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Optimization of the Fabrication of Banana Peel-Derived Activated Carbon and Application for Cu^{2+} Removal

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ABSTRACT
Activated carbons (ACs) were fabricated from chemically modified banana reel source. The response surface methodology (RSM) was used to assess the effect of the parameters including activation temperature (*T*), impregnation ratio (*IR*) and activation time (*t*) on the AC yield and the percentage of Cu (II) removal. The *RSM*–based two order regression polynomial models were found to be statistically significant by values of the coefficients of determination (R^2) closer than 1.0 and the P-values <0.0001 from analysis of variance (ANOVA). Moreover, from the predicted optimum conditions based on RSM, the confirmation experiments were performed to obtain the actual results: 31.1% and 99.6% for the AC yield and Cu (II) removal, respectively, at *T* = 519°C, *IR* = 1.8 and *t* = 43 min.

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Introduction

Activated carbon (AC), a microcrystalline and non-graphitic material, has been regarded as an efficient and versatile adsorbent because of its large surface area, good adsorption capacity, and highly micro-porous structure [1-2]. However, the high cost of commercial AC produced from traditional coal and wood has prohibited its potential applications. The agricultural by-products have recently played a crucial role in the fabrication of AC because they are the promising renewable and green raw material resources [3–5]. Banana (*Musaceae*) is one of the largest consumed and cultivated plants in some tropical countries. Banana peel is not often used as a raw material or pretreated in prior to be recharged from manufactures, which can lead to the serious environmental problems. Therefore, the use of banana peel for the synthesis of AC can meet both economical solution and environmental requirements.

AC can be fabricated by a route via physical or chemical activation.[4-7]. Physical activation is conducted by a means of carbonization in the presence of CO_2 or steam at high temperatures (700-900°C) [8]. Meanwhile, chemical activation usually refers to the pyrolysis of chemical-impregnated material, which initial precursor or its char residue is soaked with strong dehydrating reagents[9-10]. This process develops new pores with diverse sizes through the oxidative reactions between carbon atoms and activating agent molecules. In the fabrication process, chemical activation by KOH, well-known to be efficient and eco-friendly, is used to enhance porous carbon structure [11]. The purpose of present study is to investigate the effects of production parameters including activation temperature, impregnation ratio and activation time on AC yield and the percentage of Cu^{2+} removal. The predicted optimum conditions from response surface methodology are also applied to verify both the response values.

Experimental

Chemicals and Instruments

All chemicals for this study were commercially purchased from Merck and used as received without any further purification unless otherwise noted. The scanning electron microscope (SEM) was recorded by instrument S4800, Japan and used an accelerating voltage source of 10 kV with a magnification of 7000. The FT-IR spectra were recorded by using the Nicolet 6700 spectrophotometer instrument.

Production of activated carbon

The dried banana peel was first carbonized at 500°C (10°C/min) from the room temperature for 1 h under nitrogen atmosphere. The char resulting was then soaked with KOH solution for 24h. Impregnation ratio (*IR*) between KOH and the char was calculated as follows:

$$IR = \frac{w_{KOH}}{w_{Char}} \qquad (1)$$

where, w_{KOH} and w_{char} are the weight of the anhydrous KOH (g) and the char (g), respectively. The *KOH*–impregnated char samples were heated under nitrogen at various activation temperatures (*T*) for different activation time (*t*). Finally, the receiving *KOH*–activated carbon was repeatedly washed with deionized water and dried at 105 °C for 24 h. The formation yields of AC were calculated as follows:

$$AC\ yield\ (\%) = \frac{w_{AC}}{w_o}.100 \qquad (2)$$

where, w_{AC} and w_O are the weight of AC (g) and dried weight of precursor (g), respectively.

Adsorption batch

The activated carbons (0.25 g) were poured into an Erlenmeyer flask containing 50 mL of aqueous solution of Cu^{2+} 50 ppm. The mixture was agitated until obtaining absorption equilibrium. The residual Cu^{2+} concentrations were determined by AAS and the percentage of Cu^{2+} removal was calculated by the following equation:

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$$Cu^{2+}removal(\%) = \frac{C_o - C_e}{C_o}.100 \quad (3)$$

where, C_o and C_e are initial and equilibrium Cu^{2+} concentrations (ppm), respectively.

