Optimisation of durian peel based activated carbon preparation conditions for dye removal

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ABSTRACT:

Agricultural wastes are considered to be a very important feedstock for activated carbon production as they are renewable sources and low cost materials. This study present the optimize conditions for preparation of durian peel activated carbon (DPAC) for removal of methylene blue (MB) from synthetic effluents. The effects of carbonization temperature (from 673K to 923K) and impregnation ratio (from 0.2 to 1.0) with potassium hydroxide KOH on the yield, surface area and the dye adsorbed capacity of the activated carbons were investigated. The dye removal capacity was evaluated with methylene blue. In comparison with the commercial grade carbons, the activated carbons from durian peel showed considerably higher surface area especially in the suitable temperate and impregnation ratio of activated carbon production. Methylene blue removal capacity appeared to be comparable to commercial products; it shows the potential of durian peel as a biomass source to produce adsorbents for waste water treatment and other application. Optimize condition for preparation of DPAC determined by using response surface methodology was at temperature 760 K and IR 1.0 which resulted the yield (51%), surface area (786 m^2/g), and MB removal (172 mg/g).

Keywords: *Water treatment, durian shell, activated carbons, adsorption, surface area.*

1. INTRODUCTION

Water contamination by dye is a major concern for wastewater treatment, especially industrial wastewater such as textile, leather, paper, plastics [1] It is predicted that more than 100,000 commercially available dyes with over 7×10^5 tones of dyestuff produced annually [2]. To remove dyes from wastewater, one of the most effective techniques is adsorption by activated carbon. However, owing to its expensive price, the use of activated carbon for removal of color from wastewater is limited. For the aim of reducing wastewater treatment costs, therefore, the development of activated carbon

from no-cost or waste materials acquired locally is an interesting option.

A large variety source of carbonaceous materials have been used for the production of activated carbon such as coal [3, 4], coconut shell [5], sawdust [6], jute stick [7], corn cob [8], kenaf [9], rice husk [10]. Durian (Durio zibethinus Murray) is one of the important seasonal fruits in tropical Asia. The durian is distinctive for its large size, unique odor, and formidable thorn-covered husk. Direct disposal of durian peel can cause social and environmental problems since agricultural waste is already in excess amount and expected to increase in the future. Therefore several attempts have been made in order to add more value to durian peel and one of them is to convert it to activated carbon. However, there are very few studies in the production and application of activated carbon from durian peel.

Activated carbon is generally obtained using two main steps, e.g. carbonization of the raw materials below 1000^{o}C in an inert atmosphere and activation. Activated carbon can be basically obtained by physical or chemical activation [11]. Activated carbon synthesised from physical activation has wider pore size distribution and a more mesoporous structure compared to that derived from chemical activation [12]. But chemical activation offers several advantages because it is carried out in a single step, combining carbonization and activation, performed at lower temperature.

In this study, the admixed method of physical and chemical process to produce activated carbon derived from durian peel was applied. The response surface methodology (RSM) was used for optimization of DPAC preparation parameters including activation temperature (T) and impregnation ratio (IR). The response functions were used to optimize included DPAC yield, surface area and amount of adsorbed dye.

2. MATERIALS AND METHODS

Preparation of activated carbon

Durian peels were collected from local fruit stores in Ho Chi Minh city, washed with distilled water many times in order to remove dust and other inorganic impurities. After that it was cut into approximately 1cm x 1cm size and dried at 110^{o}C for 24 h to reduce its moisture content. The dried durian peels were grounded in hammer mill and then stored in desiccators to prevent it from moisture.

Potassium hydroxide (KOH, 94%) used as chemical impregnation agent were purchased from Sigma–Aldrich. For pre-treatment using chemical activating agent, 50g of dried durian peel was mixed with KOH solution (50%) with impregnation determined mass ratio of chemical activating agent to durian peel in the round bottle flask (250ml). During the impregnation period, the mixture was stirred at 200 rpm for 5h at room temperature (around 27^{o}C). The resulting slurry was poured onto porcelain disc and dried at 110^{o}C for 24h. The dried product was stored in desiccators for the carbonization step.

