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Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons

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ABSTRACT

In order to understand the adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons, the carbon yield, specific surface area, micropore area, zeta potential, and the effects of pH value, soaking time and dosage of bamboo activated carbon were investigated in this study. In comparison with once-activated bamboo carbons, lower carbon yields, larger specific surface area and micropore volume were found for the twice-activated bamboo carbons. The optimum pH values for adsorption capacity and removal efficiency of heavy metal ions were 5.81–7.86 and 7.10–9.82 by Moso and Ma bamboo activated carbons, respectively. The optimum soaking time was 2–4 h for Pb²⁺, 4–8 h for Cu²⁺ and Cd²⁺, and 4 h for Cr³⁺ by Moso bamboo activated carbons, and 1 h for the tested heavy metal ions by Ma bamboo activated carbons. The adsorption capacity and removal efficiency of heavy metal ions of the various bamboo activated carbons decreased in the order: twice-activated Ma bamboo carbons > once-activated Ma bamboo carbons > twice-activated Moso bamboo carbons > once-activated Moso bamboo carbons. The Ma bamboo activated carbons had a lower zeta potential and effectively attracted positively charged metal ions. The removal efficiency of heavy metal ions by the various bamboo activated carbons decreased in the order: Pb²⁺ > Cu²⁺ > Cr³⁺ > Cd²⁺.

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Keywords: Bamboo; Activated carbon; Adsorption capacity; Removal efficiency; Heavy metal ion

1. Introduction

Recently, the heavy metal compounds in wastewater from high industry activities have caused environmental pollution and serious symptoms of poisoning. Heavy metal pollution caused by cadmium, chromium, copper, lead, mercury, nickel and arsenic is most serious to the human body (WHO, 2004). 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 illness in humans 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 used to remove impurities from liquid solutions. It has been widely used to treat industrial and household water (Sirianuntapiboon and

Ungkprasatcha, 2007) because of its excellent adsorption properties, characterized by a high specific surface area (Cao et al., 2006). It is also used to remove metal ions from solution (Issabayeva et al., 2006). The increasing variety and amounts of potentially hazardous impurities in water have led to the increased 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) used carbonized sugi wood powder to remove mercury and other metal ions from aqueous solutions of their

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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 our previous study (Wang et al., 2008), a better adsorption effect was found for Pb²⁺ (100%), Cu²⁺ (100%) and Cr³⁺ (88–98%) using carbonized Makinoi bamboo charcoal. However, medium frequencies were observed for the adsorption effect on Cd²⁺ (40–80%) and Ni²⁺ (20–60%). For the adsorption of As⁵⁺, only some sample groups had any effect and this was very limited.

Nomanbhay and Palanisamy (2005) indicated that the metal ion adsorption effect was greatly influenced by the solution pH value, which concerns the solubility of metal ions, ion concentration of adsorbent functional groups, and degree of ionization of the adsorbate in the reaction. The surface charge of the adsorbent could be improved by changing the solution pH value. Rangel-Mendez and Streat (2002) also reported the influence of surface oxidation and solution pH value on the adsorption capacity for heavy metal ions. In order to understand the adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons after different manufacturing processes, the carbon yield, specific surface area, micropore area, zeta potential, and the effects of pH value, soaking time and dosage of bamboo activated carbon were investigated in this study. The results may provide information for estimating the benefits of utilizing bamboo in the manufacture of activated carbon.

2. Materials and methods

2.1. Bamboo materials and manufacture of bamboo activated carbons

Moso (*Phyllostachys pubescens*; oven dry density 0.77 g/cm³) and Ma (*Dendrocalamus latiflorus*; oven dry density 0.75 g/cm³) bamboos greater than 3 years old were selected for this study. These were sliced into strips 120 mm (length) × 20 mm (width) × 5–10 mm (thickness). Separate samples of the test bamboo were carbonized in a nitrogen atmosphere at varying furnace temperatures. Nitrogen gas was passed through the materials at a rate of 500 ml/min and heated at 10 °C/min to 800 °C. The sample groups were then activated by deionized water at a rate of 400 ml/h. The temperature was kept at 800 °C for 1 h, after which the heater was turned off. The activated materials, S1C1 (once-activated Moso bamboo) and S1M1 (once-activated Ma bamboo), were allowed to cool naturally inside the furnace to room temperature before they were removed for analysis.

Additional sample groups, carbonized (600 °C) Moso and Ma bamboos, were used for recarbonization in a nitrogen atmosphere at varying furnace temperatures. Similarly, nitrogen gas was passed through the materials at a rate of 500 ml/min and heated at 10 °C/min to 800 °C. The sample groups were then activated by deionized water at a rate of 400 ml/h. The temperature was kept at 800 °C for 1 h, after which the heater was turned off. The activated materials, S2C1 (twice-activated Moso bamboo) and S2M1 (twice-activated Ma bamboo), were allowed to cool naturally inside the furnace to room temperature before they were removed for analysis. All of the bamboo activated carbons were pulverized to a geometric mean particle size of 180–150 μm (80–100 mesh) and stored at room temperature.

2.2. Specific surface area and pore diameter measurement

The specific surface area of the bamboo activated carbon powder was measured using Micromeritics ASAP2010. The BET (Brunauer–Emmet–Teller) multipoint method (Jankowska et al., 1991) and Langmuir method (Gregg and Sing, 1982) were used to determine the surface area. Nitrogen (N₂) gas was used to determine the adsorption isotherms (Lowell and Shields, 1991). The micropore volume and micropore area of bamboo activated carbons were measured using the t-plot method (De Boer et al., 1966; Sing et al., 1985). For distribution measurement of meso- and macropore of bamboo activated carbons, the gas adsorption of pore diameter between 17 Å and 300 Å was investigated by the Barrett–Joyner–Halenda method (BJH method) (Barrett et al., 1951).

