



Teak Leaf-Based Activated Carbon for Phosphate Removal

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DOI 10.15294/jbat.v8i1.20169

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Article Info

Article history:
Received
November 2018
Accepted
April 2019
Published
June 2019

Keywords :
Adsorption;
Adsorbent;
Microwave;
Isotherm;
Kinetic

Abstract

The use of detergent predictably causes large quantities of phosphate ion in water bodies. It is considered to trigger eutrophication, that creates a severe reduction in water quality. Adsorption using activated carbon is one of the effective methods for the removal of phosphate from wastewater. Recently, the use of microwave irradiation in activated carbon preparation is a promising alternative to replace conventional heating using a furnace. In this study, the use of microwave heating was compared to conventional heating. The result showed that pore of activated carbon was larger than that of the char and the activated carbon prepared using 30% of $ZnCl_2$ had the adsorption performance higher than that of prepared using 20% of $ZnCl_2$. The optimum adsorption occurred at pH 4 and the equilibrium was reached after 180 minutes. The Langmuir equilibrium model was more appropriate than the Freundlich equilibrium model. While the kinetics model analyzed using pseudo-first-order, pseudo-second-order, internal diffusion, and external diffusion indicated that the pseudo second order was most suitable for the adsorption of phosphate by teak leaf activated carbon.

INTRODUCTION

The use of detergent increases with the increase in laundry industries. It predictably causes large quantities of phosphate ion in water bodies. Phosphate is a necessary nutrient for the growth of plants. However, the higher phosphate content is considered to trigger eutrophication, that causes a severe reduction in water quality (Yuan et al., 2019). Numerous methods have been developed to overcome phosphate pollution in wastewaters including electrocoagulation (Hashim et al., 2019), chitosan membrane (Karthikeyan et al., 2019) and adsorption (Yuan et al., 2019). Among of them, adsorption using activated carbon was the most effective method for the removal of phosphate from wastewater due to its effectiveness, low cost, facile design, and easy to operate (Yuan et al., 2019).

On the other hand, teak leaf waste has a high content of cellulose (28.2%), lignin (29.5%) and hemicellulose (6.8%) that can be used as a precursor in the activated carbon production. The

structure and characteristic of activated carbon are affected by the chemical composition of precursor and activation process, including the activating agent used. In this sense, the use of $ZnCl_2$ as an activating agent has been preferred due to the higher surface area obtained (Pezoti et al., 2014). Recently, the use of microwave irradiation is a promising alternative to replace conventional heating using a furnace. Microwave heating is internal and volumetric, where electromagnetic energy is converted to the thermal energy at a molecular level. As a result, it provides a shorter processing time and more uniform pore. The microwave heating has been successfully used in the preparation of activated carbon from pineapple leaf with $ZnCl_2$ activation (Mahamad et al., 2015). However, there has been no literature that particularly investigated the activated carbon preparation from the teak leaf.

Hence, the objective of this study was to prepare activated carbon from the teak leaf by $ZnCl_2$ activation. Several variables have been studied,

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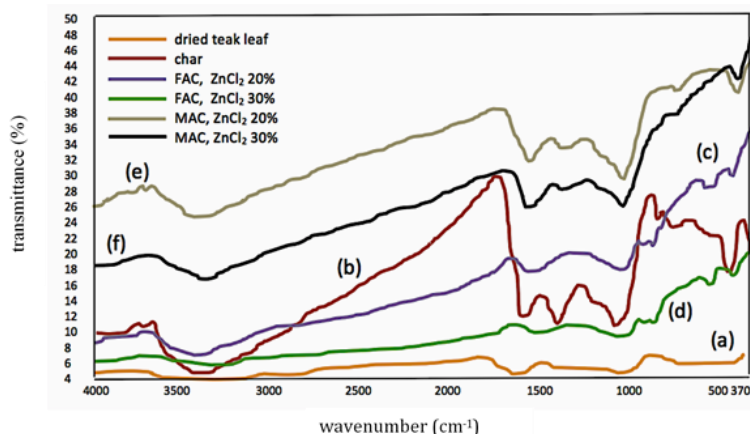


Figure 1. FTIR spectra of (a) teak leaf, (b) char, (c) FAC with ZnCl_2 20%, (d) FAC with ZnCl_2 30%, (e) MAC with ZnCl_2 20% and (f) MAC with ZnCl_2 30%

including the heating method and ZnCl_2 concentration. The obtained activated carbon was then evaluated for its feasibility as an adsorbent for phosphate removal in batch experiments. The effect of various contributing parameters to the adsorption performance, such as solution pH, initial concentration, and contact time have been investigated. The resulted data were further analyzed using two adsorption isotherm models (e.g. Langmuir and Freundlich) and five adsorption kinetic models (e.g. external diffusion, internal diffusion, pseudo-first-order, pseudo-second-order, and Elovich).