The resulting samples were carbonized in an electric furnace (Naber Therm, Germany) under nitrogen atmospheric (800 ml/min) with heating from room temperature (27^{o}C) until the desired temperature. The rate of heating was 5^{o}C/min. Then activation with CO_2 (800 ml/min) took place. Samples were held at desired temperature for 1 h before cooling down under nitrogen flow (400 ml/min). Many studies found that the activation time does not cause significant change on the activated carbon [13,14]. Therefore, the activation time was chosen 1h. The samples were grounded in micro hammer mill until it became powder (40/60 mesh) and were added to a beaker and treated with HCl 2M solution for 24 h. Consecutively, carbon powders were repeatedly washed with cool distilled water until pH of

solution reach 6.5 – 7.0. Then, the samples were dried at 110°C for 3h and stored in desiccators.

Characterization of activated carbon

The pore structural analysis of the prepared activated carbon was carried out by nitrogen adsorption at 77.3 K using Nova 2200E (Quantachrome Nova, USA). The Brunauer–Emmett–Teller (BET) surface area, pore radius and pore volume of the activated carbons were determined by application of the Brunauer–Emmett–Teller and Dubinin–Asthakov (DA) analysis software available with the instrument, respectively.

Adsorption equilibrium studies

Basic dye used in this study was methylene blue (MB) purchased from Sigma–Aldrich and it was used as received without further purification. MB has a chemical formula of $C_{16}H_{18}$ N_3SCl, with molecular weight of 319.86 g/mol. MB was chosen in this research because of its wide application and known strong adsorption into solids. The batch adsorption experiments were performed in erlenmeyer flasks (250ml) containing 4 -12 mg of the prepared activated carbon and 100 ml of methylene blue solutions with initial concentrations of 5 mg/l. The mixture was kept in an isothermal shaker at 270C for 24h with an agitation speed of 120 rpm. The concentration of MB dye solution was measured using a double beam UV–Vis spectrophoto meter (UV-VIS18-1815-01-0001, England) at 668 nm. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)}{w} V$$

where C_0 - the liquid-phase concentrations of dye initially (mg/l)

C_e - the liquid-phase concentrations of at equilibrium (mg/l)

V - the volume of the solution (l)

W - the mass of dry adsorbent used (g).

Experimental design

In this study, the respond surface with central composite design was utilized to evaluate the main and interaction effects of the factors: Activated temperature T (X_1) and impregnation ratio (IR). (X_2) on the DPAC yield (Y_1) , DPAC surface area (Y_2) and amount of MB adsorbed into the DPAC (Y_3). The complete model is based on the simultaneous variation of two factors at two levels with four experiments as the repeatability of the measurements at the center of the experimental domain implying the running of 12 trials. All factors and levels tested were reported in Table 1. The experimental data were fitted with quadratic order with interactions of polynomial response surface models, which have the following form:

$$Y = b_0 + \sum_i b_i X_i + \sum_{ii} b_{ij} X_i X_j \quad (1)$$

With i,j=1, 2

Where Y is the estimated response, X_i is the scaled independent process variable (−1=low level, 0=central level and +1=high level) and the coefficients b_0, b_i, b_{ii}, b_{ij} characterize respectively the constant, the linear and quadratic effects of the variable X_i and the interactions between X_i and X_j. To define these coefficients, it is required a star point at two levels in every variable X_i (+=1.414 and -=-1.414). Regression analysis of the data was carried out within a statistical design package ('Design-Expert' version 8.0.3, Stat Ease, Inc,).