Experimental design with RSM

Herein, RSM technique is used to optimize experimental results through second order polynomial regression equations, which describe the mathematical relationship between the response (*y)* and the set of independent values (*x*) by two-order polynomial equations. Central composite design (CCD) is used to establish given 20 experiments (Table 1). Accordingly, five level was investigated including the low (encoded –1), high (encoded +1) and rotatable (encoded ±α). Analysis of variance (ANOVA) is calculated using Design–Expert version 9.0.5.1 (DX9).

Table 1: Independent variables matrix and their encoded levels

No	Independent factors	Code	Levels				
			–α	-1	0	+1	+α
1	Activation temperature (°C)	x_1	332	400	500	600	668
2	Impregnation ratio (-)	x_2	0.16	0.5	1.0	1.5	1.84
3	Activation time (min)	x_3	9.5	30	60	90	110.5

Results and Discussion

Assessment of experimental results with DX9

The experimental and predicted results of AC yield and Cu^{2+} removal efficiency were presented in Table 2. The value range of the actual variables was designed as follows: activation temperature from 332 °C to 668°C, impregnation ratio from 0.16 to 1.84 and activation time from 9.5 min to 110.5 min. The correlation between the responses and variables was described by the following quadratic equations:

Table 2: Matrix of observed and predicted values

No	Variables			Actual (%)		Predicted (%)	
	x_1	x_2	x_3	AC yield	Cu^{2+} removal	AC yield	Cu^{2+} removal
1	400	0.5	30	20.4	92.6	20.6	92.4
2	600	0.5	30	25.3	95.3	24.7	95.8
3	400	1.5	30	27.3	94.8	27.5	95.6
4	600	1.5	30	25.3	99.4	25.1	99.0
5	400	0.5	90	20.0	95.0	20.2	95.8
6	600	0.5	90	25.7	94.5	25.4	94.1
7	400	1.5	90	23.3	97.6	23.8	97.5
8	600	1.5	90	22.7	95.1	22.5	95.7
9	332	1.0	60	19.9	90.7	19.2	90.1
10	668	1.0	60	20.9	91.4	21.6	91.4
11	500	0.16	60	26.5	95.6	26.7	95.4
12	500	1.84	60	30.2	99.8	30.0	99.5
13	500	1.0	9.5	23.3	99.8	23.5	99.5
14	500	1.0	110.5	21.3	99.9	21.1	99.6
15	500	1.0	60	22.0	99.8	23.0	98.8
16	500	1.0	60	23.4	98.1	23.0	98.8
17	500	1.0	60	22.9	97.6	23.0	98.8
18	500	1.0	60	23.6	98.5	23.0	98.8
19	500	1.0	60	22.3	99.5	23.0	98.8
20	500	1.0	60	23.8	99.0	23.0	98.8

$$AC\ yield\ (\%) = 23.0 + 0.71x_1 + 0.98x_2 - 0.73x_3 - 1.65x_1x_2 + 0.28x_1x_3 - 0.83x_2x_3 - 0.91x_1^2 + 1.90x_2^2 - 0.24x_3^2 \quad (4)$$

$$Cu^{2+}removal\ (\%) = 98.8 + 0.40x_1 + 1.21x_2 - 0.02x_3 - 0.01x_1x_2 - 1.29x_1x_3 - 0.39x_2x_3 - 2.83x_1^2 - 0.49x_2^2 + 0.28x_3^2 \quad (5)$$

The multivariable equations from response surface methodology approach allow the identification and assessment of the relative significance of factors on the process to achieve an optimal response. The proposed results of the ANOVA for response surface quadratic models, which determine the individual and interactive effects of three parameters were showed in Table 3. The significance of process can be checked by correlation coefficients (R^2) and *P*–values. In detail, the results consisting of the *P*–values were calculated to be < 0.0001 and respective R^2 coefficients were closer 1.0 revealed the quadratic models are statistically significant (95% confidence level). Moreover, high compatibility of given models continued to be confirmed by the very higher adequate precision (AP) ratios than 4.0 and by the diagnostic plots of predicted values versus actual values, which almost points distributed to the straight line (Figure 1). Otherwise, lack of fit F–test (LOF) values was recognized to be statistically insignificant and hence indicated the models fitted data well.