2.3. Adsorption capacity and removal efficiency of heavy metal ions

Standard solutions of lead nitrate [Pb(NO₃)₂], copper nitrate [Cu(NO₃)₂], chromium nitrate [Cr(NO₃)₃], and cadmium nitrate [Cd(NO₃)₂] 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, chromium nitrate, and cadmium nitrate solutions were 2.10, 2.08, 2.09, and 2.13, respectively. The bamboo activated carbons from various manufacturing conditions were first placed in a 250-ml Erlenmeyer flask. 20 ml of a standard heavy metal solution at a concentration of 10 ppm was added to the flask. The mixtures were stirred continuously in a constant temperature-controlled bath at 25 °C and left to settle before samples were taken after 2, 4, 8, 12, and 24 h (soaking time), respectively. The concentrations of heavy metal ions in the samples were measured using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy; SPECTRO GENESIS, Germany). The adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons could be expressed as follows:

$$AC = \frac{(C_i - C_f) \times V}{W_g} \quad (1)$$

$$RE (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where AC is the adsorption capacity of heavy metal ions, RE (%) is the removal efficiency of heavy metal ions, C_i (mg/l) and C_f (mg/l) are the concentration of heavy metal ions before and after adsorption experiments, respectively, V (l) is the solution volume of heavy metal ions, and W_s (g) is the dosage of bamboo activated carbon.

2.4. Zeta potential measurements

The zeta potential of bamboo activated carbon suspensions was measured using a Nano-Zetasizer 3000 (Malvern Inc.) equipped with a microprocessor unit. The zeta potential measurements were carried out as a function of equilibrium pH. The suspension pH was adjusted by addition of HCl and NaOH. A sample of 0.1 g bamboo activated carbon in 30 ml deionized water containing the desired pH values was added to an orbital shaker incubator and rinsed for 24 h at 25 °C. The samples were allowed to stand for 5 min to let particles settle. An

Table 1 – Carbon yield, specific surface area and pore properties of Moso and Ma bamboo activated carbons.

Bamboo activated carbon group	Carbon yield (%)	Specific surface area (m ² /g)		Micropore area (A _i) (m ² /g)	Pore volume (cm ³ /g)		Average pore diameter (nm)	$\frac{A_i}{A_b}$ (%)	$\frac{V_i}{V_t}$ (%)
		BET method (A _b)	Langmuir method		Total (V _t)	Micro (V _i)			
S1C1	22.6	486.80	613.15	385.51	0.2353	0.1663	1.9331	73.65	70.68
S2C1	15.4	522.90	621.47	434.05	0.2427	0.1818	1.8563	83.01	74.91
S1M1	24.3	464.70	617.55	391.95	0.2329	0.2032	2.0049	84.34	87.25
S2M1	18.5	589.65	654.25	492.49	0.2763	0.2320	1.8742	83.52	83.97

S1C1, once-activated Moso bamboo carbon; S2C1, twice-activated Moso bamboo carbon; S1M1, once-activated Ma bamboo carbon; S2M1, twice-activated Ma bamboo carbon.

aliquot taken from the supernatant was used to measure the zeta potential.

3. Results and discussion

3.1. Carbon yield, specific surface area and pore properties

Results for the carbon yield, specific surface area, and pore properties of the various Moso and Ma bamboo activated carbons are listed in Table 1. Lower carbon yields were found for the sample groups S2C1 (15.4%) and S2M1 (18.5%), whereas higher carbon yields were measured for sample groups S1C1 (22.6%) and S1M1 (24.3%). This is because the bamboo quantity decreased during the recarbonization process (twice-activated bamboo carbons). In comparison to the once-activated bamboo carbons (S1C1 and S1M1), a higher specific surface area, micropore area, micropore volume, and pore volume were observed for the twice-activated bamboo carbons (S2C1 and S2M1).

3.2. pH value of bamboo activated carbon

Table 2 shows that the pH values of the test bamboo activated carbons were 9.59–9.82 (S1C1 group), 9.32–9.44 (S2C1 group), 10.53–10.86 (S1M1 group), and 9.82–10.37 (S2M1 group), respectively. Similar results (pH values 8.25–10.15) of various bamboo activated carbons using different manufacturing conditions were found by Yatagai et al. (1995), Fujiwara et al. (2003), Wang (2004) and Sun (2006). Regardless of the different carbonization temperatures and heating rates, the pH values of bamboo activated carbons were greater than 7. However, the pH values of wood activated carbons were 4.54–6.42 for the lower carbonization temperatures (<400 °C) and 9.15–9.61 for the higher carbonization temperatures (800–1000 °C), respectively. This is because the organic acid of carbonized wood decreased with increasing carbonization temperature (Lilibeth et al., 1998).

From an SEM-EDS investigation, Lo and Wang (2007) found K, Si, Ca, Mg, and P on the surfaces of Moso bamboo activated carbons. In general, more K and Mg exist in bamboo than in wood; whereas the Ca content is equal in both bamboo and wood. The K content in bamboo carbons increased with increasing carbonization temperature. A higher percentage of K (30%) was found in bamboo carbon with an ash percentage of 17.82% (Yatagai et al., 1995). In comparison to bamboo, a lower K (10%) and ash content (1%) are found in wood.

