Adsorption Capacities of Activated Carbons Prepared from Bamboo by KOH Activation

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Abstract—The production of activated carbon from low or zero cost of agricultural by-products or wastes has received great attention from academics and practitioners due to its economic and environmental benefits. In the production of bamboo furniture, a significant amount of bamboo waste is inevitably generated. Therefore, this research aimed to prepare activated carbons from bamboo furniture waste by chemical (KOH) activation and determine their properties and adsorption capacities for water treatment. The influence of carbonization time on the properties and adsorption capacities of activated carbons was also investigated. The finding showed that the bamboo-derived activated carbons had microporous characteristics. They exhibited high tendency for the reduction of impurities present in effluent water. Their adsorption capacities were comparable to the adsorption capacity of a commercial activated carbon regarding to the reduction in COD, TDS and turbidity of the effluent water.

Keywords—Activated carbon, Bamboo, Water treatment, Chemical activation

I. INTRODUCTION

ACTIVATED carbon has been widely used as a good adsorbent for various applications including the treatment of water. The extensive application of activated carbon is mainly due to its high adsorption capacity and cheap or zero cost of the starting carbonaceous materials used for the preparation. Typically agricultural by-products or wastes such as olive cake [1], bagasse [2], coconut husk [3], and palm shell [4] are used as the starting materials to prepare activated carbon. In this study, bamboo waste discarded from the production of bamboo furniture was used as the starting material to prepare activated carbon. The bamboo waste is inevitably generated with a significant amount. Converting this waste to activated carbon will add more value to the product. Moreover it is a renewable biomass which is environmentally friendly.

Activated carbon can be prepared by a physical activation or chemical activation process. Physical activation consists of two steps: a carbonaceous material is carbonized under the oxygen-free atmosphere (carbonization process) and then activated with an activating gas such as CO_2 and H_2O (activation process). In chemical activation, both carbonization and activation processes occur simultaneously at a lower temperature and a shorter time than that in physical activation. Therefore it saves time and energy. Moreover chemical activation is reported to give activated carbon with higher specific surface area and much better developed porosity than physical activation [5, 6].

In chemical activation, several types of chemicals are used as the activating agent including $ZnCl_2$, H_3PO_4 and KOH. Different activating agents provide activated carbons with different properties. Hayashi and coworkers [7] found that the greatest specific surface areas of activated carbons were obtained at the carbonization temperature of 600 °C with $ZnCl_2$ and H_3PO_4 activation. In contrast, the maximum surface areas of activated carbons were obtained at the carbonization temperature of 800°C with alkali metal (KOH, NaOH, K_2CO_3 and Na_2CO_3) activation.

This study aimed to prepare activated carbons from bamboo furniture waste and investigated their properties and adsorption capacities for iodine, methylene blue, and other impurities in the water treatment. Bamboo-derived activated carbon was prepared by a chemical activation process using KOH as the activating agent. The carbonization was carried out at 800 °C under nitrogen atmosphere with various carbonization times.

II. EXPERIMENTAL

A. Preparation of Activated Carbon

Bamboo waste discarded from the production of bamboo furniture was cut into pieces approximately 1x1 inch^2 in size. They were washed with distilled water and dried at 105 °C for 12 h. These bamboo precursors were immersed in a potassium hydroxide (KOH) solution (25% by volume). The weight ratio of bamboo precursors to KOH was fixed at 2. Next the mixture was dehydrated in an oven overnight at 105 °C. The dried bamboo/KOH mixture then was put on a metal mesh inside a stainless steel chamber placed in an electrical furnace (Model PF2, Vecstar). Nitrogen gas (150 mL/min) was fed into the chamber and heating was initiated to start the carbonization process. The heating rate was 10 °C/min and continued until the final temperature of 800 °C was reached. The carbonization was then maintained at 800 °C for 1, 2 and 3 h. The activated carbon product was cooled down to room temperature under nitrogen atmosphere.

To remove remaining impurities such as ash, the synthesized activated carbon was washed with a hydrochloric

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(HCl) aqueous solution (5% by weight), followed by washing with distilled water several times until the pH of the washing solution was neutral. The HCl-treated activated carbon then was dried at 105 °C for 12 h and grounded into 150-180 μm prior to characterization and adsorption study. Here we assigned AC1, AC2 and AC3 for activated carbon carbonized at 800 ^{o}C for 1 h, 2 h and 3 h respectively.