MATERIAL AND METHODS

Preparation of activated carbon

Teak leaf waste used in this study was obtained from Blora, Indonesia. Before any treatment, the leaf was cleaned, washed and heated at 110°C in an oven until constant weight to remove the water content. The dried sample was then blended to a powder. The powder was entered to a furnace (Model FB1310M-33 Thermolyne, Thermo Scientific, USA) for carbonization at 500°C for 2 hours. The sample obtained was mixed with ZnCl_2 as an activator agent under various concentration (20 and 30% mass), then heated using a furnace at 700°C for 1.5 hours (FAC) or using 2.45 GHz commercial microwave oven (Model ME731K, Samsung, Malaysia) at 600 Watt for 10 minutes (namely MAC). Before microwave heating started and during the activation process, N_2 gas was flowed with a flow rate of $250\text{ cm}^3/\text{min}$. After that, the activated carbon obtained was washed with HCl, rinsed with distilled water until the pH of the

filtrate was around 7 and heated in an oven at 110°C . Activated carbon was further analyzed the specific surface area through adsorption of N_2 at 77 K using an automated gas sorption apparatus (Quantachrome, USA) with BET (Brunauer-Emmett-Teller) method, the surface morphology using a Scanning Electron Microscope (Phenom Pro X Desktop, UK), and the functional groups using Fourier Transform Infra-red Spectroscopy (Spectrum 100, Perkin Elmer, USA) recorded between 4000 and 400 cm^{-1} .

Batch adsorption studies

In the adsorption process, 0.05 gram of activated carbon was put into ten Erlenmeyer filled with 50 mL of phosphate solution with different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L). The degree of acidity (pH) of the solution was varied (2, 4, 6, 8, and 10) with the addition of 0.1 N HCl or 0.1 N NaOH. The mixture was then placed in the shaker and shaken at 250 rpm for 5-240 minutes. After the adsorption time was reached, the solution was filtered and the filtrate was analyzed for residual phosphate using a UV-Visible spectrophotometer (Model Genesys 10UV, Thermo Scientific, USA) at $\lambda_{\text{max}} 880\text{ nm}$.

RESULTS AND DISCUSSION

Characterization of activated carbon

The existence of functional groups in the char, MAC, and CAC was analyzed from FTIR spectra, recorded between 4000 - 370 cm^{-1} as can be seen in Figure 1. A wide absorption peak at 3426.54 cm^{-1} (Figure 1(a)) indicated the presence of -OH groups derived from cellulose and lignin (Njoku et al., 2014). The presence of $-\text{C}=\text{O}$ functional group