3.3. Effect of bamboo activated carbon dosage on pH value of heavy metal solution

Fig. 1 demonstrates the effects of bamboo activated carbon dosage (0 g, 0.1 g, 0.3 g, 0.5 g) on pH value of the heavy metal solution (10 ppm in each 20 ml). Generally, the pH value of the heavy metal solution increased with bamboo activated carbon dosage. For the S1C1 sample group in the test heavy metal solutions, the pH value of the heavy metal solution increased linearly with Moso bamboo activated carbon dosage. For the S2C1 sample group in the test heavy metal solutions, the pH value of the heavy metal solution remained steady when the dosage was over 0.3 g. For the S1M1 sample group in the test heavy metal solutions, the pH value of Pb²⁺ and Cu²⁺ solutions remained steady when the dosage was over 0.1 g; whereas, the pH value of Cr³⁺ and Cd²⁺ solutions remained steady when the dosage was over 0.5 g. For the S2M1 sample group in the test heavy metal solutions, the pH value of the heavy metal solutions remained steady when the dosage was over 0.1 g. The optimum pH values of the maximum adsorption capacity and the effect of the various bamboo activated carbons on increasing rate of pH value of the heavy metal solution decreased in the order: once-activated Ma bamboo carbons (S1M1 group, pH value: 8.16–9.82) > twice-activated Ma bamboo carbons (S2M1 group, pH value 7.10–7.83) > twice-activated Moso bamboo carbons (S2C1 group, pH value 6.734–7.52) > once-activated Moso bamboo carbons (S1C1 group, pH value 4.88–6.07). Ma bamboo

Table 2 – Effects of initial pH values on zeta potentials of Moso and Ma bamboo activated carbon suspensions.

Bamboo activated carbon group	pH value	Zeta potential (mV) pH = 2	Final pH value	Zeta potential (mV) pH = 7	Final pH value
S1C1	9.59–9.82	37.65	2.06	–25.18	7.4
S2C1	9.32–9.44	18.27	2.08	–33.08	7.7
S1M1	10.53–10.86	16.20	2.43	–35.24	8.7
S2M1	9.82–10.37	6.67	2.55	–36.07	8.5

For S1C1, S2C1, S1M1, and S2M1, see Table 1.

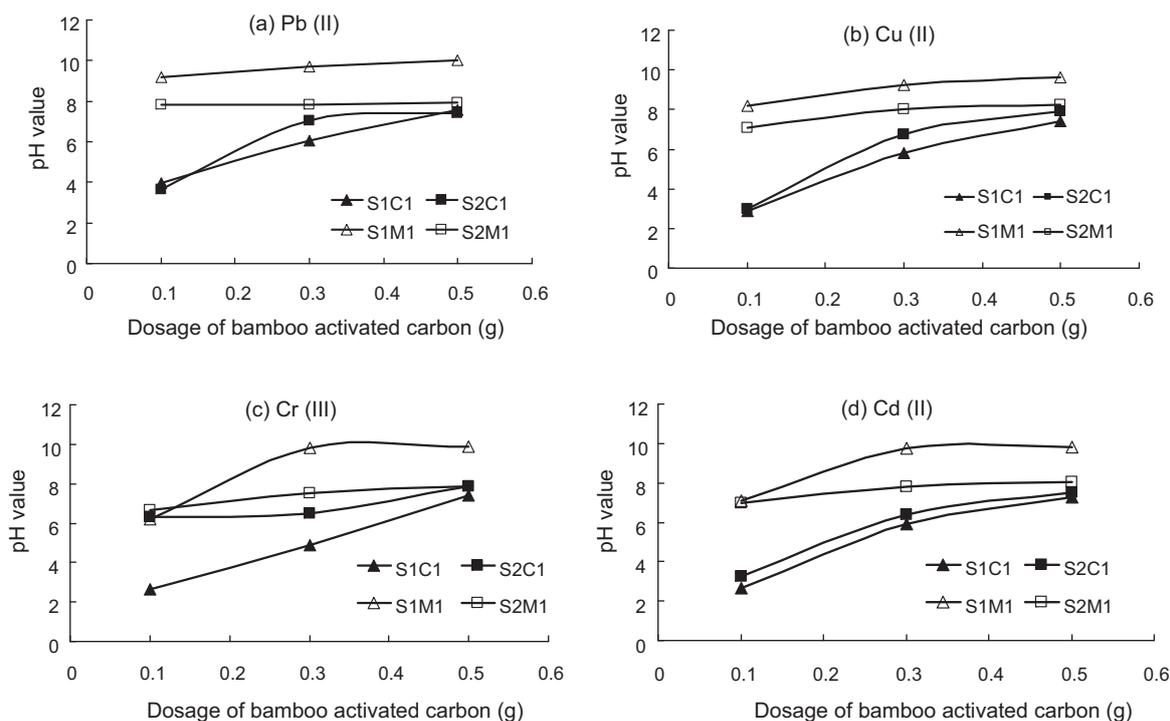


Fig. 1 – Relationship between bamboo activated carbon dosage and pH value of the heavy metal solution.

carbons with lower dosage possessed higher pH values and better adsorption capacity.

3.4. Optimum pH value of bamboo activated carbon for adsorption of heavy metal ions

Table 3 demonstrates the effects of Moso and Ma bamboo activated carbons (soaking time 24 h) on the adsorption capacity and removal efficiency of heavy metal ions (10 ppm). The pH values of the test heavy metal solutions were 2.47–2.54. The adsorption capacity increased rapidly with increasing pH value in the initial stage. However, the adsorption capacity decreased with increasing pH value after the maximum adsorption capacity was reached. The corresponding pH value defined as the optimum pH value was obtained when the maximum adsorption capacity was reached.

Table 3 shows the different optimum pH values according to the different heavy metal ions and bamboo activated carbons. The optimum pH values of Moso and Ma bamboo activated carbons were 5.81–7.52 and 7.10–9.77, respectively.

Table 3 also shows 100% removal efficiency by the S1C1 and S2C1 groups on Pb^{2+} and Cu^{2+} , and by the S1M1 and S2M1 groups on Pb^{2+} , Cu^{2+} , Cr^{3+} , and Cd^{2+} ; whereas, a 43.9–65.8% removal efficiency by the S1C1 group on Cr^{3+} and Cd^{2+} , and the S2C1 group on Cd^{2+} was observed. The optimum pH values of Moso and Ma bamboo activated carbons for maximum removal efficiency were 7.26–7.86 and 7.53–9.82, respectively.

