Research Article

Optimization of Activated Carbons Prepared by H_3PO_4 and Steam Activation of Oil Palm Shells

Daouda Kouotou,^{1,2} Horace Ngomo Manga,¹ Abdelaziz Baçaoui,²
Abdelrani Yaacoubi,² and Joseph Ketcha Mbadcam¹

¹ Physical and Theoretical Chemistry Laboratory, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon

² Applied Organic Chemistry Laboratory, Department of Chemistry, Faculty of Science Semlalia Marrakech, University Cadi Ayyad, P.O. Box 2390 Marrakech, Morocco

Correspondence should be addressed to Joseph Ketcha Mbadcam; jketcha@yahoo.com

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In this study, activated carbons were prepared from oil palm shells by physicochemical activation. The methodology of experimental design was used to optimize the preparation conditions. The influences of the impregnation ratio (0.6–3.4) and the activation temperature between 601°C and 799°C on the following three responses: activated carbon yield ($\text{R}/\text{AC}-\text{H}_3\text{PO}_4$), the iodine adsorption ($\text{I}_2/\text{AC}-\text{H}_3\text{PO}_4$), and the methylene blue adsorption ($\text{MB}/\text{AC}-\text{H}_3\text{PO}_4$) results were investigated using analysis of variance (ANOVA) to identify the significant parameters. Under the experimental conditions investigated, the activation temperature of 770°C and impregnation ratio of 2/1 leading to the $\text{R}/\text{AC}-\text{H}_3\text{PO}_4$ of 52.10%, the $\text{I}_2/\text{AC}-\text{H}_3\text{PO}_4$ of 697.86 mg/g, and the $\text{MB}/\text{AC}-\text{H}_3\text{PO}_4$ of 346.25 mg/g were found to be optimum conditions for producing activated carbon with well compromise of desirability. The two factors had both synergetic and antagonistic effects on the three responses studied. The micrographs of activated carbons examined with scanning electron microscopy revealed that the activated carbons were found to be mainly microporous and mesoporous.

1. Introduction

Nowadays, environmental pollution is becoming a serious problem to be faced. In order to purify and keep our environment clean it requires the development of optimization tools to produce highly efficient and effective adsorbents such as activated carbon. It still remains one of the most effective adsorbents owing to its well developed porous structure, large active surface area, and good mechanical properties [1–3]. Activated carbon can be prepared from a large number of materials. These materials are usually high in carbon and volatile contents but low in inorganic contents. Some of the most common precursors include coal, lignite, and wood, which are unfortunately not available in large quantity. So, researchers are intensifying their search on activated carbon produced from nonfossil sources, like lignocellulosic wastes from agriculture which are abundant and largely available

[4–8]. Amongst lignocellulosic compounds found, oil palm shells are discharged as wastes, coming mainly from industries of oil extraction. These wastes are renewable resource which can be better managed and provided a large range of useful materials. In Cameroon, like in some tropical countries such as Indonesia, Malaysia, and Thailand, large quantity of these wastes are generated annually [9–14]. To reduce these solid wastes, they can be used as starting materials for preparing activated carbons necessary for the removal of pollutants [6, 9, 10, 15–17]. Activated carbons can be prepared basically by two methods: physical activation and chemical activation. Although, oil palm shells have been successfully converted into well-developed activated carbons used for removal of various gaseous pollutants [18–22] but, there are not many works in the scientific literature that report on the optimization of the preparation of activated carbons from oil palm shells impregnated with phosphoric acid. For this

purpose, activated carbons preparation had been optimized using phosphoric acid as chemical reagent and the steam as oxidant agent. The influence of the activation temperature and the impregnation ratio, on the activated carbon yield, the iodine and methylene blue adsorption capacities were investigated using the methodology of experimental design in order to find out the significant parameters.

2. Experimental

2.1. Raw Material Sampling and Analysis. The oil palm shells were collected from Socapalm Company in the locality of Bongo-Cameroon. They were first washed with tap water then with distilled water to remove the foreign materials and dried in an oven at 105°C. The dry materials were crushed and sieved to a particle size fraction of 1 mm to 2 mm, and were stored for further experiment. The chemical analysis of oil palm shells represented in weight percent is shown in Table 1.

