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Effect of preparation conditions of oil palm fronds activated carbon on adsorption of bentazon from aqueous solutions

J.M. Salman, B.H. Hameed*

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

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ABSTRACT

Oil palm fronds (OPF) were used to prepare activated carbon (PFAC) using physiochemical activation method, which consisted of potassium hydroxide (KOH) treatment and carbon dioxide gasification. The effects of the preparation variables, which were activation temperature, activation time and chemical impregnation ratios (KOH: char by weight), on the carbon yield and bentazon removal were investigated. Based on the central composite design (CCD), two factor interaction (2FI) and quadratic models were, respectively, employed to correlate the PFAC preparation variables to the bentazon removal and carbon yield. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The optimum conditions for preparing activated carbon from OPF were found as follows: activation temperature of 850 °C, activation time of 1 h and KOH: char ratio of 3.75:1. The predicted and experimental results for removal of bentazon and yield of PFAC were 99.85%, 20.5 and 98.1%, 21.6%, respectively.

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1. Introduction

Bentazon is a post-emergence herbicide used for selective control of broadleaf weeds and sedges in beans, rice, corn, peanuts, and mint. It is one of the most commonly used herbicides in agriculture and gardening. However, through leaching or run-off from agricultural lands, deposition from aerial applications and indiscriminate discharge of industrial wastewaters, bentazon is becoming a reckoned source of contaminant to water resources with its attendant threats to ecology and environment in general [1,2]. Several methods are available for pesticides removal such as photocatalytic degradation [3,4], combined photo-Fenton and biological oxidation [5], advanced oxidation processes [6], aerobic degradation [7], nanofiltration membranes [8], ozonation [9] and adsorption [10]. Among these arrays of methods, adsorption is the most commonly reported and has enjoyed widest application in the field of hazardous waste treatment. In the same vain, activated carbon is the most widely used adsorbent material for this purpose due to its efficiency and economic viability [11]. Therefore, in recent years, many researchers have tried to produce activated carbons for removal of various pollutants using renewable and cheaper precursors which were mainly industrial and agricultural byproducts.

Oil palm (*Elaeis guianensis*) grows well in wet, humid parts of tropical Asia. The total area of planted oil palms in Malaysia stood

at 4.3 million hectares in 2007 taking Malaysia the largest producer of palm oil in the world [12]. Expectedly, large and abundant quantity of oil palm fronds (OPF) are naturally generated by this process, which presently are underutilized and are often buried in rows within the palm plantations.

A major challenge in activated carbon production from new precursors is to produce very specific carbons which are suitable for certain applications. The most important characteristic of an activated carbon is its adsorption capacity which is highly influenced by the preparation conditions. Meanwhile, in assessing the effect of the preparation conditions on quality attributes, the use of an adequate experimental design is particularly important. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more variables [13]. Optimization of experimental conditions using RSM has been widely applied in various processes including preparation of activated carbons [14].

The objective of this research was to optimize the preparation conditions of activated carbon from oil palm fronds (PFAC) and its consequent application to remove bentazon herbicide based on RSM experimental design approach.

2. Materials and methods

2.1. Adsorbate

Bentazon (99.99% purity) obtained from Sigma–Aldrich (M) Sdn Bhd, Malaysia, was used as adsorbate. Distilled water was used to prepare all solutions.

^{*} Corresponding author. Tel.: +60 45996422; fax: +60 45941013. *E-mail address:* chbassim@eng.usm.my (B.H. Hameed).

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Table 1 Experimental design matrix and results.

Run	Activated carbon preparation variables			Carbon yield	Bentazon removal
	Activation temperaturex ₁ (°C)	Activation timex ₂ (h)	Impregnation ratiox ₃	Y ₁	Y ₂
1	800	2.00	0.06	22.4	14.3
2	800	2.00	2.38	18.0	95.2
3	750	3.00	3.75	18.6	97.1
4	800	2.00	2.38	18.0	93.8
5	800	2.00	2.38	18.0	93.8
6	800	2.00	2.38	18.0	93.8
7	800	2.00	2.38	18.0	93.8
8	750	3.00	1.00	22.4	21.9
9	850	1.00	3.75	21.6	98.1
10	716	2.00	2.38	20.6	79.1
11	800	2.00	2.38	18.0	93.8
12	884	2.00	2.38	17.7	97.1
13	800	3.68	2.38	15.0	85.7
14	850	1.00	1.00	16.1	84.8
15	800	0.32	2.38	17.9	98.0
16	850	3.00	3.75	18.8	96.7
17	800	2.00	4.69	15.9	98.0
18	850	3.00	1.00	12.6	71.4
19	750	1.00	3.75	17.0	98.0
20	750	1.00	1.00	22.8	14.3

