Adsorption of Heavy Metals by Adsorbents from Food Waste Residue

X.D. FAN1,2,* and X.K. ZHANG1
1Environmental and Municipal Engineering School of Tianjin Cheng Jian University, Tianjin 300384, China
2Tianjin Key Laboratory of Aquatic Science and Technology, Tianjin 300384, China

ABSTRACT: Food waste residue is an intractable problem worldwide. The current study discussed the potential of adsorbents prepared from food waste residue (AFWR) for heavy metal removal from wastewater. The microstructure of AFWR was characterized, and kinetic studies on the simultaneous adsorption of Pb2+, Cu2+, Zn2+ and Cd2+ ions from aqueous solutions by AFWR were carried out. It was found that the adsorption of all heavy metals followed a pseudo-second-order kinetics, so that there was a competitive adsorption for Pb2+, Cu2+, Zn2+ and Cd2+. According to the experimental results, the adsorption in competition beads with the heavy metals presented an order of Cu2+ > Pb2+ > Zn2+ > Cd2+.

INTRODUCTION

RECENTLY, numerous approaches have been studied for developing more effective technologies, not only to reduce the amount of heavy metal wastewater but also to improve the quality of the treated effluent [1,2]. Among these approaches, adsorption is the most versatile and the most widely used method by far, in which activated carbon is the most commonly used adsorbent. However, the cost of activated carbon is too high [3,4], which limits its wide applications in practical industries. In view of this, inexpensive adsorbents have attracted extensive attention around the world in the past decades [5,6].

Sewage sludge is carbonaceous in nature and has volatile components in its matrix, so that it can be used as an adsorbent for metal ions [7,8]. As a matter of fact, the use of activated carbon from sewage sludge has presented a strong potential as an adsorbent material due to its functional groups [9,10]. In our preliminary investigation, we also reported the preparation of activated carbon from sewage sludge, and further examined its adsorption property for dye removal from aqueous solutions [11].

Household and municipal food waste is a tough issue worldwide, especially in the rapidly growing cities and super-cities [12,13]. An important mitigation option is the diversion of reusable materials through sorting out food waste. Accordingly, different approaches have been proposed to support the sorting and reduction of food waste, such as legislation, top-down policy, community involvement and recycling [14,15]. In recent years, the recycling of food waste gradually has become a mainstream method, and more and more attention has been paid to the reuse of food waste for environmental protection, such as fermentation of food waste mixture for cell protein, prevention of volatile fatty acids and H2 production [16,17]. Similar to sewage sludge, food waste is also carbonaceous in nature and has volatile components in its matrix [18,19]. As a result, it is probably suitable for preparing adsorbents.

The aim of this study is to investigate the feasibility of using unique adsorbents from food waste residue to achieve simultaneous removal of heavy metals produced by industrial activities. It is believed that the study is useful for low-cost industrial wastewater treatment, in which the simultaneous removal of several heavy metals is required.

EXPERIMENTAL PROCEDURE

Preparation of Adsorbents from Food Waste Residue

The food waste residue collected from Tianjin food waste Treatment Works of China was anaerobically digested and dewatered. The sample of food waste resi-
due was first dried at 105°C for 2h, and then crushed and sieved through a sieve with a uniform size of 0.05–0.1 mm. 20 g of the dried sample was heated at 500°C for 0.5 h with a heating rate of 15°C/min in the nitrogen atmosphere. Thus, the adsorbents prepared by food waste residue (AFWR) were obtained.

Chemicals

All chemicals used in this work were of analytical purity. The stock solution of Cu²⁺, Pb²⁺, Cd²⁺ and Zn²⁺ with a concentration of 1.0 g·L⁻¹ were prepared using CuSO₄, Pb(NO₃)₂, 3CdSO₄·8H₂O and (CH₃COO)₂Zn·2H₂O, respectively.