2.2. Activation Carbon Preparation. The carbonization of oil palm shells with particle size of 1 mm to 2 mm was carried out by loading 60 g of dried materials into the reactor of the horizontal furnace (CARBOLITE 1200C Tube Furnaces, KEISON Products), under N₂ gas flow (100 cm³/min), and heated up to a carbonization temperature of 800°C, at a heating rate of 10°C/min. Upon reaching 800°C, the sample is held at the same conditions for 1 hr. After carbonization, the sample is cooled at room temperature under N₂ flow 100 cm³/min. The yield of char was found to be around 30%. The carbonization product obtained, was mixed with solutions of H₃PO₄ to the impregnation ratio desired throughout 2 hours at 60°C and then dried in an oven at 110°C for 24 hours. In this work, for all the samples, the impregnation ratio was ranged from 0.6 to 3.4. A typical activation run began by loading the reactor with 10 g of the impregnated sample. After the temperature of the furnace was increased at the rate of 10°C/min, until it reached the final activation temperature of 601°C to 799°C. This temperature was maintained for 3 hours for the samples impregnated, in a flowing water vapor of 0.1 mL/min. When, the activation process is achieved, the samples were washed initially with hot distilled water and finally with cold distilled water. Then the samples known as activated carbon from oil palm shell impregnated with H₃PO₄ (AC-H₃PO₄) were dried at 110°C overnight.

2.3. Methodology of Experimental Design. The methodology of experimental design (MED) is a statistical technique for modeling and analysis of problems in which a response of interest is influenced by several factors [23]. The MED is utilized to optimize the effective parameters with a minimum number of experiments and to analyze the interactions between the parameters [24]. The two factors investigated in the present study were coded as the activation temperature (X_1) and the impregnation ratio (X_2).

The experimental design matrix and the experimental results are given in Table 2. In the 12 experiments of the matrix, each row represents an experimental run, and each column represents the variables tested.

TABLE 1: Chemical composition of oil palm shells.

Components	Weight percent (wt%)
Ash	4.0
Extract	7.0
Hydrosoluble sugar	8.0
Pectin	9.0
Cellulose	20.0
Hemicelluloses	12.0
Lignin	40.0

TABLE 2: Experimental design matrix and the corresponding experimental responses.

No. of exp	X_1	X_2	Y_1 (%)	Y_2 (mg/g)	Y_3 (mg/g)
1	-1.0000	-1.0000	58.92	602.0	565.00
2	1.0000	-1.0000	52.64	603.0	510.00
3	-1.0000	1.0000	45.10	460.0	520.00
4	1.0000	1.0000	30.73	555.0	496.00
5	-1.4142	0.0000	47.80	365.0	449.00
6	1.4142	0.0000	48.18	682.0	446.00
7	0.0000	-1.4142	48.20	444.0	524.00
8	0.0000	1.4142	27.10	539.0	528.00
9	0.0000	0.0000	59.65	444.0	300.00
10	0.0000	0.0000	64.57	476.0	297.00
11	0.0000	0.0000	62.23	460.0	293.00
12	0.0000	0.0000	55.14	413.0	293.00

X_1 : coded value of the activation temperature.

X_2 : coded value of the impregnation ratio.

Y_1 : activated carbons yield, R/AC-H₃PO₄.

Y_2 : iodine adsorption capacities, I₂/AC-H₃PO₄.

Y_3 : methylene blue adsorption capacities, MB/AC-H₃PO₄.

The three responses analyzed were the activated carbon yield, the iodine, and methylene blue adsorption capacities of activated carbon impregnated with H₃PO₄ noted, respectively, by R/AC-H₃PO₄ (Y_1), I₂/AC-H₃PO₄ (Y_2), and MB/AC-H₃PO₄ (Y_3). Each response was used to develop a model which correlates the responses to the two variables using a polynomial equation given by the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2, \quad (1)$$

where, Y is the predicted response, b_0 a constant coefficient, b_1 and b_2 are linear coefficients; b_{11} and b_{22} are quadratic coefficients; b_{12} an interaction coefficient; X_1 and X_2 , the coded values of the activated carbon preparation variables. The experimental data were analyzed using a statistical software design expert named NEMROD, (new efficient methodology of research using optimal design) for regression analysis to fit the equations developed and also to evaluate the statistical significance of the equations obtained [24].

2.4. Activated Carbon Yield, Y_1 . In activated carbon preparation, the yield is usually defined as final weight of activated carbon produced after activation, washing, and drying,

divided by initial weight of raw material, both on a dry basis [25].

