

Activated Carbon from Extracted Sawdust Waste with Alkaline Activation by Physical Mixing

Rui Wang
Shouxin Liu

Abstract

Activated carbon (AC) with high surface area and narrow pore size distribution was prepared from extracted *Larix gmelinii* (Rupr.) sawdust by alkaline activation through physical mixing. The preparation method has been optimized through the analysis of diverse experimental variables. Among them, type of activating agent and activating agent/sawdust ratio, activation temperature, and precarbonization have been studied. N₂ adsorption isotherm and scanning electron microscopy were used to determine the BET surface area, pore structure, and surface morphology. It was shown that chemical activation with KOH can be successfully used to develop an AC with a high surface area from extracted *L. gmelinii* sawdust. When the raw sawdust was precarbonized at 500°C for 1 hour, physically mixed with KOH (mass ratio of KOH/sawdust, 4:1), and activated at 750°C for 2 hours, an AC with narrow pore size distribution, a maximum surface area of 2,659.4 m²/g, and a total pore volume of 1.21 cm³/g could be obtained. Hg(II) adsorption capacity of AC produced under optimal conditions was 318.47 mg/g, much higher than the compared commercial adsorption value. With a high surface area, narrow pore size distribution, and large Hg(II) adsorption capacity, the AC prepared from extracted sawdust waste appears as a very promising adsorbent for pollution control.

Activated carbons (ACs) are high-surface-area materials prepared from various amorphous carbon-based materials and exhibit a high degree of porosity. They consist principally of carbon atoms, which form irregular cross-linked aromatic sheets randomly substituted with other heteroatoms, such as oxygen, depending on the raw material. The application of ACs has expanded into many fields, including water purification and pollution treatment, air and gas purification (motor vehicles exhaust control, cigarette filters), and the food and pharmaceutical industries.

All materials with high carbon content can be used as raw materials for AC production. Wood, lignite coal, coconut shell, and peat are some of the raw materials currently used to prepare ACs (Lafi 2001). The development of methods to reuse waste materials is greatly desired, and the production of ACs from waste materials is attractive (Fang et al. 2004). There has been increasing interest in producing ACs from agricultural and forest wastes. Their advantages as carbon feedstock include availability as renewable resources, low ash content, reasonable hardness, and their ability to produce granular ACs with high adsorption capacity. Because of their particular porous characteristics, woody materials are very relevant and attractive raw materials used to produce ACs for the adsorption of pollutants in the liquid phase. The wood industry produces a great amount of woody waste materials that might be recycled to produce

other useful products, such as extractives for natural food additives. *Larix gmelinii* (Rupr.) sawdust is a good material for extracting arabinogalactan, a useful health food or drug additive. When arabinogalactan is extracted, the sawdust is considered an industrial waste and needs further treatment, such as incineration or direct discard as a waste (Fang et al. 2004). A new environmental problem is therefore produced. Considering the increasing demand for arabinogalactan, a proper treatment of the extracted sawdust is needed. Conversion of extracted *L. gmelinii* sawdust into AC, which can be used as an adsorbent in water purification, would add to its economic value, help reduce the cost of waste disposal, and most important, provide a potentially inexpensive alternative to commercial AC.

Water pollution has become a serious problem today. Removal of toxic materials, hazardous ions, and dyes from industrial effluent is of great interest in connection with environmental and human health safety. Metal ions such as

The authors are, respectively, PhD candidate and Professor, College of Material Sci. and Engineering, Northeast Forestry Univ., No. 26 Hexing Road, Harbin, People's Republic of China, 150040 (wangrui7101@126.com, liushouxin@126.com). This paper was received for publication in September 2009. Article no. 10683.

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Hg²⁺ and Cd²⁺ have harmful effects on human physiology and other biological systems. Because of the formation of methylmercury salts, this is the most toxic form, causing irreversible damage to the central nervous system. Mercury and its salts are considered the most toxic to the environment (Khalil et al. 2002, Yardim et al. 2003). Treatment of polluted water should remove mercury and its salts without creating more toxic products or producing mercury vapor in the atmosphere. Several methods have been studied for the treatment of wastewater containing mercury compounds (Yardim et al. 2003), among which adsorbent adsorption is the most effective and widely used (Otowa et al. 1997, Park and Jang 2002). Because of its highly developed internal surface and porosity, AC exhibits higher adsorption capacity for mercury ions.

