SYNTHESIS OF ACTIVATED CARBONS ORIGINATED FROM ORANGE PEEL BY SUBCRITICAL CO_2 ACTIVATION METHOD

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ABSTRACT

Low-cost and environmental friendly activated carbons were synthesized from orange peel waste by carbonization followed by activation process using supercritical carbon dioxide. The carbonization process of orange peel waste was conducted in the electrical furnace at temperature of 800 °C for 2 h. Activation process of the impregnated orange peel was carried out in the tubular furnace for 1 h at activation temperature of 140 °C and pressure variation of 80, 125 and 170 bar. Activated carbon with highest surface area of 262.173 m^2/g was obtained by co_2 pressure of 125 bar. The activated carbons were then utilized as adsorbents for removal of methylene blue (MB) from aqueous solution. The batch adsorption study was carried out by varying the initial concentration of mb solution (2, 4, 6, 8 and 10 ppm). Experimental results showed that the adsorption kinetic of mb fitted the pseudo-second-order rate equation, where as for the adsorption isotherm model followed two models i.e. The dubinin- radushkevich and freundlich model. The adsorption mechanism was found to be governed by the intraparticle and surface diffusion mechanism.

Keywords: Activated Carbons, Adsorption, Orange Peel, Subrictical CO_2.

INTRODUCTION

In the typical textile, paper and food industries, there are many types of dye used in large amount (Ramakrishna, K.R. and Viraraghavan, T., 1997; Cheremisinoff, P.N. and Ellerbusch, F., 1980). Hence, those kinds of industries usually produce a quite large quantity of waste waters containing toxic dyes. If the waste waters are then discharged into water bodies without special treatment, it will cause very serious environmental problems (Yang, R.T., 2003). Generally, industrial dyes consist of complex aromatic structures, therefore, most of them are chemically stable and hard to be decomposed naturally (Ruthven, D.M., 1984; Chingombe *et al*., 2005). Methylene blue (MB) can be categorized as basic cationic dye because it releases a positively charged colored ion if it is dissolved in the solution. This type of dye may have serious effects on living aquatic creatures on short contact time.

Some conventional techniques can be used for the waste water treatments such as coagulation, precipitation, biological based technique and advanced oxidation process. In comparisons with other techniques, waste water treatment using adsorption has emerged as aquite popular method because it is very simple and effective to remove pollutants in small amount. There are many type of adsorbents for dye removal, one of them is activated carbon.

Activated carbon is the most widely used adsorbents due to the high surface area and easy availability. However, the high operating cost and difficulties in regeneration of activated carbon leads tomany researchers to search for more economic adsorbents. Utilization of biomass resources such as agricultural and forestry waste, can be assumed as a renewable and abundant source for supplying the demands for production of functional materials. Recently, biomass has emerged as potential raw materials for the production of carbon adsorbents.

Commonly, the preparation of activated carbon can be done using physical or chemical activation. In the physical activation process, carbonization of a carbonaceous material is followed by the activation process at specific temperature using some typical oxidizing gases such as carbon dioxide or steam or their mixtures (Nigam *et al*., 2000). Hence physical activation process is quite slow since it consists of two steps of carbon preparations. In the chemical activation approach, carbonization is conducted after the carbon precursors are mixed with the chemical impregnates such as KOH, $ZnCl_2$ or H_3PO_4 (Lee *et al*., 1999). This process is usually preferable than the physical method since it is a single operation and can be operated at lower operating temperature. However, this method is not environmental friendly due to the extensive use of chemical impregnates and it is also require high energy consumption (Khaled *et al*., 2009).