Ücer et al. (2006) reported that the optimum pH values of tannic acid immobilized activated carbons for adsorption of Cu^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} , and Fe^{3+} were 5.4, 5.7, 5.6, 5.4, and 4.0, respectively. Using activated carbon from rice hulls for adsorption of copper and cadmium ions, an optimum pH value of 5–8 was found by Teker et al. (1999). Kononova et al. (2001) indicated that the optimum pH value for adsorption of Zn^{2+} , Cu^{2+} , and Fe^{3+} using carbonaceous adsorbent

was 3.0–5.0. Amuda et al. (2007) reported that the removal efficiency of Zn^{2+} from industrial wastewater using modified activated coconut shell carbon increased linearly with increasing pH value. The removal efficiency remained steady, possibly because of ion exchange and formation of aqueous metal-OH compounds, when the pH value was greater than 6.

Kadirvelu et al. (2000) found that the maximum removal efficiency of Cu^{2+} (73%), Hg^{2+} (100%), Pb^{2+} (100%), and Cd^{2+} (100%) occurred at a pH value of 4–5 by activated carbon cloths. When activated carbon prepared from apricot stone with a pH value ranging from 1 to 6 was used, the adsorption capacity decreased from 34.70 to 7.86 mg/g for Cr^{6+} ; whereas, the adsorption capacity increased from 7.74 to 30.07 mg/g for Cd^{2+} , from 2.83 to 29.47 mg/g for Cr^{3+} , from 2.51 to 27.21 mg/g for Ni^{2+} , from 4.86 to 24.21 mg/g for Cu^{2+} , and from 6.69 to 22.85 mg/g for Pb^{2+} , respectively (Kobya et al., 2005). In their study, the maximum removal efficiency and corresponding optimum pH value were 99.99% and 1 for Cr^{6+} , 99.86% and 3 for Pb^{2+} , 99.67% and 5 for Cd^{2+} , 99.17% and 6 for Co^{2+} , 98.56% and 4 for Cr^{3+} , 97.59% and 4 for Ni^{2+} , and 96.24% and 4 for Cu^{2+} , respectively.

Lilibeth et al. (2001) found good adsorption of Hg^{2+} by sugi wood carbonized at 1000 °C (pH value 3–9); whereas, the adsorption capacity decreased when the pH value was greater than 9. Kadirvelu et al. (2004) also reported that the removal efficiency of Hg^{2+} by activated carbon made from sago waste increased with increasing pH value from 2 to 10.

From the above-mentioned references, it was concluded that the adsorption capacity of heavy metal ions by most of the various activated carbons was better at a pH value less than 7. On the contrary, the maximum adsorption capacity in our study was reached when the pH value of the test bamboo activated carbon solution was greater than 7. This is because the pH values of the test bamboo activated carbons were 9.32–10.86. According to our SEM-EDAX results, there were high amount of Si (74.5%), K, Ca and Mg metallic crystals on our

Table 3 – Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons (soaking time 24 h).

Bamboo activated carbon group	Dosage (g)	Pb(II)			Cu(II)			Cr(III)			Cd(II)		
		pH	Adsorption capacity (mg/g)	Removal efficiency (%)	pH	Adsorption capacity (mg/g)	Removal efficiency (%)	pH	Adsorption capacity (mg/g)	Removal efficiency (%)	pH	Adsorption capacity (mg/g)	Removal efficiency (%)
S1C1	0	2.54	–	–	2.48	–	–	2.47	–	–	2.54	–	–
	0.1	3.94	0.236	24.26	2.90	0.002	0.10	2.62	0	0.01	2.66	0.002	0.01
	0.3	6.07	0.675	99.87	5.81	0.587	86.43	4.88	0.328	49.54	5.90	0.197	29.91
	0.5	7.54	0.407	100.00	7.39	0.401	100.00	7.40	0.257	53.06	7.26	0.174	43.86
S2C1	0	2.54	–	–	2.48	–	–	2.47	–	–	2.54	–	–
	0.1	3.66	0.380	20.16	2.99	0.259	14.16	6.33	0.090	4.95	3.24	0.041	2.08
	0.3	7.04	0.638	100.00	6.73	0.660	99.10	6.47	0.493	71.89	6.38	0.238	37.17
	0.5	7.40	0.396	100.00	7.91	0.400	100.00	7.86	0.392	100.00	7.52	0.257	65.83
S1M1	0	2.54	–	–	2.48	–	–	2.47	–	–	2.54	–	–
	0.1	9.18	1.901	100.00	8.16	1.908	100.00	6.21	0.423	23.71	7.10	0.403	21.02
	0.3	9.70	0.676	99.98	9.25	0.650	100.00	9.82	0.634	100.00	9.77	0.670	98.44
	0.5	10.02	0.404	100.00	9.60	0.634	100.00	9.85	0.400	100.00	9.8	0.398	100.00
S2M1	0	2.54	–	–	2.48	–	–	2.47	–	–	2.54	–	–
	0.1	7.83	1.998	100.00	7.10	1.425	73.98	6.65	0.631	33.38	6.95	0.381	20.82
	0.3	7.85	0.667	100.00	8.00	0.650	100.00	7.53	0.658	100.00	7.78	0.655	99.86
	0.5	7.95	0.397	100.00	8.26	0.398	100.00	7.84	0.393	100.00	8.05	0.396	100.00

For S1C1, S2C1, S1M1, and S2M1, see Table 1.

