Preparation of Carbonaceous Heavy Metal Adsorbent from Cedar Bark Using Sulfur-Impregnation

Takaaki Wajima

Abstract—A novel carbonaceous adsorbent with heavy metal removal from aqueous solution was prepared from cedar bark using sulfur impregnation. The bark was cut to 1 cm pieces, and then immersed in 0.01 - 3 M K₂S solution to prepare sulfur-immersed materials. The immersed-materials were heated at 100-700 °C in nitrogen gas to produce the sulfur-impregnated carbonaceous adsorbent by pyrolysis. The contents of carbon and sulfur in the adsorbent and abilities of adsorbent to remove heavy metals from aqueous solution were examined. The sulfur content in sulfur-immured materials is higher than that in raw material by sulfur-immersion, while the carbon content in sulfur-immersed materials is almost the same as that in raw material. After pyrolysis, the product prepared from cedar bark immersed in 1 M K₂S solution at 400 °C indicates a maximum recovery for nickel ion, regardless of sulfur content. This product has the removal ability of the heavy metals, Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Fe³⁺ and Fe²⁺. The equilibrium adsorption capacity of the adsorbent for heavy metal ions fits the Langmuir isotherm better than the Freundlich isotherm, and the calculated maximum adsorption capacity is 0.30 - 0.74 mmol/g. The order of selectivity of the adsorbent indicates Pb²⁺ > Fe²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺ > Ni²⁺ > Fe³⁺. For adsorption of iron ion with the adsorbent, the adsorption for divalent Fe²⁺ is superior to that for trivalent Fe³⁺, while influence of co-existing anion species for the adsorption with sulfur-impregnated adsorbent is little.

Index Terms—Cedar bark, sulfur-impregnated adsorbent, pyrolysis, heavy metal removal, wastewater treatment.

I. INTRODUCTION

Japanese cedar (Cryptomeria japonica), an economically important tree plantation species, is widely distributed in Japan. The wood is used for lumber and veneer, while the bark generally is of little economic value. Usually, the bark is currently a huge residue stream for wood processing industries and is either discarded in sawmills or burned.

Activated carbon can be produced from various biomass materials. With the increasing ecological and economical significance of environmental protection, the use of waste biomass as feedstock material for the production of activated carbons is attracting increasing interest [1]-[6]. Activated carbon can be prepared from many organic materials having high carbon content, like coal [7], wood [8], [9], lignite [10], coconut shells [11], [12], activated sludge [13]; and recently, many agricultural by-products, such as walnut shells [14], palm shells [15], pecan shells [16], [17], date stones [18], almond shells [19], sugar cane bagasse [20], cotton stalks [21], physic nut [22], and rice straw [23], [24], have been used as sources for activated carbon production. However, activated carbon effectively removes organic chemicals from wastewater, but is less effective in removing metals and inorganic pollutants from aqueous solutions [25]. This is mainly due to the relatively non-polar character of activated carbon, which inhibits the attraction between charged metal species and the surface of the activated carbon (even though some functional groups may be present on the surface).

In previous studies, sulfur-impregnated adsorbents with high removal abilities for heavy metals were prepared from coal or palm shell using H₂S gas, K₂S powder, or K₂S solution [26]-[29]. According to the Pearson theory, the sulfur, as a soft base, should interact with heavy metals such as Zn²⁺, Pb²⁺, Cd²⁺ and Ni²⁺ (soft acids) rather than with oxygen (a hard base) in the activated carbon [30], [31]. From these results, it would be possible to produce a low cost heavy metal adsorbent from agricultural wastes, and could be applied to recover the metal ions from wastewater.

In this study, we attempted to prepare a carbonaceous heavy metal adsorbent from cedar bark using sulfur-impregnation, and estimate its removal ability for heavy metals from aqueous solution.

II. MATERIALS AND METHODS

A. Raw Bark

Raw cedar bark, which was collected from one of the company in Akita prefecture, Japan, first cut into 1 cm length, then washed with distilled water, and dried and stored for use. Properties of cedar bark sample are shown in Table I. All reagents used in this study were purchased from Wako Chemical Co., Japan at analytical grade.

<table>
<thead>
<tr>
<th>TABLE I: PROPERTIES OF CEDAR BARK SAMPLE</th>
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<tr>
<td>Moisture (g/100g dry matter)</td>
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<tr>
<td>Ash (g/100g dry matter)</td>
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<tr>
<td>Volatile matter + fixed carbon (g/100g dry matter)</td>
</tr>
<tr>
<td>C (%)</td>
</tr>
<tr>
<td>H (%)</td>
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<tr>
<td>N (%)</td>
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<td>S (%)</td>
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B. Preparation of Adsorbent

20 g of sample was immersed in 200 mL of K₂S solution with 0.05 – 3 mmol/L for 24 h, then filtered, and dried in a drying oven overnight to obtain sulfur-immersed samples. These samples were pyrolyzed using a horizontal reactor (Fig. 1) as follows. Sulfur-immersed samples were put in a ceramic board, and installed in a transparent quartz tube of 0.45 mm inside diameter and 1 m in length. Before pyrolysis, N₂ gas was injected into the tube for 30 min at a rate of 1.0 L/min to replace the air in the tube. The product was heated in an
electric furnace at 100 – 700 °C for 1 h, with a continuous flow of N₂ gas at a rate of 1.0 L/min. After heating, the solid was cooled to room temperature with a steady N₂ gas flow (1.0 L/min) in the tube, then washed with distilled water and dried in a drying oven overnight to obtain the sulfur-impregnated adsorbent (Product).