The synthesis of activated carbon by sub critical CO_2 activation method can be an alternative method next to the physical and chemical activation method because of it is a green method. Specifically, it can produced activated carbons with a strong mechanical characteristics and more developed meso-porous structure (Alam *et al*., 2009). From the literature, it can be said that sub/supercritical CO_2 can be usedas a good and effective activating agent of carbon materials since it has a mixture properties between gas and liquid such as a low viscosity, a high diffusive properties, a high specific density, and a high dissolving property (Gottipati *et al*., 2010). Therefore, it is expected that the sub/supercritical CO_2 activation method can be used for the preparation of activated carbons with a good mechanical strength (El-Hendawy *et al*., 2001).

In this work, low-cost and environmental friendly activated carbons were synthesized from orange peel waste by carbonization process followed by activation process using subcritical carbon dioxide. The orange peel derived activated carbons were then used in adsorbents for the removal of the methylene blue (MB) dyes from solutions.

METHODS

Synthesis of orange peel based activated carbons

Orange peel waste was firstly collected locally from the beverages stores in Bandung. It was then washed by distilled water, dried at the oven and crushed to the mesh size of +100/-200. The orange peel waste was then carbonized at 450 °C using nitrogen gas for 1 h. After the final temperature was achieved, the gas flow was changed to carbon dioxide and activation was done for 2 h by changing the activation temperature (140, 200 and 250 ^{o}C) and maintaining the pressure at 80 bar. The carbon product was then cooled down to room temperature by the flow of nitrogen gas. It was then with distilled water to remove remaining chemical impregnates. The surface characterization of the activated carbon (AC) was examined by N_2 adsorption at 77 K. The BET procedure was used to determine the surface area of activated carbons.

Analysis of methylene blue

For the synthetic dye solution, methylene blue (MB) was used as a dye adsorbate. Double distilled water was used to prepare the solutions and reagents. The UV spectrophotometer was the main instrument to measure the concentration of MB in the synthetic solution. The calibration curves were then constructed based on the Lambert-Beer Law which was reflected by the linear plot for the varying MB concentration.

Batch equilibrium studies

For the adsorption experiments, batch adsorption studies of MB onto the activated carbons were conducted by varying the initial concentration of MB. First of all, the equilibrium conditions was firstly determined by observing the concentration of MB until it reached a constant value. This experiment was done in the Erlenmeyer flasks in which MB solutions (200 mL) with different initial concentrations were placed in the flasks. Activated carbons with a mass of 0.5 g was added to the MB solutions under isothermal conditions (30 °C) for about 24 - 48 h until it reached equilibrium conditions. The initial pH was adjusted to 7 by adding hydrochloric acid or sodium hydroxide. The flasks were then removed from the shaker. The final concentration of MB dyes solution was then measured using calibration curves. Before conducting the concentration measurements, the

solution was filtered. Every experiment was repeated twice with the same conditions. The concentration of MB dyes at the equilibrium conditions, *q*e (mg g^{-1}), was determined by the following equations

$$q = \frac{(C_i - C_e)\,V}{m} \quad (1)$$

where C_i and C_e (mg/L) are the concentrations of MB dyes at initial and equilibrium conditions, respectively. *V* is the volumeof the solution (L), and *m* is the mass of activated carbon used for adsorption (g).

Batch kinetic studies

The procedures of kinetic experiments were the same as the equilibrium experiments. The concentration of MB at time *t*, q_t (mg g^{-1}), was calculated by:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (2)$$

where C_0 and C_t (mg/L) are the MB concentrations at initial and any time *t*, respectively. *V* is the volume of the solution (L), and *m* is the mass of activated carbon used for adsorption (g).

DISCUSSION

Figure 1 showed the N_2 adsorption–desorption isotherms of the orange peel based activated carbons prepared by sub-critical CO_2 activation method. The isothermal plots of activated carbons demonstrated a type III characteristics. This type is characterized by a well-defined plateau, which confirms its mesoporosity. It can be seen that hysteresis loop for the samples is found between the relative pressures (P/P_0) of 0.45 to 1.

