# One-step synthesis of magnetic activated carbons for methylene blue dye removal: activation conditions and adsorption studies

# Lee Lin Zhi<sup>a,b</sup>, Muhammad Abbas Ahmad Zaini<sup>a,b,\*</sup>

<sup>a</sup>Centre of Lipids Engineering and Applied Research (CLEAR), Ibnu-Sina Institute for Scientific & Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia, emails: chloey.leelinzhi@hotmail.com (L.L. Zhi), abbas@cheme.utm.my (M.A.A. Zaini)

<sup>b</sup>School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

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### ABSTRACT

Magnetic activated carbon (MAC) was prepared from palm kernel shell by one-step synthesis using zinc chloride and ferric chloride. The effects of process variables, namely activation temperature and time on carbon yield, methylene blue (MB) adsorption, and magnetic recovery were investigated. The synthesis conditions were evaluated by response surface methodology. The MACs were characterized for yield, specific surface area, morphology, and magnetic percentage. The suitable process conditions for activation were found to be 600°C and 2 h, which resulted in activated carbon with 53% yield, maximum MB capacity of 84.7 mg/g, and magnetic recovery of 96.3%. The MB adsorption is mainly influenced by the specific surface area of MAC. Isotherm and kinetics models were employed to examine the adsorption data. The Langmuir model gave the best conformity, suggesting monolayer adsorption of MB molecules. The Dubinin–Radushkevich model proposed that the process may be controlled by physisorption, while the adsorption rate obeyed the pseudo-second-order model. The one-step synthesis using a composite activating agent can simplify the preparation process and yields a promising MAC for dye removal from water.

Keywords: Activation condition; Adsorption; Magnetic activated carbon; One-step synthesis

### 1. Introduction

Activated carbon (AC) is extensively used as an adsorbent for adsorption due to its large porous surface area, controlled pore structure, and inert properties [1]. Various carbonaceous raw materials can be used to prepare AC, especially agricultural by-products such as coconut shells [2], corn cobs [3], apricot stone [4], and so on. Often, these materials are underutilized and can, to some extent cause handling and disposal problems in some countries. Hence, converting them into AC is a feasible solution to environmental issues. palm kernel shell (PKS) is among the promising candidate of porous AC because of its high lignin content, low cellulose content, and less fibrous structure [1]. In this work, the preparation of magnetic activated carbon (MAC) from PKS was investigated [5–7].

The global production of AC is believed to escalate to 1.9 million tonnes with an annual growth rate of 10.3%. This growth is mainly due to strong demand for environmental pollution control to purify polluted water from natural disasters such as earthquakes and tsunami. China is the largest manufacturer and exporter of AC, accounting for about half of the global production with an export volume of  $210 \times 10^3$  tons in 2012 [8]. In industrial applications,

<sup>\*</sup> Corresponding author.

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the adsorbent has to be replaced frequently to maintain the removal performance. Consequently, landfilling and incineration are the common ways to dispose spent AC. The amount of exhausted AC in Malaysia, for example, is nearly 1,300 tonnes in 2012, which requires a surmounting cost of RM 3.9 million for disposal. Thus, green regeneration approaches are sought for a sustainable environment, wherein the recovery of spent AC from the treated water is the key success of the study [9].

A huge amount of raw material is required for the mass production of AC. In Malaysia, about 20 million tons of crude palm oil was produced in 2017. For every 10 tons of crude palm oil produced during the milling process, 5.2 tons fiber, 2.2 tons shell, 8.5 tons empty fruit bunch and other wastes are generated [10]. In 2015, the palm oil industry recorded production of 88 million tons of solid biomass, which includes oil palm frond, oil palm trunk, empty fruit bunch, PKS, and mesocarp fiber. Of these, about 5.61 million tons belong to PKS, hence a promising candidate for AC production due to its sustainable supply.