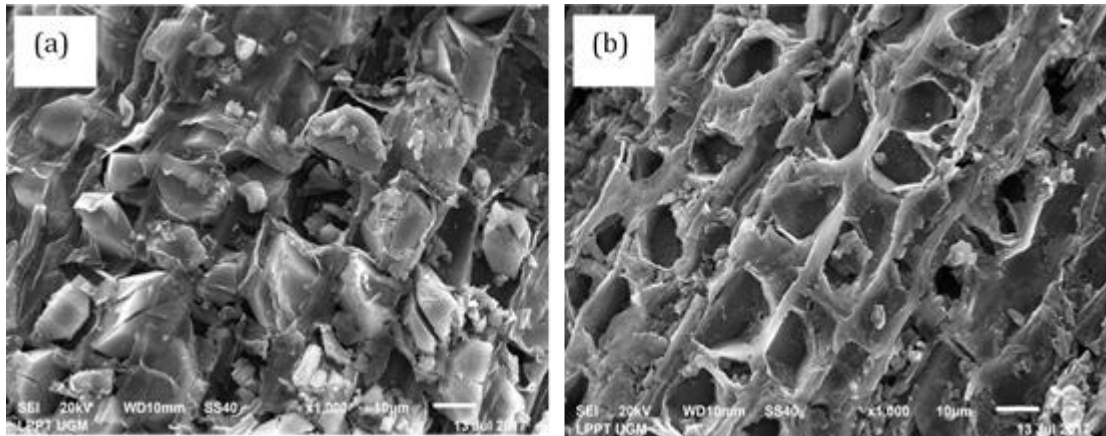


Figure 2. SEM from (a) char and (b) MAC with $ZnCl_2$ 30%

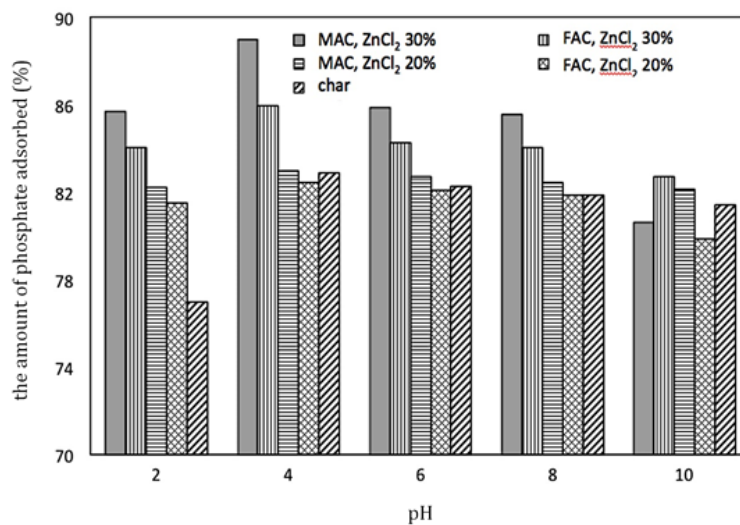


Figure 3. Effect of pH to the amount of phosphate adsorbed (time: 240 min, phosphate concentration: 100 mg/L, adsorbent dose: 0.05 gram)

derived from lignin was indicated by an absorption peak at 1320.86 cm^{-1} while the presence of $-C-O-C$ groups derived from cellulose was indicated by absorption peak at 1065.04 cm^{-1} . The peak observed at 1640.07 cm^{-1} may be attributed to the $C=C$ group indicated the presence of carbon chains on the teak leaves before the carbonization process. After the carbonization process (Figure 1(b)), the position and intensity of some peaks being changed. Peak around 3426.54 cm^{-1} shift to 3416.53 cm^{-1} , peak around 1065.04 cm^{-1} shift to 871.76 cm^{-1} and peak around 1640.07 cm^{-1} shift to 1610.94 cm^{-1} , indicating the dissolution of several carbon bonds. It led to the formation of the new pores. Figure 1(f) shows that chemical activation process with $ZnCl_2$ 30% using microwave heating produced the best character compared to other treatment because it has the highest $Zn-O$ group which can help in the adsorption process, indicated by an absorption peak at 470.58 cm^{-1} .

BET surface area of char and MAC with $ZnCl_2$ 30% was $6.69\text{ m}^2/\text{g}$ and $219.79\text{ m}^2/\text{g}$, respectively. The larger surface area led to the higher phosphate adsorbed, so the use of microwave heating is a promising alternative.

The morphology of char and MAC with $ZnCl_2$ 30% was described in Figure 2. Char produced from teak leaf without activation (Figure 2(a)) had several pores, but the pore size was small and several pores were blocked by tarry substances. Whereas, MAC with $ZnCl_2$ 30% (Figure 2(b)) had a larger and uniform pore size.

Adsorption performance of activated carbon

The adsorption performance of activated carbon toward phosphate was studied by varying pH, initial concentration, and contact time. The effect of pH on the amount of phosphate adsorbed was described in Figure 3. In a certain pH range (2-10), the amount of phosphate adsorbed increased

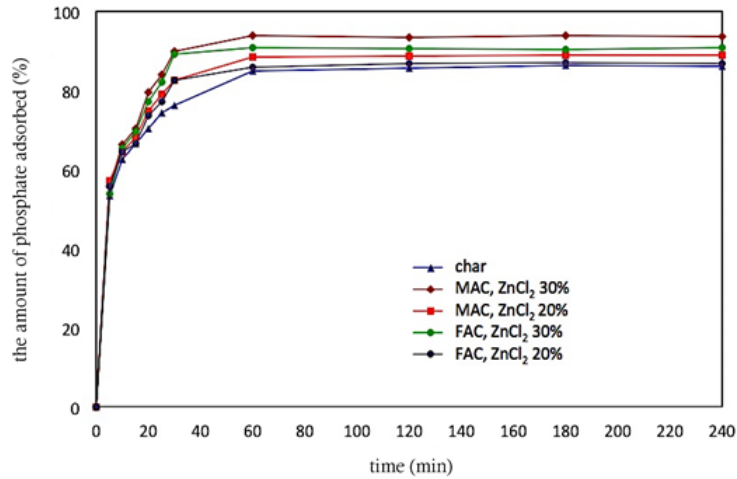


Figure 4. Effect of contact time to the amount of phosphate adsorbed (pH: 4, phosphate concentration: 100 mg/L, adsorbent dose: 0.05 gram).