Effect of variables on the AC yield and Cu^{2+} removal

Figure 2 describing the effects of variables: the activation temperature (x_1), impregnation ratio (x_2) and activation time (x_3) on the formation yield of activated carbon and the percentage of Cu^{2+} removal, by means of a couple of factors, were investigated at various fractional points and the other was immobilized at center point. According to three-dimensional response surface Figure 2A, the AC yield was dependent on both impregnation ratio and activation temperature. Increasing the temperature from 332 °C to 668 °C was unfavorable for the formation of activated carbon while a large amount of KOH activation agent (high *IR*–values) was used to promote the yield. An appropriate range of conditional parameters to maximize the yield of activated carbon was found to be lower levels of temperature and higher levels of impregnation ratio. Referring to observation in Figure 2B, *KOH*–activated carbon fabricated from synthesis strategy of around 500 °C activation temperature could remove almost copper ions from aqueous solution (approximately 99.5 %) regardless of any fluctuation values of impregnation ratio.

Figure 2C revealed the unremarkable influences of activation temperature and activation time on the yield of activated carbon. By changing the wide range of both influential factors (temperature of 332–668 °C and time of 9.5–110.5 min), the result was merely obtained in the narrow range (<5% of yield). According to Figure 2D, the optimum activation temperature was repeatedly recognized at around 500 °C while activation time played a minor role for the process to eliminate Cu^{2+}.

The effects of activation time and impregnation ratio on the activated carbon yield and the removal of Cu^{2+} was plotted in Figure 2E and 2F. According to the response surfaces in Figure 2E, the yield of activated carbon was generally dependent on both activation time and impregnation ratio. As it can be seen that the maximum yield of activated carbon could be reached by decreasing the activation time and increasing the impregnation ratio. The yield was obtained to be about 33% at IR of 1.84 and time of 9.5 min. According to Figure 2F, the Cu^{2+} removal efficiency was insignificantly influenced by preparation conditions. The change of these preparation conditions only fluctuated a narrow range of yield (< 5%). As reported studies, the

Table 3: ANOVA for response surface quadratic models

Response	Source	Sum of squares	Degree of freedom	Mean square	F-value	Prob. > F	Comment
AC yield (%)	Model	126.30	9	14.03	30.17	< 0.0001 [s]	Mean = 23.51
	x_1	6.86	1	6.86	14.76	0.0033 [s]	CV % = 2.9
	x_2	13.19	1	13.19	28.36	0.0003 [s]	R^2 = 0.9645
	x_3	7.27	1	7.27	15.63	0.0027 [s]	$R^2_{(adj.)}$ = 0.9325
	$x_1 x_2$	21.78	1	21.78	46.82	< 0.0001 [s]	AP = 22.384
	$x_1 x_3$	0.61	1	0.61	1.30	0.2807 [n]	
	$x_2 x_3$	5.44	1	5.44	11.71	0.0065 [s]	
	x_1^2	12.04	1	12.04	25.88	0.0005 [s]	
	x_2^2	51.85	1	51.85	111.47	< 0.0001 [s]	
	x_3^2	0.85	1	0.85	1.82	0.2074 [n]	
	Residuals	4.65	10	0.47			
	Lack of Fit	1.99	5	0.40	0.75	0.6207 [n]	
	Pure Error	2.66	5	0.53			
Cu^{2+} removal (%)	Model	157.65	9	17.52	26.41	< 0.0001 [s]	Mean = 96.7
	x_1	2.20	1	2.20	3.31	0.0988 [n]	CV % = 0.84
	x_2	20.09	1	20.09	30.29	0.0003 [s]	R^2 = 0.9596
	x_3	0.0053	1	0.0053	0.0079	0.9308 [n]	$R^2_{(adj.)}$ = 0.9233
	$x_1 x_2$	0.0013	1	0.0013	0.0019	0.9662 [n]	AP = 16.510
	$x_1 x_3$	13.26	1	13.26	19.99	0.0012 [s]	
	$x_2 x_3$	1.20	1	1.20	1.81	0.2081 [n]	
	x_1^2	115.38	1	115.38	173.95	< 0.0001 [s]	
	x_2^2	3.30	1	3.30	4.97	0.0498 [s]	
	x_3^2	1.14	1	1.14	1.72	0.2184 [n]	
	Residuals	6.63	10	0.66			
	Lack of Fit	3.10	5	0.62	0.88	0.5558 [n]	
	Pure Error	3.54	5	0.71			