Recent studies have shown that physical mixing of the activating agent and starting carbonaceous material instead of impregnation was much more effective for porosity development of alkaline activation. AC with high specific surface areas (over 1,500 m²/g) can be achieved (Lillo-Ródenas et al. 2003).

The purpose of this work was to prepare high-surface-area ACs from extracted *L. gmelinii* sawdust waste through alkaline activation by physical mixing and to examine the effects of preparation conditions (type of activating agent, activating agent/sawdust ratio, and precarbonization and activation temperature) on pore structure of the AC. The application of the prepared AC for adsorptive removal of Hg(II) was also investigated.

Experimental

Raw materials

L. gmelinii sawdust previously extracted for arabinogalactan by an ultrasonic method was used as raw material (Fang et al. 2004). Results of the proximate, ultimate, and component analyses of this sawdust are given in Table 1. The composition of lignocellulosic materials influences the structure of the AC in terms of porosity. If lignocellulosic materials contain a comparatively large percentage of lignin content, the BET surface area (S_{BET}) of the AC is high

Table 1.—Proximate, ultimate, and component analyses of the extracted sawdust.

Type of waste biomass	Extracted <i>Larix gmelinii</i> sawdust (% wt/wt)
Proximate analysis (as received)	
Moisture	8.8
Volatile matter	64.28
Fixed carbon	21.62
Ash	5.3
Ultimate analysis (as received)	
C	46.1
H	6.0
N	<0.3
S	<0.3
O (by difference)	45.5
Component analysis (as received)	
Extractive	6.01
Hemicellulose	16.84
Lignin	28.47
Cellulose	44.08

(Gergova et al. 1994). It is obvious that the extracted sawdust waste has high lignin and carbon and low ash content, indicating that this precursor is suitable for the preparation of AC. Prior to use, the raw sawdust was washed with water to remove impurities and then dried at 105°C for 24 hours. The dried material was crushed and sieved to a uniform size of 1.4 to 2.0 mm. Nitrogen was used to provide the inert atmosphere. KOH, NaOH, and HgCl₂ were agent grade and purchased from Shanghai Agent Corporation (Shanghai, China). The commercial AC was supplied by Tangshan Jianxin Activated Carbon Corporation (Tangshan, China).

Preparation of AC

The samples activated with NaOH or KOH were prepared by physical mixing using a alkaline/precursor ratio of 1.0:1 to 4.5:1 (weight terms) at room temperature. It should be emphasized that the process is done in the absence of water. In order to investigate the effect of precarbonization, the raw sawdust was first precarbonized in N₂ atmosphere at 500°C for 1 hour and then the char was physically mixed with an activating agent. After physical mixing, the mixture was activated in a horizontal cylindrical furnace reactor (inside diameter = 45 mm) at 500°C to 900°C for 2 hours. The temperature was ramped at the rate of 5°C/min with a N₂ flow rate of 20 mL/min. The activated products were cooled to room temperature and washed with deionized water. These samples were poured into a beaker containing 0.1 mol/dm³ HCl (250 cm³) and stirred for 1 hour. Finally, they were washed with hot water until the pH of the washing solution was about 6 to 7 and then dried at 105°C for 12 hours.

Characterization and analysis

S_{BET} of carbons were determined on the ASAP 2010 surface area and porosimetry system by nitrogen adsorption at 77 K. Prior to taking measurements, the samples were outgassed at 300°C under nitrogen flow for 3 hours. The *t*-plot method was applied to calculate the micropore volume and external surface area. The total pore volumes were estimated to be the liquid volumes of adsorbate (N₂) at a relative pressure of 0.98. Morphology of the prepared AC was observed using scanning electron microscopy (SEM; QUANTA 200, FEI, and Holland). Iodine values were determined according to ASTM Standard D4607-94 (standard test method for determination of the iodine number of AC).