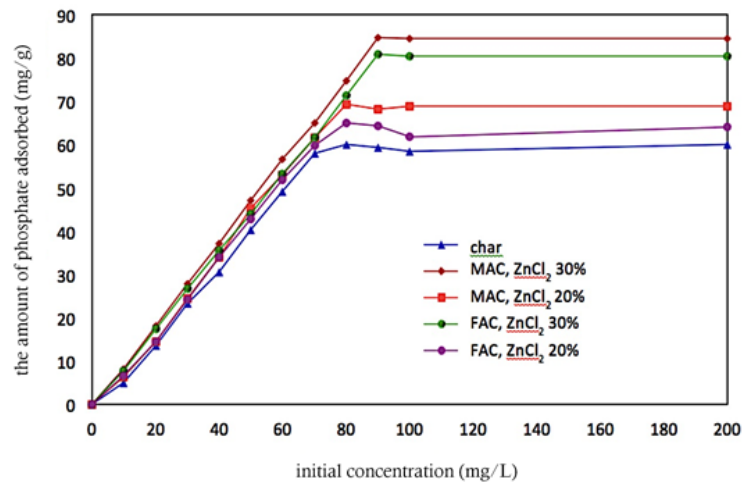


Figure 5. Effect of initial concentration to the amount of phosphate adsorbed (pH: 4, time: 240 min, adsorbent dose: 0.05 gram).

with the increasing pH up to certain pH value and then decreased with further increasing pH. The decreasing may be related to the formation of negative surface charges on the activated carbon, which was influenced by the solution pH. In the acid medium (pH 4), the positively charged species start dominating and activated carbon surface disposed to acquire positive charge while the adsorbate species (i.e. phosphate) have negatively charged. As a result, the electrostatic attraction between the active site in the adsorbent surface and phosphate molecules was dominating. The increase of solution pH led to the decrease of positively charged species and activated carbon surface disposed to acquire the negative charge. It caused the decrease of phosphate adsorbed due to electrostatic repulsive between negatively charged of activated carbon surface and negatively charged

of phosphate molecules. While the amount of phosphate adsorbed at pH 2 was lower than that of at pH 4. It may be due to in the lower pH, phosphate disposed to form phosphoric acid (H_3PO_4) having larger molecule size, so the effectiveness of the adsorption process decreased. The amount of phosphate adsorbed by MAC with $ZnCl_2$ 30% was higher than that of by $ZnCl_2$ 20% due to the greater concentration of $ZnCl_2$ used led to the larger of pores size of activated carbon.

The microwave heating technique was seen more effective than the furnace heating technique due to microwave heating was internal and volumetric so the pore size produced was more uniform. It led to the phosphate adsorbed increased.

The effect of contact time toward the amount of phosphate adsorbed describes in Figure 4. The phosphate adsorption process was rapid at

the initial stage, but it gradually slowed down until the equilibrium was reached. It may be due to a large number of vacant active sites were available for phosphate adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Once equilibrium was attained, the amount of phosphate adsorbed was constant.

The effect of initial concentration on the phosphate adsorption was investigated at pH 4 in the range of concentration was 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, and 200 mg/L, as can be seen in Figure 5. The amount of phosphate adsorbed increased with the increase of initial concentration and remain constant after equilibrium reached. The initial concentration provides an important driving force to overcome all mass transfer resistance of phosphate between the aqueous and solid phase. Hence, the higher initial concentration of phosphate will enhance the adsorption process.

Adsorption isotherm

Adsorption isotherm was used to describe the adsorption mechanism of phosphate molecules on the activated carbon surface. In this study, the Langmuir and Freundlich isotherm model has been studied. The Langmuir isotherm, based on the fact that the monolayers adsorption occurs in homogeneous sites on the adsorbent surface, was given by Eq. (1) (Astuti et al., 2017).

$$C_{\mu} = \frac{C_{\mu m} K_L C_e}{1 + K_L C_e} \tag{1}$$

where K_L is the adsorption equilibrium constant (L/mg), $C_{\mu m}$ is the amount of phosphate required to form a monolayer on unit mass of adsorbent (mg/g) and C_{μ} is the amount phosphate adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L) which is defined as Eq. (2) as follows (Astuti et al., 2017):

$$C_{\mu} = \frac{C_i - C_e}{m} \times V \tag{2}$$

where C_i is the initial concentration of phosphate in aqueous solution (mmol/L), C_e is the concentration of phosphate in the solution at equilibrium (mmol/L), V is the volume of phosphate solution (L) and m is the mass of activated carbon (g).