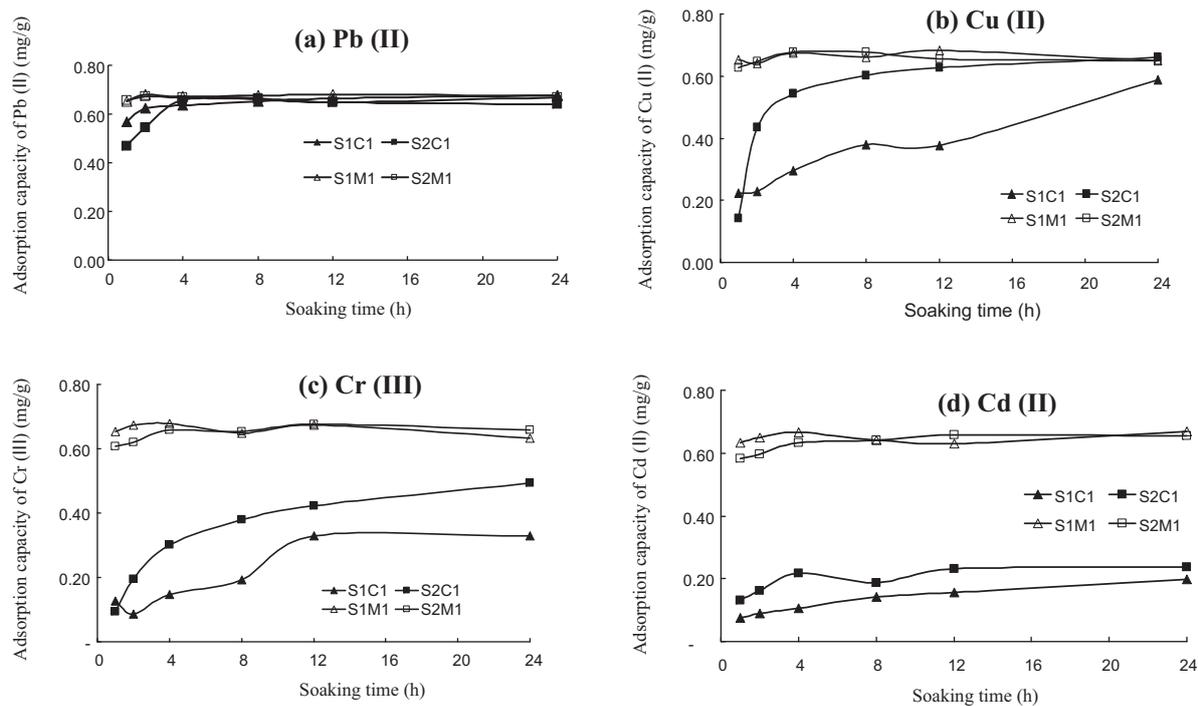


Fig. 2 – Relationship between the adsorption capacity of heavy metal ions and soaking time (0.3 g bamboo activated carbon).

bamboo carbons which gave the effect of pH above 7 during adsorption processes.

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

Fig. 2 shows the effects of soaking time on adsorption capacity of heavy metal ions using 0.3 g of the test bamboo activated carbons. The results indicate that the adsorption capacity of Pb^{2+} increased with increasing soaking time. The increased rate of the adsorption capacity remained steady after a soaking time of 2–4 h for Moso bamboo activated carbons and 1 h for Ma bamboo activated carbons, respectively. After 24-h soaking, the adsorption capacity of Pb^{2+} was 0.638–0.675 mg/g for Moso bamboo activated carbons and 0.667–0.676 mg/g for Ma bamboo activated carbons, respectively (Fig. 2a). The results also showed that the removal efficiency increased with increasing soaking time. After 1-h and 2-h soaking with Moso bamboo activated carbon, the removal efficiency of Pb^{2+} was 71.6–86.4% and 79.3%, respectively. The Ma bamboo activated carbon had better removal efficiency for Pb^{2+} (98.8–99.9% and 100% after 1-h and 24-h soaking, respectively).

Fig. 2b demonstrates that the adsorption capacity of Cu^{2+} increased with increasing soaking time. The increased rate of the adsorption capacity remained steady after a soaking time of 8 h for the S1C1 group, 4 h for the S2C1 group, and 1 h for the S1M1 and S2M1 groups, respectively. After 24-h soaking, the adsorption capacity of Cu^{2+} was 0.587–0.660 mg/g for the S1C1 and S2C1 groups and 0.650 mg/g for the S1M1 and S2M1 groups, respectively. The results also showed that the removal efficiency increased with increasing soaking time. After 1-h soaking with the test specimens, the removal efficiency of Cu^{2+} was 33.2% for the S1C1 group, 21.9% for the S2C1 group, 100% for the S1M1 group, and 93.5% for the S2M1 group, respectively. After 24-h soaking with the test specimens, the removal efficiency of Cu^{2+} was 86.43% for the S1C1 group, 99.10% for the S2C1 group, and 100% for the S1M1 and S2M1 groups, respectively.

Fig. 2c shows that the adsorption capacity of Cr^{3+} increased with increasing soaking time. The increased rate of the adsorption capacity remained steady after a soaking time of 4 h for the S1C1 and S2C1 groups, and 1 h for the S1M1 and S2M1 groups, respectively. After 24-h soaking, the adsorption capacity of Cr^{3+} was 0.328 mg/g for the S1C1 group, 0.493 mg/g for the S2C1 group, 0.634 mg/g for the S1M1 group, and 0.658 mg/g for the S2M1 group, respectively. The results also indicated that the removal efficiency increased with increasing soaking time. After 1-h soaking with the test specimens, the removal efficiency of Cr^{3+} was 8.74% for the S1C1 group, 14.4% for the S2C1 group, 100% for the S1M1 group, and 91.7% for the S2M1 group, respectively. After 24-h soaking with the test specimens, the removal efficiency of Cr^{3+} was 49.54% for the S1C1 group, 71.89% for the S2C1 group, and 100% for the S1M1 and S2M1 groups, respectively.