B. Characterization of Activated Carbon

Proximate and ultimate analyses of bamboo precursor were carried out using thermogravimetric analyser (TGA, ASTM D5142-90) and CHNO analyser (ASTM D5373-93) respectively. Heating value was determined with Bomb calorimeter. The physical properties (BET surface area and pore volume) of AC1, AC2 and AC3 were determined with nitrogen adsorption at its normal boiling point (-196 ^{o}C). The ASTM D4607-94 method was employed to evaluate the adsorption capacities for iodine of AC1, AC2 and AC3.

C. Adsorption Study

The adsorption capacity of AC3 for methylene blue was tested in a batch system. Aqueous solutions of methlyene blue with various concentrations (100, 200, 300, 400 and 500 mg/L) were prepared. 0.2 g of AC3 was added into flasks containing 200 mL of the prepared methylene blue solutions. The flasks were placed in a thermostatic shaker bath and shaken at 150 rpm and 30 ± 1 ^{o}C. Samples (1 mL each) were taken at several time intervals and rapidly centrifuged in order to separate activated carbons from the solutions. The clarified supernatant solutions were then analysed with a double beam UV/VIS spectrophotometer (UV500 model, UNICAM) at 668 nm. The concentrations of methylene blue were determined from a prepared calibration curve which was linear over the concentration range used in this study. Dilution of dye solutions was required if their absorbances were higher than 0.7.

The amount of methylene blue adsorbed on activated carbon per unit mass of activated carbon, q_t (mg g^{-1}), at any time t was determined from equation (1):

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of methylene blue at initial time and time t, respectively. V is the volume of solution (L), and m is the amount of activated carbon (g).

To study the adsorption capacities of AC1, AC2 and AC3 for water treatment, a water sample was taken from the effluent of Bangbua Wastewater Treatment plant, Bangkok, Thailand. This represents municipal wastewater. The sample had initial chemical oxygen demand (COD), total dissolved solid (TDS), turbidity and UV254 of 437 mg/L, 1.8 mg/L, 62.1 NTU and 1.6352 1/m respectively. The adsorption study was performed in a batch system containing 1 L of the water sample. Various amounts (6, 8, 10 and 12 g) of AC1, AC2 and

AC3 were added and the mixtures were stirred at 150 rpm for 1 h. After adsorption, the mixtures were suddenly centrifuged in order to separate activated carbons from the solutions. The clarified supernatant solutions were subjected to analysis. The reductions of COD, TDS, turbidity and UV254 were used to indicate the removal efficiency of bamboo-derived activated carbons for water treatment. A commercial activated carbon (CAC) in powder form was kindly supplied by C. Gigantic Carbon Co., Ltd and used for comparison.

III. RESULTS AND DISCUSSION

A. Properties of Bamboo and Bamboo-derived Activated Carbon

Properties of bamboo are presented in Table I. The result shows that bamboo has high volatile and carbon contents. High carbon content is a favorable property of the starting carbonaceous material to be used for the production of activated carbon. The carbon content of our bamboo is in agreement with those of Indian and Hong Kong bamboos which are 43.8 and 47.6% respectively [8].

Specific surface areas and pore volumes of AC1, AC2 and AC3 are presented in Table II. The bamboo-derived activated carbons with KOH activation have high specific surface areas and pore volumes. This is in agreement with that reported in the literature [6]. For bamboo-derived activated carbon, the use of KOH as an activating agent gives activated carbon with

TABLE I
PROPERTIES OF BAMBOO

Properties	Bamboo
Heating value (cal g^{-1})	4,072.7
Proximate Analysis (%)	
Moisture content	2.44
Volatile matter	69.63
Ash	6.51
Fixed carbon	21.42
Ultimate Analysis (%)	
Carbon	45.53
Hydrogen	4.61
Nitrogen	0.22
Oxygen, sulfer and others†	49.65

Note: † by difference

greater specific surface area and pore volume than the use of other activating agents (HCl, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, ZnCl$_2$ and KOH) [9, 10].