The activated carbons yield, $R(\%)$ was calculated using the following formula:

$$R(\%) = \frac{m}{m_0} \times 100, \quad (2)$$

where, m and m_0 are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

2.5. Iodine Adsorption Capacities, Y_2 . Iodine was considered as probe molecule for assessing the adsorption capacity of adsorbent for solutes of molecular sizes $< 10 \text{ \AA}$. The iodine number is defined as the milligrams of iodine adsorbed by 1 g of carbon. The iodine adsorption was determined using the sodium thiosulfate volumetric method [26]. The iodine number was estimated by mixing the activated carbon with 0.02 N iodine solution shaken occasionally and then by titration of the solution against $\text{Na}_2\text{S}_2\text{O}_3$, $5\text{H}_2\text{O}$.

2.6. Methylene Blue Adsorption Capacities, Y_3 . Methylene blue was considered as probe molecule for assessing the adsorption capacity of adsorbent for solutes of molecular sizes $> 15 \text{ \AA}$. The methylene blue number is the milligrams of methylene blue adsorbed by 1 g of carbon [27]. The concentration of methylene blue was measured by using a beam UV-visible spectrophotometer Anthelie data at the maximum absorbance wavelength of 660 nm.

The iodine and methylene blue adsorption capacities, Cads (mg/g) were calculated using the following formula:

$$\text{Cads} = \frac{(C_0 - C_e)V}{m}, \quad (3)$$

where, C_0 and C_e (mg/L) are the liquid-phase concentrations of iodine at initial and at equilibrium, respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

3. Results and Discussion

3.1. Responses Analysis and Interpretation. A polynomial regression equation was developed using NEMROD to analyze the correlation between the factors (activation temperature and impregnation ratio) and the responses (activated carbon yield, adsorption capacities of iodine and methylene blue). The experiments at the center point (experiments 9 to 12) of the complete design matrix were used to determine the experimental error and to verify the reproducibility of experimental data. The activated carbon yield ranged from 27.10 to 64.57% whereas the iodine and methylene blue numbers obtained ranged from 365 mg/g to 682 mg/g and from 293 mg/g to 565 mg/g, respectively. The results obtained revealed that, the adsorption capacities are higher for lower activation temperature (experiment 5 for $\text{I}_2/\text{AC-H}_3\text{PO}_4$ and experiment 1 for $\text{MB}/\text{AC-H}_3\text{PO}_4$) corresponding to the ratio ranging between 1/1 and 2/1. However, lower adsorption capacities are obtained for activation temperature higher

than 700°C with the same ratio (experiment 6 for $\text{I}_2/\text{AC-H}_3\text{PO}_4$ and experiment 11 for $\text{MB}/\text{AC-H}_3\text{PO}_4$). According to the results of activated carbon yields, the lowest value was obtained for 3.4/1 and the highest value for 2/1 independently of the activation temperature which remained the same at temperature 700°C .

The polynomial model equations in terms of coded factors are given as follows:

$$\begin{aligned} Y_1 &= 61.220 - 2.642X_1 - 7.581X_2 - 5.128X_1^2 \\ &\quad - 11.348X_2^2 - 3.253X_1X_2, \\ Y_2 &= 444.75 + 75.18X_1 + 3.19X_2 + 66.19X_1^2 \\ &\quad + 30.44X_2^2 + 13.0X_1X_2, \\ Y_3 &= 295.75 - 10.405X_1 - 6.668X_2 + 84.876X_1^2 \\ &\quad + 124.127X_2^2 + 7.75X_1X_2. \end{aligned} \quad (4)$$

Conventionally, a positive sign in front of the coefficients indicates synergistic effects, whereas negative sign indicates antagonistic effects. So, we can see that for the response Y_2 , the effects of the two variables are synergistic, but they are antagonistic for the response, Y_1 and Y_3 . The value of the correlation coefficient (R^2) helps to evaluate the quality of the model developed. When the correlation coefficient is closer to unit, it means that the model is better fit thus the predicted values are closer to the experimental values for the response. The R^2 values were 0.981, 0.993, and 0.970 for Y_1 , Y_2 , and Y_3 , respectively. It indicated that 98.1%, 99.30%, and 97% of the total variation in the activated carbon yield, $\text{I}_2/\text{AC-H}_3\text{PO}_4$, and $\text{MB}/\text{AC-H}_3\text{PO}_4$, respectively, were due to the experimental data analyzed. The R^2 values of 0.981, 0.993 and 0.970 for Y_1 , Y_2 , and Y_3 were considered relatively high indicating that there was a good agreement between the experimental and predicted activated carbon yield, iodine, and methylene blue numbers from the model.

