Songklanakarin J. Sci. Technol.
30 (2), 185-189, Mar. - Apr. 2008

Songklanakarin Journal
of Science and Technology
http://www.sjst.psu.ac.th

Original Article

Adsorption of phenol from diluted aqueous solutions by activated carbons obtained from bagasse, oil palm shell and pericarp of rubber fruit

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Received 2 April 2007; Accepted 29 April 2008

Abstract

Activated carbons prepared from bagasse, oil palm shell and pericarp of rubber fruit were used to study the adsorption of phenol from aqueous solution. The obtained activated carbons were characterized for iodine number, BET surface area, surface functional groups, and point of zero charge (pH_{pzc}). Adsorption of phenol in aqueous solution at pH 2 and pH 12 were determined by UV-Visible spectrophotometer at 30°C. The adsorption data were fitted to Freundrich isotherm. The adsorption capacity of phenol of the different types of activated carbon was approximately the same.

Key words: activated carbon, phenol, adsorption isotherm

1. Introduction

The rapid growth of several industries in Thailand, such as rubber latex industries, oil refineries, pharmaceutical, and dye industries etc. has generated environmental contaminations from waste water, and phenol is one of the toxic compounds that should be concerned about. Exposure to phenol by any route can cause severe poisoning. Its vapor can irritate the respiratory system and eyes. The solid form can cause skin to burn (Armour, 1991).

Activated carbons have been remarkably cited to be capable of adsorbing organic compounds, such as organic dyes, volatile organic compounds, mineral oils, poly aromatic hydrocarbons, and phenol. Examples from applications of activated carbons in different processes are groundwater purification, the de-chlorination of process water, water purification for swimming pools, and the polishing of treated effluent. A variety of activated carbons are available commercially, but they are very expensive. Hence, in this work we produce the activated carbons from agricultural wastes, such as bagasse, oil palm shell, and pericarp of rubber fruit by chemical activation with zinc chloride. Adsorption of phenol in aqueous solution at pH 2 and pH 12 are consequently studied at 30°C. The adsorption isotherm will be investigated systematically. The influence of acidic surface of activated carbons will also be elucidated.

2. Materials and Methods

2.1 Preparation of raw materials

The raw materials were dried in the sun and cut into small pieces approximately 1 inch, except oil palm shell, which were not cut after drying. Each raw material was dried again in the oven at 110°C for 3 h, then kept in the dessicator.

2.2 Carbonization and chemical activation

The carbonization of each raw material was conducted in a muffle furnace at 400°C for 1 h by placing the raw material into a stainless steel box with cover. After carbonization the residual char was grounded in a laboratory jar

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mill to pass between a 25-50 mesh sieve. Then, the chemical activation was performed by mixing the grounded char with concentrated solution of $ZnCl_2$ at ratio 1:2. The sample was activated at 600°C for 3 h in the muffle furnace (Sirichote *et al.*, 2002). The obtained activated carbon was washed with 1% HCl. In the next step, it was soaked in hot water for five minutes and subsequently the water was drained off through a Buchner funnel. This step was repeated two more times to obtain a neutral pH value. Finally, it was dried in the oven at 110°C for 24 h.

2.3 Characterization of the activated carbons

1) Iodine number

The iodine number of obtained activated carbons was analyzed using the method of the American Standard of Testing Material (1999) (ASTM D4607-94).

2) BET Surface area and pore size distribution

Nitrogen adsorption isotherms at 77 K were used to determine the specific surface area and the pore size distribution of the activated samples by Coulter apparatus, model SA 3100 using Brunauer-Emmett-Teller (BET) and t-plot equations, respectively. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model (Barrett *et al.*, 1951).

3) Fourier-transform infrared spectrometry (FT-IR)

The FT-IR spectra of raw materials, carbonized carbons, and activated carbon were recorded by FT-IR spectrophotometer and diffuse reflectance accessory, Spectrum GX, Perkin Elmer within the range of 400-4,000 cm^{-1}. The KBr pellets were prepared by activated carbon-KBr mixtures at a ratio of approximately 1:300.

4) Point of zero charge measurements

The point of zero charge (pH_{pzc}) means the pH at which the total number of positive and negative charges on its surface becomes zero (Jia *et al.*, 2002). The pH_{pzc} values of each activated carbon was measured by preparing a solution of 0.1 M NaCl in preboiled water in order to eliminate CO_2. Each 100 mL of NaCl solutions of two different pH values at 2 and 12 was prepared and adjusted by adding either diluted HCl or NaOH. The activated carbons were dried in the oven at 110°C for 3 h, then weighted out 0.1500 g and 0.5000 g and placed in 50.00 mL of adjusted NaCl solutions in 125 mL conical flasks. All the flasks were sealed to avoid contact with air and left at room temperature for 48 h. The samples were filtered through filter paper No.1 by neglecting the first 5 mL of the filtrate. The final pH of filtrate was measured.