Fig. 2d shows that the adsorption capacity of Cd^{2+} increased with increasing soaking time. The increased rate of the adsorption capacity remained steady after a soaking time of 8 h for the S1C1 group, 4 h for the S2C1 group, and 1 h for the S1M1 (0.670 mg/g) and S2M1 (0.655 mg/g) groups, respectively. After 24-h soaking, the adsorption capacity of Cd^{2+} was 0.197 mg/g for the S1C1 group, and 0.238 mg/g for the S2C1 group, respectively. The results also indicated that the removal efficiency increased with increasing soaking time. After 1-h soaking with the test specimens, the removal efficiency of Cd^{2+} was 11.5% for the S1C1 group, 19.5% for the S2C1 group, 96.4% for the S1M1 group, and 87.8% for the S2M1 group, respectively. After 24-h soaking with the test specimens, the removal efficiency of Cd^{2+} was 29.91% for the S1C1 group, 37.17% for the S2C1 group, 98.44% for the S1M1 group, and 99.86% for the S2M1 group, respectively.

Our experimental results revealed that the optimum soaking time was 2–4 h for Pb^{2+} , 4–8 h for Cu^{2+} and Cd^{2+} , and 4 h for Cr^{3+} by Moso bamboo activated carbons, and 1 h for the tested heavy metal ions by Ma bamboo activated carbons. The adsorption capacity and removal efficiency of heavy metal ions of the various bamboo activated carbons decreased

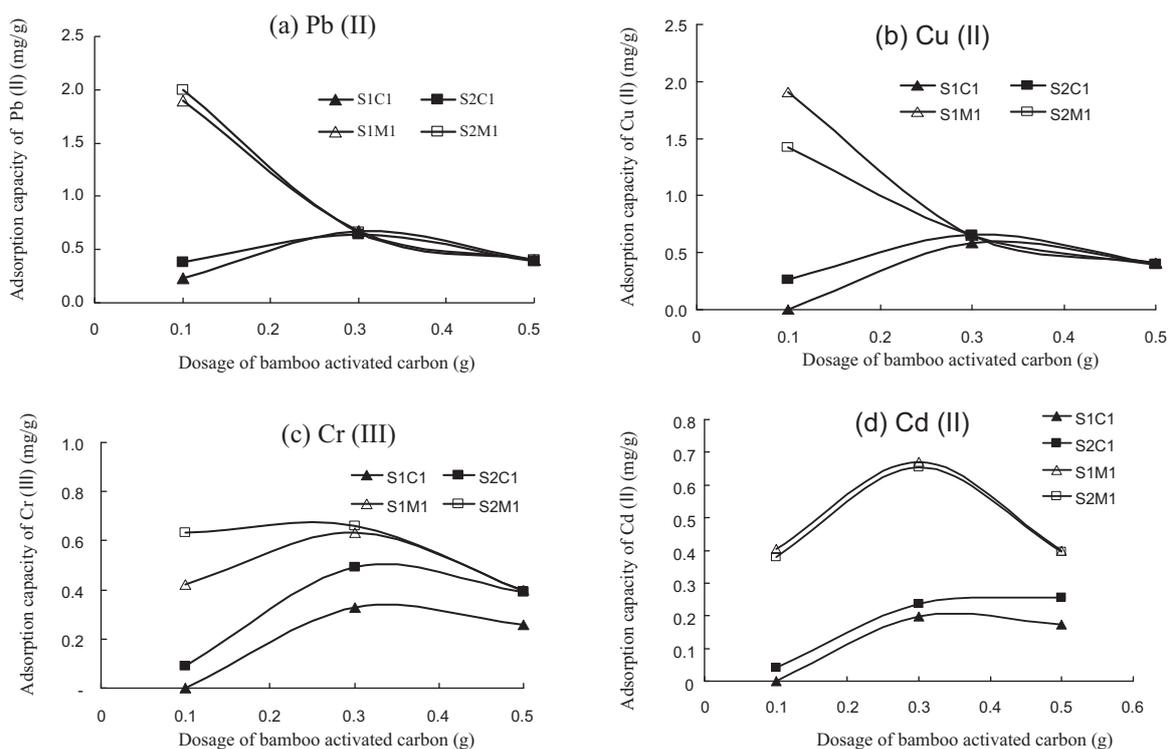


Fig. 3 – Relationship between the adsorption capacity of heavy metal ions and bamboo activated carbon dosage.

in the order: twice-activated Ma bamboo carbons > once-activated Ma bamboo carbons > twice-activated Moso bamboo carbons > once-activated Moso bamboo carbons. Ücer et al. (2006) also reported that the removal efficiency increased with increasing soaking time up to 60 min. An optimum soaking time (20–60 min) for removal of metal divalent ions was found by Brown et al. (2000). Amuda et al. (2007) indicated that the Zn^{2+} removal efficiency increased with increasing soaking time up to equilibrium adsorption.

The optimum adsorption time for S1C1 and S2C1 bamboo carbons was greater than data by other authors mostly because the results presented here were set to 100% removal efficiency and we extended the adsorption to 24 h. In general, the removal efficiencies of Pb(II), Cu(II), Cr(III) and Cd(II) by S1M1 and S2M1 in 1 h were high and better than those of other authors as 99.9%, 100%, 100%, 96.4% and 98.8%, 93.5%, 91.7%, 87.8%, respectively. And the optimum adsorption time was longer (4–8 h) and the removal efficiency lower (20–77%) for S1C1 and S2C1 might due to the average pore diameter tended to be less than 2 nm which meant the pores were majorly micropores.

3.6. Effects of bamboo activated carbon dosage on adsorption capacity and removal efficiency of heavy metal ions

Fig. 3 shows that the adsorption capacity of Pb^{2+} , Cu^{2+} , Cr^{3+} , and Cd^{2+} increased with increasing dosage of Moso bamboo activated carbons. The increased rate of the adsorption capacity remained steady by using 0.3 g Moso bamboo activated carbons. However, the adsorption capacity of Ma bamboo activated carbons reached an optimum by using 0.1 g of Pb^{2+} and Cu^{2+} , and 0.3 g Cr^{3+} and Cd^{2+} , respectively.

