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Research Article

Preparation of Mesoporous-Activated Carbon from Branches of Pomegranate Trees: Optimization on Removal of Methylene Blue Using Response Surface Methodology

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Mesoporous activated carbon prepared from branches of pomegranate trees (BP) using physiochemical activation (potassium hydroxide treatment and carbon dioxide gasification). Based on the central composite design (CCD), two factor interaction (2FI) and quadratic models were respectively employed to correlate the activated carbon preparation variables. The effects of the activation temperature, activation time, and chemical impregnation ratios on the carbon yield, methylene blue (MB) removal were investigated. 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 branches of pomegranate trees (BP) were found to be activation temperature of 620.5°C, activation time of 1.4 h, and chemical impregnation ratio of 1.5. The carbon yield was found to be 16% while the removal of methylene blue was found to be 92.5%.

1. Introduction

Dyes are widely used by textile industries to color their products. One of the major problems concerning textile wastewaters is colored effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms [1]. Methylene blue (MB) dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. Therefore, the treatment of effluent containing such dye is of interest due to its esthetic impacts on receiving waters [2].

Activated carbon is the most widely used adsorbent material for adsorption due to its efficiency and economic feasibility. Utilization of activated carbon can be in the form of powder, granular, and fiber or cloth. Activated carbon-cloth having very high specific surface area coupled with high adsorption capacity and mechanical strength has gained increasing attention in recent years. Activated carbon is used for the removal of many pollutants from waste water by adsorption [3].

However, commercially available activated carbon is expensive. In the last years, special emphasis on the preparation of activated carbons from several agricultural by-products has been given due to the growing interest in low cost activated carbons from renewable resources, especially for application concerning treatment of wastewater. Researchers have studied the production of activated carbon from palm tree [4], cassava peel [5], bagasse [6], date pits [7], olive stones [8], fir woods and pistachio shells [9], and jute fiber [10]. The advantage of using agricultural by-products as raw materials for manufacturing-activated carbon is that these raw materials are renewable and potentially less expensive to manufacture.

The focus of the research is to evaluate the adsorption potential of branches of pomegranate trees-based activated carbon for methylene dye due to the fact that the branches of pomegranate trees are a very abundant and inexpensive material. MB was chosen in this study because of its known strong adsorption onto solids and it often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. MB which is the most commonly used material for dying cotton, wood, and silk has a molecular weight of 373.9 g mol^{-1}, which corresponds to methylene blue hydrochloride with three groups of water. The equilibrium data of adsorption studies were processed to understand the adsorption mechanism of the dye molecules onto the activated carbon.

2. Experimental

2.1. Adsorbate. Methylene blue (MB) supplied by Sigma-Aldrich was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all solutions. Table 3 listed the properties of MB dye used.

2.2. Preparation and Characterization of Activated Carbon. Branches of pomegranate trees (BP) are used as precursors for preparation of activated carbon. The precursor was first crushed into pieces of (1-2 cm) then was washed to remove dirt from its surface and was then dried in an oven at 75°C for three days. The dried precursors was crushed and screened to particle size of 1–4 mm and carbonized at 400°C under nitrogen flow for 2 h using stainless steel vertical tubular reactor placed in a tube furnace. The char produced was mixed with KOH pallets with different impregnation ratio (IR), as calculated using (1):

$$\mathrm{IR} = \frac{w_{\mathrm{KOH}}}{w_{\mathrm{char}}}, \tag{1}$$

where w_{KOH} is the dry weight (g) of KOH pellets and w_{char} is the dry weight (g) of char. Distilled water was then added to dissolve all the KOH pallets. The mixture was then dehydrated in an oven overnight at 100°C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature. Once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for different period of time. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot distilled water and 0.1 molar hydrochloric acid until the pH of the washing solution reached [11] 6-7.

2.3. Characterization of the Prepared Activated Carbon. Scanning electron microscopy (SEM) analysis was carried out on the activated carbon prepared under optimum conditions, to study its surface texture and the development of porosity. Brunaeur, Emmett and Teller (BET) suggested to determine the pore size distributions, the surface area, and pore characteristics of activated carbons using Micromeritics (Model ASAP 2020, USA).