Table 1. Factors and levels tested for the designed experiment

Xi (i=1,2,3) coded variable	Z1	Z2
	T (K)	IR (-)
+1	923	1.0
-1	673	0.2
0	798	0.6
+=1.414	975	1.17
-=-1.414	621	0.03

2.5 Desirability Function

The approach to optimization of multiple responses is to utilize the simultaneous optimization technique popularized by Derringer, G., and Suich, R., [15]. It is one of the most widely used methods in industry which is based on the idea that the "quality" of a product or process that has multiple quality characteristics, with one of them outside of some "desired" limits, is completely unacceptable. Their procedure makes use of desirability functions. The common approach is to first transform each response y_i into an individual desirability function $d_i(y_i)$ that varies over the range 0 $d_i(y_i)$ 1, where it takes a range of between 0 and 1, and increases as the corresponding response value becomes more desirable.

In this study, the target is Larger Better (LB). Therefore, the objective is , $\max_x \hat{y}_i(\hat{\theta}; x)$,

$$d_i(\hat{y}_i) = \begin{cases} 0 & if\ \hat{y}_i(x) \le L_i \\ \left(\dfrac{\hat{y}_i(x) - L_i}{T_i - L_i}\right)^r & if\ L_i \le \hat{y}_i(x) \le T_i \\ 1 & if\ \hat{y}_i(x) > T_i \end{cases}$$

ıates of polynomial regression coefficients obtained by least square method. The L_i is lower acceptable values of y_i, while T_i is target values desired for i^{th} response, where $L_i<T_i$. At this point, r is the parameters that determine the shape of $d_i(y_i)$. A value of r=1 means that the desirability function is linear, r>1 means that the desirability function is convex, more importance should be attached to close with the target value, and when the shape of the $d_i(y_i)$ is concave when the value is 0<r<1 which means less importance to be attached.

3. RESULTS AND DISCUSSION

Experimental results

The different formulations of the factorial design consisted of all possible combinations of two factors at all levels and were conducted in a fully randomized order. The face-centered design was used to evaluate both the main and the interaction effects of the operating conditions on the DPAC process. To determine the experimental error, the experiment at the centre point was replicated four times on different days. The matrix of the experiments and the response results for every experiment are listed in Table 2, and sorted by standard order (StO) for easier comparison. The highest amount of the DPAC yield was 67% obtained at the temperature 621 K and IR 0.6. Whilst the highest DPAC surface area and amount of MB adsorbed were 880 m^2/g and 225 mg/g and 225, respectively which was obtained at temperature 798 K and IR 1.2. It illustrates the complicated affect of operating condition on the yield and properties of DPAC.

Table 2. Experimental matrix and values of observed responses

StO	Z1	Z2	Y1	Y2	Y3
1	673	0.2	63.25	553.25	88.25
2	923	0.2	46.32	505.31	83.75
3	673	1.0	57.85	654.51	116.24
4	923	1.0	43.36	680.38	135.18
5	621	0.6	67.25	425.16	71.24
6	975	0.6	41.35	445.75	78.65
7	798	0.0	52.43	750.68	140.31
8	798	1.2	43.12	880.21	225.36
9	798	0.6	46.26	804.35	170.08
10	798	0.6	46.58	815.64	171.21
11	798	0.6	46.83	812.52	170.92
12	798	0.6	45.97	807.24	171.68

Statistical data analysis

Analysis of variance (ANOVA)

For the statistical analysis of experimental results, center method was used to calculate the

estimated coefficients of the polynomial functions of response surfaces for the DPAC yield (Y_1), DPAC surface area (Y_2) and amount of MB adsorbed into the DPAC (Y_3). The analysis of variance (ANOVA) is presented in Table 3 for three response functions.