When the activation time was increased, higher specific surface area and pore volume were obtained. This corresponds to the literature [11, 12]. Compared with the commercial activated carbon, our activated carbons synthesized from bamboo have greater specific surface area and pore volume.

B. Adsorption Study

Iodine adsorption capacities of AC1, AC2 and AC3, which were carbonized for 1, 2 and 3 h respectively, are shown in Fig. 1. Our activated carbons have iodine adsorption

capacities in the rage of 811.2-850.4 mg/g. When the carbonization time was increased, the synthesized activated carbon has higher iodine adsorption capacity. This corresponds to the greater specific surface area with longer

TABLE II
BET SURFACE AREAS AND PORE VOLUMES OF AC1, AC2 AND AC3

Activated carbon	BET surface area (m^2/g)	Pore volume (cm^3/g)
AC1	1281.7	0.4246
AC2	1493.4	0.4805
AC3	1532.8	0.4911
CAC	1169.1	0.4121

carbonization time (see Table II). The relationship between iodine adsorption capacity and carbonization time was found to be linear ($R^2 = 0.9365$). However our synthesized activated carbons still have lower iodine adsorption capacities than the commercial activated carbon which has iodine adsorption capacity of 1076.0 mg/g.
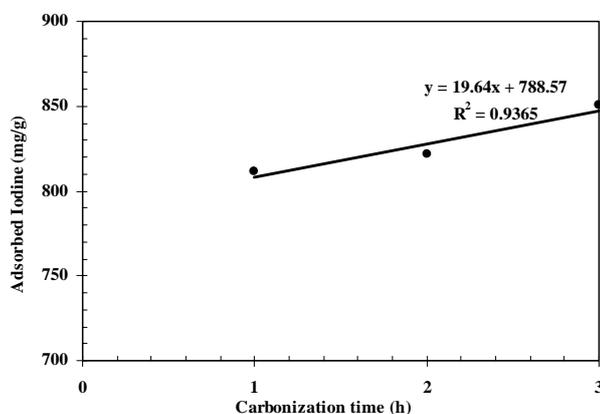
Fig. 1 Effect of carbonization time on iodine adsorption capacity

According to Thai Industrial Standards Institute, the standard iodine number for a commercial activated carbon must not be lower than 600 mg/g. Referred to this criterion, the synthesis of activated carbon from bamboo with chemical activation using KOH as the activating agent has a potential to be developed to a commercial scale.

Adsorption capacities of AC3 for methylene blue at different initial concentrations of methylene blue are shown in Fig. 2. The activated carbons rapidly adsorb methylene blue within the first few minutes of the adsorption time. Then the adsorption capacities become constant. At these points, the adsorption equilibrium is attained, implying that the amount of methylene blue adsorbed onto the activated carbon is equal to that desorbed from the activated carbon.
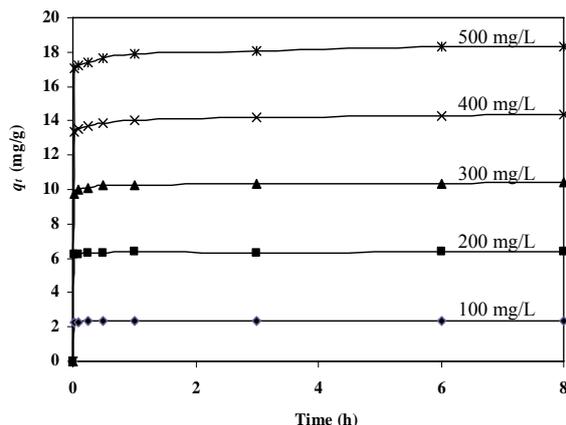
Fig. 2 Adsorption capacities for methylene blue of AC3

When the initial concentrations of methylene blue are between 100 and 300 mg/L, adsorption equilibrium can be achieved in 3 h. When the initial concentrations of methylene blue are between 400 and 500 mg/L, adsorption equilibrium can be achieved in 6 h. The equilibrium adsorption capacities of AC3 increase with the initial concentrations of methylene blue: 2.4, 6.4, 10.4, 14.4 and 18.3 mg/L for the initial concentrations of 100, 200, 300, 400 and 500 mg/L. It is important to note that the adsorption capacity for methylene blue is quite low compared to that for iodine. This implies that our activated carbons have microporous structure. Iodine number can be typically used as a measure of the micropore (less than 2 nm) content whereas methylene blue as a measure of the mesopore (2-5 nm) content of the activated carbon [13, 14]. Moreover Wu and coworkers [6] similarly found that the KOH-activated carbons mainly consisted of micropores.