2.4. Design of Experiments for Preparation of Activated Carbon. Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables [12]. A standard design called a central composite design (CCD) was applied in this work to study the variables for preparing the activated carbons. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [13]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (six replicates).

The activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The activated carbon preparation variables studied were (x_1) activation temperature; (x_2) activation time, and (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 impregnation ratio are the important parameters affecting the characteristics of the activated carbons produced [14]. The number of experimental runs from the central composite design (CCD) for the three variables consists of eight factorial points, six axial points, and six replicates at the centre points indicating that altogether 20 experiments were required, as calculated from (2):

$$N = 2^n + 2n + n_c = 2^3 + 2 \times 3 + 6 = 20, \tag{2}$$

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

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. Each response (Y_i) for carbon yield and MB removal 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 [15] (3):

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \sum b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j, \tag{3}$$

where Y is the predicted activated carbon yield or MB removal 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 or MB removal variables [16].

The activated carbon was derived from these precursors by physiochemical activation method which involved the use of KOH treatment and followed by gasification with CO_2. The parameters involved in the preparation were varied using the response surface methodology (RSM). The three variables studied were x_1, activation temperature, x_2, activation time, and x_3, KOH/char impregnation ratio (IR).

The most important characteristic of an activated carbon is its adsorption uptake or its removal capacity which is highly influenced by the preparation conditions. Besides, activated carbon yield during preparation is also a main concern in activated carbon production for economic feasibility. Therefore, the responses considered in this study were Y_1 activated carbon yield, Y_2 removal of MB.

2.5. Activated Carbon Yield. The experimental activated carbon yield was calculated based on the following equation (4):

$$\%\ \text{Yield} = \frac{w_c}{w_o} \times 100, \tag{4}$$

Table 1: ANOVA for response surface quadratic model for BPAC yield.

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	16.08	9	1.79	13.5	0.0001
X_1	0.16	1	0.16	1.28	0.2839
X_2	0.84	1	0.84	6.66	0.0274
X_3	8.51	1	8.51	67.89	<0.0001
X_1^2	0.24	1	0.24	1.90	0.1979
X_2^2	4.13	1	4.13	32.93	0.0002
X_3^2	2.88	1	2.88	22.95	0.0007
X_1X_2	0.080	1	0.080	0.64	0.4430
X_1X_3	0.080	1	0.080	0.64	0.4430
X_2X_3	0.000	1	0.000	0.000	1.0000

Table 2: ANOVA results for MB removal by BPAC.

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	1843.81	9	204.87	14.77	0.0001
X_1	*414.38*	*1*	*414.38*	*29.87*	0.0003
X_2	*0.83*	*1*	*0.83*	*0.060*	0.8119
X_3	*1002.34*	*1*	*1002.34*	*72.25*	0.0001
X_1^2	*16.84*	*1*	*16.84*	*1.21*	0.2964
X_2^2	*0.56*	*1*	*0.56*	*0.040*	0.8448
X_3^2	*164.55*	*1*	*164.55*	*11.86*	0.0063
X_1X_2	*220.50*	*1*	*220.50*	*15.89*	0.0026
X_1X_3	*0.50*	*1*	*0.50*	*0.036*	0.8532
X_2X_3	*32.00*	*1*	*32.00*	*2.31*	0.1598

Table 3: Some properties of the MB used.

Properties	
Chemical formula	$C_{16}H_{18}ClN_3S{\cdot}3H_2O$
Molecular weight	373.9 g/mol
Type	Basic dye
Solubility	Soluble in water
Solution pH	6.5
Wave length	668 nm