Table 3. ANOVA for response surface quadratic model

Model	**Sum of Squares**	**Mean Square**	**R Squared**	**F Value**	**p-value Prob > F**	
DPAC yield (Y_1)	760	152	0.984	75	< 0.0001	significant
DPAC surface area (Y_2)	276732	55346	0.989	112	< 0.0001	significant
amount of MB adsorbed (Y_3)	24501	4900	0.951	23	0.0007	significant

The analysis results showed that, three respond functions with quadratic model were statistically significant. The values of p-value or "Prob > F" are < 0.05 at 95% confidence. Furthermore, the Models F-value of 75, 112, 23 imply the models are significant. The polynomial regression models were in good agreement with the experimental results with the coefficients of determination from 0.95 to 0.98. The fit of the empirical models also can be seen clearly the Fig. 1 a,b,c of the predicted value versus the experimental value of the three functions.

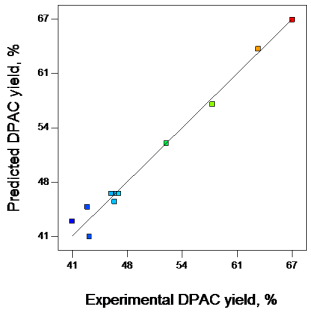

Figure 1.a. Predict versus experimental yield of DPAC

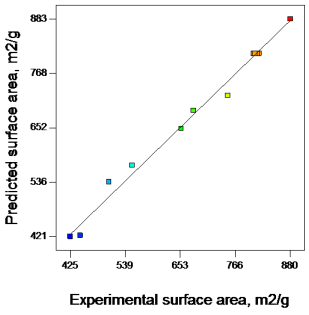

Figure 1.b. Predict versus experimental surface area of DPAC

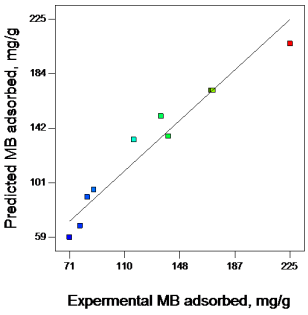

Figure 1.c. Predict versus experimental MB adsorbed

Effect of operation conditions on the yield of activated carbon

For the production of commercial activated carbons, relatively high product yields are expected. The yield of activated carbon depended on the carbonization temperature of the raw materials. In addition pre-treatment with different amount of KOH plays an important role on the yield of product. Fig. 1a, b, c describes the effect of carbonization temperature and pre-treatment with different IR on the yield of activated carbon.

In the response surface methodology, the effects of factors on the response functions are determined by the value of coefficient of coded factor and their significance. The great value of coefficient illustrates the high effect of the factor

on the response function and Values of "Prob > F" less than 0.05 indicate model terms are significant. These values greater than 0.10 indicate the model terms are not significant. The value of coefficients of coded and factual factors of response surfaces yield of active carbon are presented in Table 4.

Table 4. Regression coefficient of polynomial functions of response surfaces of DPAC yield

Factor	Coefficient Estimate		Standard	p-value	
	Coded factor	Factual factor	Error	Prob > F	
Intercept	46.41	290.73	0.71		
A-T	-8.51	-0.52	0.50	< 0.0001	*Significant*
B-IR	-2.69	-24.69	0.50	0.0018	*Significant*
AB	0.61	0.01	0.71	0.4250	
A^2	4.36	0.00	0.56	0.0002	*Significant*
B^2	1.10	6.86	0.56	0.0995	

The results shown in Table 5 that A, B and A^2 are significant model terms ("Prob>F"<0.05). It means the both T and IR affect to the yield of DPAC.