Adsorption of Hg(II)

The adsorption capacity of the prepared AC toward Hg(II) ion was measured using an aqueous solution of HgCl₂. The adsorbate stock solution (1,000 mg/liter) was prepared by dissolving HgCl₂ in distilled water. This stock solution was diluted to obtain standard solutions containing 20 to 1,000 mg/liter of Hg(II). Batch equilibrium adsorption studies were carried out with 0.2 g of adsorbent and 100 mL of HgCl₂ solution with the desired concentration in a conical flask. The stoppered flasks containing the adsorbent and the adsorbate were agitated for predetermined time intervals at 25°C on a mechanical shaker. At the end of agitation, the suspensions were filtered through microporous filter paper. The amount of the Hg(II) in the final filtrate was determined

spectrometrically using an atomic adsorption spectrophotometer (TAS-900; Pgeneral Company, China).

Results and Discussion

The properties of ACs are dependent not only on the nature of the raw carbonaceous materials but also on the means of preparation (Wu et al. 2005). In this study, we present the effect of different parameters involved in the alkaline activation process, including activating agent type, precarbonization, activation temperature, and mass ratio of activating agent to raw materials, on the porosity of the final AC.

Effect of activating agent

Figure 1 compares the S_{BET} and iodine values of ACs prepared using two different activating agents with various mass ratios of activating agent/sawdust at 750°C for 2 hours. It can be seen that chemical activation with both hydroxides (NaOH and KOH) by physical mixing can be successfully applied to the extracted *L. gmelinii* sawdust waste. Different porosity developments are achieved as a function of activating agent and mixed ratio. Specific surface areas from 1,098 to 2,189 and 713 to 1,179 m²/g were achieved for KOH and NaOH activation, respectively. KOH exhibited better performance and produced higher porosity than NaOH. The AC prepared with an activating agent/sawdust ratio of 4:1 had a maximum S_{BET} of 2,189 and 1,179 m²/g for KOH and NaOH activation, respectively. The poor performance of NaOH was believed to be due to its higher corrosive nature, which led to a stronger stoichiometric reaction and partially collapsed generated micropore structures (Hu and Srinivasan 1999, Zou and Han 2001):



where M = Na, K.

Effect of mass ratio of KOH to raw materials

The mass ratio of activating agent to starting material is one of the most important parameters for chemical activation (Zou and Han 2001, Babel and Jurewic 2004). Using the extracted sawdust as starting material, KOH as activating agent, and a fixed activation temperature at 750°C for 2 hours, the effects of mass ratio of KOH to raw

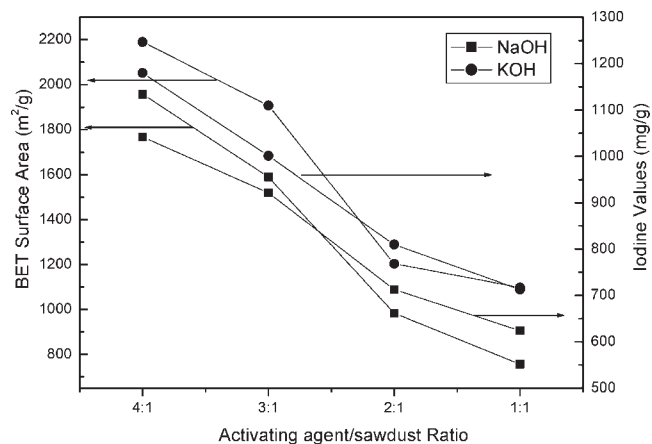


Figure 1.—Effect of activating agent type on the properties of AC.

materials on the porosity development of ACs are shown in Figure 1. S_{BET} and iodine values of prepared AC were proportional to the ratio of KOH/sawdust up to 4. At a higher ratio of 4.5:1, a decrease in the surface area and iodine values was observed. The result suggested that the impregnation ratio strongly affects characteristics of the AC and that the appropriate impregnation ratio of 4 should be selected for the production of the AC with the highest surface area. The decrease of porosity at higher mixed ratio should be attributed to the widening of micropores. In addition, it was reported that for a high impregnation ratio, KOH did not reach the interior of the raw particles, remained as a solid on the external surface, and was not involved in the chemical activation (Hu and Srinivasan 1999, Zou and Han 2001).