Adsorption Experiments

Adsorption experiments were conducted at 25°C. 0.50 g of AFWR and 25 mL heavy metal ion solution with desired concentration were added into a conical flask of 100 mL, and then the mixture was stirred by a shaking thermostat machine at a speed of 120 rpm for 2h (the contact time excluded). In kinetic experiments, Pb²⁺, Cd²⁺ and Ni²⁺ ion solutions of 10 mg·L⁻¹ were used, and the adsorption time varied between 0 and 400 min. The filter liquor was analyzed for the concentration of residual heavy metal ion by using Agilent 3510 atomic absorption spectrophotometer. The amount of adsorption (q) was calculated according to the following equation:

\[ q = \frac{(C_0 - C_e)V}{m} \]  

(1)

Where \( C_0 \) and \( C_e \) are the initial and equilibrium heavy metal ion concentrations (mg·L⁻¹), respectively; \( V \) is the volume of the solution (L); and \( m \) is the amount of adsorbent used (g). All the adsorption experiments were conducted in duplicate, and the mean values were adopted.

Scanning Electron Microscope (SEM)

SEM images were recorded to visualize the sample morphology. Pore structure and structural changes could be observed by SEM.

RESULTS AND DISCUSSION

A field emission scanning electron microscope was used to observe the surface morphology of AFWR (Figure 1). As can be seen, there are some fibrous structures and sheet structures, and those fibrous structures cover on or intersperse in the sheet structures. Since fiber bundles can form a larger number of macropores or micropores, the fibrous structures are relatively loose compared with the sheet structures, thus improving the adsorption performance of AFWR. Notably, the sheet structures also play an important role in the adsorption; namely, they can provide the support for the fiber structures.

Competitive Adsorption

In general, the competitive ability of heavy metals can be represented by competitive adsorption coefficients. For example, the coefficient of Cu²⁺ can be expressed as follows together with Pb²⁺, Zn²⁺ and Cd²⁺ [20]:

\[ a_{(Cu^{2+})} = \frac{q_e / C_0(Cu^{2+})}{q_e / C_0(Pb^{2+}) + q_e / C_0(Zn^{2+}) + q_e / C_0(Cd^{2+})} \]  

(2)

Where \( q_e \) is the adsorbed amount (mg·g⁻¹) at equilibrium state, and \( C_0 \) is the initial concentration. According to the above expression, the bigger the competitive adsorption coefficient, the higher the competitive ability of heavy metals.

\[ a_{(Cu^{2+})} + a_{(Pb^{2+})} + a_{(Zn^{2+})} + a_{(Cd^{2+})} = 1 \]  

(3)
Table 1. The Competitive Adsorption Coefficients of Different Heavy Metal Ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Competitive Adsorption Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb²⁺</td>
</tr>
<tr>
<td>Cu²⁺-Zn²⁺</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu²⁺-Pb²⁺</td>
<td>0.26</td>
</tr>
<tr>
<td>Cu²⁺-Cd²⁺</td>
<td>0.12</td>
</tr>
<tr>
<td>Pb²⁺-Zn²⁺</td>
<td>0.33</td>
</tr>
<tr>
<td>Pb²⁺-Cd²⁺</td>
<td>0.28</td>
</tr>
<tr>
<td>Zn²⁺-Cd²⁺</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu²⁺-Pb²⁺-Zn²⁺</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu²⁺-Pb²⁺-Cd²⁺</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu²⁺-Zn²⁺-Cd²⁺</td>
<td>0.23</td>
</tr>
<tr>
<td>Pb²⁺-Zn²⁺-Cd²⁺</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu²⁺-Zn²⁺-Cd²⁺-Pb²⁺</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 1 showed that the competitive adsorption coefficients with an individual heavy metal are larger than those with multi-metals. For example, the coefficients with two metals are about 0.50, whereas those with four kinds of heavy metals are below 0.30. Although the adsorption of Cd²⁺ is the lowest in this study, its competitive adsorption coefficient still exceeds 0.23, indicating the feasibility of simultaneous adsorption of heavy metals from aqueous solutions by AFWR.

