Effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal

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Abstract

The objective of this study was to investigate the effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal. Results show that the specific surface area and iodine number of bamboo charcoal activated at 900 °C were larger than those of bamboo charcoal activated at 800 °C. The specific surface area of bamboo charcoal activated at 800 °C was larger than that of charcoal activated by steam. However, a contrary result was observed when the activation temperature was 900 °C.

The total volume and proportion of micropores in bamboo charcoal activated by carbon dioxide were greater than those in the other sample groups. However, the total volume and bulk volume of meso- and macropores, and average pore diameter for bamboo charcoal activated by steam were greater than those in the other sample groups.

Using 5 g bamboo charcoal (10–30 mesh) with a soaking time of 24 h, a better adsorption effect on Pb²⁺ (100%), Cu²⁺ (100%), and Cr³⁺ (88–98%) was found. However, medium frequencies were observed for the adsorption of Cd²⁺ (40–80%) and Ni²⁺ (20–60%). Very limited adsorption of As⁵⁺ was detected in this study.

For the same charcoal grain sizes, the adsorption capacity of 0.5 g of charcoal was better than that of 0.1 g. The improved adsorption effect of the sample group activated by steam was compared with the sample group activated by carbon dioxide.

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1. Introduction

In the past, the heavy metal compounds in wastewater have been causing environmental pollution and serious symptoms of poisoning. Recently, this environmental damage has been monitored by modern technology. However, the environmental pollution still occurs because of problems of management of the liquid phase environment. Heavy metal pollution caused by lead, copper, chromium, cadmium, nickel and arsenic is most serious to the human body. Concentrations of 0.005 mg/l (for Pb²⁺ and Cr³⁺), 0.001 mg/l (for Cd²⁺, Ni²⁺, and As⁵⁺) and 0.1 mg/l (for Cu²⁺), will cause humans to fall ill and can even be fatal (Kawarada et al., 2005). The removal of heavy metal ions is an important problem in the field of water purification.

Activated carbon is one of the materials being used to remove impurities from liquid solutions. It has been widely used to treat industrial and household water (Sirianuntapiboon and Ungkaprasatcha, 2007) because of its excellent adsorption properties, characterized by a high specific surface area (Cao et al., 2006). The increasing varieties and amounts of potentially hazardous impurities in water have led to increasing use of activated carbon. The problem associated with its use as a water purifier is largely economic; activated carbon is expensive. As this
problem limits its use on a large industrial scale, more economical materials are needed. Although much work has been done on the use of activated carbon for water purification, heavy metal pollution is still a problem.

In order to reduce the cost of activated carbon, Pulido et al. (1998) have used carbonized sugi wood powder to remove mercury and other metal ions from aqueous solutions of their salts. They indicated that wood powder carbonized at 1000 °C achieved the best removal of heavy metal ions among the wood-based materials and was even better than commercial activated carbon in both single and mixed solutions.

In addition to plantation wood, bamboo is an important material due to its rapid growth and a shortage of timber in Taiwan. Makino bamboo is a multipurpose species grown in Taiwan for fuel wood, food (bamboo shoots), construction materials, handicrafts, mat boards, and pressboards and for several other uses. In order to develop an innovative processing system which can significantly increase the value of the utilization of bamboo, manufacturers have studied the use of Makino bamboo charcoal for the removal of impurities from liquid solutions. However, the influence of the manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal is still not well known. In the light of the above, the present study was carried out to investigate the effects of manufacturing conditions on the adsorption capacity for heavy metal ions (including Pb2+, Cr3+, Cd2+, Ni2+, As5+, and Cu2+) by Makino bamboo charcoal. The results can provide information for estimating the benefits of utilizing Makino bamboo in the manufacture of charcoal.

2. Methods

2.1. Bamboo materials and manufacturing conditions of bamboo charcoal

Four-year-old Makino bamboo (Phyllostachys makinoi Hayata) was selected for this study. These were sliced into strips 12 cm (length) × 2 cm (width) × 0.5–1.0 cm (thickness). Separate samples of Makino bamboo were carbonized in a nitrogen atmosphere at varying furnace temperatures between 800 and 900 °C. Nitrogen gas was passed through the materials at a rate of 500 ml/min and heated at 10 °C/min. The temperature was kept at the target level for 2 h, after which the heater and gas flow were turned off. The carbonized materials were allowed to cool naturally inside the furnace to room temperature. After cooling, the sample group GC-1 was re-carbonized with the above conditions and then activated by carbon dioxide; the sample groups GH-1 and GH-4 were activated by steam; the sample group GC-2 was activated by carbon dioxide; the sample group G-1 was without activation. The activation temperature was kept at 800 and 900 °C for 2 h, respectively. The activated materials were allowed to cool naturally inside the furnace to room temperature before they were removed for analysis. The manufacturing conditions of Makino bamboo charcoal are shown in Table 1.