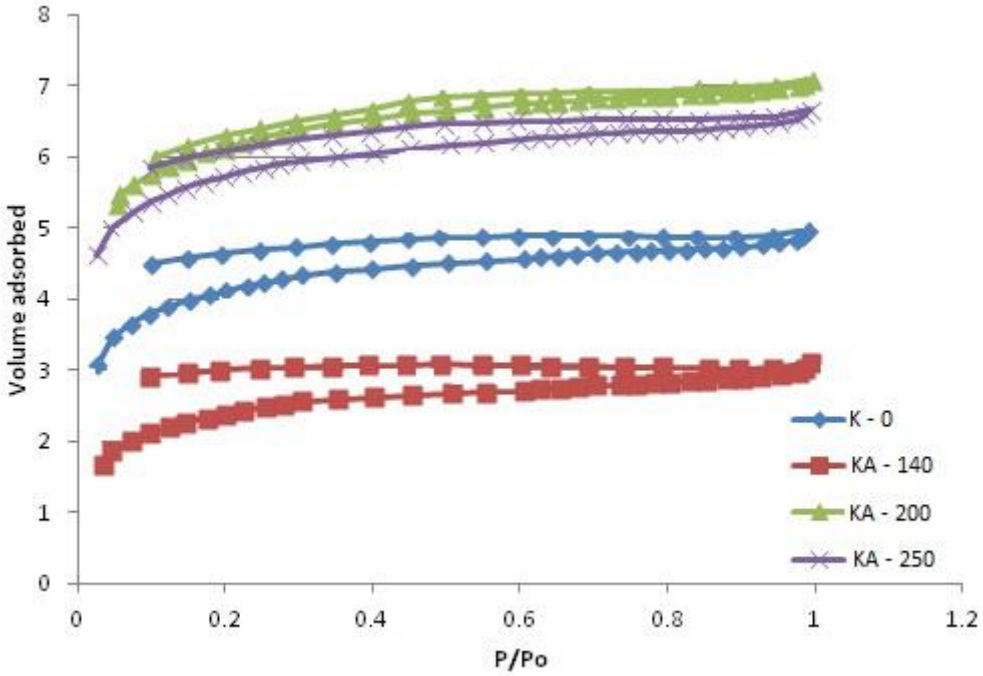

Figure. 1 Adsorption/desorption isotherm of N_2 gas on the orange peel based activated carbons prepared at different activating temperature. (K-0 : carbon samples before subcritical CO_2 activation)

Table 1 shows the surface properties of the carbon products obtained by varying the activation temperature. It can be seen that the highest surface is shown by the sample activated at temperature of 200 °C.

Table 1. Surface characteristicsof orange peel based activated carbons.

Samples	Activation Temperature (°C)	BET Surface Area (m^2/g)
KA- 140	140	169.507
KA - 200	200	415.938
KA - 250	250	287.099

Figure 2 shows the plots of pore size distribution (PSD) of carbon samples synthesized by sub-critical CO_2 activation method with varying activation temperature. It can be seen that all carbon samples can be classified as mesoporous carbons.

