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Activated carbons from KOH-activation of salacca peels as low cost potential adsorbents for dye removal

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ABSTRACT

Salacca peel was used to prepare activated carbon (AC) by chemical activation with potassium hydroxide (KOH). The activated carbon with the largest surface area and most developed porosity was then used in the batch adsorption experiments of methylene blue (MB). Activated carbons with a surface area of around 1939 m^2/g were obtained. The adsorption equilibrium and kinetics of MB dyes from aquaeous solution on AC were also investigated. Adsorption isotherms of MB were correlated with the Langmuir, Freundich, Dubinin Radushkevich and Tempkin equations, and the heat of adsorption was determined. It was revealed that the Langmuir adsorption equation was more appropriate to represent the adsorption procedure of MB dyes compared to the other equations. Two simplified kinetic models including pseudo first- order and -second-order equations were used to evaluate the adsorption processes. The results indicated that the adsorption of MB dyes could be described properly by a pseudo-second-order equation. The kinetic parameters of this model were calculated and discussed. Copyright © 2016 VBRI Press.

Keywords: Salacca peel; activated carbons; chemical activation; dyes; langmuir models.

Introduction

Nowadays, the water pollution is becoming a serious problem in our modern society due to the discharge of non-degradable, toxic and hazardous compounds. The major sources of these kind of pollutants are the untreated effluents containing reactive dyes released from various industries such as paper, food and textile industries. Even a low concentration of dyes resulted in carcinogenic and mutagenic reactions [**1**]. Hence, it becomes very crucial to reduce the content of dyes from industrial wastewater to tolerable levels before discharging it into natural water bodies.

Most of the current waste water treatment technologies are either costly or uneffective for all types of pollutants. Additionally, the modern industries are now facing increasing pressure from the environmental regulatory boards to replace the conventional treatment technologies with eco friendly ones. Adsorption using activated materials is one of the most effective methods for the removal of wide range of pollutants.

Adsorption is a unit operation in which mass transfer of solutes occurs from bulk of gas or liquid to adsorbents. During adsorption, atoms, molecules or ion from bulk of gas or liquid are attached on the solid adsorbents via intermolecular forces [**2**]. Adsorption has been extensively used as separation methods in chemical, petroleum, and food industries especially for removing contaminants in waste water treatment. Although other separation methods including oxidation, precipitation and biological methods are used, adsorption is still important method in waste water treatment [**3**].

Activated carbon is one of the most preferred adsorbent over other adsorbents due to its high surface area and easy availability. However, the high operating cost and difficulties in regeneration of activated carbon leads to many researchers to search for more economic adsorbents. Use of biomass consisting mainly of agricultural and forestry waste, can be regarded as a renewable energy source with great potential to supply the global material demands. Biomass has already been utilized as adsorbents to remove dye and heavy metals from waste water including rice husk, saw dust, sugar cane waste, jackfruit waste, and cassava peels [**4-13**].

Salacca is a very important fruit product in Indonesia that has been cultivated throughout Indonesia. In Indonesia, salak has been cultivated throughout the islands and the fruit is widely used as fresh fruit. According to the Ministry of Agriculture of Indonesia in 2011, salak production in Indonesia has increased from 423.5 t in 2000 to 862.5 t in 2009. Fresh fruits of this cultivar have also been exported to Singapore, United Kingdom, Malaysia, Thailand, Hongkong and Saudi Arabia [**14**]. Salacca belongs to a group of palms, which are 1.5 - 5 m high, extremely spiny and sprout their leaves from the ground level. Salak palms grow as under-storey plants in the low lands of tropical rain forests in Indonesia and other Southeast Asian countries. Fruits of salak are located in tight; globose bunches, round, 2.5 - 10 cm x 5 - 8 cm across. They are covered with

regularly arranged scales developing from the peel of the fruit (pericarp) giving it the appearance of a snake or reptiles´skin. The aromatic fruits enclose a soft, translucent pulp with a taste comparable to a combination of apple, pineapple and banana [**15**].