2.2. Preparation and characterization of activated carbon

Oil palm fronds (OPF) used for preparation of activated carbon was collected from the oil palm field within Engineering Campus, Universiti Sains Malaysia, Malaysia. OPF (after removing leaflets) were firstly cut into pieces (1-2 cm), washed with water to remove dirt from its surface and subsequently dried overnight at 105 °C. The dried fronds pieces were crushed to the size (1-4 mm) and then carbonized at 700 °C under purified nitrogen (99.995%) flow (150 cm³/min) for 2 h in a stainless steel vertical tubular reactor placed in a tubular furnace (the heating rate was fixed at 10°C/min). The char produced was then soaked in potassium hydroxide (KOH) solution with different impregnation ratios (KOH:char). The mixture was then dehydrated in an oven overnight at 105 °C to remove moisture and then activated under carbon dioxide (CO₂) atmosphere at different temperatures. Once the final temperature was reached, the gas flow was switched over from nitrogen to CO₂ while activation was held for varying periods of time. The activated product was then cooled to room temperature and washed with hydrochloric acid (0.1 M) and hot distilled water until the pH of the washed solution reached 6.5-7.

The surface area and pore characteristics which include the pore volume and pore size distribution were analyzed using Micromeritics (Model ASAP 2020, USA surface area and porosity analyzer) through nitrogen adsorption isotherm at 77 K. In order to determine the morphology of PFAC surface, the sample prepared at the optimum condition was examined using Scanning Electron Microscope. The analysis was conducted using a Field Emission Scanning Electron Microscope (SEM) (Leo Supra 35 VP).

2.3. Adsorption studies

Batch adsorption was performed in 20 sets of 250 mL Erlenmeyer flasks. In a typical adsorption run, 100 mL of bentazon solutions with initial concentration of 100 mg/L was placed in a flask. 0.30 g of PFAC, with particle size of 1–3 mm, was added to the flask and kept in an isothermal shaker (120 rpm) at 30 °C until equilibrium was attained. The concentrations of bentazon solutions before and after adsorption were determined using a double beam UV–vis spectrophotometer (UV-1601 Shimadzu, Japan) at its maximum wavelength of 232 nm. The percentage removal at equilibrium was calculated by the following equation:

$$% \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

where C_o and C_e are the liquid-phase concentrations of bentazon at initial state and at equilibrium (mg/L), respectively [15,16].

2.4. Activated carbon yield

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The experimental activated carbon yield was calculated based on the following equation:

$$\text{Yield}(\%) = \frac{W_c}{W_o} \tag{2}$$

where w_c and w_o are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

2.5. Design of experiments

The various process parameters for preparing the activated carbon was studied with a standard response surface methodology (RSM) design called a central composite design (CCD). This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, and also to analyze the interaction between the parameters [17]. Generally, the CCD consists of a 2^n factorial runs with 2n axial runs and n_c center runs (6 replicates).

In this work, the activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The variables studied were (i) x_1 , activation temperature; (ii) x_2 , activation time and (iii) x_3 , KOH:char impregnation ratio. These three variables together with their respective ranges were chosen based on the literature and preliminary studies. Activation temperature, activation time and chemical impregnation ratio are the important parameters affecting the characteristics of the activated carbons produced [14,18]. The number of experimental runs from the central composite design (CCD) for the three variables consists of 8 factorial points, 6 axial points and 6 replicates at the centre points indicating that altogether 20 experiments were required, as calculated from the following equation:

$$N = 2^{n} + 2n + n_{c} = 2^{3} + 2 \times 3 + 6 = 20$$
(3)

where *N* is the total number of experiments required and n is the number of process variables.

Table 2

Analysis of variance (ANOVA) response surface 2FI model for PFAC yield.

Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob > F
Model	97.67	6	16.28	7.24	0.0015
<i>x</i> ₁		1	20.10	8.94	0.0104
<i>x</i> ₂		1	7.33	3.26	0.0941
<i>x</i> ₃		1	5.72	2.55	0.1346
<i>x</i> ₁ <i>x</i> ₂		1	7.05	3.14	0.1000
<i>x</i> ₁ <i>x</i> ₃		1	56.55	25.15	0.0002
<i>x</i> ₂ <i>x</i> ₃		1	0.92	0.41	0.5339
Residual		13	2.25		
Luck of fit		8	3.65		
Pure error		5	0.00		

The complete design matrix of the experiments carried out, together with the results obtained, is shown in Table 1. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The two responses were activated carbon yield (Y_1) and bentazon removal (Y_2). Each response was used to develop an empirical model which correlated the response to the three preparation process variables using a second degree polynomial equation as given by the following equation [19]:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{i_i} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j$$
(4)

where Y is the predicted response, b_o the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i , x_j are the coded values of the activated carbon preparation variables.

3. Results and discussion

3.1. SEM and BET analysis

The surface morphology of the PFAC produced was examined using scanning electron microscopy. Fig. 1 shows the SEM image of PFAC prepared at optimum condition. It can be seen that the surface of PFAC contains a well-developed pores where there is a good possibility for Bentazon to be adsorbed into the surface of the pores. The BET surface area, Langmuir surface area, total pore volume and the pore size were 1237.13 m²/g, 1856.65 m²/g, 0.667 cm³/g and 2.16 nm, respectively.



Fig. 1. SEM image of PFAC prepared at optimum condition (Magnification = $500 \times$).

3.2. Development of regression model equation

A polynomial regression equation was developed by using CCD to analyze the process variable (factors) interactions by identifying the significant factors contributing to the regression model. The complete design matrixes together with both the response values obtained from the experimental work are given in Table 1. Runs 2, 4,5,6,7 and 11 at the center point were used to determine the experimental error. Bentazon removal was found to range from 14.3 to 98.1%, whereas the activated carbon yield obtained ranged from 12.6 to 22.8%.

For response of bentazon removal the quadratic model was selected as suggested by the software. For carbon yield, the two factor interaction (2FI) model was selected by the software. The final empirical models in terms of coded factors (parameters) after excluding the insignificant terms for carbon yield (Y_1) and bentazon removal (Y_2) are shown in Eqs. (5) and (6), respectively.

$$Y_1 = 18.37 - 1.21x_1 - 0.73x_2 - 0.65x_3 - 0.94x_1x_2 + 2.66x_1x_3 + 0.34x_2x_3$$
(5)

$$Y_{2} = 94.19 + 10.98x_{1} - 2.11x_{2} + 24.77x_{3} - 3.15x_{1}^{2} - 1.82x_{2}^{2}$$
$$-14.45x_{3}^{2} - 2.69x_{1}x_{2} - 15.04x_{1}x_{3} + 0.44x_{2}x_{3}$$
(6)

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient value. The R^2 values for Eq. (5) and Eq. (6) were 0.7697 and 0.9701, respectively. This indicated that 76.97% and 97.01 of the total variation in the carbon yield and bentazon removal, respectively, was attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. The R^2 of 0.7697 for Eq. (5) was considered as moderate to validate the fit, which might lead to a larger variation in the carbon yield predicted from the model. The R^2 of 0.9701 for Eq. (6) was considered relatively high, indicating that there was a good agreement between the experimental and the predicted bentazon removal from this model.

The ANOVA for the 2FI model for PFAC yield is listed in Table 2. The Model *F*-value of 7.24 and Prob > *F* of 0.0015 implied that the model was significant as well. In this case, x_1 , x_2 , and x_1x_2 were significant model terms whereas x_3 , x_1x_2 and x_2x_3 were insignificant to the response. Fig. 2(a) shows the three-dimensional response surfaces which were constructed to show the effects of the PFAC preparation variables (activation temperature and chemical impregnation ratio) on the carbon yield (Y_1).