III. RESULTS AND DISCUSSION

A. Sulfur-impregnated Adsorbent

Effect of pyrolysis temperature on the properties of the product was examined.

Fig. 2 shows the XRD pattern of raw cedar bark, sulfur-immersed cedar bark immersed in 1 mol/L K₂S solution for 24 h, and the product pyrolyzed at 100 – 700 °C. The peaks of cellulose were indicated in cedar bark, sulfur-immersed cedar bark and the product pyrolyzed at 100 °C and 200 °C, while those in the product pyrolyzed above 300° C are decreasing to indicate broad pattern. It means that cellulose structure was decomposed at pyrolysis above 300 °C to form amorphous structure in the product.

C. Heavy Metal Removal

The adsorption capabilities of the products for heavy metals were examined. 0 - 10 mmol/L of Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Fe³⁺ and Fe²⁺ solutions were prepared with Zn(NO₃)₂, 6H₂O, Cu(NO₃)₂·3H₂O, Ni(NO₃)₂, Pb(NO₃)₂, Cd(NO₃)₂·8H₂O, Fe(NO₃)₃·9H₂O, FeCl₃·6H₂O and FeCl₂·4H₂O powders, respectively. 0.1 g of the product was added to 10 mL of heavy metal solution in a 50 mL centrifuge tube, and was shaken in a reciprocal shaker for 24 h. After shaking, the slurry was centrifuged, and the concentrations of heavy metal ions in the supernatant were analyzed to calculate the corresponding adsorption amounts (qₑ (mmol/g)):

\[ qₑ = \frac{(M₀ - Mₑ) \cdot V}{w} \]  

Here, \( V \) is the volume of solution (L) and \( w \) is the weight of sample (g).
Fig. 3 shows the contents of carbon and sulfur in cedar bark, sulfur-immersed cedar bark, and the product pyrolyzed at 100 - 700 °C. The contents of carbon and sulfur in raw cedar bark are 42.7 % and 0.7 %, respectively. The carbon content of the samples after sulfur-immersion and pyrolysis at 100 °C and 200 °C are almost same as those of raw cedar bark, while the products pyrolyzed above 300 °C are higher contents of carbon (50 - 60 %) than raw cedar bark. The sulfur content of the sample increase after sulfur immersion (almost 3 %), and gradually increase with increasing the pyrolysis temperature above 300 °C. It may be caused by the decomposition of organic matters, such as cellulose, as shown in Fig. 2, in the products by pyrolysis.

Fig. 4 shows the recovery of nickel using raw cedar bark, sulfur-immersed cedar bark, and the product pyrolyzed at 100 - 700°C. Nickel recovery of raw cedar bark is 7.9 %, that of sulfur-immersed cedar bark is 55 %, and the product after pyrolysis at 100 °C, 200 °C and 300 °C are approximately 60 %. With increasing temperature of pyrolysis above 300 °C, nickel recovery of the products pyrolyzed at 400 °C is high (80 %), then decrease to approximately 40 %. The product pyrolyzed at 400 °C indicates the highest nickel recovery.

Fig. 5 shows the contents of carbon and sulfur in the product pyrolyzed at 400 °C from cedar bark immersed in 0 - 3 mol/L K₂S solution for 24 h. With increasing K₂S concentration, carbon content decreases, while sulfur content increases.

Fig. 6 shows the recovery of nickel using the product pyrolyzed at 400 °C from cedar bark immersed in 0 - 3 mol/L K₂S solution for 24 h. With increasing K₂S concentration to 1 mol/L, nickel recovery of the product increases, and above 1 mol/L, that of the product decreases.

From these results, the carbonaceous adsorbent with the highest ability for nickel recovery can be prepared from cedar bark by pyrolysis at 400 °C after immersion in 1 M K₂S solution.