Note: [s] significant at $p < 0.05$, insignificant at $p > 0.05$. X_1, X_2 and X_3 are the main factors. X_1^2, X_2^2 and X_3^2 are the square factors. X_1X_2, X_1X_3 and X_2X_3 are the interaction factors.

Table 4: Model confirmation

Sample	T (°C)	IR (-)	t (min)	Desirability	AC yield (%)		Cu^{2+} removal (%)	
					Predicted	Tested	Predicted	Tested
AC519	519.0	1.8	43	1.0	30.4	31.1	100.0	99.6

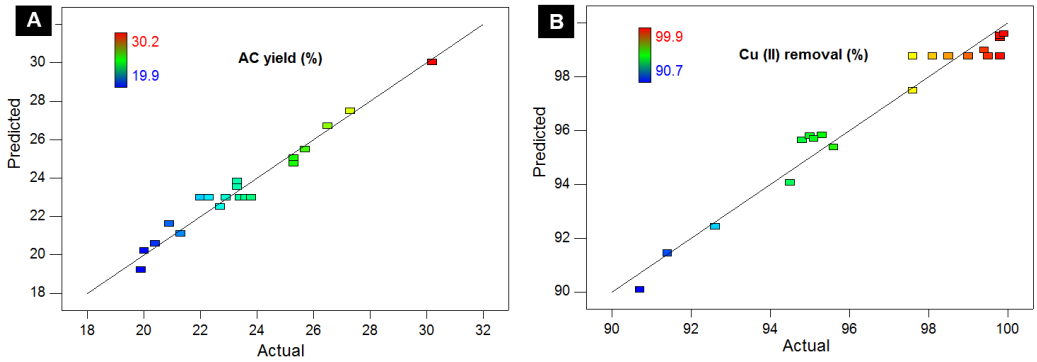

Figure 1: Actual versus predicted plot of regression models of AC yield (A) and Cu^{2+} removal (B)

structural formation of activated carbon must occur at appropriate activation temperature (commonly more than 350 °C), and hence very low temperature can be unfavorable for the fabrication of activated carbon. But the higher temperature could reduce the activated carbon yield. Increasing the percentage of Cu^{2+} removal by increasing *IR*–value for the production of activated carbon can be explained due to chemical agent plays a crucial role in the development of new pore and functional groups, which are essential for absorption of transition metal ions on the surface of the adsorbent material. According to data in Table 4, the predicted optimal conditions based experiment was further conducted to verify the suitability of the proposed models: T = 519°C, IR = 1.8 and t = 43 min.