Rearrange of Eq. (1) to the linear form is given by Eq. (3) as follows (Astuti et al., 2017):

$$\frac{C_e}{C_{\mu}} = \frac{1}{C_{\mu m}} C_e + \frac{1}{K_L C_{\mu m}} \tag{3}$$

A plot of C_e/C_{μ} versus C_e should yield straight line if Langmuir isotherm is obeyed by the adsorption equilibrium data. The value of $C_{\mu m}$ and K_L can be calculated from the slope and intercept of the graphed line, respectively. In contrast to the Langmuir model, Freundlich isotherm based on the fact the presence of energetically heterogeneous adsorption sites, which is defined as Eq. (4) while the linear form is given by Eq. (5).

$$q_e = k_F C_e^{1/n} \tag{4}$$

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where K_F (L/g) and n are the Freundlich equilibrium constants. The value of K_F and n can be calculated from the slope and intercept of the graphed line of Eq. (5), respectively. The value of Langmuir, and Freundlich constants and the correlation coefficients on the linear regression can be seen in Table 1. Data in Table 1 shows that the Langmuir model is seen in accordance with the experimental data due to the correlation coefficient for the Langmuir isotherm is closer to unity than that of Freundlich isotherms. It is an indication of high chemical interaction between active sites on the activated carbon and phosphate molecules.

Table 1. Isotherm constants and correlation coefficient for phosphate adsorption onto activated carbon from teak leaves.

Isotherm parameter	Value
Langmuir	
$C_{\mu m}$	0.9241
K_L	24.372
R^2	0.9769
Freundlich	
K_F	1.4811
N	2.5139
R^2	0.4027

Adsorption kinetics

In this study, five kinetics models were analysed, including external diffusion, internal diffusion, pseudo-first-order, pseudo-second-order, and elovich. The linear form of the models was

Table 2. Kinetics model constants and correlation coefficient for phosphate adsorption onto Activated Carbon from Teak Leaves.

Isotherm parameter	Value
External diffusion	
A'	0.3107
k_f	1.9652×10^{-05}
R^2	0.739
Internal diffusion	
k_{id}	7.0049
R^2	0.5574
Pseudo first order	
q_e	21.301
k_1	0.0253
R^2	0.8297
Pseudo second order	
q_e	85.4701
k_2	0.0041
R^2	0.9996
Elovich	
A	65.708
B	0.0715
R^2	0.8144

expressed by Eq. (6)-(10), respectively (Astuti et al., 2017).

$$\ln \left[\left(\frac{C_t}{C_i} \right) - \left(\frac{A'}{m_s K_L} \right) \right] = \ln A' - \left(\frac{k_f S_s}{A'} \right) t \quad (6)$$

$$\log q_t = \log k_{id} + \frac{1}{2} \log t \quad (7)$$

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2,303} \right) t \quad (8)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (9)$$

$$q_t = \left(\frac{1}{\beta} \right) \ln(\alpha\beta) + \left(\frac{1}{\beta} \right) \ln t \quad (10)$$

where C_i (mmol/L) is the concentration of phosphate in aqueous solution at the time t , k_f is the external mass transfer coefficient (L/mg), m_s is the concentration of adsorbent in the liquid phase (mg/L), S_s is particle surface area (cm²), q_e and q_t are the amount of phosphate adsorbed at equilibrium (mg/g) and at time t (mg/g), respectively, k_{id} is the rate constant of intraparticle diffusion, k_1 is the rate constant of pseudo-first-order model (min⁻¹), k_2 is the rate constant of pseudo-second-order model (g/mg min), α and β are Elovich constants and t is time (min). While m_s and A' is given by Eq. (11) and (12), respectively (Astuti et al., 2017).

$$m_s = \frac{m}{V_s} \quad (11)$$

$$A' = \frac{m_s K_L}{1 + m_s K_L} \quad (12)$$

The value of the kinetic models constant can be calculated from the slope and intercept of the graphed line of Eq. (6)-(10), and the result was described in Table 2. Data in Table 2 shows that pseudo-second-order model is seen in accordance with experimental data due to the correlation coefficient is closer to unity than the others.

CONCLUSIONS

MHAC with ZnCl₂ 30% is the best characteristic, and it leads to higher adsorption performance. The optimum adsorption occurred at pH 4, and the equilibrium was reached after 180 minutes. The Langmuir equilibrium model was more appropriate than the Freundlich equilibrium model. While the kinetics model analyzed using pseudo-first-order, pseudo-second-order, internal diffusion, and external diffusion indicated that the pseudo-second-order was most suitable for the adsorption of phosphate by teak leaf activated carbon.

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