2.4 Adsorption of phenol from aqueous solutions

The determination of the equilibrium time of phenol adsorption at pH 2 and pH 12 were carried out in a 125 mL stoppered conical flask by adding 0.1500 g of activated carbon to 50.00 mL of phenol solution. The concentrations of phenol were 50, 100 and 500 ppm in a buffer solution of pH 2 and pH 12. All flasks were kept in a thermostat shaker at 30°C for 2, 3, 4, 5, 7, 9, 10, 12, and 15 h for phenol concentrations of 50 and 100 ppm. For the phenol concentration of 500 ppm the flask was shaken for 1, 3 ,5, 10, 15, and 20 h. The concentrations of phenol solution at pH 2 and pH 12 were varied in the range 20 to 600 ppm by fixing the weight of activated carbons at 0.1500 g. After shaking in a thermostat shaker at 30°C for 24 h, the contents were filtered. Then the concentrations of the left over filtrate were determined by UV-Visible spectrophotometer using a buffer solution as reference at the maximum absorption wavelength, 270 nm for pH 2 and 287 nm for pH 12.

3. Results and Discussion

A photo of each raw material, carbonized char, and activated carbon is shown in Figure 1.

The values of the iodine number (IA) and BET surface area (S_{BET}) of all activated carbons are shown in Table 1.

The FT-IR analysis can be used to identify the presence of the surface functional groups in the activated carbons. A comparision of the functional groups on the surfaces of the raw materials, carbonized carbons, and acti-

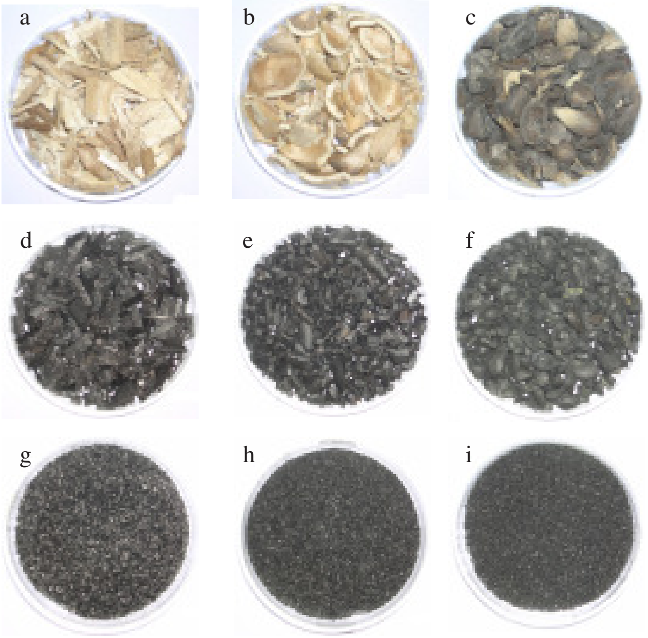

Figure 1. The photographs of the raw materials, bagasse (a), pericarp of rubber fruit (b) and oil palm shell (c), carbonized char (d, e, f), and the activated carbon (g, h, i), respectively.

Table 1. Iodine number and BET surface area of the obtained activated carbons at 600°C with sample to $ZnCl_2$ ratio of 1:2

Raw materials	IA (mg/g)	S_{BET} (m^2/g)
Bagasse (B)	939	1076
Pericarp of rubber fruit (PR)	868	877
Oil palm shell (OP)	808	770

vated carbons is shown in Table 2. The FT-IR spectra of the raw materials, carbonized carbons, and activated carbons are shown in Figure 2 to 4.

From the results shown in Table 2 it can be concluded that the C=O stretching of carbonyl in carbonized acid at 1,700 cm^{-1}, C=C stretching of the aromatic compound and alcohol at 1,500 cm^{-1}, and C-O stretching of carboxylic acid at 1,200 cm^{-1} disappeared for carbonized carbons and activated carbons when compared to the raw materials. Both carbonized carbons and activated carbons have the same functional groups. These indicate that the activation process does not change the surface functional group but causes an increase of their surface area.

For the determination of pH_{pzc} of the activated carbons the values of the final pH (pH_f) were plotted versus their corresponding initial pH values (pH_i) as shown in Figure 5 for 0.1500 g of activated carbon. From the graphs, the values of pH_{pzc} of activated carbons are determined from the points where the initial pH equals the final pH. The pH_{pzc} values are shown in Table 3.