Effect of activation temperature

The surface area of the carbon depends largely on the activation temperature. With the increase of activation temperature, the reaction rate between the activator of KOH and the carbon increases fast. Using KOH and a ratio of 4:1 (wt/wt, agent/precursor), the effect of activation temperature is presented in Figure 2. It is clear that the activation temperature had a significant influence on the porosity development. The increase in temperature can result in an increase of the surface area because of the generation of new micro- and mesopores. The carbon with the highest surface area and iodine values was obtained at 750°C. A further increase in temperature at 800°C and 900°C may cause pore widening and pore collapse (Park and Jung 2002). According to our experiments, the effect of temperature on the S_{BET} and iodine value at various mass ratios of alkaline to sawdust exhibited a similar tendency with that of 4:1. Thus, for space considerations here, the result of 4:1 was selected, and the others are not shown. This showed that for the extracted waste sawdust, the activation at the suitable temperature of 750°C produced the best results.

Effect of precarbonization

The porosity of AC is highly dependent on the history of carbonization and activation (Zou and Han 2001, Carvalho et al. 2003). KOH activation was more effective for the highly ordered materials. Generally, compared with raw, the structure order of carbonized lignocellulosics was enhanced

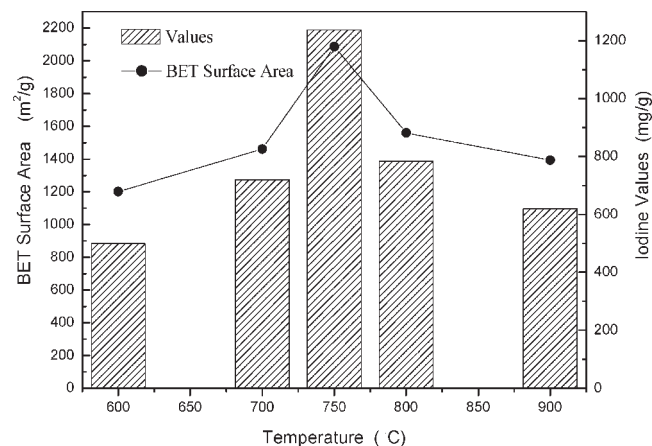


Figure 2.—Effect of activation temperature on the BET surface area and iodine values of AC.

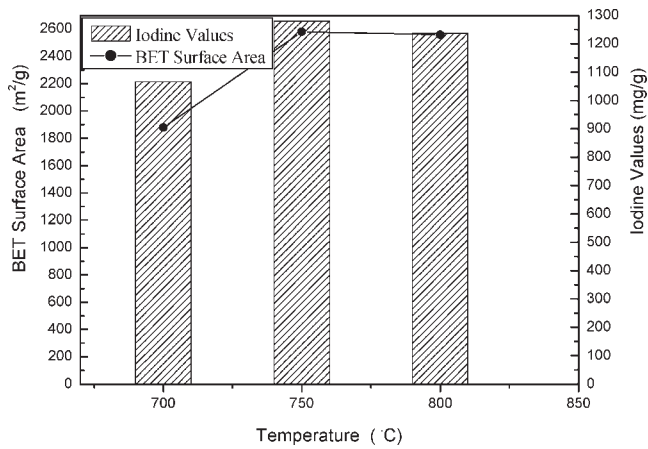


Figure 3.—Effect of precarbonization (500°C) on the BET surface area and iodine values of AC.

greatly because of the removal of volatiles: tars. In this work, the raw sawdust was precarbonized at 500°C for 1 hour. The obtained carbon was then physically mixed with KOH and activated at 700°C, 750°C, and 800°C, respectively. It can be seen from Figure 3 that precarbonization was an important factor for the porosity development. Precarbonization led to a higher S_{BET} and iodine values of prepared AC.

With the aim of producing ACs with the maximum S_{BET} and adsorption capacity, we conducted a large number of experiments to evaluate the effect of each preparation parameter. The maximum values of S_{BET} and adsorption capacity were achieved under the following conditions: carbonized at 500°C; KOH as the activator, with a mass ratio of KOH/carbonized sawdust of 4:1; and an activation temperature of 750°C. Under these conditions, S_{BET} and iodine values of 2,659.4 m²/g and 1,242.3 mg/g, respectively, could be obtained. The carbon with the highest surface area was further analyzed in terms of surface morphology and porosity.