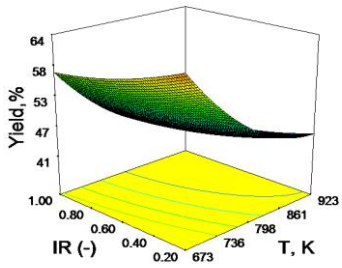

Figure 2. Three-dimensional plot of the yield of DPAC

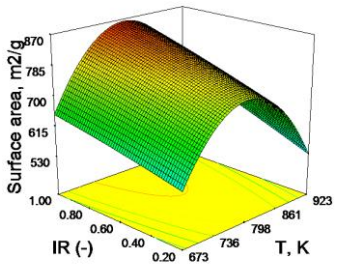

Figure 3. Three-dimensional plot of surface area of DPAC

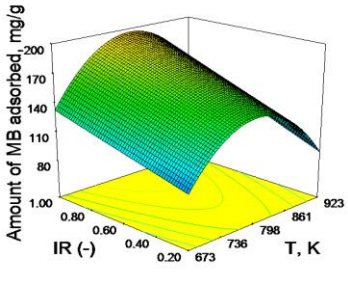

Figure 4. Three-dimensional plot of MB adsorbed

As observed in Fig. 2, activated temperature and IR have quite significant effect on the yield of product. With increasing activation temperature (from 673K to 923K), the yield of activated carbon decrease. It may be explain that the weight loss rate is higher primarily because at high temperature a large amount of volatiles can be easily released. On the case of activated carbon affected by IR, the yield of activated carbon was slightly decreased with the increasing of IR.

Effect of operation conditions on pore structure of DPAC

The nitrogen adsorption–desorption curve provides qualitative information on the adsorption mechanism and porous structure of carbonaceous materials. Identifying the pore structure of activated carbons by nitrogen adsorption at 77.3K is an essential procedure

before applying them onto liquid phase experiments. Table 5 present the summarizing of the value of coefficients of coded and factual factors of response surfaces surface area of DPA.

Table 5. Regression coefficient of polynomial functions of response surfaces of DPAC surface area

Factor	Coefficient Estimate		Standard Error	p-value Prob > F	
	Coded factor	Factual factor			
Intercept	809.94	-7021.28	11.10		
A-T	0.88	19.60	7.85	0.9143	
B-IR	57.44	-120.77	7.85	0.0003	*Significant*
AB	18.45	0.37	11.10	0.1475	
A^2	-194.01	-0.01	8.78	< 0.0001	*Significant*
B^2	-4.02	-25.11	8.78	0.6632	

In the case of DPAC surface area B, and A^2 are significant model terms which is the values of "Prob > F" less than 0.05. Fig. 3 demonstrated the three-dimensional plots of DPAC surface area as a function of the actual process variables based on the empirical model of the process.

The value of coefficients of coded factors and the Fig. 4 illustrated the complicated affect of operating conditions on the DPAC surface area. It can be seen that the DPAC surface area increased whilst the temperature increased at low value but with high operating temperature, the DPAC surface area decreased whilst the temperature increased. Most of the case, the values of DPAC surface area were high at high IR.

Adsorption capacities of DPAC for MB

Adsorption isotherms are usually determined under equilibrium conditions. A series of contact time experiments for MB dye have been carried out at different initial concentration 5 mg/l and at room temperature. Fig. 4 shows the effect of temperature and IR on the adsorption capacities of activated carbon. As shown in Fig. 4 adsorption capacities of activated carbon synthesized with pre-treatment by KOH solution for MB had higher value of adsorption capacities when the IR increasing. In term of the effect of temperature, there was a suitable temperature to produce the high adsorption capacities DPAC.

Table 6. Regression coefficient of polynomial functions of response surfaces amount of MB adsorbed

Factor	Coefficient Estimate		Standard Error	p-value Prob > F	
	Coded factor	Factual factor			
Intercept	170.97	-2021.38	7.28		
A-T	3.11	5.45	5.15	0.5675	
B-IR	24.96	-32.41	5.15	0.0029	*Significant*
AB	5.86	0.12	7.28	0.4518	
A^2	-53.77	0.00	5.76	< 0.0001	*Significant*
B^2	0.17	1.08	5.76	0.9771	

It was shown in Table 6 that in the case of DPAC adsorption capacities, B, A^2 are significant model terms which is the Values of "Prob > F" less than 0.05.