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

2.6. Adsorption Studies. Batch adsorption was performed in 20 sets of 250 mL Erlenmeyer flasks. In a typical adsorption run, 100 mL of methylene blue solution with initial concentration of 100 mg/L was placed in a flask. 0.30 g of the prepared activated carbon (BPAC), with particle size of 2 mm, was added to the flask and kept in an isothermal shaker (120 rpm) at 30°C until equilibrium was attained. The concentrations of dye solution before and after adsorption were determined using a double-beam UV-vis spectrophotometer (UV-1700 Shimadzu, Japan). The maximum wavelength of the methylene blue was found to be 668 nm. The percentage removal of dye at equilibrium was calculated by the following equation (5):

$$\%\ \text{removal} = \frac{(C_o - C_e)}{C_o} \times 100, \quad (5)$$

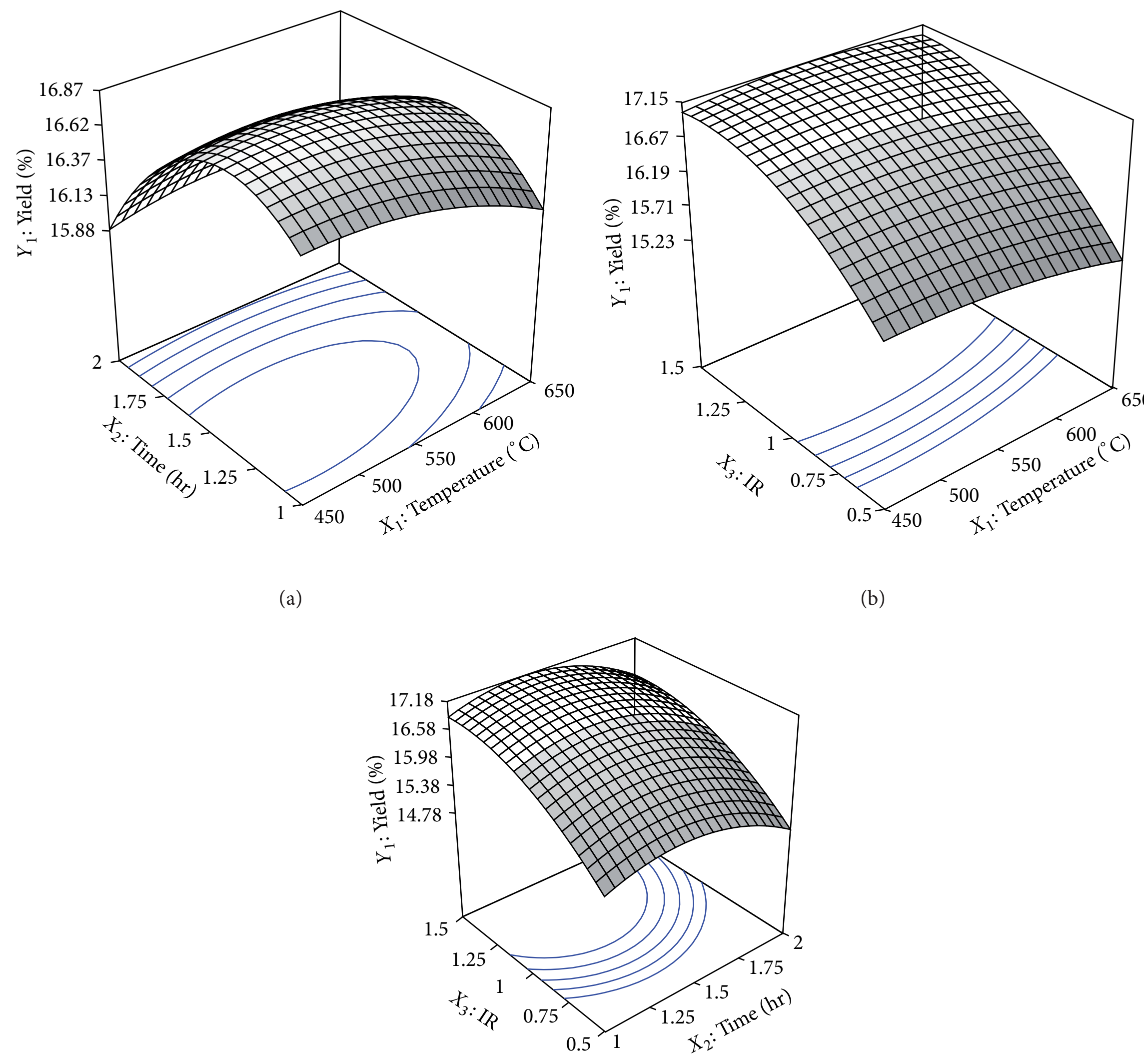
where C_o and C_e (mg/L) are the concentration of dye at initial and at equilibrium, respectively [17].