The results from Table 3 imply that all activated carbons have acidic surfaces since the pH_{pzc} values are less than 7. Increasing the weight of activated carbons 3.3 times with equal volume of the solution will decrease the pH_{pzc} values and a higher number of protons will be released into the solution. The pH of OP and PR are close together and

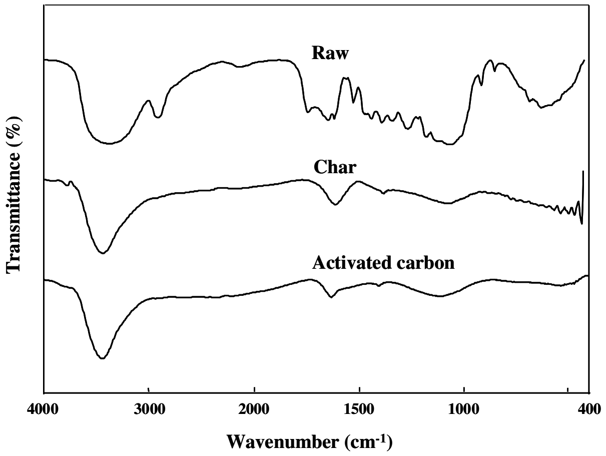

Figure 2. Comparison of the FT-IR spectra of the raw material, carbonized char, and activated carbon obtained from bagasse.

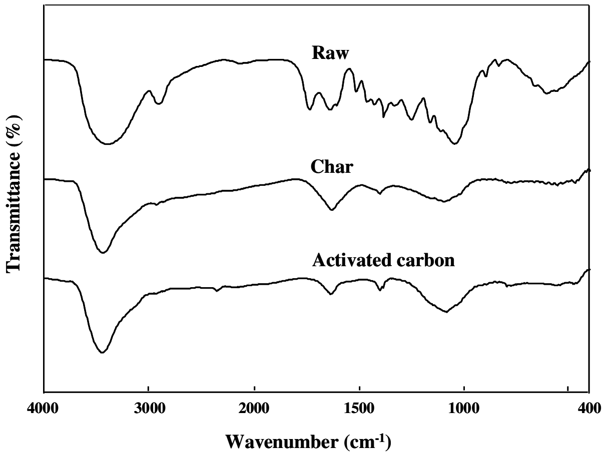

Figure 3. Comparison of the FT-IR spectra of the raw material, carbonized char, and activated carbon obtained from pericarp of rubber fruit.

Table 2. The appearances of functional groups on surfaces of raw materials, carbonized carbons and activated carbons by $ZnCl_2$, B = bagasse, PR = pericarp of rubber fruit, OP = oil palm shell, R = raw material, C = carbonized char, AC = activated carbon by $ZnCl_2$, I = appear, - = disappear

Wavenumber (cm^{-1})	Vibrational mode	Functional group	B			PR			OP		
			R	C	AC	R	C	AC	R	C	AC
3400	O-H stretching	H_2O, phenol, alcohol	I	I	I	I	I	I	I	I	I
2900	C-H stretching	CH_2, CH_3	I	I	I	I	I	-	I	I	I
1700	C=O stretching	carboxyl in carboxylic acid	I	-	-	I	-	-	I	-	-
1600	C=O stretching	carbonyl in ketone									
	C=C stretching	aromatic compound	I	I	I	I	I	I	I	I	I
			I	I	I	I	I	I	I	I	I
1500	C=C stretching	aromatic compound	I	-	-	I	-	-	I	-	-
1400	O-H bending	alcohol, carboxylic acid	I	I	I	I	I	I	I	I	I
1200	C-O stretching	carboxylic acid	I	-	-	I	-	I	I	-	-
1100	C-O stretching	alcohol	I	I	I	I	I	I	I	I	I

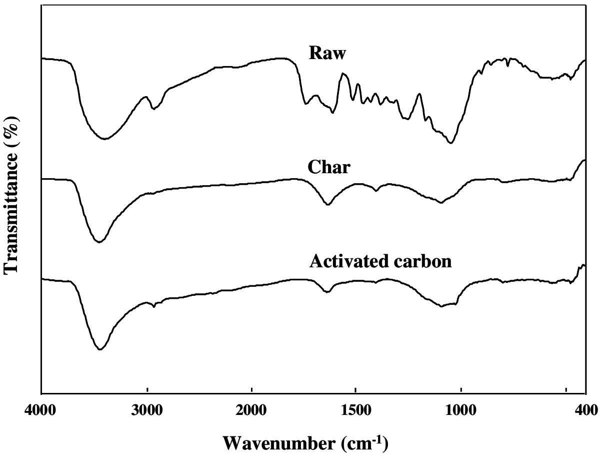

Figure 4. Comparison of the FT-IR spectra of the raw material, carbonized char, and activated carbon obtained from oil palm shell.