**B. Heavy Metal Adsorption**

The adsorption isotherms of various metal ions with the adsorbent, which was prepared by pyrolysis at 400 °C after immersion in 1 M K₂S solution, are shown in Fig. 7 and Fig. 8. In Fig. 7, the high adsorbed amount (approx. 0.7 mmol/g) is confirmed for Pb²⁺, the adsorbed amounts for Zn²⁺, Cu²⁺,
and Cd$^{2+}$, are approximately 0.5 mmol/g, and the low adsorbed amounts for Ni$^{2+}$ and Fe$^{2+}$ are about 0.4 mmol/g and 0.3 mmol/g, respectively. In Fig. 8, the isotherms for three types of iron ion, Fe(NO$_3$)$_3$, FeCl$_3$, and FeCl$_2$, are compared. In the case of Fe(NO$_3$)$_3$ and FeCl$_3$, although different co-existing anions, NO$_3^-$ and Cl$^-$, are present in the solution, the adsorption behaviors for Fe$^{3+}$ are almost same (about 0.3 mmol/g). In the case of FeCl$_3$ and FeCl$_2$, the adsorption for divalent Fe$^{2+}$ (approx. 0.6 mmol/g) is superior to that for trivalent Fe$^{3+}$.

The adsorption behaviors of the product for metal ions are determined by the isotherm models. Several isotherm models are available to describe the equilibrium sorption distribution with the Langmuir and Freundlich models being commonly used to fit experimental data. The linear forms of the Langmuir and Freundlich models are given by:

$$ C_e/q_e = 1/(Q_{max} \cdot K_F) + C_e/Q_{max} $$

$$ \ln(q_e) = \ln(K_F) + (1/n) \ln(C_e) $$

where $q_e$ is the amount of metal ions adsorbed at equilibrium (mmol/g); $Q_{max}$ (mmol/g) and $K_F$ (L/mg) are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites and a measure of adsorption energy (equilibrium adsorption constant), respectively. $K_F$ and $n$ are Freundlich constants.

**TABLE II: QMAX CALCULATED USING LANGMUIR MODEL FOR VARIOUS METAL IONS**

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Zn$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{max}$ (mmol/g)</td>
<td>0.55</td>
<td>0.56</td>
<td>0.45</td>
<td>0.74</td>
<td>0.50</td>
<td>0.34</td>
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</tbody>
</table>

**TABLE III: QMAX CALCULATED FROM LANGMUIR MODEL FOR IRON IONS**

<table>
<thead>
<tr>
<th>Iron Ions</th>
<th>Fe(NO$_3$)$_3$</th>
<th>FeCl$_3$</th>
<th>FeCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{max}$ (mmol/g)</td>
<td>0.34</td>
<td>0.30</td>
<td>0.68</td>
</tr>
</tbody>
</table>

For all metal ions, the correlation regression coefficients ($R^2$) of Langmuir model ($R^2 = 0.99 - 1.00$) indicate a better fitting than the Freundlich model ($R^2 = 0.12 - 0.99$) and the maximum adsorption capacity of the product for various metal ions calculated from Langmuir model were given in Table II and Table III. The order of selectivity of the adsorbent indicates Pb$^{2+}$ > Fe$^{2+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$ > Ni$^{2+}$ > Fe$^{3+}$, and the adsorbed amount for Fe$^{2+}$ is twice as high as that for Fe$^{3+}$.

**IV. CONCLUSION**

The carbonaceous adsorbent with the removal ability for heavy metals can be prepared from cedar bark using pyrolysis followed by sulfur immersion treatment. The product prepared from cedar bark immersed in 1 M K$_2$S solution via pyrolysis at 400 °C has a maximum ability for nickel ion recovery. This product has the removal ability of the heavy metals, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$. The equilibrium adsorption capacity of the adsorbent for heavy metal ions fits the Langmuir isotherm better than the Freundlich isotherm, and the calculated maximum adsorption capacity is 0.30 - 0.74 mmol/g. The order of selectivity of the adsorbent indicates Pb$^{2+}$ > Fe$^{2+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$ > Ni$^{2+}$ > Fe$^{3+}$. For adsorption iron ion with the adsorbent, the adsorption for divalent Fe$^{2+}$ is superior to that for trivalent Fe$^{3+}$, while influence of co-existing anion species for the adsorption with sulfur-impregnated adsorbent is little.

These results suggested that sulfur-impregnated adsorbent to apply for heavy metal removal from wastewater can be prepared from cedar bark.

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**REFERENCES**


Takaaki Wajima was born in February 1976 in Saga Prefecture, Japan. He has been an associate professor in the Department of Urban Environment Systems, graduated from School of Engineering, Chiba University, Japan, since 2013. He received his bachelor’s degree and master’s degree in resource engineering from Kyoto University, Japan, in 1998 and 2000, respectively, and his PhD in environmental mineralogy and technology from Kyoto University, Japan, in 2004. His main PhD research theme was “Micro-porous materials synthesized from paper sludge ash at low temperature, and its chemical mineralogy.” In 2004, he moved to the Institute of Ocean Energy at Saga University to work as a postdoctoral researcher, and from 2007 to 2013, he was an assistant professor at Akita University, Japan. His main research interests are waste recycling, resource recovery, and environmental purification.