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Morphology and Sorption Kinetic Studies of L-Type Activated Carbons Prepared from Oil Palm Shells by ZnCl₂ and H₃PO₄ Activation

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Abstract: The aim of this investigation was to study the morphology and sorption kinetic studies of an L-type activated carbon prepared from Oil Palm Shells (OPS) by way of the two stage activation method in self-generated atmosphere using a muffle furnace. Both L-type dehydrating agents, zinc chloride and phosphoric acid were used as the chemical activation agent. For the $ZnCl_2$ samples, the optimum adsorption capacity was obtained when the samples were subjected to semi-carbonization of 400°C, 5 M $ZnCl_2$ impregnating solution, followed by pyrolysis at 400°C. Whereas for the H_3PO_4 samples, semi-carbonization of 400°C followed by 4.5 M H_3PO_4 impregnating solution and pyrolysis at 400°C has shown to produced the optimum adsorption capacity. All activated carbons were fitted well in the Langmuir adsorption isotherm and the pseudo-second-order kinetics. These results demonstrated that this agricultural waste has the potential to be converted into high-capacity adsorbent for the remediation of waste waters.

Key words: L-type activated carbons, two-stage activation, oil palm shells

INTRODUCTION

Over the decades, various raw materials have been used to prepare activated carbons using both chemical and physical activations. These adsorbent materials have many applications (Bansal *et al.*, 1988) presenting porous structures consisting of micropores (pore width <20 A°), mesopores (20-500 A°) and macropores (>500 A°). Activated carbons can be prepared by chemical activation technique which involves impregnating the precursor with a strong dehydrating agent, such as H_3PO_4 or $ZnCl_2$ at 450-600°C to simultaneously form and activate the carbon matrix producing an L-type activated carbon or by physically activating the raw materials (prepared without any chemical activation), which will produce H-type activated carbon. The differences between the L-type and H-type activated carbons are listed in Table 1. Any cheap substance with a high carbon and low ash content can be used as a starting material for the production of active carbon. In older production procedures preference was given to recent and younger fossil materials-wood, peat and wastes of vegetable origin (fruit stones, nutshells, sawdust) which can be activated easily and give high quality products (Davidson *et al.*, 1968). Malaysia is one of the world's foremost palm oil producers; as such it has an abundant agricultural waste such as Oil Palm Shells (OPS). Greater awareness to the cost of impact of agricultural waste to the environment has resulted in various attempts to turn these large quantities of agricultural waste into a value added product. In this work, L-type activated carbons were prepared from OPS

Table 1: The differences between the L-type and H-type activated carbons

L-type activated carbons	H-type activated carbons
Lower activating temperature. Activating temperature of 450-600°C, with the appropriate impregnating chemical agent such as H_3PO_4 or $ZnCl_2$ were used.	Higher activating temperature. Activating temperature of 800-1000°C with the appropriate activating vapor/gas (in the reaction chamber) such as H_2O or CO_2 were used
Surface oxygen groups present, originates from the precursor materials.	Surface oxygen groups results from partial oxidation mechanism by the activation atmosphere
Wider micropores present due to the formation of smaller polyhexagon sheets but with larger aliphatic and hydrogen content.	Smaller micropores present due to different polyhexagon sizes being linked by oxygen bridging in the intersheet spacings
Pore size distribution obtained by N_2 adsorption indicates that L-type carbons have large micropores but narrow mesopores.	Pore size distribution obtained by N_2 adsorption indicates that H-type carbons have narrow micropores but wider mesopores
Lower particle size reduction and higher yields in chemically activated carbons.	Higher particle size reduction and lower yields in physically activated carbons

Albornoz *et al.* (1999), Laine and Yunes (1992), Laine *et al.* (1989) and Lopez *et al.* (1996)

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using H_3PO_4 and $ZnCl_2$ in a two stage activation method. However, the use of H_3PO_4 is much preferable than $ZnCl_2$ as due to the fact that later would cause serious corrosion problems, difficulty in chemical recovery and is toxic to the environment.