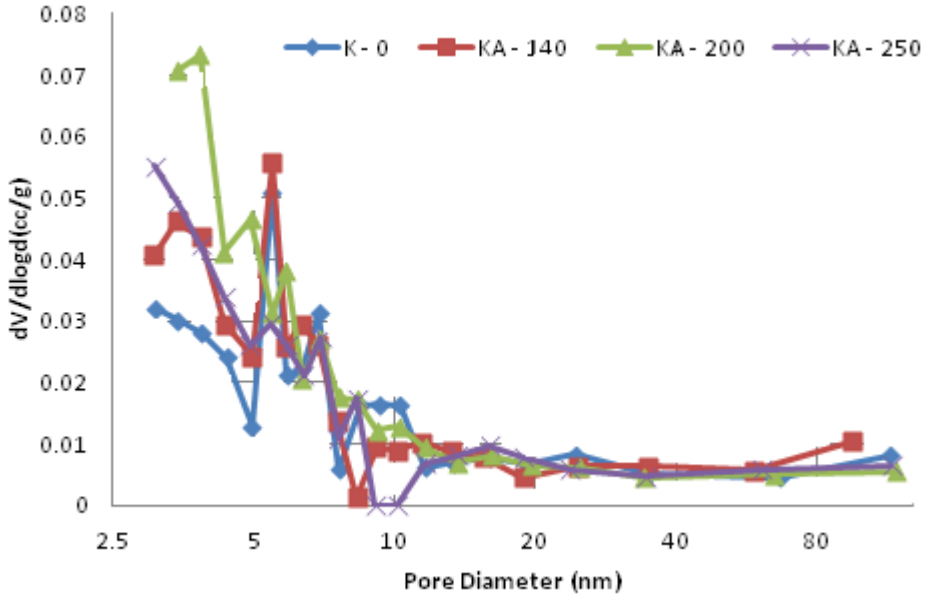

Figure 2. The plots of pore size distribution of the orange peel basedactivated carbons prepared at different activating temperature. (K-0 : Carbon samples before subcritical CO_2 activation)

The adsorption isotherm models are usually used to correlate the concentration of MB dye in the liquid and the solid phase at the equilibrium conditions. The data of equilibrium conditions were then fitted by different isotherm models. From these models, we can determine the maximum capacity of adsorption process (El-Hendawy *et al.*, 2005). Figure 3shows the adsorption isotherms of MB dye on the activated carbon. From the analysis of adsorption isotherm, we can use it further for investigating the interaction between solutes and adsorbents. It can be used further for optimization and design purpose.

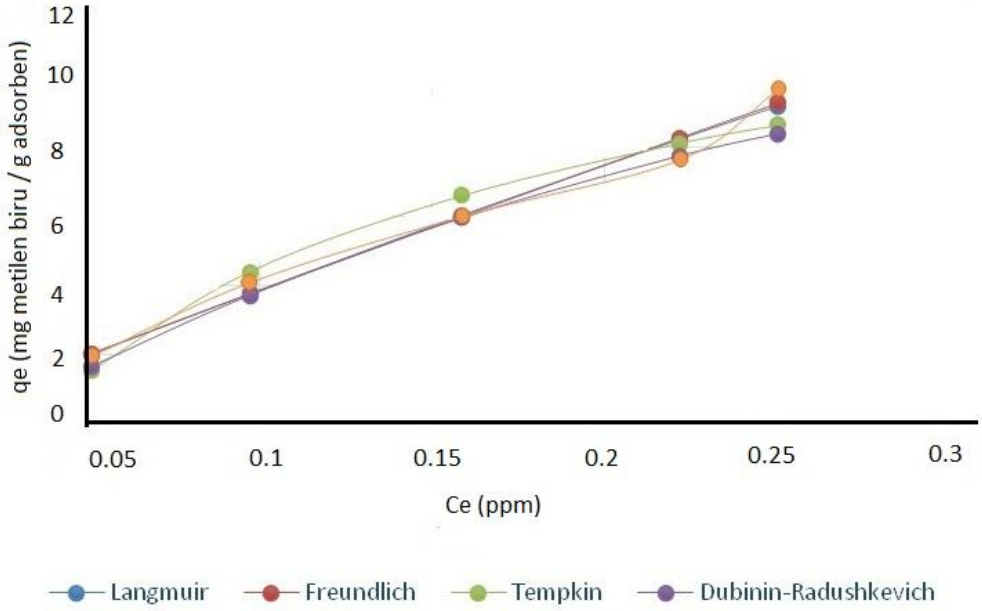

Figure 3. The plots of adsorption isotherm of methylene blue onto activated carbon.