ACs are generally effective for wastewater treatment. However, the recovery of exhausted AC from water can be challenging. The traditional approach thru filtration often leads to filter blockage and poor recovery, thus restricting wide applications of AC in many fields [11]. Magnetic separation is a rapid technique to remove spent adsorbent from the treated solution. In recent years, MACs have been widely studied to adsorb organic and inorganic pollutants from wastewater [2,12,13]. However, the preparation of MAC is complicated by multiple processing steps, comprising activation and magnetization. The established methods for magnetization are chemical co-precipitation and high-temperature impregnation, where the former involves the precipitation of iron salts in hot alkaline suspension [2,14,15], while the latter comprises high-temperature pyrolysis to impregnate magnetic elements in AC [10,16,17]. Nonetheless, the attachment of magnetic particles could block the existing pores of AC, leading to inferior adsorption capacity when compared to the un-modified one [11]. A simple synthesis method of MAC, combining activation and magnetization in a single step has been introduced, assuming that iron could also serve as an activating agent on top of the magnetic element. In related work, however, ferric chloride-activated carbon yields a low removal performance as compared with its zinc chloride counterpart [18]. In this work, an attempt has been made to boost the adsorptive properties of MAC by ZnCl, and FeCl, as a composite activating agent.

The performance of AC is highly influenced by its preparation conditions [19]. Besides, the yield is a crucial economic factor in the process synthesis, while the magnetic ratio indicates the inherent properties of MAC for physical recovery upon adsorption treatment. Therefore, a response surface methodology (RSM) of Design-Expert software version 6.0.4 was used to analyze and evaluate the interactive effect of several independent variables to find the compromise optimum for more than one response in the synthesis of MAC [20]. Consequently, the adsorption equilibrium and kinetics provide theoretical interpretations of adsorption mechanisms [1]. The present work was aimed to evaluate the activation conditions of MAC for dye removal. The effect of activation temperature and time were

evaluated for MAC yield, magnetic percentage, and maximum removal capacity, while methylene blue dye (MB) was used as the primary response to probe the adsorption performance of MACs.

## 2. Methodology

#### 2.1. Preparation and characterization of MAC

PKS was obtained from the palm oil factory in the Johor state of Malaysia. Methylene blue (MB, MW = 319.85 g/mol, C.I. No. 52015, and  $\lambda_{max}$  = 603 nm) was supplied by HmbG Chemicals (Hamburg, Germany). Zinc chloride (ZnCl<sub>2</sub>, 99.5%) and hydrochloride acid (HCl, 37.0%) were purchased from R&M Marketing, Essex, U.K. Ferric chloride (FeCl<sub>3</sub>, 98.0%) was purchased from Merck Schuchardt, Germany. Analytical-grade reagent of chemicals was used.

MACs were prepared from PKS by chemical activation. Raw PKS was crushed and sieved to a size <1 mm, and washed few times with distilled water to remove impurities and dirt. ZnCl<sub>2</sub> and FeCl<sub>3</sub> were mixed with dried PKS at weight ratios of 0.5:0.5:1 (ZnCl<sub>2</sub>:FeCl<sub>3</sub>:PKS) [21]. The designation of AC is listed in Table 1. The composite activating agent was first dissolved in water and stirred at 90°C for 1.5 h to homogenize the mixture. Upon oven-drying at 110°C, the impregnated PKS was subjected to carbonization in a furnace at different temperatures of 300°C-800°C for 1-3 h. The resultant products were soaked in 0.1 M HCl overnight to remove excess chemicals and minerals, followed by hot distilled water washing to a solution pH of 4. Then, the samples were oven-dried and ready to use for characterization and adsorption. The experimental data were used in RSM to determine the suitable activation conditions. Design-Expert software version 6.0.4 was used as the analysis tool.

The carbon yield was calculated as:

$$Yield = \frac{m}{m_0} \times 100\%$$
(1)

where *m* (g) is the mass of MAC and  $m_0$  (g) is the mass of dried PKS. A simple magnetic test was carried out using a N52 neodymium block magnet (50 mm × 50 mm × 25 mm) to observe the relationship between activation conditions and the recovery of MAC. The recovery of MAC was calculated as:

Recovery of MAC = 
$$\frac{\text{Mass of AC attracted by magnet}(g)}{\text{Total mass of AC}(g)} \times 100\%$$
(2)

The specific surface area ( $S_{\text{BET}}$ ) of MAC was determined using a Pulse Chemisorb 2705 with liquid N, at 77 K.