The ANOVA for activated carbon yield (Y_1) is given in Tables 3 and 4.

It can be seen, from the ANOVA, that, the coefficients of the impregnation ratio ($b_2 = -7.581$) and their quadratic term ($b_{22} = -11.348$) were significant model terms whereas the coefficient of the activation temperature ($b_1 = -2.642$) was least insignificant. The coefficient of the quadratic term of activation temperature ($b_{11} = -5.128$) and the interaction term ($b_{12} = -3.253$) were least moderated to the response Y_1 .

According to the ANOVA of results obtained, the coefficients of the activation temperature ($b_1 = 75.18$) as given in Tables 5 and 6 and its quadratic term ($b_{11} = 66.19$) were found to have significant effects on the iodine adsorption. The coefficient of the activation temperature term imposes the greater effect on $\text{I}_2/\text{AC-H}_3\text{PO}_4$. The coefficients of the quadratic term of the impregnation ratio ($b_{22} = 30.44$) and the interaction term ($b_{12} = 13.00$) were considered moderated, while the coefficient of the impregnation ratio term ($b_2 = 3.14$) imposed the least effect on the iodine adsorption (Y_2).

Tables 7 and 8 summarized the ANOVA of methylene adsorption capacity. The coefficients of the quadratic term of

TABLE 3: Analysis of variance of the activated carbon yield, R/AC-H₃PO₄ (Y₁).

Source of variation	Sum of square	Degree of freedom	Square mean	Rapport	Signif.
Regression	1.43660E + 0003	5	2.87320E + 0002	62.2320	0.0150***
Residual	2.77015E + 0001	6	4.61692E + 0000		
Total	1.46430E + 0003	11			

*** most significant effect, ** less significant effect, * not significant effect.

TABLE 4: Statistical estimations of coefficients: R/AC-H₃PO₄ (Y₁).

Name	Coefficient	F.Inflation	Ecart-type	t. exp.	Signif. %
b_0	61.220		1.074	56.98	<0.01***
b_1	-2.642	1.00	0.760	-3.48	1.33*
b_2	-7.581	1.00	0.760	-9.98	0.0130***
b_{11}	-5.128	1.04	0.849	-6.04	0.117**
b_{22}	-11.348	1.04	0.849	-13.36	<0.01***
b_{12}	-3.253	1.00	1.074	-3.03	2.30*

*** most significant effect, ** less significant effect, * not significant effect.

the activation temperature ($b_{11} = 84.876$) and impregnation ratio ($b_{22} = 124.127$) were found to have significant effects on MB/AC-H₃PO₄, with the quadratic effects of impregnation ratio imposing the greatest effect on the carbons prepared. The coefficients of the activation temperature ($b_1 = -10.405$) and the interaction term ($b_{12} = 7.750$) seem to have moderate effects, whereas the coefficient of the impregnation ratio term ($b_2 = -6.668$) found to have the least effects on the MB/AC-H₃PO₄.

3.2. *Activated Carbon Yield (R/AC-H₃PO₄), Y₁.* Figure 1 shows the two- and three-dimensional response surfaces which were constructed to present the most important factors on the activated carbon yield.

The analysis of the graphs below showed that, an increase of the activation temperature between (630–770)°C and the impregnation ratio between 1/1 to 3/1, the activated carbons yield decreased from 56.47 to 36.89%. Other authors also obtained similar range of activated carbon yield, with precursors activated with phosphoric acid: peach stones, 42–44% [28], coconut shells, 49–52% [29]. We can see that a thermal treatment at the same temperature under an inert atmosphere followed by the impregnation with H₃PO₄, involves a remarkable degradation of the microstructure. Such degradation conducted to relatively important mass losses. This mass effect becomes more and more noticeable as temperature increases, which results in a progressive decrease of the global yield of the process. This latter assertion is consistent with the results obtained by Ould-Idriss et al., [30] for olive-tree activated with H₃PO₄. The activation temperature has a negative effect on carbon yield. This was expected because at a higher temperature, more volatiles are released, resulting in a lower yield. However, when the activation temperature exceeds 700°C, most of the volatiles have been released; therefore, the yield maintain almost a constant value. A similar trend has been reported in some studies for ZnCl₂ chemical activation [31, 32]. The response