2.2. Specific surface area measurement

The specific surface area of the bamboo charcoal powder was measured using Micrometrics ASAP2010. The BET (Brunauer-Emmet-Teller) multipoint method and Langmuir method were used to determine the surface area. Nitrogen (N2) gas was used to determine the adsorption isotherms.

2.3. Iodine number measurement

The iodine number of the Makino bamboo charcoal was measured according to ASTM D4607-94 (1999): (1) Transfer 0.5 g Makino bamboo charcoal to a clean, dry 250-ml Erlenmeyer flask equipped with a ground glass stopper. (2) Pipet 10 ml of 5 wt% hydrochloric acid solution into each flask containing Makino bamboo charcoal. (3) Stopper each flask and swirl gently until the carbon is completely wetted. (4) Loosen the stoppers to vent the flasks, place on a hot plate in a fume hood, and bring the contents to a boil. Allow to boil gently for 30 ± 2 s to remove any sulfur which may interfere with the test results. (5) Remove the flasks from the hot plate and cool to room temperature. (6) Pipet 100 ml of 0.1 N iodine solution into each flask. Immediately stopper the flasks, and shake the contents vigorously for 30 ± 1 s. (7) Quickly filter each mixture by gravity through one sheet of folded filter paper (Whatman No. 2 V or equivalent) into a beaker. For each filtrate, use 10 ml of 0.1 N potassium iodide solution into each beaker. Add 10 ml of standardized 0.1 N sodium thiosulfate solution to each filtrate and titrate each filtrate with standardized 0.1 N sodium thiosulfate solution.

<table>
<thead>
<tr>
<th>Sample group</th>
<th>Carbonization times</th>
<th>Highest carbonization temperature (°C)</th>
<th>Activator</th>
<th>Activator injection rate</th>
<th>Activation temperature (°C)</th>
<th>Activation time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH-1</td>
<td>1</td>
<td>800</td>
<td>H2O</td>
<td>400 (ml/h)</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>GC-1</td>
<td>2</td>
<td>800</td>
<td>CO2</td>
<td>400 (ml/min)</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>G-1</td>
<td>1</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>GH-4</td>
<td>1</td>
<td>900</td>
<td>H2O</td>
<td>400 (ml/h)</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>GC-2</td>
<td>1</td>
<td>900</td>
<td>CO2</td>
<td>400 (ml/min)</td>
<td>900</td>
<td>2</td>
</tr>
</tbody>
</table>

* The pH values of GH-1, GC-1, G-1, GH-4, and GC-2 solutions (according to ASTM D3838-80) are 8.96, 9.23, 10.16, 9.12, and 9.40, respectively.
thiosulfate solution until the solution is a pale yellow. Add 2 ml of the starch indicator solution and continue the titration with sodium thiosulfate until one drop produces a colorless solution. (10) Record the volume of sodium thiosulfate used for determination of the amount of iodine adsorbed on to the carbon (mg/g).

2.4. Adsorption experiment

Standard solutions of lead nitrate [Pb(NO₃)₂], copper nitrate [Cu(NO₃)₂], nickel nitrate [Ni(NO₃)₂], chromium nitrate [Cr(NO₃)₃], cadmium nitrate [Cd(NO₃)₂], and arsenic acid [H₂AsO₄] in distilled water were prepared at 10 ppm concentrations on the basis of weight by weight (w/w) of each metal molecule. The pH values of lead nitrate, copper nitrate, nickel nitrate, chromium nitrate, cadmium nitrate, and arsenic acid solutions are 2.10, 2.08, 1.98, 2.09, 2.13, and 2.10, respectively. The charcoals from various manufacturing conditions were first placed in a 250-ml Erlenmeyer flask. Twenty milliliter of a standard heavy metal solution with a concentration of 10 ppm was added to the flask. The mixtures were stirred continuously in a constant temperature-controlled bath at 20 °C and left to settle before samples were taken after 1, 2, 4, 8, 12, 24, and 48 h (soaking time), respectively. The concentrations of heavy metal ions in the samples were measured using the ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy; SPECTRO GENESIS, Germany).