#### 2.2. MB adsorption

Fifty mL of MB solution of varying initial concentrations in the range of 20–400 mg/L was brought into contact with 50 mg of MAC. The mixture was allowed to equilibrate at 30°C and 120 rpm for 72 h. The equilibrium concentration of

Table 1 Designation of magnetically activated carbons

Sample	Activation temperature (°C)	Activation time (h)
ZMAC-3	300	1
ZMAC-4	400	1
ZMAC-5	500	1
ZMAC-6	600	1
ZMAC-7	700	1
ZMAC-8	800	1
ZMAC-6,2	600	2
ZMAC-6,3	600	3
ZMAC-7,2	700	2
ZMAC-7,3	700	3

MB was analyzed using a HALO VIS-10 visible spectrophotometer with a wavelength of 603 nm.

The adsorption capacity of MAC was calculated as:

$$Q_e = \frac{\left(C_0 - C_e\right)}{m} V \tag{3}$$

where  $Q_e$  (mg/g) is the equilibrium capacity,  $C_0$  (mg/L) is the initial dye concentration,  $C_e$  (mg/L) is the equilibrium concentration, V (L) is the volume of dye solution and m (g) is the mass of MAC.

Langmuir, Freundlich, Redlich–Peterson, and Dubinin– Radushkevich models were applied to interpret the equilibrium data. The Langmuir model describes the monolayer coverage of adsorbate on the surface of the adsorbent, and is expressed as [22]:

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \tag{4}$$

where  $Q_m$  (mg/g) is the maximum removal capacity, and b (L/mg) is the coefficient related to the affinity of adsorbent at low adsorbate concentration. The dimensionless equilibrium parameter of Langmuir,  $R_L$  represents the nature of adsorption, either irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ). The  $R_L$  is given as:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

The Freundlich equation is applied to represent the non-ideal, multilayer adsorption onto heterogeneous adsorbent [22]. The Freundlich isotherm is given as:

$$Q_e = K C_e^{\frac{1}{n}}$$
(6)

where K and n are the Freundlich constants. The Redlich– Peterson (R–P) model is a hybrid of Langmuir and Freundlich models. It is applicable for a broad range of concentration, either in the heterogeneous or homogeneous system [23]. The R–P model is expressed as:

$$Q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}}$$
(7)

where  $K_R$  (L/g) and  $\alpha_R$  are the R–P isotherm constants and  $\beta$  is an exponent that exists between 0 and 1. The Dubinin–Radushkevich (D–R) isotherm is mainly employed to describe the adsorption mechanism onto the heterogeneous surface by Gaussian energy distribution [22]. The D–R equation is expressed as:

$$Q_e = Q_s \exp\left(-K_{\rm ad}\varepsilon^2\right) \tag{8}$$

where  $K_{ad}$  (mol<sup>2</sup>/kJ<sup>2</sup>) is the D–R isotherm constant,  $Q_s$  (mg/g) is the theoretical isotherm saturation capacity and  $\varepsilon$  is the Polanyi potential as expressed in Eq. (9). The Polanyi potential drives the movement of molecules near the adsorbent surface, similar to gravity or electric fields [24].

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{9}$$

where T (K) is the absolute temperature and R (8.314 J/mol K) is the gas constant. The physical and chemical adsorption is distinguished by the mean free energy, E per molecule of the adsorbate.

$$E = -\frac{1}{\sqrt{2K_{\rm ad}}}\tag{10}$$

Ion exchange reaction could be involved in the adsorption if the magnitude of E is in the range of 8 to 16 kJ/mol [25].

Fifty mg of MAC was added into 50 mL of MB solution, from which a small volume was withdrawn from the mixture at different time intervals for adsorption kinetics [26]. The selection of  $C_0$  depends on the performance of MAC in equilibrium adsorption. The  $C_0$  with a saturation point of  $Q_e$  was chosen to determine the equilibrium time for maximum adsorption, while  $C_0$  with at the lower stage was selected to study the effect of  $C_0$  on the adsorption mechanism. The effect of time on adsorption was determined as:

$$Q_t = \frac{\left(C_0 - C_t\right)}{m} V \tag{11}$$

where  $Q_t$  (mg/g) is the capacity at time *t* and  $C_t$  (mg/L) is the dye concentration at time *t*.

