lower than that adsorbed and desorbed the first time. These results indicate that Z-FA and dilute sodium hydroxide solution were useful for recovering W from aqueous solutions.

**References**