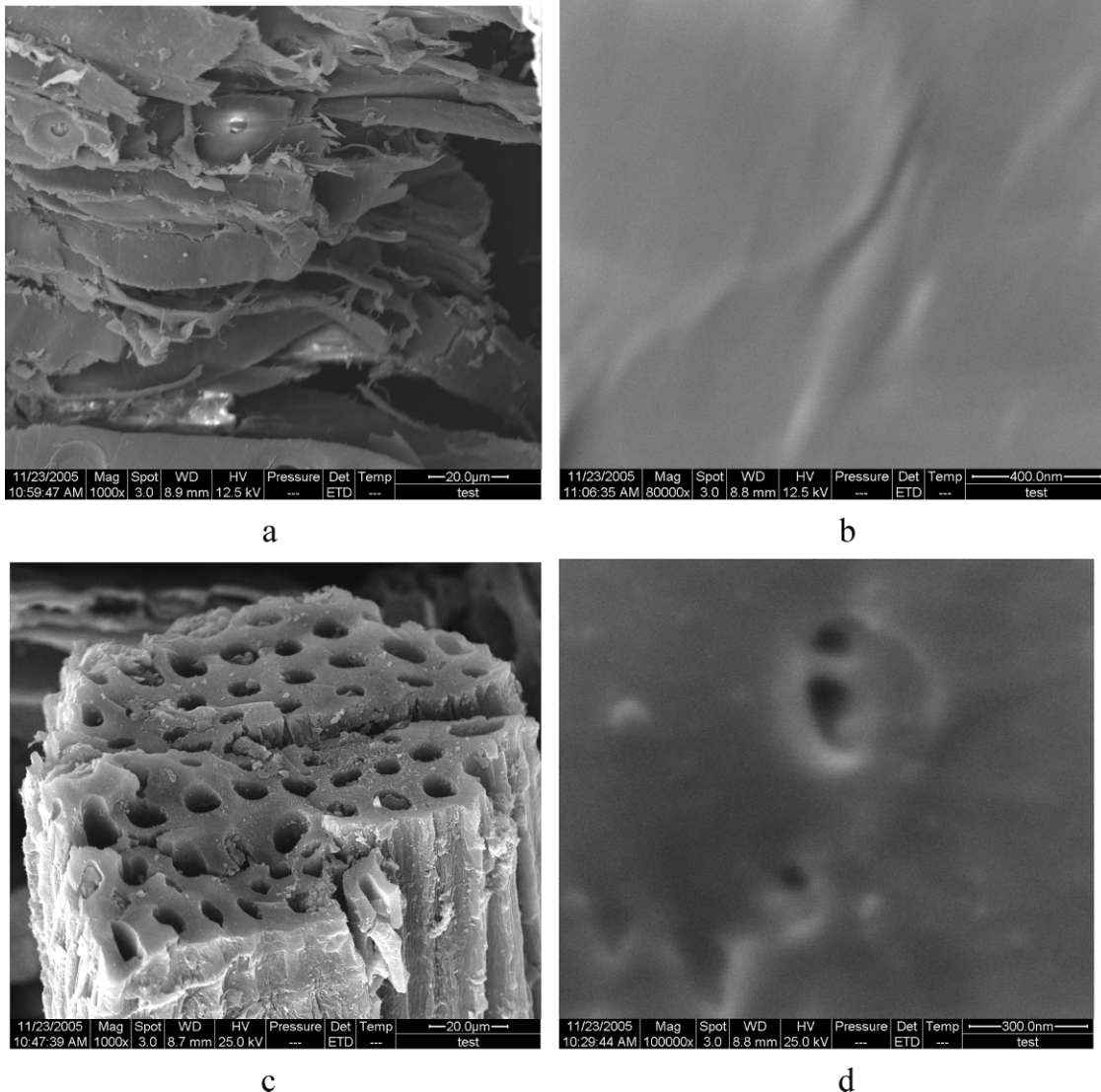
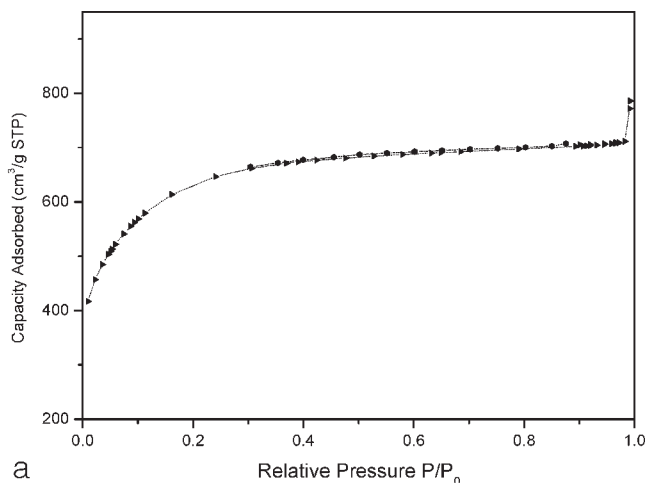
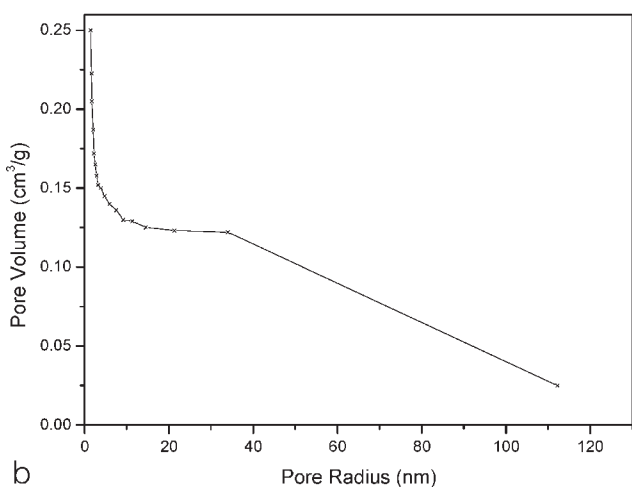