MATERIALS AND METHODS

The OPS were obtained from Desa Kin Loong Palm Oil Mill in Keningau, Sabah, Malaysia. Prior to the impregnation process, the OPS were washed with distilled water and dried in an oven at 110°C for 24 h. This was done to remove sand, branch fibers and dirt from contaminating the samples as explained in our earlier studies (Anuar *et al.*, 2001, 2002, 2003, 2004). The samples were divided into two 8 batches series and each batch of sample had 20 g of OPS. Impregnation process was done using H_3PO_4 and $ZnCl_2$ as the dehydrating agents with the impregnation ratio to OPS as shown in Table 2. The flask was then placed in an orbital shaker model 721 Protech for a week. The samples were then dried overnight in an oven at 110°C. A muffle furnace model Carbolite RHF 1500 was used to semi-carbonized the samples at various temperatures (400-600°C) for 1 h as the first stage followed

by an activation stage at various temperatures (400-600°C) for 30-45 min as the second stage. All experiments were conducted in a laboratory scale muffle furnace under static conditions in a self-generated atmosphere covering process parameters such as impregnation ratio, time and temperature which was previously describe by (Srinivasakannan and Abu Bakar, 2004). The impregnated precursors were exposed straightaway to semi-carbonization and activation temperatures unlike the specific temperature progression methods as described in our earlier works (Anuar *et al.*, 2001, 2002, 2003, 2004).

After the allotted time, the samples were extracted from the furnace and placed immediately in a dessicator until it reached room temperature. The activated carbons were then refluxed in distilled water to remove all metals ions, tar and ash followed by distilled water (10 times) to remove the dehydrating agents. The activated carbons were dried in an oven at 110°C for a week, after which, yield percentage, pH, morphological and sorption kinetic studies of the selected activated carbon were preformed. However, in this study, only the morphological and reaction kinetics of the prepared activated carbons will be discussed.

Table 2: Preparation and activation parameters for $ZnCl_2$ and H_3PO_4 activated carbons

Sample $ZnCl_2(Z)$ $H_3PO_4(H)$	Semi-carbonization	Activation	Impregnation ratio $ZnCl_2$ or H_3PO_4 (mol L^{-1})/OPS (g)
Z/H1	400°C in 1 h	400°C in 45 min	3.5:20
Z/H2	400°C in 1 h	400°C in 45 min	4.0:20
Z/H3	400°C in 1 h	400°C in 45 min	4.5:20
Z/H4	400°C in 1 h	400°C in 45 min	5.0:20
Z/H5	400°C in 1 h	400°C in 30 min	4.0:20
Z/H6	400°C in 1 h	500°C in 30 min	4.0:20
Z/H7	400°C in 1 h	600°C in 30 min	4.0:20
Z/H8	600°C in 1 h	400°C in 45 min	4.5:20