surface showed a curvature indicating that the interaction effect between activation temperature and impregnation ratio on the yield is pronounced. This result obtained is in agreement with the work done by Ahmad et al. [33]. The activated carbon yield was found to decrease with the increasing of activation temperature and impregnation ratio, this trend is in accordance with the work done by other authors [33, 34]. The two variables were found to have significant effects on the activated carbon yield, and also antagonistic interactions occurred between activation temperature and impregnation ratio. This behavior was attributed to the fact that, the reaction of lignocellulosic compounds with phosphoric acid begins as soon as the components are mixed. The acid first attacks hemicelluloses and lignin because cellulose is more resistant to acid hydrolysis [35]. Here the acid will hydrolyze glycosidic linkages in lignocellulosic and cleave aryl ether bond in lignin. These reactions are accompanied by further chemical transformations that include dehydration, degradation, and condensation. As the temperature increases, the aromatic condensation reactions also take place among the adjacent molecules, which resulted in the evolution of gaseous products from the hydroaromatic structure of carbonized char leading to decreased yield of carbon. This observation is consistent with other authors [36]. According to the polynomial equation, the impregnation ratio is another critical parameter that affects the activated carbon yield. From the figures, it is obvious that activated carbon yield decreased as the impregnation ratio increased. Here the excess of phosphoric acid will promote gasification of char and increased the total weight loss of carbon. The same result was also observed by other researchers [35–37]. The phosphoric acid chemical assumed a dehydration agent role during activation. It inhibits the formation of tars and any other liquids that could clog up the pores of the sample. So the movement of the volatiles through the pore passages would not be hindered, and volatiles will be subsequently released from the carbon surface during activation. Therefore the activated carbon yield decreased. Similar trends were also reported by Lua and Yang [38] and Guo and Lua [39] in their studies on the preparation of activated carbon from pistachio-nut shell and oil palm shells, respectively.

3.3. *The Iodine Number Results (I₂/AC-H₃PO₄), Y₂.* Figure 2 presented the two- and three-dimensional response surfaces constructed to show the most important variable on the response Y₂.

From the above graphs, we noticed that, as the activation temperature increases from (630 to 770°C) and the impregnation ratio from 1/1 to 3/1, the iodine adsorption

TABLE 5: Analysis of variance of iodine adsorption, $I_2/AC-H_3PO_4$ (Y_2).

Source of variation	Sum of square	Degree of freedom	Square mean	Rapport	Signif.
Regression	7.599E + 0004	5	1.519E + 0004	176.7482	<0.01 ***
Residual	5.159E + 0002	6	8.598E + 0001		
Total	7.650E + 0004	11			

*** most significant effect, ** less significant effect, * not significant effect.

FIGURE 1: Variation of the activated carbon yield (Y_1) in the plan temperature-ratio.

FIGURE 2: Variation of the iodine adsorption, $I_2/AC-H_3PO_4$ (Y_2) in the plan temperature-ratio.

FIGURE 3: Variation of the methylene blue adsorption, MB/AC-H₃PO₄ (Y₃) in the plan temperature-ratio.

FIGURE 4: Variation of the function of desirability as a function of both activation temperature and impregnation ratio.

also increases. The two factors studied, activation temperature and impregnation ratio had a synergistic effect on the response Y₂. For the impregnation ratio, this could be attributed to the impregnation with phosphoric acid which permits to have more mesopores than micropores. We can deduce that, from the deeply attack of our material by phosphoric acid, it resulted in the opening of more sites of adsorption of iodine. Micropores favored the adsorption of

smaller molecules like iodine although no clear correlation with the mesopore volume was found indicating that adsorption of smaller molecules in large micropore and mesopore is feasible. As we observed the increase of iodine number, we can assume the presence of both types of pores: micropores and mesopores. This is in accordance with Juang et al. [40] who studied the role of microporosity of activated carbons in phenol adsorption and who concluded that adsorption of

FIGURE 5: SEM micrographs of raw material and optimum activated carbon AC-H₃PO₄.TABLE 6: Statistical estimations of coefficients: I₂/AC-H₃PO₄ (Y₂).