Fig. 4a shows that the removal efficiency for Pb^{2+} increased with increasing dosage of Moso bamboo activated carbons and reached 99.87% by using 0.3 g of the S1C1 group and reached

100% by using 0.3 g of the S2C1 group, respectively. However, the test groups (S1M1 and S2M1) at a dosage of 0.1 g had 100% removal efficiency for Pb^{2+} . Fig. 4b shows that the removal efficiency for Cu^{2+} increased with increasing dosage of Moso bamboo activated carbons and reached 86.43% by using 0.3 g of the S1C1 group, reached 99.10% by using 0.3 g of the S2C1 group, and reached 100% by using 0.5 g of the S1C1 and S2C1 groups, respectively. The test groups (S1M1 at a dosage of 0.1 g and S2M1 at a dosage of 0.3 g) had 100% removal efficiency for Cu^{2+} . Fig. 4c shows that the removal efficiency for Cr^{3+} was very poor by using 0.1 g Moso bamboo activated carbons. However, the removal efficiency increased with increasing dosage of Moso bamboo activated carbons and reached 53.06% by using 0.5 g of the S1C1 group, and reached 100% by using 0.5 g of the S2C1 group, respectively. The removal efficiency was 23.71% for the S1M1 group at 0.1 g and 33.38% for the S2M1 group at 0.1 g. The test groups (S1M1 and S2M1 at a dosage of 0.3 g) had 100% removal efficiency for Cr^{3+} . Fig. 4d shows that the removal efficiency for Cd^{2+} increased with increasing dosage of Moso bamboo activated carbons and reached 43.86% by using 0.5 g of the S1C1 group and reached 65.83% by using 0.5 g of the S2C1 group, respectively. Similarly, the removal efficiency increased with increasing dosage of Ma bamboo activated carbons and reached 98.44% and 99.86% by using 0.3 g of the S1M1 and S2M1 groups, and reached 100% by using 0.5 g of the S1M1 and S2M1 groups, respectively.

The adsorption capacity and removal efficiency of heavy metal ions by the various bamboo activated carbons decreased in the order: twice-activated Ma bamboo carbons > once-activated Ma bamboo carbons > twice-activated Moso bamboo carbons > once-activated Moso bamboo carbons. This is partly because the specific surface area, pore volume, and micropore area of twice-activated bamboo carbons were larger than those of once-activated bamboo carbons. Furthermore, the average pore diameter of twice-activated bamboo carbons was smaller than that of once-activated bamboo carbons

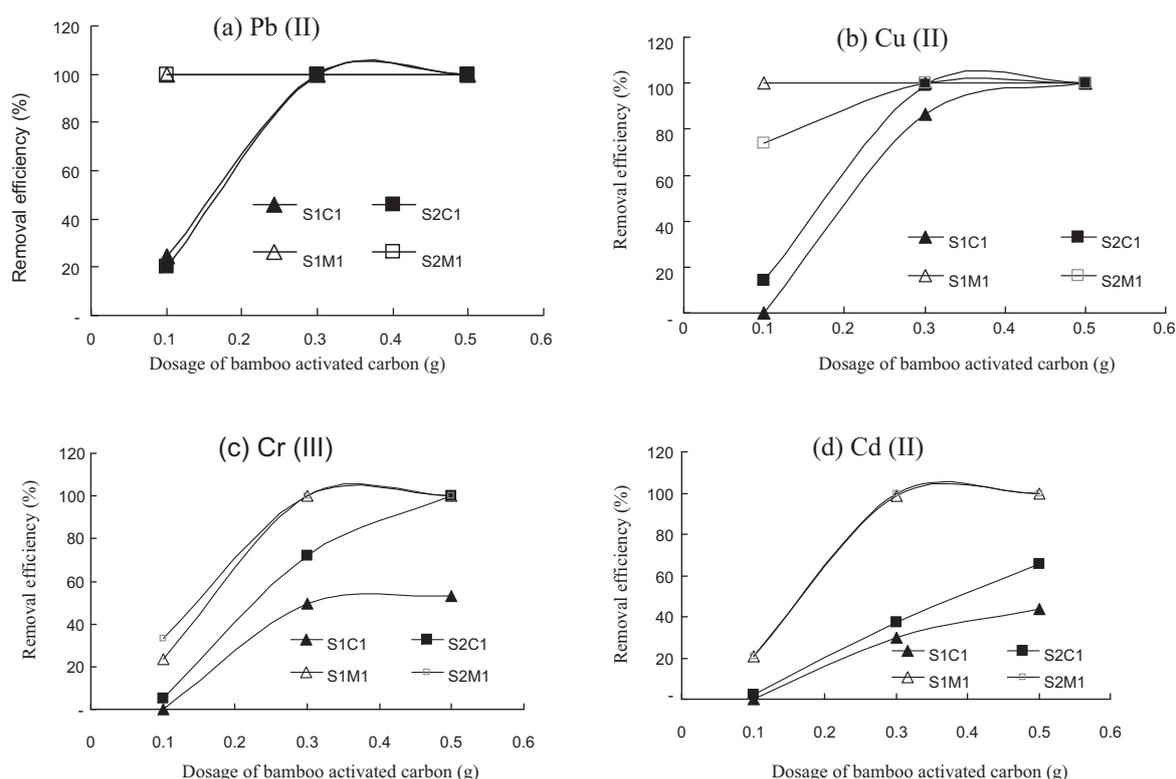


Fig. 4 – Relationship between the removal efficiency of heavy metal ions and bamboo activated carbon dosage.