Due to abundant amount of salacca (salak) peel in Indonesia, it needs to be considered as cheap and renewable precursors for production of activated carbons for methylene blue (MB) dye removal. The activated carbons were prepared from salacca peel by chemical activation method using KOH. This would help in placing value on this fruit waste and provide a potentially cheap alternative to existing commercial activated carbons. To the best of our knowledge, no report has been documented on the use of salacca based activated carbon as a low-cost alternative adsorbent for MG dye removal from aqueous solution. Kinetics and isotherms parameters governing the adsorption process were studied and reported.

Experimental

Materials synthesis

The carbonaceous precursor selected was salacca peel. The peels were crushed and sieved to particle sizes of 2.0-2.8 mm. The powders were initially subjected to the pre-carbonization process at temperature of 500 °C for 1 h. After this process, the salacca peel powders were impregnated with solution of KOH with different mass concentration (10 %, 15 % and 20 %-w) by varying impregnation ratios (weight of KOH to weight of salacca peel) from 1:1, 2:1 and 4:1. The salacca peel powders were impregnated for 20 h. The slurries were then heated at 80 °C for 24 h to dryness. Next, samples were pyrolyzed under N_2 flow at 800 °C for 1 h. Prepared activated carbons were washed with 0.1 M HCl and then with distilled water until the pH of the washing water was neutral (pH 7).

Characterizations

Characterization in terms of specific surface area, pore volume, and pore diameter of the obtained activated carbons was determined by N_2 adsorption at with surface area and pore size analyzer using the Brunnaeur-Emmet-Teller (BET) method. The micropore volume was calculated by using t-Plot micropore volume. The pore size distribution was determined by using Barrett–Joyner–Halenda (BJH) model.

Batch adsorption

Methylene blue (MB) was used as a model cationic dye for this experiment. MB dye was purchased and was used without further purification. The stock solution (500 ppm) of MB dye was prepared by dissolving 0.5 g of MB in 1 L of distilled water. The experimental solutions of desired concentration were prepared by diluting stock solution with distilled water. The concentration of MB dye was measured at maximum wavelength of 668 nm using UV–visible spectrophotometer.

Adsorption experiments were carried out with 100 mL experimental volume of the dye solution in 250 mL flasks. The solution pH was kept at its original value and was not controlled during the experiment. Adsorption equilibrium experiments were conducted with adsorbent dose of 0.04 g/L, temperature of 25 °C and varying dye concentration. The desired carbon dose was mixed with dye solution, and was then agitated at a rate of 200 rpm in a shaking incubator. Adsorption kinetics and thermodynamic experiments were carried out using initial dye concentration (10–50 ppm) at the equilibrium experimental conditions whereas dye samples were withdrawn at regular time intervals for their residual dye analysis.

The adsorption capacity (qe) and color removal efficiency (R) were calculated using following Eqs. (1) and (2), respectively:

$$q_e\ (mg/g) = (C_0 - Ct)V.\ M \quad (1)$$

$$R\ (\%) = (C_0 - C_t) / C_0 \quad (2)$$

where, C_0 is the initial dye concentration (mg/L), Ct is the residual dye concentration (mg/L) at time t, V is the volume (L) of aqueous solution, and M is the mass of the adsorbent (g).

Results and discussion

Activated carbon is chemically activated by KOH impregnant. The effect of impregnation ratio and mass concentration of KOH on the characteristics of activated carbons such as surface area, volume, pore diameter and yield gains will be discussed in this section. The results of the characteristics of the activated carbon are shown in **Table 1**.

Table 1. Characterization of Activated Carbons.

Sample	Impregnation ratio	KOH Concentration	BET Surface Area (m^2/g)	Pore volume (cc/g)	Pore Diameter (Å)	% Yield
KA1:1-10%	1:1	10%	723	0.453	25.04	24.75
KA1:2-10%	1:2	10%	813	0.608	29.87	21.50
KA1:4-10%	1:4	10%	1488	0.888	23.87	20.25
KA1:1-15%	1:1	15%	743	0.482	25.96	23.50
KA1:2-15%	1:2	15%	1006	0.602	23.93	18.00
KA1:4-15%	1:4	15%	1820	1.034	22.72	21.25
KA1:1-20%	1:1	20%	804	0.485	24.15	21.75
KA1:2-20%	1:2	20%	874	0.566	25.93	19.75
KA1:4-20%	1:4	20%	1939	1.088	22.45	14.50

From **Table 1**, it can be seen that the BET surface area of activated carbons can be increased as the impregnation ratio is increased from 1:1 to 1:4. The range of BET surface area is between 723 and 1939 m^2/g. The same trend can be observed by increasing the mass concentration of KOH from 10 % to 20 %. The error ranges for all measurements of BET surface area, pore volume and pore diameter were about 5 %.