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM): Scanning electron microscope was used to study the morphological structure on the prepared activated carbons. Figure 1 shows the morphological structure of the H_3PO_4 prepared activated carbons whereas, Fig. 2 shows the morphological structure of the $ZnCl_2$ prepared activated carbons. H3 and H8 showed microporous structures but H2, H6 and H6 showed clear honey-comb and tunnel-like
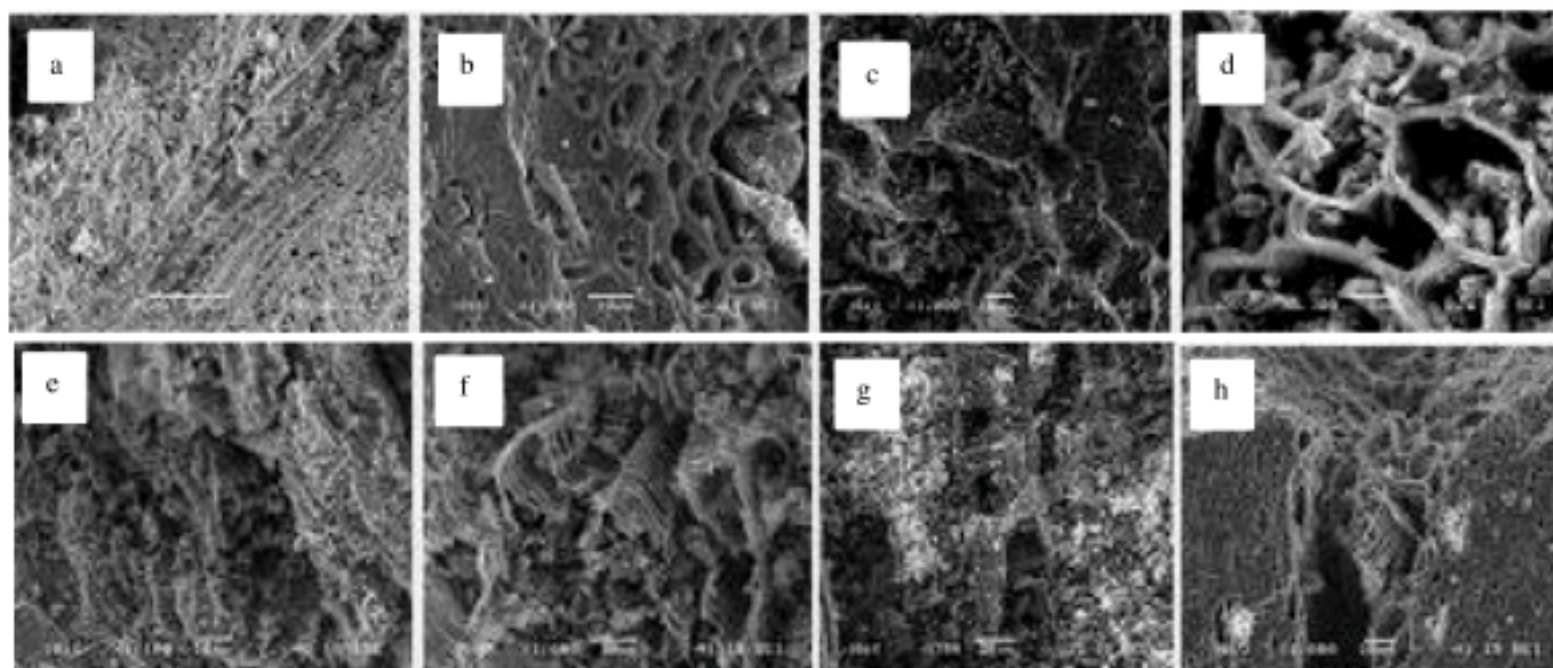