Figure 4.—SEM pictures of material sawdust (a, b) and prepared AC (c, d).



a



b

Figure 5.—Nitrogen adsorption–desorption isotherms at 77 K (a) and pore size distribution (b) of AC prepared under the optimum condition.

SEM and N₂ adsorption isotherm

Figure 4 shows SEM pictures of raw material sawdust and the AC prepared with the highest S_{BET} . Significant structural changes occurred for the sawdust after two-stage activation. The irregular edge of sawdust disappeared, and the prepared AC particles appeared with a regular shape. This probably is due to the strong corrosion effect of KOH. Comparing Figure 4b with Figure 4d, it is clear that additional new pores, which have never been observed on the starting materials, have been formed during KOH activation.

Figure 5a shows the nitrogen adsorption–desorption isotherms at 77 K on AC prepared under the optimal

Table 2.—Pore structure characteristics of AC prepared under the optimum condition.

S_{BET} (m ² /g)	Micropore area (m ² /g)	External surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Avg pore size (nm)
2,659.4	696.62	1,339.78	1.21	0.38	2.38

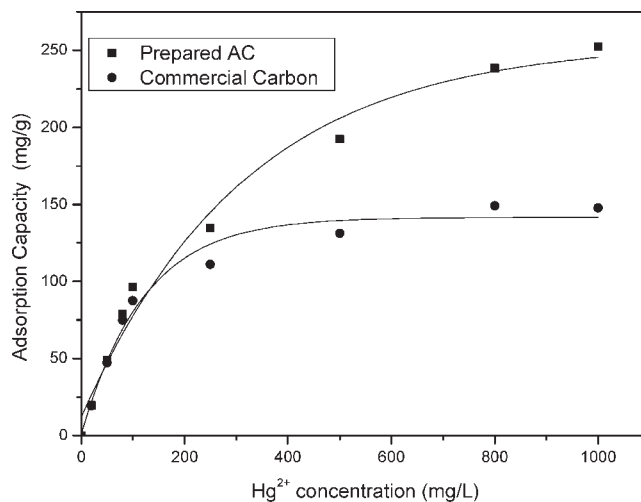


Figure 6.—Adsorption isotherm of Hg(II) on prepared AC and a compared commercial carbon.