3. Results and Discussion

3.1. SEM and BET Analysis. The surface morphology of the prepared activated carbon was examined using scanning electron microscope (Model Leo Supra 50VP Field Emission, UK). The surface of activated carbon prepared contains a well-developed pores where there is a good possibility for dye to be absorbed into the surface of the pores.

The Brunauer-Emmett-Teller (BET) surface area and the average pore diameter were 535 m^2/g and 2.96 nm, respectively, using Micromeriticsue (Model ASAP 2020, USA).

3.2. Preparation of Pomegranate Trees Branches Activated Carbon Using DOE. The complete design matrix for the yield response of activated carbon prepared from branches of pomegranate trees (BPAC) with the removal of methylene blue solution from the experimental works include 20 runs, five runs from them at the center point were conducted to



(c)

Figure 1: Three-dimensional response on the yield of BPAC, (a) the variables activation temperature and activation time, (b) the variables activation temperature and IR, and (c) activation time and IR.

determine the experimental error and the reproducibility of the data.

The yield of activated carbon and the removal of methylene blue were influenced not only by the preparation variables but also depending on the type and nature of the original precursors as different precursors would have different physical and chemical characteristics.

3.3. Pomegranate Trees Branches Activated Carbon Yield. The experimental data revealed that the activation time have the greatest effect on the BPAC yield response and gave the highest F value of 13.5. The information presented in Table 1 gave indication that activation time and IR have effect on the activated carbon yield. The quadratic effect of activation time and IR on the yield of BPAC was higher compared to the activation temperature on the same response. It appears that the interaction between activation temperature and activation time have more effect on the BPAC yield.

Figures 1(a), 1(b), and 1(c) show the three-dimensional response and the interaction effects between the parameters considered on the yield of BPAC. Figure 1(a) depicts the effect of activation temperature and activation time on the response with IR being fixed at zero level (IR = 1.5). Figure 1(b) depicts the effect of activation temperature and IR on the same response with activation time fixed at zero level (time = 1.4), while Figure 1(c) depicts the effect of activation time and IR on the same response with activation temperature fixed at zero level (temperature = 620°C).

In general, the BPAC yield was found to decrease with increasing activation temperature, activation time, and chemical impregnation ratio. The increase in activation temperature would increase the removal of volatiles and impurities from the sample due to thermal decomposition and carbon monoxide emission via C-CO_2 reaction, this resulted into a decrease in sample weight [16]. The development of porosity of the activated carbons by KOH activation