The highest surface area of activated carbons is about 1939 m^2/g for KOH concentration of 20 % and impregnation ratio of 1:4. From the average pore size diameter, it can be observed that the activated carbons can be classified as mesoporous carbons. However the yield is decreased from 24.75 % to 14.50 % when the impregnation ratio is increased from 1:1 to 1:4.

Fig. 1 shows the pore size distribution of activated carbons obtained by impregnation ratio of 1:2 and 1:4, it can be seen that the activated carbons belong to the mesoporous structure.

The porous structure of activated carbons obtained by impregnation ratio of 1:2 and 1:4 is also confirmed by the observation using scanning electron microscope (SEM), as

shown in **Fig. 2**. It seems that the porous structure is formed during the activation process using KOH impregnants.

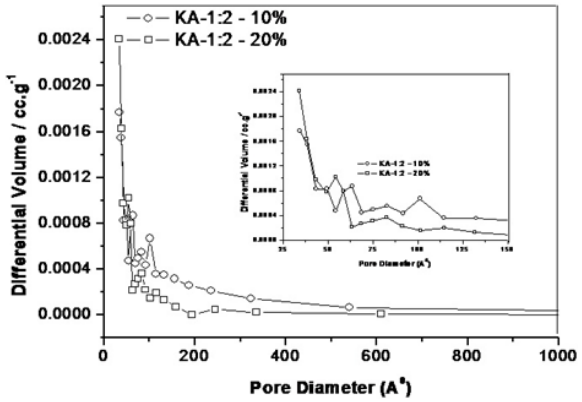

Fig. 1. Pore size distribution of activated carbons (Inset: The zone between 25 and 150 A^0)

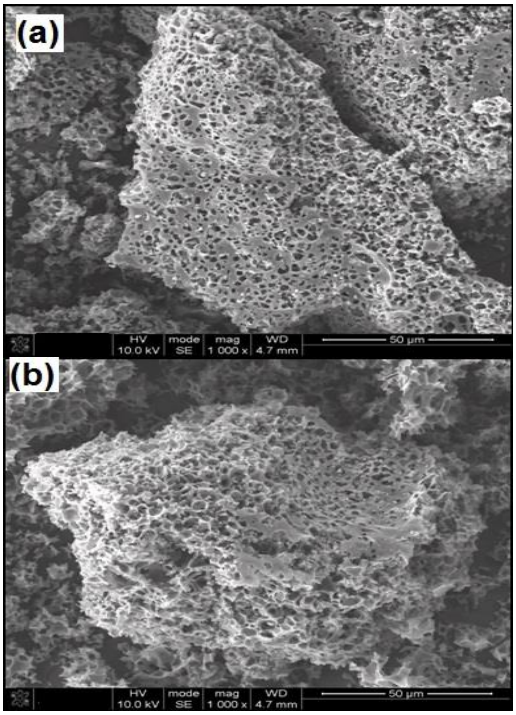

Fig. 2. SEM image of salacca peel based activated carbons prepared by impregnation ratio of (a) 1:2 and (b) 1:4.

Isothermal adsorption model

Adsorption experiments performed with adsorption process using activated carbon with the highest surface area (1939 m^2 /g).

There are four Isothermal Adsorption models tested in this experiment, namely Langmuir, Freundlich, Temkin and Dubinin Radushkevich. In the experiment, the isothermal adsorption model that best matches the data will be obtained. Parameters of isothermal adsorption models were shown in **Table 2**. Based on the value of R^2, it can be seen that the adsorption process follows the Langmuir isothermal adsorption models. Isothermal Adsorption Langmuir describe molecules adsorbed only attached to the outer layer of activated carbon surface or only form a monolayer and the absence of interaction between adsorbed molecules.

Table 2. Parameters for adsorption isothermal models.