Adsorption isotherm study is carried out on the four type of isotherms, Langmuir, Freundlich, Tempkin and Dubinin Radushkevic model. The applicability of the isotherm equation is compared by observing the correlation coefficients. Based on the correlation coefficients, the most suitable model is the Dubinin Radushkevich isotherm model, as shown in Table 2.

Table 2. Dubinin Radushkevich Isotherms constant for Adsorption of MB onto activated carbons.

Sample	Activation Temperature (^oC)	q_m (mg/g)	K (L/mg)	E (KJ/mol)	R^2
K – 0	-	18.2	4×10^{-8}	3.54	0.961
KA – 140	140	12.0	7×10^{-8}	2.67	0.937
KA – 200	200	15.9	4×10^{-8}	3.54	0.988
KA – 250	250	13.3	5×10^{-8}	3.16	0.857

The Dubinin Radushkevich (D-R) model, which assume a heterogeneous surface or a non-constant adsorption potential as the Langmuir model (Tseng *et al*., 2005), was used to test the experimental data. It could be used to differentiate between physical and chemical adsorption of MB. The following form of D-R models model is used :

$$\ln(q_e) = \ln(q_m) - K\varepsilon^2 \quad (3)$$

where K is the coefficient correlated with the averaged free energy of adsorption (mol^2/J^2) and ε = is the Polanyi potential [J /mol] , which is defined as RT Ln (1+1/Ce) where R = universal gas constant (8.314 $J.mol^{-1}.K^{-1}$); and T = temperature (K)]. The constants of q_m and β can be calculated using linear regression method. Hence, it can be seen that the D-R equation represented the most representative to the experimental data than the other models. The average sorption energy, E, can be determined using the following equation :

$$E = \frac{1}{\sqrt{2K}} \quad (4)$$

It was found that the magnitude of E was less than 8 $kJ.mol^{-1}$. It indicated that the adsorption process was the type of physical adsorption.

Two kinetic models such as pseudo-first-order and pseudo-second-order kinetic were applied for the experimental results. The pseudo-first-order kinetic model proposed (Foo et al., 2010) was usually used to predict sorption kinetic and was defined as:

$$Ln(q_e - q_t) = Ln\,(q_e) - k_1 t \quad (5)$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively and k_1 (1/h) is the adsorption rate constant.

The pseudo-second-order equation (Langergren *et al.*, 1998) is expressed by :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 (g/mg h) is the rate constant of second-order adsorption.

The values of all constants R^2obtainedfrom the plots for adsorption of MB dye on the adsorbent at 25 °C are reported in Table3. It wasobserved that the R^2 values obtained for the pseudo-second-order model was higher than that of first order model. This shows that the adsorption of MB dye on the adsorbent follows apseudo second-order kinetic model.

Table 3. Adsorption Kinetic Model Parameters.

Pseudo first order model

No.	Sample	Activation Temperature (^oC)	Qe(mg/g)	K_1 (min^{-1})	R^2
1	K – 0	-	2.03	7.68	0.993
2	KA – 140	140	1.89	43.4	0.940
3	KA – 200	200	2.01	25.3	0.955
4	KA – 250	250	1.97	34.6	0.963

Pseudo second order model

No.	Sample	Activation temperature (^oC)	Qe (mg/g)	K_2 (min^{-1})	R^2
1	K – 0	-	2.03	6.41	0.999
2	Ka – 140	140^{o}C	2.17	0.00748	0.992
3	Ka – 200	200^{o}C	2.15	0.0142	0.998
4	Ka – 250	250^{o}C	2.19	0.00964	0.996

CONCLUSIONS

The present investigation showed that orange peel can be effectively used as a raw material for the preparation of activated carbon using subcritical CO_2 activation process. Activated carbons were then used as adsorbents for the removal of methylene blue dye from aqueous solution. Methylene blue is foundto adsorb strongly on the surface of activated carbon. Adsorption behaviour is described by a Dubinin Radushkevich type isotherm. Kinetic data follows pseudo second-order kinetic model.

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