Kinetic models, namely the pseudo-first-order, pseudosecond-order, and intraparticle diffusion models were used to explain the adsorption mechanisms. The pseudo-firstorder model describes the adsorption reaction based on removal capacity [27], and is given as:

$$Q_t = Q_e \left( 1 - e^{-k_t t} \right) \tag{12}$$

where  $k_1$  (h<sup>-1</sup>) is the pseudo-first-order rate constant. This equation is valid only for the initial adsorption period prior

to equilibrium. The pseudo-second-order model relates the fraction of available sites as the driving force of the process. It can be expressed as:

$$Q_{t} = \frac{k_{2}Q_{e}^{2}t}{1 + k_{2}Q_{e}t}$$
(13)

where  $k_2$  (g/mg h) is the pseudo-second-order rate constant. The intraparticle diffusion model describes the diffusion-controlled kinetics. The model is expressed as

$$q_t = k_d t^{1/2} + c \tag{14}$$

where  $k_d$  (g/mg h) is the rate constant for intraparticle diffusion and *c* is the intercept at the *y*-axis. A straight line of  $q_t$  vs.  $t^{1/2}$  curve passes through origin signifies that the pore diffusion as the sole rate-limiting step.

#### 3. Results and discussion

#### 3.1. Effect of activation conditions

Table 2 shows the performance of MACs prepared at different activation temperatures and times. Generally, an increase in activation temperature increases the adsorption capacity and recovery but decreases the yield. While, an increase in activation time often results in decreasing yield, removal capacity, and recovery. Analysis of variance (ANOVA) was performed to rationalize the suitability of the model by identifying the significance of factors and the interaction between the influential factors and the responses [19,28].

Table 3 shows the ANOVA tables and regression of models for carbon yield, maximum adsorption capacity ( $Q_m$ ) and MAC recovery. The high  $R^2$  and  $R_A^2$  values, which are greater than 0.9 represent a good explanation of the variability by the models for yield,  $Q_m$  and MAC recovery [29].

From Table 3a, the model *F*-value of 34.41 signifies that the model is significant at a confidence interval of 95%. The model terms, *A* and  $A^2$  are significant as the Prob. > *F* values are lesser than 0.05. While, the model terms *B*,  $B^2$  and

Tab	le 2			
Pre	paration	of MACs	from	PKS

*AB* are not significant as indicated by the values greater than 0.1. The final equation in terms of actual factors for carbon yield was obtained as:

$$Yield = -18.22 + 0.37 A - 0.0004 A^2$$
(15)

From Table 3b, the *F*-value of 8.14 shows that the model is significant at a confidence interval of 95%. The model terms *A*,  $A^2$  and *AB* are significant, while  $B^2$  is not significant. The final equation in terms of actual factors for  $Q_m$  was obtained as:

$$Q_m = -415.0 + 1.25A + 236.8B - 0.0008A^2 - 0.36AB$$
(16)

In Table 3c, the model is significant at a confidence interval of 95% as demonstrated by the *F*-value of 18.06. None of the model terms are significant because of no Prob. > *F* values are lesser than 0.05. The final equation in terms of actual factors for MAC recovery is:

MAC recovery = 
$$-206.4 + 156.1B$$
 (17)

The predicted responses for yield,  $Q_m$  and MAC recovery were evaluated using Eqs. (15)-(17), respectively. From Eqs. (15)-(17), the respective negative constants of -18.22, -415.0, and -206.4 are the expected mean of the responses when all independent variables, A and B are equal to 0. Since *A* and *B* values in this work would never become 0, the intercept has no intrinsic meaning and has an independent relationship between the responses and the variables. The constants are negative due to the range of independent variables is higher than the range of the responses. Generally, the overall relationships between the variables give a substantial outcome in a regression model, while the constants are needed to predict the magnitude of responses. The positive coefficient represents a synergistic effect whereas the negative signpost signifies an antagonistic effect towards the responses. It can be clearly observed that the linear terms of A and B are positive coefficients, thus providing a positive influence on the responses. It can be noted that these responses increase proportionally with the increment of