The competitive adsorption characteristics of Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ are studied. Table 2 shows the metal removal from multi-metal solution (10 and 20 mg·L⁻¹) and individual heavy metal solutions (10 mg·L⁻¹), respectively. As can be seen, the heavy metal adsorption in individual heavy metal solutions is better than that in multi-metal solution. For individual heavy metal solutions, Cu²⁺ and Cd²⁺ can be removed by AFWR more efficiently, of which the removal of Cu²⁺ is the highest in competitive adsorption. In contrast, the removal of Zn²⁺ is remarkably reduced since most active sites are occupied by other heavy metal ions. That is to say, the adsorption in competition beads with the following heavy metals presents an order of Cu²⁺ > Pb²⁺ > Zn²⁺ > Cd²⁺. This result suggests that the presence of Cd²⁺ and Zn²⁺ has little impact on the adsorption of other heavy metal ions. It is noticed that although the adsorption of Cd²⁺ is the minimum in this study, its removal still exceeds 5.0 mg·L⁻¹, which further confirms the feasibility of simultaneous adsorption of heavy metals from aqueous solutions by AFWR.

### Adsorption kinetics

Adsorption kinetics of Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ are analyzed using the Elovich pseudo-first-order rate equation [21]:

\[
a \log(q_e - q_t) = \log q_e - \frac{K_1}{2.303m}
\]  

(4)

Where \(q_e\) is the adsorbed amount (mg·g⁻¹) at equilibrium state, \(q_t\) is the adsorbed amount (mg·g⁻¹) at time \(t\) and \(K_1\) is the rate constant of pseudo-first-order adsorption (min⁻¹). \(q_e\) and \(K_1\) can be calculated from the slope and intercept of the plot of \(\log(q_e - q_t)\), respectively (Figure not shown here). In fact, the calculated equilibrium adsorption capacity, \(q_e\) (Cal.), should be in accordance with the experimental value \(q_e\) (exp.) [22]. However, in this study, although the correlation coefficient values (R²) are high, the experimental \(q_e\) values do not agree with the calculated ones (Table 3).

The adsorption kinetics can also be described by pseudo-second-order equation [21]:

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

(5)

Where \(K_2\) is the rate constant of pseudo-second-order adsorption (g·mg⁻¹·min⁻¹). \(K_2\) and \(q_e\) can be calculated from the slope and intercept of the plot of \(t/q_t\), respectively. It is found that the calculated \(q_e\) agrees well with the experimental \(q_e\) (Table 3). The large correlation coefficient of the pseudo-second-order model and the consistency between the calculated \(q_e\) and the experimental data both demonstrate that the adsorption of heavy metal ions (Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺) onto AFWR can be approximated by the pseudo-second-order model more favorably than by the pseudo-first-order model. This result suggests that the adsorption mechanism for heavy metal ions is the pseudo-second-order kinetic model based on the adsorption rather than the mass transfer from the solution to the adsorbent surface [22]. Hence, the rate-limiting step may be the chemical adsorption involving valance forces by sharing or exchanging electrons between heavy metal ions and the adsorbent.
CONCLUSIONS

AFWR can be used as an effective adsorbent with a high removal percentage for the simultaneous adsorption of all heavy metals (Pb$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$) from aqueous solutions, and the adsorption kinetics follow the pseudo-second-order equation. The competitive adsorption results show that the presence of competitive ions can reduce the removal percentage of each heavy metal ion. During competitive adsorption, the adsorption beads with the heavy metals presents an order of Cu$^{2+}$ > Pb$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the Tianjin City Application Basis and Advanced project, and the Young and Middle-aged Talents Plan provided by Tianjin of China.

REFERENCES


Table 1. The Fitting Kinetics Parameters for Adsorption.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$ exp (mg·g$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>5.10</td>
<td>0.816</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>3.01</td>
<td>0.735</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>2.99</td>
<td>0.793</td>
</tr>
</tbody>
</table>