Optimal operating condition and responses

The optimization process was carried out to determine the optimum value of three responses with multivariate factors. In this case, this is difficult to optimize for the whole three responses because interest region of factors is difference. Therefore, when the high yield expected, the surface area and absorbed capacity can be low. Hence, function of desirability was applied to compromise between responses. In this work, desired goals for variables were set in range and the responses were chosen at maximum values. The number solution was done by using a statistical design package ('Design-Expert' version 8.0.3, Stat Ease, Inc,). Optimum DPAC preparation conditions and responses were shown in Table 7 with the values of predicted and experimental response.

Table 7. Optimal operating condition and responses

Optimising condition	T (K)	IR (-)	Yield of DPAC (%)	Surface area (m^2/g)	Amount of MB adsorbed (mg/g)
Prediction	726	1.0	50.81	787.84	173.09
Experimental values	726	1.0	51.23	786.12	172.15

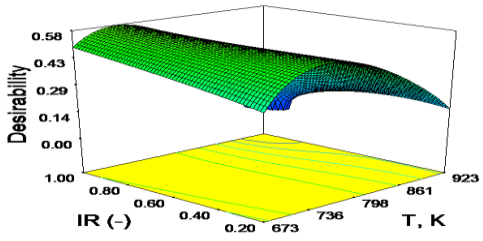

Figure 5. The plot of optimal desirability versus the operating parameters

Fig. 5 showed the plot the values of desirability depend on the operating parameters. It was shown that to reach the nearest optimal condition, low temperature and high IR should be chosen. The optimal condition in the investigated domain was determined to be at temperature 726K and highest IR 1.0. The experimental values were in good agreement with the predictive values from the models with relatively small error. It was proved that the empirical mathematical model which describes the effects of process variables on the studied response can be predicted the response behaviour over the whole experimental field.

4. CONCLUSION

Activated carbon prepared from durian peel by pre-treatment with KOH were performed with various impregnation ratio and activation temperatures. The experimental design approach was used in this study allowed the determination of the significant effects and polynomial functions that describe the effects of operating condition. The optimum DPAC preparation conditions were found to acquire high yield, high surface area of activated carbon and great adsorption capacities for methylene blue.

Tối ưu quá trình than hóa vỏ sầu riêng ứng dụng trong xử lý chất màu

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Viện Kỹ thuật nhiệt đới và bảo vệ môi trường

TÓM TẮT:

Các chất thải nông nghiệp được coi là một nguyên liệu rất quan trọng đối với sản xuất than hoạt tính bởi chúng là các nguồn nguyên liệu tái tạo và vật liệu chi phí thấp. Nghiên cứu này trình bày các điều kiện tối ưu cho quá trình than hóa vỏ sầu riêng làm than hoạt tính để loại bỏ màu xanh methylen từ nước thải tổng hợp. Ảnh hưởng của nhiệt độ than hóa (từ 673K đến 923K) và tỷ lệ KOH (0,2-1,0) lên năng suất , diện tích bề mặt và khả năng hấp thụ chất màu của than hoạt tính được định lượng trong nghiên cứu này. Khả năng loại bỏ chất màu được đánh giá với xanh methylen . So với một số loại than hoạt tính thương mại , than hoạt tính từ vỏ sầu riêng có diện tích bề mặt cao hơn đáng kể đặc biệt là trong điều kiện nhiệt độ và tỷ lệ KOH thích hợp. Khả năng loại bỏ xanh methylen của than hoạt tính từ vỏ sầu riêng cũng tương tự với các sản phẩm thương mại , kết quả này cho thấy tiềm năng của vỏ sầu riêng có thể là một nguồn sinh khối để sản xuất chất hấp phụ nhằm xử lý nước thải và các ứng dụng khác. Điều kiện tối ưu cho quá trình than hóa vỏ sầu riêng được xác định bằng cách sử dụng phương pháp bề mặt đáp ứng được ở nhiệt độ 760 K và tỉ lệ KOH là 1.0; kết quả ở điều kiện tối ưu cho năng suất (51%) , diện tích bề mặt (786 m2 / g) , và khả năng loại bỏ xanh methylen là (172 mg / g) .