MAC	Activation	Activation	Yield (%)	$Q_m (mg/g)$	Recovery of
	temperature (°C)	time (h)			MAC (%)
ZMAC-3,1	300	1	64.5	11.8	0.00
ZMAC-4,1	400	1	64.5	48.3	0.14
ZMAC-5,1	500	1	64.0	47.8	38.4
ZMAC-6,1	600	1	59.7	51.5	53.2
ZMAC-7,1	700	1	31.9	52.9	99.1
ZMAC-8,1	800	1	11.0	0.51	99.4
ZMAC-6,2	600	2	53.0	84.7	96.3
ZMAC-6,3	600	3	47.1	77.5	92.8
ZMAC-7,2	700	2	24.3	4.22	99.4
ZMAC-7,3	700	3	22.7	0.22	95.4
RSM 1	577	2.13	54.0	84.7	92.3

Table 3a	
ANOVA table f	or carbon yield

Source	Sum of squares	DF	Mean square	<i>F</i> -value	Prob. $> F$
Model	3,570.15	5	714.03	34.41	0.0022
Α	507.31	1	507.31	24.45	0.0078
В	0.67	1	0.67	0.032	0.8663
$A^2$	572.66	1	572.66	27.60	0.0063
$B^2$	2.73	1	2.73	0.13	0.7353
AB	42.75	1	42.75	2.06	0.2245
Residual	83	4	20.75		
Corrected total	3,654.14	9			
Standard deviation		4.56	$R^2$		0.9773
Mean		44.26	$R_A^2$		0.9489

DF: Degree of freedom; A: activation temperature; B: activation time.

Table 3b ANOVA table for  $Q_m$ 

Source	Sum of squares	DF	Mean square	<i>F</i> -value	Prob. > $F$
Model	8,209.17	5	1,641.83	8.14	0.0320
Α	3,197.15	1	3,197.15	15.84	0.0164
В	1,510.66	1	1,510.66	7.49	0.0521
$A^2$	2,513.23	1	2,513.23	12.45	0.0243
$B^2$	2.23	1	2.23	0.011	0.9213
AB	2,882.05	1	2,882.05	14.28	0.0195
Residual	807.27	4	201.85		
Corrected total	9,016.44	9			
Standard deviation		14.21	$R^2$		0.9105
Mean		37.96	$R_A^2$		0.7685

DF: Degree of freedom; A: activation temperature; B: activation time.

Table 3c ANOVA table for MAC recovery

Source	Sum of squares	DF	Mean square	<i>F</i> -value	Prob. $> F$
Model	14,767.54	5	2,953.51	18.06	0.0075
Α	237.29	1	237.29	1.45	0.2948
В	880.40	1	880.40	5.38	0.0811
$A^2$	7.60	1	7.60	0.046	0.8399
$B^2$	342.4	1	342.4	2.09	0.2215
AB	351.39	1	351.39	2.15	0.2166
Residual	654.18	4	163.55		
Corrected total	15,421.72	9			
Standard deviation		12.79	$R^2$		0.9576
Mean		67.41	$R_A^2$		0.9046

DF: Degree of freedom; A: activation temperature; B: activation time.

variables. Conversely, the quadratic terms of  $A^2$  and AB are negative coefficients, rendering negative implications on the yield and  $Q_m$ .

Residual represents the difference between the observed values and the predicted ones in the linear regression model.

The normal probability plots as shown in Fig. 1 is important to check the sufficiency of the statistical model. The normal probability plot displays the data close to a straight line if the residuals are normally distributed [29]. From Fig. 1, there is good agreement between the predicted values and the actual



Fig. 1. Residual diagnostics of the fitted model for (a,b) yield, (c,d) Q<sub>m</sub> and (e,f) MAC recovery.

experimental data for yield,  $Q_m$  and MAC recovery, which represent the excellent reliability of the model with high  $R^2$  of 0.9773, 0.9105, and 0.9046, respectively.

The 3D response provides the effect of factor level on each response as illustrated in Fig. 2. From Fig. 2a, the increase in activation temperature from 300°C to 800°C has resulted in the decrease of MAC yield from 64.5% to 11.0%, while no significant change in yield was observed with increasing activation time from 1 to 3 h. This is supported by Eq. (15), in which the activation temperature is a significant factor. Fig. 2b shows that  $Q_m$  increases with increasing temperature and time to some extent, before it decreases with



Fig. 2. Model graphs of crossed design for (a) yield, (b)  $Q_{\rm m'}$  and (c) MAC recovery.

further increases in both operating parameters. Activation temperature and time are significant factors affecting  $Q_m$  as given in Eq. (16). Although the recovery of MAC shows an increasing trend with activation temperature, the temperature by itself is not a significant factor for this response. Maximum MAC recovery can be achieved when the activation time is greater than 2 h for all studied temperatures as revealed in Fig. 2c.