3. Results and discussion

3.1. Effects of manufacturing conditions on the specific surface area and iodine number

Results for the carbon yield, specific surface area, and iodine number of various Makino bamboo charcoals are listed in Table 2. A low carbon yield (12.3%) was found for the sample group GH-4, whereas high carbon yields (25.2–25.8%) were measured for sample groups GH-1 and G-1. However, a high specific surface area was observed for the sample group GH-4, whereas high carbon yields (25.2–25.8%) were measured for sample groups GH-1 and G-1. Kitamura and Katayama (2001) indicated that the specific surface area of the sample group GH-4 has the most generous time for activation. As shown in Table 2, the iodine number or specific surface area measured by the BET method increased with decreasing carbon yield. Table 2 also shows a high correlation between the iodine number and the specific surface area as measured by the BET method. The following linear regression equation was obtained using an F-value test:

\[ \text{Iodine number} = 0.6366 \times \text{specific surface area} + 174.34, \quad R^2 = 0.83. \]

3.2. Pore diameter, volume quantity and proportion of different pore diameters

The frequency of pore diameters can be used as an indicator of adsorption capacity in an activated carbon material. The sample groups GH-4 and GC-2 were chosen for pore diameter investigations by the BJH method (Barrett et al., 1951). Values for the volume quantity and proportion of different pore diameters, calculated by the BJH method, are shown in Table 3. The volume quantity and proportion of micropores for sample group GC-2 (activated by carbon dioxide) were larger than those for sample group GH-4 (activated by steam). However, the volume quantity and proportion of meso- and macropores, the bulk volume and the average pore diameter were greater for sample group GH-4. As shown in Table 2, the specific surface area (from the BET method) of GH-4 and GC-2 were 794 m²/g and 594 m²/g, respectively. There is a high frequency of micropores in GH-4 and GC-2. However, the frequency of mesopores was higher in GH-4 than in GC-2.

Wu et al. (1999) investigated the distribution of pore diameters from bamboo charcoal (Phyllostachys bambusoides) activated at 850 °C for 2 h. It was found that the largest and average pore diameter were around 3.8 nm and 2.63 nm, respectively. There are high frequencies of micro- and mesopores. Daud and Ali (2004) also reported a high

<table>
<thead>
<tr>
<th>Sample group</th>
<th>Carbon yield (%)</th>
<th>Specific surface area (m²/g)</th>
<th>Iodine number (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH-1</td>
<td>25.2</td>
<td>473.9</td>
<td>628.6</td>
</tr>
<tr>
<td>GC-1</td>
<td>21.6</td>
<td>570.0</td>
<td>755.3</td>
</tr>
<tr>
<td>G-1</td>
<td>25.8</td>
<td>563.6</td>
<td>747.4</td>
</tr>
<tr>
<td>GH-4</td>
<td>12.3</td>
<td>794.1</td>
<td>1073.1</td>
</tr>
<tr>
<td>GC-2</td>
<td>22.6</td>
<td>594.3</td>
<td>787.3</td>
</tr>
</tbody>
</table>
frequency of micropores in activated carbons from palm shell and coconut shell using an activation temperature of 850 °C. Furthermore, the volume quantity of macropores increased significantly at an activation temperature of 600 °C. However, the increased frequency of mesopores was not evident. In addition, micro- and mesopores increased along with a decrease of the carbon yield when the activation temperature was 800 °C and the activator was carbon dioxide. In comparison to the charcoal activated by steam, the frequency of micro- and mesopores was higher, whereas the frequency of meso- and macropores was lower. The volume quantity of meso- and macropores increased significantly with increasing activation temperature (750–800 °C), when steam was used as an activator. Compared to commercial activated carbon with a pore diameter of 1.7–2.9 nm and with a specific surface area of 650–1200 m²/g as used for the purification of wastewater (Wu et al., 1999), the Makino bamboo charcoal manufactured in this study can meet this standard.

3.3. Effects of soaking time on adsorption capacity of heavy metal ions

The results indicate that Makino bamboo charcoal activated by steam (GH-4: 0.1 g, 60–100 mesh) with a soaking time of 24 h had better adsorption capacity for Pb²⁺ (2.9 ppm) and Cu²⁺ (1.7 ppm), but poorer adsorption capacities were found for Cr³⁺ (0.7 ppm with a soaking time of 12 h), Ni²⁺ (0.7 ppm with a soaking time of 24 h), Cd²⁺ (0.2 ppm with a soaking time of 48 h), and As⁵⁺ (0.05 ppm with a soaking time of 24 h). Fig. 1 shows no evidence for any effect of soaking time on the heavy metal ion adsorption capacity of Makino bamboo charcoal (GC-2: 0.1 g, 60–100 mesh) activated by carbon dioxide. Our results reveal that the sample group GC-2 had better adsorption capacities for Pb²⁺ and Cu²⁺, but values were lower than those for the sample group GH-4. Furthermore, lower adsorption capacities for Cr³⁺, Ni²⁺, Cd²⁺, and As⁵⁺ were also found in this study.