Langmuir Model			
q_m (mg solute/mg activated carbons)	k_l (L/ mg solute)		R^2
0.674	4.01		0.869
Freundlich Isotherm Model			
N	kf (mg solute/mg activated carbon)		R^2
15.15	0,544		0.712
Temkin Model			
a (L/mg solute)	b	b (j/mol)	R^2
1202604	0.039	63527	0.683
Dubinin-Radushkevich Isotherm Model			
q_m (mg solute/mg karbon aktif)	k_d (mol^2/J^2)	E (joule/mol)	R^2
0.666	7×10^{-8}	2672	0.841

Adsorption kinetic models

Adsorption kinetics is determined by the active carbon with sample code KA1: 4-20 %. There are two models were used to examine the kinetics of the adsorption process is a model pseudo-first order and pseudo-second order. 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 [**16**] was usually used to predict sorption kinetic and was defined as:

$$Ln(q_e - q_t) = Ln\,(q_e) - k_1 t \quad (3)$$

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

Table 3. Parameter for Pseudo 1st order model.

Konsentrasi awal	q_e (mg solute/mg carbon)	k ($minute^{-1}$)	R^2
30 ppm	0.417	0.0138	0.971
40 ppm	0.411	0.0160	0.97
50 ppm	0.433	0.0140	0.877
55 ppm	0.369	0.0184	0.907

The pseudo-second-order equation [**17**] is expressed by,

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{t}{q_e} \quad (4)$$

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

The values of all constants obtained from the plots for adsorption of MB dye on the adsorbent at 25 °C are reported in **Table 3**. It was observed 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.

From the results shown in **Tables 3** and **4**, it is found that pseudo-order kinetic model is more in accordance with the data of the kinetic model pseudo-first order. This can be seen from the value of R^2 model of pseudo-second order which is almost close to a value of 1.

Table 4. Parameter for Pseudo 2nd order model.

Konsentrasi awal	q_e (mg solute/mg carbon)	k (1/(mg solute. minute))	R^2
30 ppm	0.686	0.081	0.999
40 ppm	0.673	0.095	0.998
50 ppm	0.733	0.0995	0.997
55 ppm	0.667	0.124	0.999

The value of k_2 on pseudo-order kinetic model tends to rise as shown **Table 4** with respect to the initial concentration of the dye solution due to the increase in the driving force (the difference in concentration of the adsorption process). The plot of experimental data versus the pseudo first and second order model can be seen in **Fig. 3** for MB initial concentration of 55 and 50 ppm.

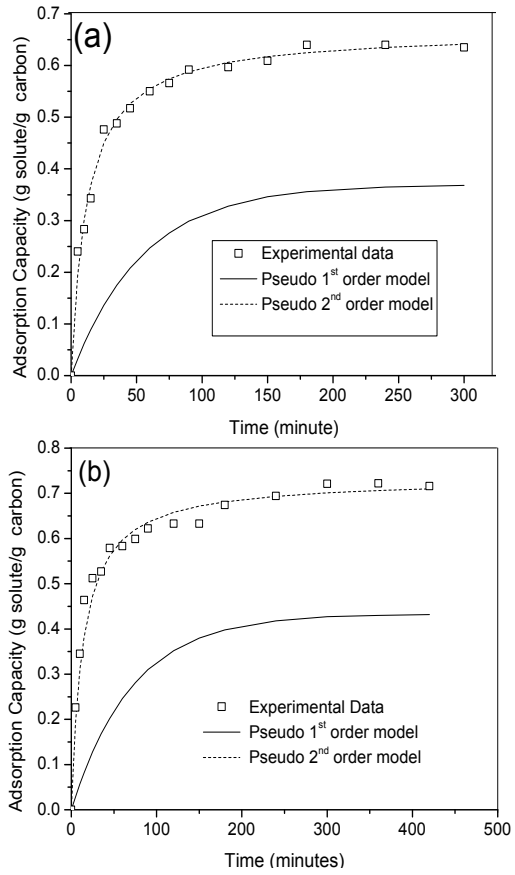

Fig. 3. Comparison of experimental data and fitted kinetic adsorption models for MB initial concentration of (a) 55 ppm and (b) 50 ppm.

Conclusion

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

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