The rapid adsorption of methylene blue on AC3 can suggest that the adsorption takes place mainly on the external surface of the activated carbon. If the major sites for adsorption were on the internal surface within the pores of the activated carbon, the adsorption should take long contact time due to the effect of pore diffusion. Hameed and coworkers [15] have reported longer equilibrium times for adsorption of methylene blue on bamboo-derived activated carbons: 6 h for initial concentrations of methylene blue of 100-300 mg/L and 24 h for initial concentrations of 400-500 mg/L. Moreover, a methylene blue molecule has 1.43 nm width [6], which might be difficult to diffuse through micropores (<2 nm diameter) of our activated carbons. Chan and coworkers [16] found that their high-surface-area activated carbons derived from bamboo had maximum pore diameter of 2 nm.The low adsorption capacities for methylene blue of AC3 compared to those reported in the literature [6, 15] indicate that bamboo-derived activation carbon is inefficient for the removal of methyl blue from aqueous solution.The removal efficiencies for COD of the synthesized activated carbons are presented in Fig. 3. Our synthesized activated carbons can reduce COD in the range of 86.5-93.2%. The removal efficiencies for COD of AC1 and AC2 are very similar to the efficiency of the

commercial activated carbon (CAC). AC3 was found to reduce COD in the water sample more greatly than AC1, AC2 and CAC. Increasing dosages of activated carbons slightly improve their removal efficiencies for COD. Compared to previous studies concluded by Ahmad and Hameed [17], the activated carbons synthesized in this study show relatively large percentage of COD removal.
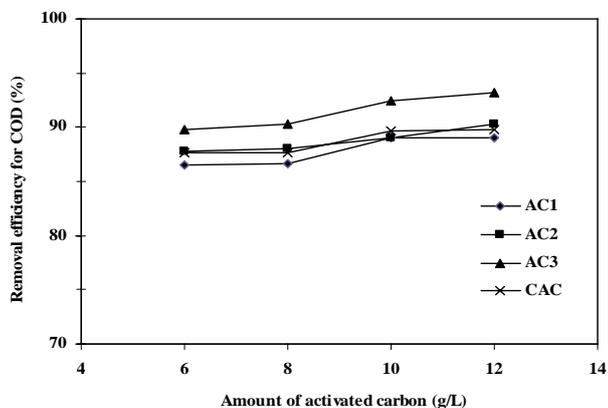
Fig. 3 Removal efficiencies for COD of AC1, AC2, AC3 and CAC

The efficiencies of activated carbons for removing total dissolved solid in the water sample are presented in Fig. 4. Our synthesized activated carbons can reduce TDS in the range of 77.8-94.6%. AC3 prepared from the longest carbonization time (3 h) at 800 $^{\circ}$C has higher removal efficiency for TDS than AC2 and AC1 respectively. The efficiency of AC3 is closed to that of CAC when the dosages of AC3 are in the range of 8-12 g/L. The removal efficiencies for TDS are obviously different among AC1, AC2 and AC3, unlike the removal efficiencies for COD in Fig. 3. This is because that COD and TDS are measures of different components. COD value represents the quantity of dissolved organic substances that can be chemically oxidized. In other words, it is an indication of biodegradable pollutants in the wastewater. TDS is a measure of all inorganic and organic substances dissolved in water in molecular, ionized or micro-granular (colloidal sol) form.
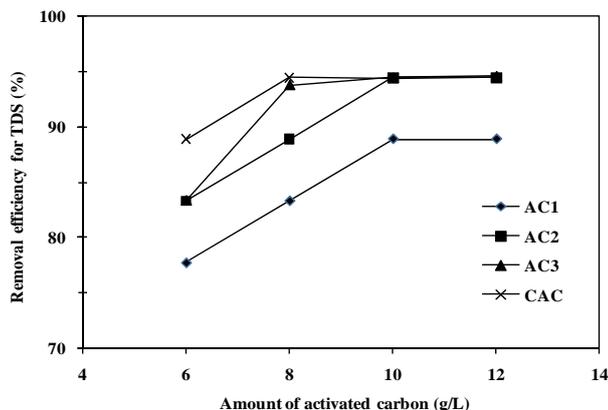
Fig. 4 Removal efficiencies for TDS of AC1, AC2, AC3 and CAC