Fig. 1: The electron micrographs of activated carbons impregnated by H_3PO_4 (a) H1 (x500), (b) H2 (x1500), (c) H3 (x1000), (d) H4 (x3300), (e) H5 (x1100), (f) H6 (x1600), (g) H7 (x700) and (h) H8 (x1000)
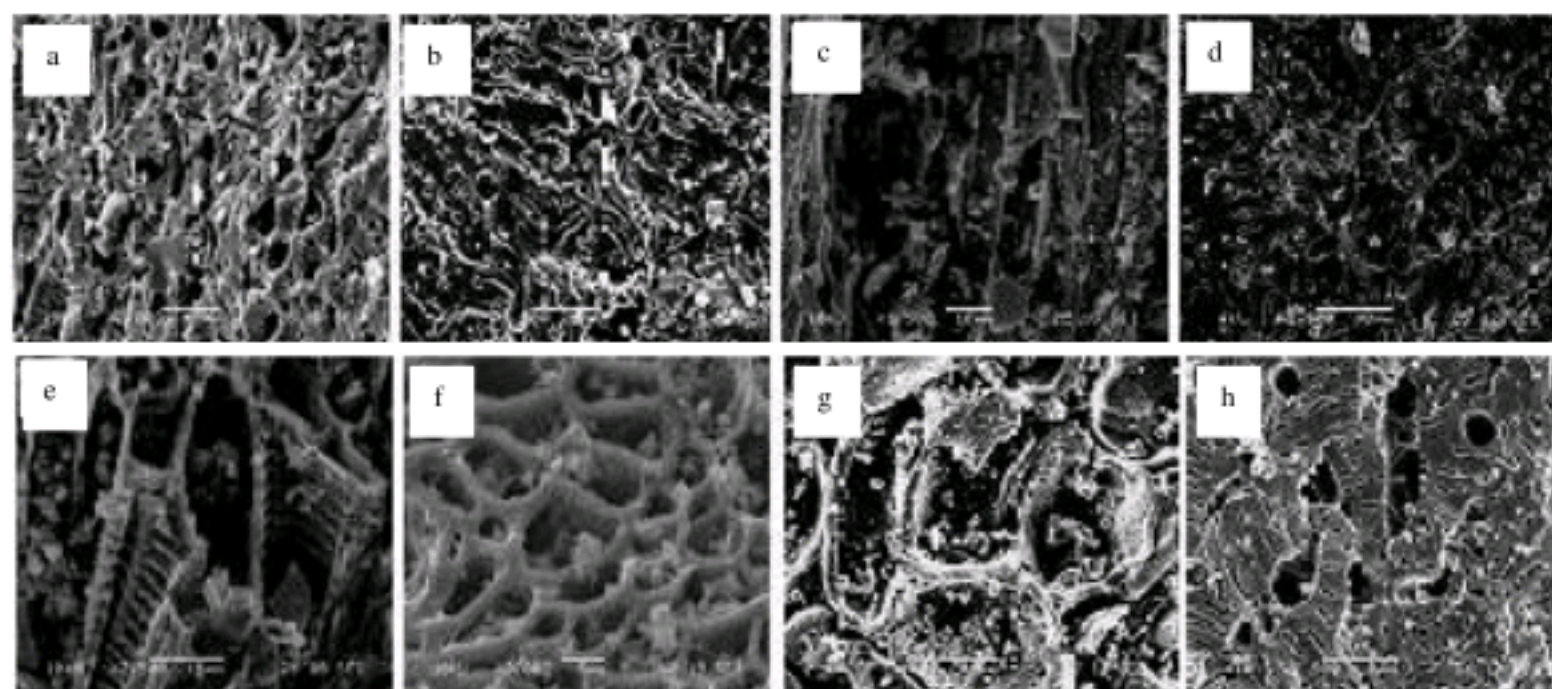
Fig. 2: The electron micrographs of activated carbon impregnated by $ZnCl_2$ (a) Z1 (x2000), (b) Z2 (x2500), (c) Z3 (x1500), (d) Z4 (x2500), (e) Z5 (x2500), (f) Z6 (x3000), (g) Z7 (x2000) and (h) Z8 (2500)

structures, indicating pore enlargement. H5 and H7 showed damaged or altered surfaces. This shows that a low H_3PO_4 dehydrating agent ratio (4.0 mol L^{-1}) and a high activation temperature (600°C) cause damage to the porosity structure of the carbon. Z4 shows a microporous structure but Z5 and Z6 showed clear honey-comb and tunnel-like structures, indicating pore enlargement. However, these two figures show the similar traits in which the increases of chemical activator ratio, the pores will be developed and generated. As the increases of activation temperature and time (to a certain extend), there will be more pores (including pore enlargement) produced.

Adsorption capacity: In order to understand the adsorption of the adsorbents, the equilibrium data were evaluated according to the Freundlich and Langmuir isotherm. A linearised plot of Freundlich and Langmuir isotherm for both dehydrating agents obtained for activated carbon are shown in Table 3 and 4. Langmuir equation is based on a theoretical model and assumes that the maximum adsorption corresponds to monolayer capacity and energy of adsorption. The Langmuir equation is given by Eq. 1 (Gregg and Sing, 1982).

$$\frac{Ce}{Xe} = \frac{1}{bn_m} + \frac{Ce}{n_m} \qquad (1)$$

where, Ce is the equilibrium concentration (mg L^{-1}), Xe is the amount adsorbed at equilibrium (mg g^{-1}), n_m and b is the Langmuir constant.

The Freundlich equation is an empirical model that considers heterogeneous adsorptive energies on the adsorbents surface. The Freundlich equation is given as Eq. 2 (Jankowska *et al.*, 1991).