Từ khóa: *Xử lý nước thải, vỏ sầu riêng, than hoạt tính, hấp phụ, bề mặt riêng.*

REFERENCES

[1]. H. M´etivier-Pignon, C. Faur-Brasquet, P.L. Cloirec, Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultrafiltration to treat coloured wastewaters, Sep. Purif. Technol. 31,3–11(2003).

[2]. J.W. Lee, S.P. Choi, R. Thiruvenkatachari, W.G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, Dyes Pigments 69, 196-203(2006).

[3]. Jibril, B. Y., R. S. Al-Maamari, G. Hegde, N. Al-Mandhary, and O. Houache, Effects of Feedstock Pre-Drying on Carbonization of KOH-mixed Bituminous Coal in Preparation of Activated Carbon, J. Anal. Appl. Pyrolysis, 80, 277 (2007).

[4]. Pietrzak, R., H. Wachowska, P. Nowicki, and K. Babel, Preparation of Modified Active Carbon from Brown Coal by Ammoxidation, Fuel Process. Technol., 88, 409 (2007).

[5]. Achaw, O. W. and G. Afrane, The Evolution of the Pore Structure of Coconut Shells during the Preparation of Coconut Shell-based Activated Carbons, Microporous Mesoporous Mater., 112, 284 (2008).

[6]. Ismadji, S., Y. Sudaryanto, S. B. Hartono, L. E. K. Setiawan, and A. Ayucitra, Activated Carbon from Char Obtained from Vacuum Pyrolysis of Teak Sawdust: Pore Structure Development and Characterization,'' Bioresour. Technol., 96, 1364 (2005).

[7]. Asadullah, M., M. A. Rahman, M. A. Motin, and M. B. Sultan, Preparation and Adsorption Studies of High Specific Surface Area Activated Carbons Obtained from the Chemical Activation of Jute Stick, Adsorp. Sci. Technol., 24, 761 (2006).

[8]. Cao, Q., K. C. Xie, Y. K. Lv, and W. R. Bao, Process Effects on Activated Carbon with Large Specific Surface Area from Corn Cob, Bioresour. Technol., 97, 110 (2006).

[9]. Cuerda-Correa, E. M., A. Macias-Garcia, M. A. D. Diez, and A. L. Ortiz, Textural and Morphological Study of Activated Carbon Fibers Prepared from Kenaf, Microporous Mesoporous Mater., 111, 523 (2008).

[10]. Deiana, C., D. Granados, R. Venturini, A. Amaya, M. Sergio, and N. Tancredi, Activated Carbons Obtained from Rice Husk: Influence of Leaching on Textural Parameters, Ind. Eng. Chem. Res., 47, 4754 (2008).

[11]. Ahmadpour, A. and D. D. Do, The Preparation of Active Carbons from Coal by Chemical and Physical Activation, Carbon, 34, 471 (1996).

[12]. Azargohar, R. and A. K. Dalai, Steam and KOH Activation of Biochar: Experimental and Modeling Studies, Microporous Mesoporous Mater., 110, 413 (2008).

[13]. Sudaryanto, Y., S. B. Hartono, W. Irawaty, H. Hindarso, and S. Ismadji, High Surface Area Activated Carbon Prepared from Cassava Peel by Chemical Activation, Bioresour. Technol., 97, 734 (2006).

[14]. Diao, Y. L., W. P. Walawender, and L. T. Fan, Activated Carbons Prepared from Phosphoric Acid Activation of Grain Sorghum, Bioresour. Technol., 81, 45 (2002).

[15]. Derringer, G., and Suich, R., Simultaneous Optimization of Several Response Variables, Journal of Quality Technology, 12, 4, 214-219 (1980).