The removal efficiencies for turbidity of the synthesized activated carbons are in the range of 74.3-84.4% as shown in Fig. 5. When the amounts of activated carbon are increased, the removal efficiencies for turbidity increase. The removal efficiency for turbidity of AC3 is comparable to that of CAC. Turbidity is the cloudiness or haziness of a fluid caused by suspended solids; therefore, the removal efficiency for turbidity represents the adsorption capacity of activated carbon for suspended substances in water.
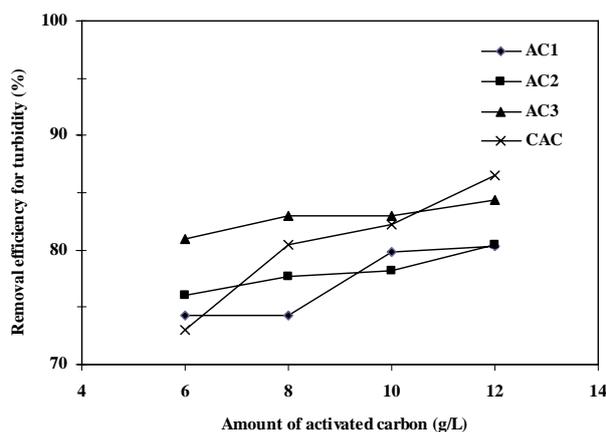
Fig. 5 Removal efficiencies for turbidity of AC1, AC2, AC3 and CAC

The removal efficiencies for UV254 of the activated carbons are in the range of 55.4-75.4% as shown in Fig. 6. When the amounts of activated carbon are increased, the removal efficiencies for UV254 increase. However our synthesized activated carbons have lower efficiencies in reducing UV254 in the water sample than the commercial activated carbon.
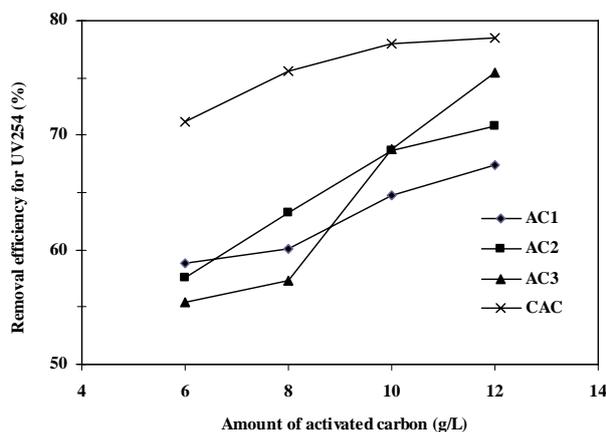
Fig. 6 Removal efficiencies for UV254 of AC1, AC2, AC3 and CAC

IV. CONCLUSION

The activated carbons synthesized from bamboo waste using KOH activation have greater specific surface areas (1281.7-1532.8 m^2/g) and pore volumes (0.4246-0.4911

cm^3/g) than a commercial activated carbon. They have iodine numbers between 811.2 and 850.4 mg/g which are greater than the standard value specified by Thai Industrial Standards Institute, implying a potential to be developed to a commercial scale. Increasing carbonization time improves the specific surface area, pore volume and iodine adsorption capacity of bamboo-derived activated carbon. Lower adsorption capacity for methylene blue compared to iodine indicates microporous structure of the activated carbons. In water treatment, the synthesized activated carbons can reduce COD, TDS, turbidity and UV254 significantly. The synthesized activated carbons have removal efficiencies comparable to the commercial activated carbon regarding to COD, TDS and turbidity.

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