Table 3: Correlation coefficient of Langmuir and Freundlich model of activated carbon impregnated by H_3PO_4

Activated carbon	Correlation coefficient (R^2)	
	Langmuir model	Freundlich model
H1	0.0240	0.0326
H2	0.8233	0.7286
H3	0.9375	0.1184
H4	0.3664	0.3855
H5	0.7915	0.2501
H6	0.2381	0.1172
H7	0.0295	0.0449
H8	0.9362	0.5832

$$Xe = KC^{1/n} \qquad (2)$$

Equation 2 can be rearranged to linear form:

$$\log Xe = \log K + \frac{1}{n} \log Ce \qquad (3)$$

where, K and n are the Freundlich constants.

The result from Table 3 and 4 show that correlation coefficient of Langmuir model are higher than Freundlich model. This result indicates that the freundlich equation does not fit the experimental results very well. On the other hand, the Langmuir equation gives a satisfactory fitting and the modeling result are shown in Table 3 and 4. It supports that at the acidic solution, the methylene blue is adsorbed on the macropores and mesopores and on a certain fraction of micropores and adsorption could be just a single layer adsorption. However, the values of correlation coefficient of Langmuir model from Table 4 are better than the value from Table 3. This means that the adsorption ability of activated carbon impregnated by $ZnCl_2$ is better than that of activated carbons impregnated by H_3PO_4.

Table 4: Correlation coefficient of Langmuir and Freundlich model of activated carbon impregnated by $ZnCl_2$

Activated carbon	Correlation coefficient (R^2)	
	Langmuir model	Freundlich model
Z1	0.7618	0.0517
Z2	0.7787	0.0980
Z3	0.9116	3E-050
Z4	0.9474	0.2011
Z5	0.9249	0.9005
Z6	0.8745	0.8249
Z7	0.8933	0.1526
Z8	0.9408	0.0839

Table 5: Correlation coefficient of activated carbon impregnated by $ZnCl_2$ and H_3PO_4

Samples	Correlation coefficient (R^2)	
	Activated carbon ($ZnCl_2$)	Activated carbon (H_3PO_4)
1	0.8680	0.9995
2	0.9978	0.9991
3	0.9279	0.7428
4	0.9138	0.8731
5	0.9006	0.9696
6	0.9702	0.9950
7	0.9981	0.9972
8	0.8508	0.9988

Kinetics and dynamics of adsorption: Table 5 shows the correlation coefficient of activated carbon impregnated by $ZnCl_2$ and H_3PO_4. The kinetics and dynamics of adsorption of methylene blue on activated carbon can be studied by applying the Lagergren first-order and pseudo-second order rate equations for the determination of the rate constant. Lagergren kinetic first-order and the pseudo-second-order equations have been most widely used for the adsorption of an adsorbate from an aqueous solution, which are expressed by the Eq. 4 and 5.

The Lagergen first-order equation is given as Eq. 4

$$Log(q_e - q_t) = \log q_e - \frac{k_{ad} t}{2.303} \quad (4)$$

The pseudo-second order equation is given as Eq. 5

$$\frac{t}{q_t} = \frac{1}{k_{ad} q_e^2} + \frac{1}{q_e} t \quad (5)$$

where, q_e and q_t are the amount of dye adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium time and time t, respectively and k_{ad} is the rate constant. The result shows that both types of activated carbon are fitted best to pseudo-second order.

CONCLUSION

Oil palm shells were used as raw materials for the production of activated carbons using H_3PO_4 and $ZnCl_2$ as the activation agents, which demonstrated promising results. Morphological studies showed the relationship between the dehydrating agent impregnating ratios and activation time and temperature had an effect on the porosity size and structure. The kinetics for the pyrolysis of the impregnated OPS for the production of activated carbons was also investigated and corroborated with the morphological studies, indicated that both type of carbons fitted best to the Langmuir isotherm and pseudo-second-order kinetics, indicating a monolayer type adsorption. These results are very supportive of a high quality activated carbon production from an abundant waste material.

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