In the synthesis of MACs, relatively high product yield is desirable. But at the same time, achieving superior adsorption performance and magnetic properties are also essential. However, it is difficult to optimize these responses under the same condition because the feasible regions of different factors are different. For example, a good adsorption performance is normally shown by MAC with a small yield. Hence, to compromise between these responses, the desirability function was applied using Design-Expert software. The goals for both variables, namely activation temperature and time were set as 'in range' with experimental limitations. For the responses, the objectives of yield,  $Q_m$  and MAC recovery were set as 'maximize'. The experimental conditions with the highest desirability were selected as shown in Table 2. From Table 2, ZMAC-6,2 (activation at 600°C for 2 h) displayed the highest  $Q_m$  of 84.7 mg/g with a comparable yield of 53.0% and MAC recovery of 96.3%. It was observed that the experimental data are in good agreement with the RSM predicted values with relatively small errors of 1.9%, 0%, and 4.2% for yield, Q<sub>m</sub> and MAC recovery, respectively.

#### 3.2. Characteristics of MACs

The textural properties of MACs are shown in Table 4. The increase of activation temperature and time usually increases the specific Brunauer–Emmett–Teller (BET) surface area. High temperature accelerates char burning-off, thus intensifies the formation of pores and enhances the BET surface area. However, excessive retention at a higher temperature and longer activation period may collapse the existing pores, thus decreasing the surface area [30]. Therefore, the one-step synthesis is preferably carried out at 600°C and 2 h.

Generally, AC with high surface area tends to offer more interaction probabilities for high adsorption capacity as shown in Fig. 3. A high surface area provides more active sites, which are accessible to accommodate adsorbate molecules [11]. From Table 4, ZMAC-6,2 with a BET area of 941.8 m<sup>2</sup>/g exhibits a greater  $Q_m$  of 84.75 mg/g among all MACs studied. However, MACs that are highly microporous may interfere with the diffusion of dye molecules, hence no much improvement in adsorption capacity can be seen from the increase of surface area.

Fig. 4 illustrates the ability of magnetic stirrer to attract MAC, indicating it was successfully synthesized with magnetic properties.

#### 3.3. Adsorption of MB

Fig. 5 shows the performance of MACs in MB removal. All MACs demonstrate an increasing pattern of equilibrium capacity ( $Q_e$ ) to a saturation point which is known as maximum uptake. At lower dye concentration, there are plenty of available sites for adsorption, so the adsorption percentage is concentration-dependent until the active sites are completely occupied at higher concentrations. Consequently, there is no further increase in adsorption with increasing concentration, at which  $Q_m$  is achieved [31].

Table 5 summarizes the isotherm constants of MB adsorption by MACs. The Langmuir model shows the

Table 4 Textural properties of MACs

MAC	Temperature (°C)	Time (h)	$Q_m$ (mg/g)	BET surface area (m²/g)	Microporosity (%)	Average pore size (nm)
ZMAC-6,1	600	1	51.55	917.7	97.50	1.696
ZMAC-7,1	700	1	52.91	413.1	95.16	1.712
ZMAC-8,1	800	1	0.302	2.350	34.97	2.544
ZMAC-6,2	600	2	84.75	941.8	96.58	1.674
ZMAC-6,3	600	3	77.52	439.3	96.22	1.698



Fig. 3. Effect of BET surface area of MACs on MB removal capacity.

correlation of determination ( $R^2$ ) close to 1, indicating its applicability to describe the MB adsorption by MACs. The adsorption process is assumed to take place on the homogenous surface of MAC via the formation of a monolayer of MB molecules. Furthermore, the *n* values of the Freundlich model for all MACs are greater than 1, revealing the adsorption obeys the ordinary Langmuir isotherm [32].



Fig. 5. Equilibrium adsorption of MB by MACs (solution volume = 50 mL; concentration = 20-400 mg/L; adsorbent mass = 0.05 g; pH =  $3.2 \pm 0.2$ ; temperature =  $30^{\circ}$ C; contact time = 72 h).



Fig. 4. Image of magnet test on MAC by a magnetic stirrer.