Name	Coefficient	F inflation	Ecart-type	t. exp.	Signif. %
b_0	444.75		4.64	95.93	<0.01***
b_1	75.18	1.00	3.28	22.93	<0.01***
b_2	3.19	1.00	3.28	0.97	37.0
b_{11}	66.19	1.04	3.67	18.06	<0.01***
b_{22}	30.44	1.04	3.67	8.30	0.0281***
b_{12}	13.00	1.00	4.64	2.80	3.06*

*** most significant effect, ** less significant effect, * not significant effect.

phenol is not completely restricted to occur within the micropores. On the other side mesopores clearly favor adsorption of larger molecules contrary to micropores which adsorbed small ones. Another fine analysis of results showed that the activated carbon prepared with the ratio of 1/1 (experiments 1 and 2), ratio of 3/1 (experiments 3 and 5), and ratio 3.4/1 (experiment 8) iodine adsorption capacities were higher (601, 603, 460, 555, and 539 mg/g, resp.). We can attribute these adsorption capacities to micropores. Whereas for the activated carbons prepared with the ratio 2/1 (experiments 5, 6, 9, 10, 11, and 12) present a decrease of the iodine adsorption, so we can attribute them to adsorption into mesopores. From our results obtained, it indicates that the activated carbons prepared with a low impregnation ratio (between 1/1 and 2/1) have higher iodine numbers consequently more microporous structure, while for impregnation ratio equals to 2/1, the iodine numbers seems to decrease consequently the activated carbons are mostly mesoporous. The observation confirmed the coexistence of two types of pores. The increase of of the SEM of AC-H₃PO₄ as given in Figure 5 iodine numbers at low impregnation ratio can be attributed to the effect of H₃PO₄, which inhibits the formation of tar and promotes the release of volatiles to produce more micropores than mesopores. But when the impregnation ratio is higher than 2/1, the more swelling impregnated material and stronger release of volatiles in the activation process will lead to a widening of pores; micropores formed are subsequently converted to

mesopores and even probably macropores. Our results are in good agreement with the work related to ZnCl₂ chemical activation [41]. And also from the polynomial equation, the impregnation ratio was the most significant factor on the iodine number response.

3.4. The Methylene Blue Numbers Results (MB/AC-H₃PO₄), Y₃. Figure 3 shows the two- and three-dimensional response surfaces which were constructed to present the most important factors on the MB/AC-H₃PO₄.

The polynomial equation showed that the linear term of the activation temperature and the impregnation ratio had antagonistic effects on the methylene blue adsorption capacity. The activation temperature has the most significant effects. However the coefficient of the interaction term had a synergetic effect on the MB/AC-H₃PO₄. This was expected as the increase in activation temperature would entail an opening and enlargement of the pores, which enhanced the adsorption of MB/AC-H₃PO₄ [42] but decreased the yield. Similar phenomenon were observed in the activated carbon derived from coconut husk and oil palm fiber for adsorption of methylene blue dye and 2,4,6-TCP by other authors [42, 43]. Moreover, Auta and Hameed [44] in their work on the optimized waste tea activated carbon for adsorption of methylene blue and acid blue 29 dyes using response surface methodology arrived to the same observation that activation temperature and impregnation ratio helped in the development of pores and surface area of the adsorbent which contributed to the adsorption of dyes. Currently, the chemical activation with H₃PO₄ conducted to obtain activated carbons with a well-developed mesoporosity, which is favorable to adsorb larger molecules like methylene blue. Also, it conducted to have more acidic groups at the activated carbon surface. Guo and Lua [45] also observed these acid groups for activated carbon prepared from the same precursor. Consequently, the higher the percentage of mesopores, the higher the adsorption of methylene blue. This is completed by the electrostatic interactions occurring between methylene blue and the deprotonated acidic groups. The same trend had been shown by Altenor et al. [46]. The activated carbon

TABLE 7: Analysis of variance of methylene blue adsorption, MB/AC-H₃PO₄ (Y₃).

Source of variation	Sum of squares	Degree of freedom	Mean square	Rapport	Signif.
Regression	1.2410E + 0005	5	2.48215E + 0004	2142.8652	<0.01***
Residual	3.8473E + 0003	6	6.4121E + 0002		
Validity	3.8125E + 0003	3	1.270E + 0003	109.7139	0.130**
Error	3.4750E + 0001	3	1.1583E + 0001		
Total	1.2795E + 0005	11			

*** most significant effect, ** less significant effect, * not significant effect.

TABLE 8: Statistical Estimations of coefficients: MB/AC-H₃PO₄ (Y₃).