(Table 1). 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 have also reported the positive influence of acid functional groups and surface oxidation on the adsorption capacity for heavy metal ions (Rangel-Mendez and Streat, 2002; Pendyal et al., 1999; Ahmendna et al., 2000; Dong et al., 2000; Manju et al., 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 activated carbons, with larger specific surface area, more functional groups and metal oxide compounds had better adsorption capacity for Pb^{2+} , Cu^{2+} , Cr^{3+} , and Cd^{2+} .

The removal efficiency of heavy metal ions by the various bamboo activated carbons decreased in the order: $Pb^{2+} > Cu^{2+} > Cr^{3+} > Cd^{2+}$.

In comparison to the research of Ücer et al. (2006), the maximum removal efficiencies of Cu^{2+} and Cd^{2+} heavy metal ions by the tannic acid carbons were 89.0% and 60.1% in 1 h, while the maximum removal efficiencies of Cu^{2+} and Cd^{2+} heavy metal ions by the Ma bamboo carbons were 93.5–100% and 87.8–96.4% in 1 h, respectively (see Fig. 4), which were more effective.

As for Moso bamboo carbons, the removal efficiencies in 1 h of Cu^{2+} and Cd^{2+} heavy metal ions were 21.9–33.2% and 11.5–19.5% in 1 h, respectively, with enough longer adsorption time the removal efficiencies could be raised to 25–55% (8 h) and 20–77% (4 h).

3.7. Effects of initial pH values on zeta potentials of Moso and Ma bamboo activated carbon suspensions

Table 1 shows that the specific surface area, pore volume, and micropore area of the S1M1 group were not larger than

those of the S2C1 group. However, the adsorption capacity and removal efficiency of heavy metal ions by the S1M1 group were better than those of the Moso bamboo carbons. In order to understand the reasons for this, the zeta potentials of Moso and Ma bamboo activated carbons were investigated.

Table 2 indicates that the suspension of bamboo activated carbons in distilled water were alkaline (9.32–10.86). At the initial pH 2, the zeta potential of S1C1 and S2C1 were 37.65 and 18.27, and those of S1M1 and S2M1 were 16.20 and 6.67, respectively. When the initial pH of the solution was 7, the zeta potential of S1C1 and S2C1 were -25.18 and -33.08 , and those of S1M1 and S2M1 were -35.24 and -36.07 , respectively. Thus, the bamboo activated carbon acts as a negative surface and attracts positively charged metal ions. The surfaces of S1M1 and S2M1 were more negatively charged than those of S1C1 and S2C1, therefore adsorption of positively charged Pb^{2+} , Cu^{2+} , Cd^{2+} and Cr^{3+} was more effective. Feng et al. (2009) reported that maximum adsorption occurs at pH 6.0 (94.6%) but adsorption decreases when pH is increased further. The minimum adsorption at pH 2.0 may be due to the fact that there are more protons available at lower pH to protonate active groups on the biomass surface, and compete with metal ions in the solution. At higher pH values, the lower number of H^+ ions and the greater number of ligands with negative charges results in greater copper adsorption. As pH increases the adsorbent surface becomes more and more negatively charged and therefore the adsorption of positively charged Cu^{2+} species is favorable (Nuhoglu and Oguz, 2003). At $pH \geq p_{Hpzc}$, the surface charge of activated carbon is negative, thus Cd^{2+} ions, which are positively charged, can easily bind to negatively dissociated forms of the surfactant's active groups and can form complexes with its surface groups (Chi et al., 2009). Cationic heavy metals including Cd^{2+} are removed from aqueous solution due to their interaction with anionic functional groups on the surface of activated carbon.

The zeta potential measurement was majorly for finding the reason for why Ma bamboo carbons and especially S1M1 carbon were better than Moso bamboo carbons with similar the specific surface area, pore volume, micropore area and FTIR spectroscopy. We could find that S1M1 possessed biggest absolute value of zeta potential at pH 7 and the final pH was higher (pH 8.7).

Higher zeta potential means higher electron charge, with further evaluation of zeta potential to BET specific area, Langmuir specific area and micropore area ratios, S1M1 possessed higher absolute values of 0.076, 0.057, 0.090, respectively, than other bamboo carbons. This implied a higher area charge density.

4. Conclusions

The adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons were investigated in this study. The optimum pH values of the maximum adsorption capacity and the effect of the various bamboo activated carbons on increasing rate of pH value of the heavy metal solution decreased in the order: once-activated Ma bamboo carbons (S1M1 group, pH value: 8.16–9.82) > twice-activated Ma bamboo carbons (S2M1 group, pH value 7.10–7.83) > twice-activated Moso bamboo carbons (S2C1 group, pH value 6.73–7.52) > once-activated Moso bamboo carbons (S1C1 group, pH value 4.88–6.07). Ma bamboo carbons with lower dosage possessed higher pH values and better adsorption capacity. The optimum pH values were 4.88–7.52 and 7.10–9.82 by Moso and Ma bamboo activated carbons, respectively. The optimum soaking time was 2–4 h for Pb²⁺, 4–8 h for Cu²⁺ and Cd²⁺, and 4 h for Cr³⁺ by Moso bamboo activated carbons, and 1 h for the tested heavy metal ions by Ma bamboo activated carbons. The removal efficiencies of Pb(II), Cu(II), Cr(III) and Cd(II) by S1M1 and S2M1 in 1 h were high and better than those of other authors as 99.9%, 100%, 100%, 96.4% and 98.8%, 93.5%, 91.7%, 87.8%, respectively. And the optimum adsorption time was longer (4–8 h) and the removal efficiency lower (20–77%) for S1C1 and S2C1 might due to the average pore diameter tended to be less than 2 nm which meant the pores were majorly micropores. The Ma bamboo activated carbons had a lower zeta potential and effectively attracted positively charged metal ions. The removal efficiency of heavy metal ions by the various bamboo activated carbons decreased in the order: Pb²⁺ > Cu²⁺ > Cr³⁺ > Cd²⁺.

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