Analysis of variance (ANOVA) was further carried out to justify the adequacy of the models. The ANOVA for the quadratic model for bentazon removal is listed in Table 3. From the ANOVA

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Table	3

ANAIVSIS ULVANAIUC LANUVATTESDUNSE SUTACE UUAUTAUC INDUCTIULDENIAZUN TEINU	Analy	vsis of variance (ANOVA) respons	e surface quadratic	model for bentazon	removal
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Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	Prob > F
Model	15005.12	9	1667.24	36.02	< 0.0001
<i>x</i> ₁	1646.92	1	1646.92	35.58	0.0001
<i>x</i> ₂	60.68	1	60.68	1.31	0.2789
<i>x</i> ₃	8378.50	1	8378.50	181.02	< 0.0001
x_1^2	142.92	1	142.92	3.09	0.1094
x_2^2	47.91	1	47.91	1.04	0.3329
x_3^2	3007.11	1	3007.11	64.97	< 0.0001
$x_1 x_2$	57.78	1	57.78	1.25	0.2900
$x_1 x_3$	1809.01	1	1809.01	39.08	< 0.0001
<i>x</i> ₂ <i>x</i> ₃	1.53	1	1.53	0.033	0.8593
Residual	462.84	10	46.28		
Luck of fit	461.21	5	92.24	282.37	< 0.0001
Pure error	1.63	5	0.33		

response surface quadratic model for bentazon removal, the Model (*F*-value) of 36.02 and (Prob > *F*) of 0.0001 implied that the model was significant. In this case, x_1 , x_3 and x_1x_2 were significant model terms whereas x_2 , x_1^2 , x_2^2 , x_1x_3 and x_2x_3 were insignificant to the



Fig. 2. (a) Three-dimensional response surface plot of bentazon removal (effect of activation temperature and chemical impregnation ratio, t = 1 h). (b) Three-dimensional response surface plot of PFAC yield (effect of activation temperature and chemical impregnation ratio, t = 1 h).

Table 4

Predicted and experimental results of carbon yield and bentazon removal.

Item	Predicted results	Experimental results	Error
Carbon yield	20.5	21.6	5.1
Bentazon removal (%)	99.85	98.10	1.75

response. Fig. 2(b) shows the three-dimensional response surfaces which was constructed to show the effects of the activated carbon preparation variables (activation temperature and chemical impregnation ratio) on the Bentazon removal (Y_2).

The results of this investigation corroborated Sudaryanto et al. [20] reports that activation time gave no significant effect on the pore structure of activated carbon produced from cassava peel, but the pore characteristics changed significantly with the activation temperature and the KOH impregnation ratio. Sentorun-Shalaby et al. [21] also found that activation time did not show much effect on the surface area obtained for activated carbons prepared from apricot stones using steam activation, while at high KOH impregnation ratio, the microporosity of their product was attributed to possible intercalation of potassium metal in the carbon structure. In this work, the high adsorption capacity for bentazon displayed by the PFAC may therefore, be due to the above speculated intercalated potassium or creation of expanded surface area within the carbon microstructure by the alkaline purging.

3.3. Process optimization

The activated carbon produced should have accepted carbon yield and also a high bentazon removal for economical viability. However, to optimize these two response factors under the same conditions is difficult because the interest regions of the two factors were different. This phenomenon is expected, because the higher the KOH fraction used in the activation process, the higher will be the etching of the impurities and salts within the char matrix leaving behind a more porous but lighter activated carbon, thus recording higher adsorption capacities at the expense of activated carbon gross weight. Therefore, in order to compromise between these two responses, the function of desirability was applied using Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The experimental conditions with the highest desirability were selected to be verified.

The optimum condition for preparation of activated carbon was activation temperature of 850 °C, activation time of 1 h and chemical impregnation ratio of 3.75. The predicted and experimental results of carbon yield and bentazon removal obtained at optimum condition are listed in Table 4. It can be found that the errors between predicted and experimental carbon yield and bentazon removal are 5.1 and 1.75%, respectively.

4. Conclusions

Oil palm fronds were used as precursor to produce an activated carbon with high surface area, sufficient yield of carbon and high bentazon removal. A CCD was conducted to study the effects of three activated carbon preparation variables: activation temperature, activation time and chemical impregnation (KOH:char) ratio, on the removal of bentazon and activated carbon yield. A quadratic model and a 2FI model were respectively employed to correlate the preparation variables to the removal of bentazon and carbon yield. Through analysis of the response surfaces derived from the models, activation temperature and chemical impregnation (KOH:char) ratio were found to have significant effects on the removal of bentazon, with chemical impregnation ratio imposing the greatest effect on this response. Activation temperature was found to have the greatest effect on carbon yield. The optimum condition for preparation of activated carbon was activation temperature of 850 °C, activation time of 1 h and chemical impregnation ratio of 3.75.

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