The results also indicate that the Ni²⁺ adsorption capacities of the sample groups GH-4 (0.5 g, 10–30 mesh) and GC-2 (0.5 g, 10–30 mesh) increased with increasing soaking time. The adsorption capacities of Ni²⁺ with a soaking time of 24 h were 7.0 ppm and 3.2 ppm for the sample groups GH-4 and GC-2, respectively.

The adsorption process of heavy metal ions by charcoal includes external diffusion, internal diffusion and adsorption. The metal ion adsorption speed is mainly influenced by external diffusion and internal diffusion (Weber et al., 1991). The adsorption forces of the hydrophobic surface of bamboo charcoal are larger when the charcoal pit size is closer to the size of the heavy metal cation (Abe et al., 2001). However, compared to chemical adsorption forces, the adsorption forces of the hydrophobic surface of bamboo charcoal are weaker. It is possible that the adsorbed heavy metal ions will be desorbed (Lo, 2001).

In this study, a small quantity of charcoal (0.1 g) and a high concentration heavy metal ions (10 ppm) were tested. The adsorption process ceased after a relatively short duration. In this procedure, the sample group GH-4 with the larger specific surface area was able to adsorb more heavy metal ions with no soaking time influence. However, the desorption of adsorbed heavy metal ions can occur with the sample group GC-2 during the soaking process because of its smaller specific surface area. The results reveal that the Ni²⁺ adsorption capacities shown in tests with 0.5 g of charcoal were better than those with 0.1 g. The 0.5 g sample of charcoal had a larger specific surface area than the 0.1 g sample. The adsorption capacities of Ni²⁺ increased with increasing soaking time. This evidence of an increased rate of adsorption capacity of charcoal was observed with soaking time of up to 4 h.

3.4. Effects of manufacturing conditions on the adsorption capacity of heavy metal ions

Fig. 2 reveals the effects of manufacturing conditions on the charcoal’s adsorption capacity for heavy metal ions.
(10 ppm). 0.5 g of bamboo charcoal (10–30 mesh) with a soaking time of 2 h was examined. Results reveal that all the tested sample groups had better adsorption capacities for Pb$^{2+}$ (10 ppm), Cu$^{2+}$ (10 ppm), and Cr$^{3+}$ (8.8–9.8 ppm). Fig. 2 also demonstrates that the Ni$^{2+}$ adsorption capacities of tested materials carbonized at 800°C increased with increasing specific surface area. Furthermore, the Ni$^{2+}$ adsorption capacities of tested materials carbonized at 900°C and activated by steam or carbon dioxide increased linearly with increasing specific surface area ($R^2 = 0.989$). Moreover, the sample groups GH-1, GC-1, and GH-4 showed better adsorption capacities for Cd$^{2+}$ than the other sample groups. However, the $R^2$ value was low. For all tested bamboo charcoals, no significant effect on the adsorption capacity for As$^{5+}$ was observed. In particular, the sample groups GH-1 and GC-1 did not show any effect at manufacturing temperatures of 800°C.

Lo (2001) reported that the Pb$^{2+}$ adsorption capacity of charcoal was mainly affected by the functional groups on the charcoal surface. The carboxylic groups on adsorbents can play an important role in the adsorption of Cu$^{2+}$, Pb$^{2+}$, and Ni$^{2+}$ (Kadirvelu et al., 2000). Many researchers also reported the positive influence of acid functional groups and surface oxidation on the adsorption capacity for heavy metal ions (Pendyal et al., 1999; Ahmendna et al., 2000; Dong et al., 2000; Manju et al., 2002; Rangel-Mendez and Streat, 2002; Machida et al., 2005). Wang (2004) indicated that K, Ca, Mg, Fe, Mn, Si, and Cl can be found on the bamboo charcoal surface. After surface oxidation, they may form metal oxide compounds, which contribute to the adsorption of heavy metal ions. Bamboo charcoal, with larger specific surface area, more functional groups and metal oxide compounds had better adsorption capacity for Pb$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, and Ni$^{2+}$.