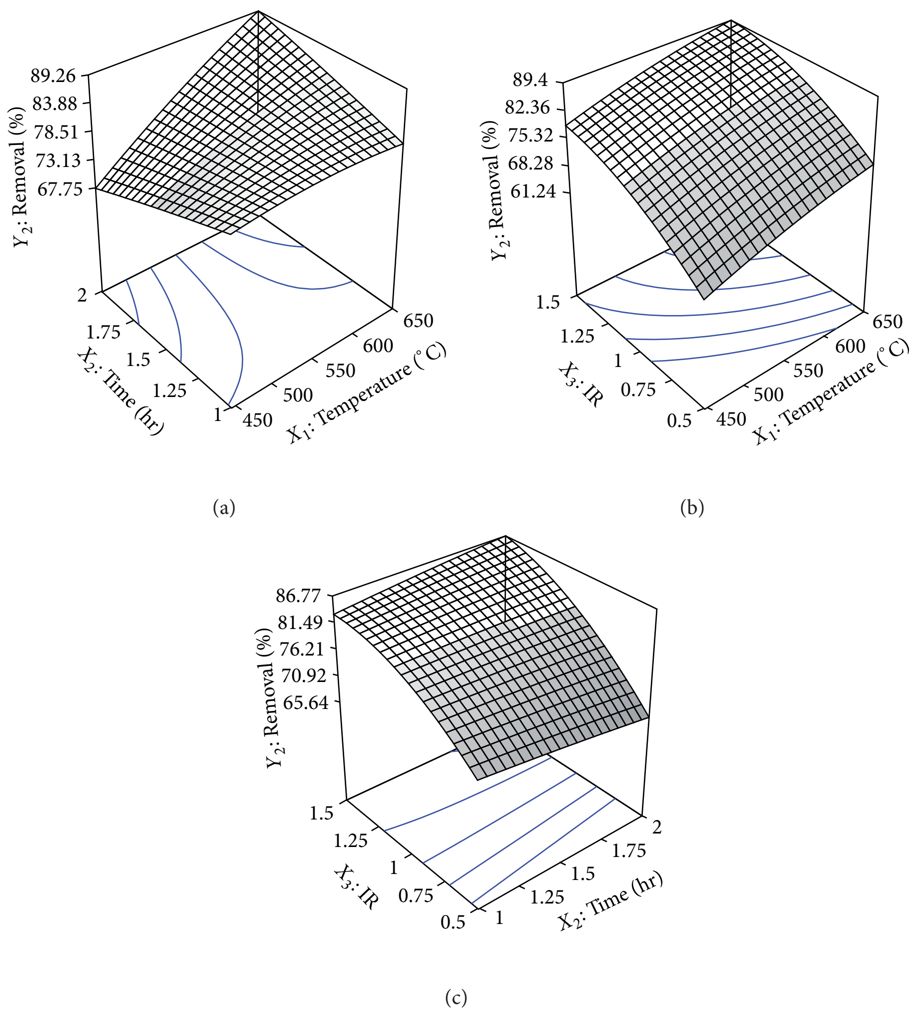


Figure 2: Three-dimensional response between the variables activation temperature, time and IR for the removals of methylene blue onto BPAC, (a) the variables activation temperature and activation time, (b) the variables activation temperature and IR, and (c) activation time and IR.

is associated with gasification reaction. It is assumed that KOH is reduced to metallic potassium during the preparation process. The yield was strongly affected by the chemical impregnation ratio where an increased impregnation ratio decreased the yield and the carbon burn off increased. This was because when higher impregnation ratio was used, the weight losses were due to increase of volatile products release as a result of intensification in the dehydration and elimination reactions [17, 18].

3.4. Methylene Blue Removal onto Prepared Activated Carbon. The experimental values obtained for the removal of methylene blue and its response (Table 2) which gave indication that revealed that the activation temperature and time have significant effects, while IR have the significant quadratic effect. The interaction effect between activation temperature with activation time was significant. However, the interaction effect between activation temperature with IR and between activation times with IR were insignificant.

Figures 2(a), 2(b) and 2(c), show the three-dimensional response and the interaction effects between the variables activation temperature, activation time, and IR on the MB removal. It would be observed from these figures that the removal of MB on BPAC generally increase with increase of activation temperature and IR.

3.5. Optimization of Operation Parameters. In order optimize the preparation conditions for activated carbon used for methylene blue removal, the targeted criteria was set as maximum values for the two responses of activated carbon yield (Y_1) and MB removal (Y_2) while the values of the three variables (activation temperature, activation time, and IR) were set within the range of values studied. It was found that the optimum preparation activation temperature, activation time, and IR needed were 620.5°C, 1.4 h, and 1.5, respectively.

4. Conclusion

Branch pomegranate tree were used as precursor to prepare mesoporous-activated carbon with high surface area, sufficient yield of carbon, and high dye removal. A central composite design was conducted to study the effects of three activated carbon preparation variables, which were the activation temperature, activation time, and chemical impregnation ratio on the activated carbon yield and the removal of methylene blue. Through analysis of the response surfaces derived from the models, the BPAC yield was found to decrease with increasing activation temperature, activation time, and chemical impregnation ratio. It was found that the removal of methylene blue increases with the increasing of activation temperature and IR. The optimum conditions to prepare BPAC were obtained using 620°C activation temperature, 1.4 h activation time, and 1.5 KOH: char impregnation ratio.