Name	Coefficient	F inflation	Ecart-type	t. exp.	Signif. %
b_0	295.750		1.702	173.80	<0.01***
b_1	-10.405	1.00	1.203	-8.65	0.240**
b_2	-6.668	1.00	1.203	-5.54	1.01*
b_{11}	84.876	1.04	1.345	63.09	<0.01***
b_{22}	124.127	1.04	1.345	92.26	<0.01***
b_{12}	7.750	1.00	1.702	4.55	1.82*

*** most significant effect, ** less significant effect, * not significant effect.

samples activated by phosphoric acid are negatively charged due to deprotonated acidic groups such as carboxylic acid. Thus there is a net linear increase of methylene blue uptake. The methylene blue being cationic dye has a high affinity for the negatively charged surfaces. Electrostatic interactions are clearly involved in methylene blue adsorption mechanism [47]. The phosphoric acid activation led not only to much more acidic activated carbons by increasing the impregnation ratio but also to the opening of pores. Moreover, due to its higher molecular weight of 373.9 g/mol and a minimum molecular size about 1.3 nm, mesopores favor methylene blue adsorption. That can explain the more favorable adsorption of methylene blue. The same observation was made on vetiver roots activated carbons [48, 49]. It can be seen that increasing activation temperature (at the same impregnation ratio) from 600 to 841°C reduced the amount of methylene blue adsorption. This can be explained by a decrease of acidic functional groups and increase the basic surface groups of the carbon. The increase of activation temperature will make several functional groups decompose to form CO and CO₂. This phenomenon is due to the instability of acidic groups at high temperatures [50]. Thus, basic groups are increased as the temperature is increased. These groups can be formed during cooling of the activated carbon after the heating process. This cooling process enables the fixation of oxygen in the active sites [50]. Similar result was also obtained by Guo and Rockstraw [51].

3.5. Optimization of AC-H₃PO₄. The production of commercial activated carbon is based on the quality and the quantity of products obtained. Hence, it is desirable to prepare activated carbon with higher yield and a high adsorption capacity. From experimental data, the activation carbon yield and the iodine and methylene blue numbers responds opposite to each other with the two factors studied. So, to

compromise these two factors, the function of desirability is applied by considering the same weight for all the two factors on the three responses.

3.6. Model Validation. According to the software, the desirability profiles of activated carbon yield (Y₁), the iodine and methylene blue adsorption (Y₂ and Y₃) showed the levels of the variables constraints chosen, which produced the most desirable predicted responses of the variables studied. It ranged from (30–60)%; (550–900) mg/g and (250–500) mg/g, respectively, for R/AC-H₃PO₄, I₂/AC-H₃PO₄, and MB/AC-H₃PO₄. The predicted values were 53.44%, 675.58 mg/g, and 453.31 mg/g which conducted to the degree of satisfaction of 78.14%, 2.23%, and 48.76%, respectively, for Y₁, Y₂, and Y₃. The constraints were chosen relatively close to obtain the maximum yield and adsorption capacities of activated carbon prepared. The 3D surface provided information about the optimum conditions of the experiment (Figure 4). The optimum condition for preparation of activated carbon from oil palm shell was found to be an activation temperature of 770°C and impregnation ratio of 2/1. At the optimum conditions, the R/AC-H₃PO₄, the I₂/AC-H₃PO₄, and the MB/AC-H₃PO₄ were 52.10%, 697.86 mg/g, and 346.25 mg/g, respectively. It was observed that, the experimental values obtained were in good agreement with the values predicted from the polynomial model, with relatively small errors between the predicted and experimental values which were only 1.26%, 8.61, and 3.57 which indicated the success of the process of optimization exercise.

4. Conclusion

The influences of two factors, activation temperature and impregnation ratio on the yield and the adsorption capacities of iodine and methylene blue were investigated. The ANOVA was used to identify the significant factors. The experimental data of the responses were found to agree satisfactorily with the model predicted. The optimum conditions for preparation of activated carbons were found to be an activation temperature of 770°C and an impregnation ratio of 2/1. The optimum conditions resulted in activated carbons with the yield, the I₂/AC-H₃PO₄ and MB/AC-H₃PO₄ of 52.10%, 697.86 mg/g and 346.25 mg/g, respectively. The micrograph of the sample showed the pores with different sizes, suggesting the mixture of micro- and mesopores. The results of this study indicate the potential of oil palm shells to be a feedstock

for production of activated carbon of significant quantity and quality.

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