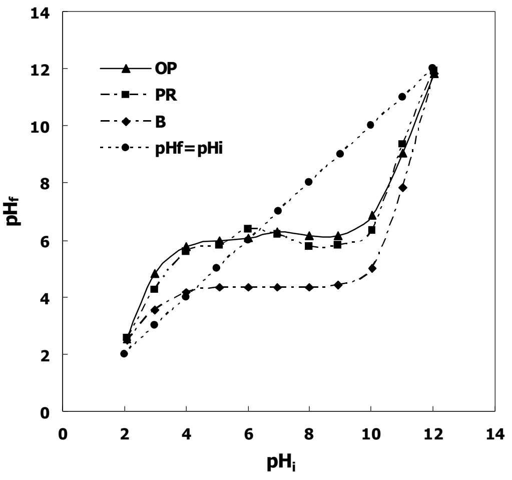

Figure 5. Final (pH_f) versus initial pH (pH_o) for 0.1500 g of different activated carbons. OP = oil palm shell, PR = pericarp of rubber fruit, B = bagasse

Table 3. Point of zero charge (pH_{pzc}) of 0.1500 g and 0.5000 g of activated carbons, B = bagasse, PR = pericarp of rubber fruit, OP = oil palm shell

Sample	pH_{pzc} (0.1500 g sample)	pH_{pzc} (0.5000 g sample)
B	4.2	4.0
PR	6.4	5.4
OP	6.1	5.6

higher than B. The surface of activated carbon B is the most acidic one, while the surface acidity of OP and PR are not much different.

For fitting the adsorption isotherm the adsorbed amounts of phenol are plotted against their equilibrium concentrations at pH 2 and pH 12 by using program sigma plot 2000 as shown in Figure 6. The Fruendlich isotherm is used to fit these graphs according to the following equation (Shaw, 1980):

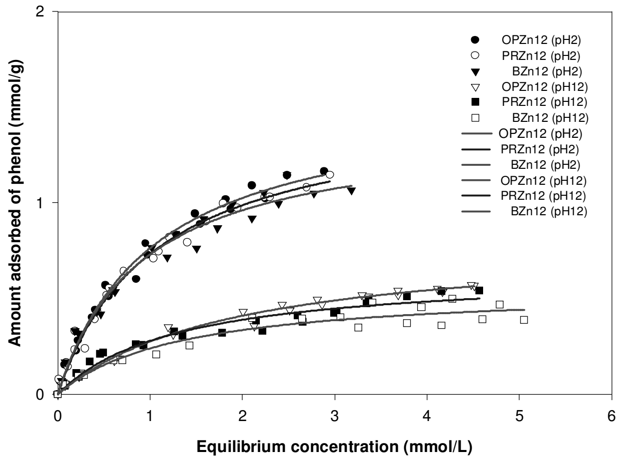

Figure 6. Adsorption isotherms of phenol at 30 °C on the activated carbons.

Table 4. The Fruendlich isotherm parameters for phenol adsorption at pH 2 and pH 12. K = the adsorption capacity constant, 1/n = the reciprocal of the empirical parameter depending on the concentration of phenol in aqueous solution, and R^2 = the correlation coefficient

Activated carbon	K	1/n	R^2	pH
OP	0.7091	0.5260	0.9853	2
PR	0.6804	0.5211	0.9817	
B	0.6788	0.4768	0.9743	
OP	0.2671	0.5277	0.9801	12
PR	0.2612	0.4816	0.9786	
B	0.2249	0.4513	0.9167	

$$Q = KC_e^{1/n}$$

where Q is the amount of phenol per unit weight of activated carbon, C_e is the concentration of phenol in the solution at equilibrium, K is the adsorption capacity constant, and n is the empirical parameter depending on the concentration of phenol in aqueous solution.

The Fruendlich isotherm parameters for phenol adsorption at pH 2 and pH 12, including the R^2 values, are listed in Table 4.

The values of K in Table 4 indicate that the adsorption capacity of phenol at pH 2 is greater than at pH 12. At pH 2 the surfaces of activated carbons are protonated and have acidic surfaces with positive charges. Phenol behaves as a weak base that interacts with the acidic surface of activated carbons by dispersion electron donor-acceptor interaction. In contrary, at pH 12 the surfaces of activated carbons have negative charges and the molecules of phenol are in the form of the phenolic anion. These cause the electrostatic repulsion between the surfaces and phenolic anions. At pH 2 the adsorption capacities of phenol for three kinds of activated carbons are approximately the same. At pH 12 the experiment shows the same adsorption capacities among all kinds of activated carbons.

Acknowledgements

This work was supported by the Department of Chemistry, the Faculty of Science, Prince of Songkla University, Hat Yai and partially supported by the Center of Innovation in Chemistry: Postgraduate Education and Research Program in Chemistry. The authors thank the Department of Chemical Engineering, Prince of Songkla University, Hat Yai for help in measuring the BET surface area and pore size distribution.

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