conditions. The adsorption isotherms were type I with a steep initial uptake (<0.1), and there was almost no desorption hysteresis, indicating that a high level of microporosity and narrow pore size distribution were achieved. This was further well demonstrated with the result of pore size distribution (Fig. 5b). Table 2 lists the results of S_{BET} , micropore surface area, external surface area, and total volume. The results confirm that the extracted waste sawdust used was appropriate for the preparation of an AC with high surface area and narrow pore size distribution by KOH activation through physical mixing. The proper preparation conditions allowed us to produce microporous AC with a micropore volume up to 1.21 cm³/g and an S_{BET} of 2,659.4 m²/g.

Hg(II) adsorption

The adsorption isotherms of the prepared AC and the compared commercial AC are shown in Figure 6. The adsorption isotherms were basically of type I, obeying the Langmuir equation. This indicated that monomolecular micropore filling adsorption occurred (Hu and Srinivasan 1999, Park and Jung 2002). Langmuir isotherm constants were calculated from the following equation:

$$\frac{c}{q} = \frac{c}{q_m} + \frac{1}{q_m k_L} \quad (2)$$

where q_m and k_L are Langmuir constants determined from the slope and intercept of the plot, indicative of maximum adsorption capacity (milligrams per gram) of AC and energy adsorption, respectively, and c and q are the equilibrium concentration and equilibrium amount of the adsorbed Hg(II) on AC. The adsorption capacity (q_m), the

Table 3.—Langmuir parameters of Hg(II) adsorption on prepared AC and a commercial carbon.

Sample	q_m	k_L	R
Commercial AC	167.22	0.0083	0.99
Prepared AC	318.47	0.0036	0.99

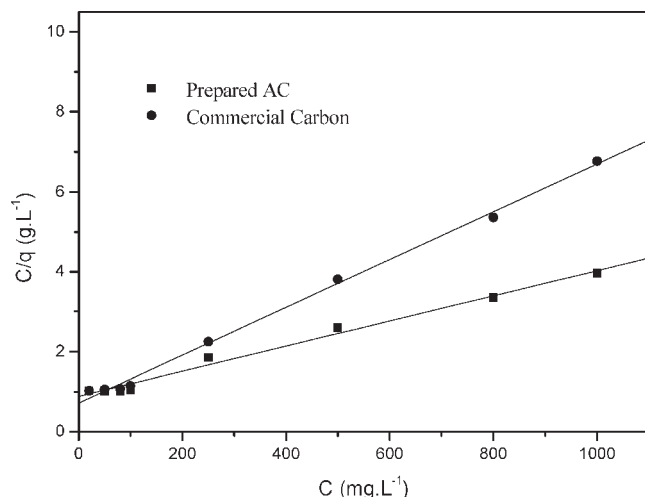


Figure 7.—Adsorption of Hg(II) on carbons treated by the Langmuir equation.

Langmuir constant (k_L), and the relative coefficient (R) are listed in Table 3. The adsorption result of Hg(II) on AC treated by the Langmuir equation is presented as Figure 7. According to the data of Figure 7 and Table 3, the adsorption capacity of the prepared AC was much higher than the capacity of the commercial AC. These results indicate that AC prepared from extracted sawdust is a suitable and effective adsorbent for the removal of Hg(II) from aqueous solutions.

Conclusions

Extracted waste sawdust was a suitable material for preparation of AC with a high surface area and narrow pore size distribution. The type of activating agent, ratio of activating agent/precursor, activation temperature, and precarbonization were the main parameters. The optimal preparation parameters of AC from extracted sawdust were as follows: carbonized at 500°C, KOH as the activator and with the mass ratio of KOH/carbonized sawdust of 4:1, and an activation temperature of 750°C. AC prepared under these optimum conditions had an S_{BET} of 2,659.4 m²/g and iodine values of 1,242.3 mg/g. The prepared AC exhibited a higher adsorption capacity (318.47mg/g) for Hg(II) than

what was exhibited by commercial carbon. The adsorption of Hg(II) fit the Langmuir isotherm well.

Acknowledgments

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