3.5. Effects of charcoal grain sizes and quantity on adsorption capacity of heavy metal ions

Fig. 3 indicates the effects of charcoal grain size on the adsorption capacity for heavy metal ions (10 ppm). 0.5 g of bamboo charcoal (GH-4, GC-2: 10–30 mesh and 60–100 mesh) with a soaking time of 24 h was investigated. Results show that the tested sample groups had better adsorption capacities for Pb$^{2+}$ (10 ppm), Cu$^{2+}$ (10 ppm), and Cr$^{3+}$ (10 ppm). The sample groups tested also had greater adsorption capacity for Cd$^{2+}$ (about 9 ppm). In this case no significant effect of charcoal grain size on adsorption capacity was observed. Smaller grain sizes showed better effects than larger grain sizes for all tested charcoals. Machida et al. (2005) reported that the specific surface area of charcoal and its adsorption capacity increased with decreasing grain size. In addition, the gap area of charcoal for adsorption of heavy metal ions increased because of small charcoal grain sizes (Liang and Lin, 1999). In this study, the sample group GH-4 (activated by steam) had a good adsorption capacity because of its large volume quantity, whereas the sample group GC-2 (activated by carbon dioxide) had a good adsorption capacity because of its high frequency of micropores.

The diameters of Pb$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Ni$^{2+}$, Cd$^{2+}$, and As$^{5+}$ are 0.0940 nm, 0.0620 nm, 0.0615 nm, 0.0690 nm, 0.0800 nm, and 0.0500 nm, respectively (Lin, 1993). They are smaller than those of sample groups GH-4 (1.99 nm) and GC-2 (1.92 nm) (Table 3). As a result, desorption of heavy metal ions was not commonly observed during the adsorption process (Abe et al., 2001). The adsorption capacity was influenced by the diameter of the heavy metal cation and the distribution of charcoal pore diameters. Kadirvelu et al. (2000) reported that Pb$^{2+}$ was highly...
adsorbed by mesopore charcoal. In this study, the percentages of mesopores in sample groups GH-4 and GC-2 were 75.87% and 68.36%, respectively.

It was also found that the Pb\(^{2+}\) adsorption capacity by Makino bamboo charcoal (GH-4) increased with increase of charcoal quantity and reached maximum adsorption capacity with 0.3 g of charcoal.

Fig. 4 demonstrates the effect of different manufacturing conditions (GH-4 and GC-2) and charcoal quantities (0.1 g and 0.5 g) on the adsorption capacity of heavy metal ions. Compared to 0.1 g of bamboo charcoal, the heavy metal ion adsorption capacity of 0.5 g of bamboo charcoal was more than five times better.

4. Conclusions

The effects of manufacturing conditions on the adsorption capacity of heavy metal ions using Makino bamboo charcoal were investigated in this study. Our results show that the specific surface area and iodine number of bamboo charcoal activated at 900 °C (GH-4 and GC-2) were greater than those of bamboo charcoal activated at 800 °C (GH-1 and GC-1). In comparison to bamboo charcoal activated at 800 °C by carbon dioxide (GC-1), the specific surface area was larger than that of charcoal activated by steam (GH-1). However, a contrary result was observed when the activation temperature was 900 °C.

The volume quantity and proportion of micropores in bamboo charcoal activated by carbon dioxide (GC-1 and GC-2) were greater than those of the other sample groups. However, the volume quantity and bulk volume of meso- and macropores, and average pore diameter for the Makino bamboo charcoal activated by steam (GH-1 and GH-4) were greater than those in the other sample groups.

Using 5 g bamboo charcoal (10–30 mesh) with a soaking time of 24 h, a better adsorption effect was found for Pb\(^{2+}\) (100%), Cu\(^{2+}\) (100%), and Cr\(^{3+}\) (88–98%). However, medium frequencies were observed for the adsorption effect on Cd\(^{2+}\) (40–80%) and Ni\(^{2+}\) (20–60%). The average Cd\(^{2+}\) and Ni\(^{2+}\) adsorption capacities of various charcoal groups were (in decreasing order) GH-4 > GC-1 > GH-1 > GC-2 > G-1, and GH-4 > GC-1 > GH-1 > G-1 > GC-2, respectively. For the adsorption of As\(^{5+}\), only the sample groups GC-2, GH-1 and G-1 had any effect and this was very limited.

Our results indicate that the sample group GC-2 had better adsorption capacity for Pb\(^{2+}\) and Cu\(^{2+}\), but values were lower than those of sample group GH-4. Furthermore, smaller adsorption capacities for Cr\(^{3+}\), Ni\(^{2+}\), Cd\(^{2+}\), and As\(^{5+}\) were also detected in this study. For the same grain sizes, the adsorption capacities of 0.5 g charcoal were better than those for 0.1 g. Better adsorption by the sample group activated by steam was observed in comparison to the sample group activated by carbon dioxide.

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