References

[1] B. H. Hameed, I. A. W. Tan, and A. L. Ahmad, "Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology," *Journal of Hazardous Materials*, vol. 158, no. 2-3, pp. 324–332, 2008.

[2] B. H. Hameed, A. T. M. Din, and A. L. Ahmad, "Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies," *Journal of Hazardous Materials*, vol. 141, no. 3, pp. 819–825, 2007.

[3] A. Demirbas, "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review," *Journal of Hazardous Materials*, vol. 167, no. 1–3, pp. 1–9, 2009.

[4] I. A. W. Tan, B. H. Hameed, and A. L. Ahmad, "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon," *Chemical Engineering Journal*, vol. 127, no. 1–3, pp. 111–119, 2007.

[5] Rajeshwarisivaraj, S. Sivakumar, P. Senthilkumar, and V. Subburam, "Carbon from Cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution," *Bioresource Technology*, vol. 80, no. 3, pp. 233–235, 2001.

[6] W. T. Tsai, C. Y. Chang, M. C. Lin, S. F. Chien, H. F. Sun, and M. F. Hsieh, "Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation," *Chemosphere*, vol. 45, no. 1, pp. 51–58, 2001.

[7] B. S. Girgis and A. N. A. El-Hendawy, "Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid," *Microporous and Mesoporous Materials*, vol. 52, no. 2, pp. 105–117, 2002.

[8] A. H. El-Sheikh, A. P. Newman, H. K. Al-Daffaee, S. Phull, and N. Cresswell, "Characterization of activated carbon prepared from a single cultivar of Jordanian Olive stones by chemical and physicochemical techniques," *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 1, pp. 151–164, 2004.

[9] F. C. Wu, R. L. Tseng, and R. S. Juang, "Comparisons of porous and adsorption properties of carbons activated by steam and KOH," *Journal of Colloid and Interface Science*, vol. 283, no. 1, pp. 49–56, 2005.

[10] S. Senthilkumaar, P. R. Varadarajan, K. Porkodi, and C. V. Subbhuraam, "Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies," *Journal of Colloid and Interface Science*, vol. 284, no. 1, pp. 78–82, 2005.

[11] J. M. Salman and B. H. Hameed, "Removal of insecticide carbofuran from aqueous solutions by banana stalks activated carbon," *Journal of Hazardous Materials*, vol. 176, no. 1–3, pp. 814–819, 2010.

[12] D. C. Montgomery, *Design an Analysis of Experiments*, John Wiley & Sons, New York, NY, USA, 2001.

[13] R. Azargohar and A. K. Dalai, "Production of activated carbon from Luscar char: experimental and modeling studies," *Microporous and Mesoporous Materials*, vol. 85, no. 3, pp. 219–225, 2005.

[14] A. Baçaoui, A. Yaacoubi, A. Dahbi et al., "Optimization of conditions for the preparation of activated carbons from olive-waste cakes," *Carbon*, vol. 39, no. 3, pp. 425–432, 2001.

[15] N. F. Zainudin, K. T. Lee, A. H. Kamaruddin, S. Bhatia, and A. R. Mohamed, "Study of adsorbent prepared from oil palm ash (OPA) for flue gas desulfurization," *Separation and Purification Technology*, vol. 45, no. 1, pp. 50–60, 2005.

[16] M. K. B. Gratuito, T. Panyathanmaporn, R. A. Chumnanklang, N. Sirinuntawittaya, and A. Dutta, "Production of activated carbon from coconut shell: optimization using response surface methodology," *Bioresource Technology*, vol. 99, no. 11, pp. 4887–4895, 2008.

[17] I. Pavlovic, C. Barriga, M. C. Hermosín, J. Cornejo, and M. A. Ulibarri, "Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite," *Applied Clay Science*, vol. 30, no. 2, pp. 125–133, 2005.

[18] I. A. W. Tan, A. L. Ahmad, and B. H. Hameed, "Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology," *Chemical Engineering Journal*, vol. 137, no. 3, pp. 462–470, 2008.