The Langmuir constant, *b* is related to the energy of adsorption. ZMAC-6,3 displays the highest *b*, suggesting favorable adsorption at low MB concentration. It indicates a high affinity between the active sites of ZMAC-6,3 and MB molecules. This could be associated with the reactive carbon surface as a result of a long activation period [33]. All MACs possess  $R_L$  values in the range 0 to 1, showing that the adsorption process is favorable and reversible.

From Table 4, the R–P constant, β approaching unity agreed well with Langmuir isotherm. In D–R isotherm, *E* is the mean free energy of adsorption, and *E* < 8 kJ/mol is assumed due to physical adsorption [34]. Thus, it is suggested that the adsorption of MB by MACs is physisorption. The maximum adsorption capacity,  $Q_s$  in the D–R model are close to  $Q_m$  of the Langmuir model. The sum of the squares of errors (SSE) of the R–P model is the lowest, indicating the best fit of equilibrium data by this isotherm model. ZMAC-6,2 had the highest SSE due to the magnitude and SSE tends to increase to the higher end of initial concentrations [35].

Table 6 summarizes the performance of various MACs in literature. ZMAC-6,2 demonstrates a comparable BET surface area with the other MACs prepared from different precursors, although its adsorption capacity is somewhat lower. This could be due to its rich microporosity (96.6%) with an average pore size of 1.67 nm, which may somewhat unfavorable for MB adsorption. The average pore size of adsorbent is at least 2 times larger than the adsorbate molecular size for smooth diffusion and adsorption. The dimension of most dyes is around 1 nm, thus complicate the penetration into the channels of micropore-rich AC [36]. Do et al. [16] reported a 303 mg/g capacity of

	constants
Table 5	Isotherm

		Langmuiı	r model			Fr	eundli	pom de	[]		Redlich.	-Peterson m	odel			Dubinin–R	adushk	evich model	
MIAC	$Q_m (mg/g)$	b (L/mg)	$R^2$	$R_{_L}$	SSE	и	K	$R^2$	SSE	$K_{_R}$ (L/g)	β	$\alpha_{_R}$ (L/mg)	$R^2$	SSE	$K_{ m ad}$	$Q_s (mg/g)$	$R^2$	E (kJ/mol)	SSE
ZMAC-6	51.5	0.184	1.000	0.012	98.4	6.63	22.8	0.873	112	33.7	0.932	0.965	0.998	51.5	14.5	49.9	0.959	0.186	339
ZMAC-6,2	84.7	0.393	0.991	0.006	811	6.20	35.9	0.907	354	652	0.867	16.0	0.999	311	1.56	80.1	0.815	0.567	1,047
ZMAC-6,3	77.5	0.436	0.997	0.005	496	7.19	36.7	0.897	291	331	0.903	7.29	0.999	183	1.00	74.5	0.864	0.706	743
ZMAC-7	52.9	0.154	0.996	0.015	149	9.30	28.9	0.898	84.0	772	0.925	22.8	0.999	61.3	5.76	50.1	0.949	0.295	402

Table 6 Maximum adsorption capacity of dye removal by various MACs

MAC	$S_{ m BET}( m m^2/g)$	$R_{ m mi}$ (%)	Average pore size (nm)	Dye	$Q_m (mg/g)$	Reference
Powdered MAC	I	I	1	MB	47.6	[37]
Powdered MAC	429	I	18.1	MB	105	[14]
Coconut shell MAC	1,110	83.3	15.0	Methylene orange	303	[16]
Peanut shell MAC	1,236	66.0	1	MB	405	[12]
Coconut shell MAC	372	74.3	2.26	Sunset yellow	22.31	[18]
Palm kernel shell MAC (ZMAC-6,2)	942	96.6	1.67	MB	84.8	This study
S = BET surface area; R _ = microporosity.						
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Table 7 Kinetic constants of ZMAC-6,2

$C_0 (mg/L)$	$Q_{e, \exp} \ (\mathrm{mg/g})$		Pseudo-fir	st-order			Pseudo-seconc	l-order		Intrapa	uticle diffusior	_
		$k_1(h^{-1})$	$Q_e (mg/g)$	$R^2$	SSE	$k_2$ (g/mg h)	$Q_e$ (mg/g)	$R^2$	SSE	$k_d$ (g/mg h)	c (mg/g)	$R^2$
50	42.72	0.554	34.94	0.944	182	0.0029	46.30	0.974	136	4.818	4.968	0.970
250	66.38	1.452	56.35	0.383	760	0.0058	68.49	0.986	487	4.401	38.62	0.835

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methylene orange adsorption by mesoporous coconut shell MAC with a surface area of 1,110 m<sup>2</sup>/g. The average pore size of 15.0 nm is more than sufficient for dye adsorption when compared to that of ZMAC-6,2 (1.67 nm). It is obvious that mesopore-rich MAC provides more active sites for dye molecules. Meanwhile, micropore-rich MAC may restrict the access of dye molecules, thus leading to low adsorption performance. This is also true for low surface area MAC even though the average pore size is accessible to dye molecules as reported by Cazetta et al. [18]. Nevertheless, the microporous MACs in this work may as well be appropriate for other related industrial applications such as odor and air pollution control and heavy metals removal.

Fig. 6 shows the rate of MB adsorption by ZMAC-6,2 at concentrations of 50 and 250 mg/L. At initial contact time, rapid adsorption is promoted due to plentiful surface sites. In the course of adsorption, some sites are still unoccupied due to repulsion between the readily adsorbed MB molecules on ZMAC-6,2 surface and the molecules in the bulk phase. The repulsive lateral interaction among the neighboring MB molecules reduces the bond of the energy of the MB-MAC surface, hence triggers the desorption of MB molecules from the adsorption layer, a point at which the equilibrium is attained. Rapid adsorption happens at the outer surface, while the adsorption decelerated inside the pores. Adsorption increased gradually with time evincing the formation of a monolayer on the surface of AC [21].

Table 7 shows the kinetic constants for MB adsorption by ZMAC-6,2. The regression and SSE show the applicability of the pseudo-second-order model to describe the rate of adsorption. It is proposed that the overall driving force of adsorption is due to the availability of active sites on ZMAC-6,2 [38]. ZMAC-6,2 shows a higher  $k_2$  at high  $C_0$  because of the decrease in solid-phase mass transfer-resistant, rendering a greater driving force for MB removal [21].

From Table 7, the intercept, *c* of the intraparticle diffusion model depicted that pore diffusion is not the sole rate-controlling step. A greater *c* value signifies a greater contribution of film diffusion in the rate-controlling step, or in other words, the boundary layer is thicker. It was observed that *c* value is higher at higher  $C_{0'}$  which indicates the higher contribution of film diffusion due to competition among free MB molecules to access the pores. Therefore,



Fig. 6. Rate of MB adsorption by ZMAC-6,2 at  $C_0 = 50$  and 250 mg/L (solution volume = 50 mL; adsorbent mass = 0.05 g; pH =  $3.2 \pm 0.2$ ; temperature =  $30^{\circ}$ C).

film diffusion is proposed as the rate-limiting step in MB adsorption onto ZMAC-6,2. The overall mechanism can be described by film diffusion of MB molecules through the boundary layer, followed by pore diffusion in the pores of MAC, and physical interaction between MB molecules and MAC. Often, film diffusion is the rate-determining step in a process controlled by physisorption. The physisorption happens due to (a) van der Waals forces, (b) electrostatic interaction, (c) hydrogen bonding and (d) hydrophobic-hydrophobic interaction between MB molecules and MAC surface. It is suggested that physisorption could also occur via monolayer coverage of MB molecules since the average pore size is close to that of dye molecules, which is agreed well with Langmuir isotherm.

# 4. Conclusion

MAC was produced from PKS by one-step synthesis using  $ZnCl_2$  and  $FeCl_3$  as a composite activating agent. Activation temperature shows a significant effect on carbon yield and adsorption capacity, while activation time displays a considerable influence on adsorption capacity and recovery of MAC. The one-step synthesis of MAC can be suitably performed at 600°C for 2 h. At this condition, MAC possesses a 941.8 m<sup>2</sup>/g surface area and a yield of 53%, with an 84.7 mg/g MB capacity and recovery of 96.3%. The results were also predicted with less than 10% error by RSM. The adsorption data were well fitted into Langmuir and pseudo-second-order models. The one-step synthesis is a promising approach to produce MAC for wastewater treatment.

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