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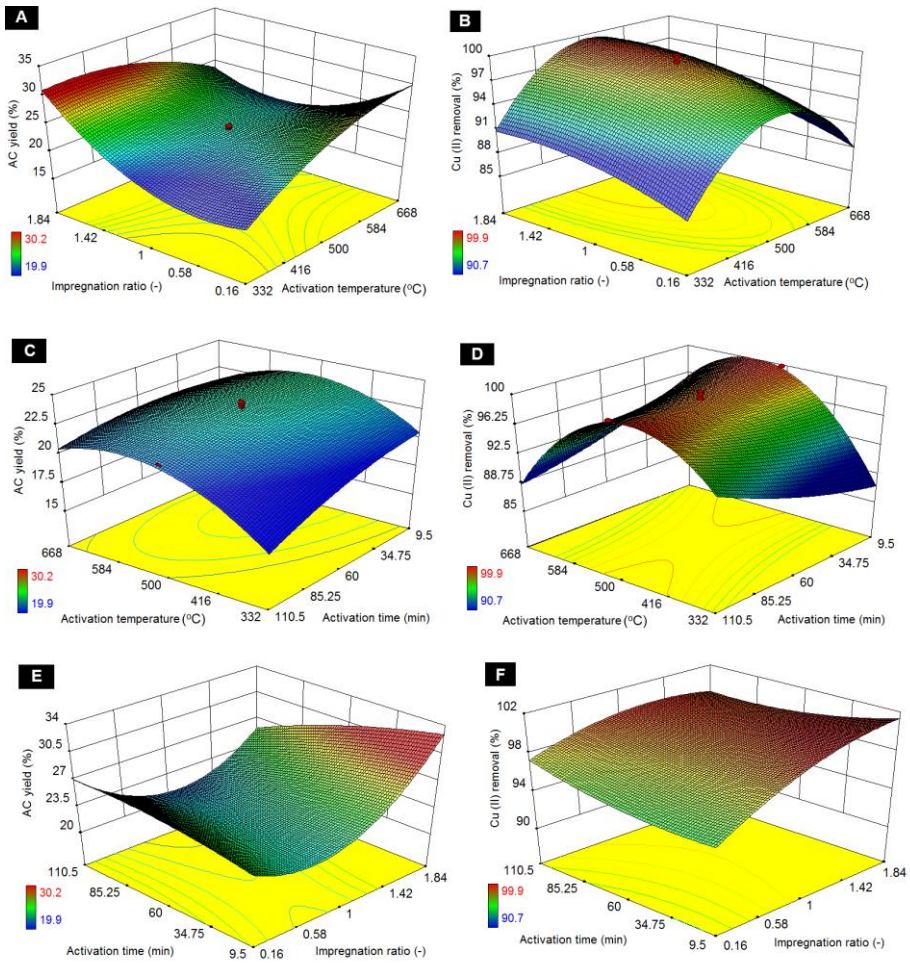

Figure 2: Effect of temperature T, IR and time t = 60 min on the AC yield (A) and Cu^{2+}removal (B); Effect of temperature T, time t, and IR = 1.0 on the AC yield (C) and Cu^{2+} removal (D); Effect of time t, IR and temperature T = 500 °C on AC yield (E) and Cu^{2+} removal (F)

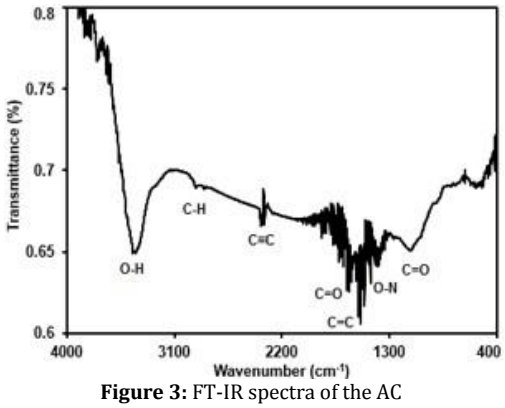

Figure 3: FT-IR spectra of the AC

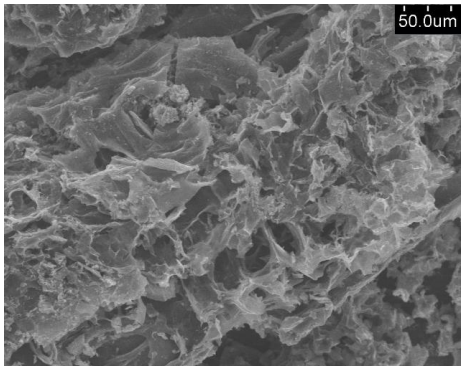

Figure 4: SEM image of the AC

Thereby, the tests for AC yield and Cu^{2+} removal were obtained at 31.1 % and 99.6% which is nearly closed to the predicted values of 30.4 % and 100 %, respectively. These results demonstrate the high compatibility of the proposed models with the experimental data.

Characterization of synthesized activated carbon

The FT–IR spectrum in Fig. 3 indicated the as–synthesized *KOH*–activated carbon possesses a various kind of functional groups on the surface. In detail, the presence of stretching vibration of broadband around 3400 cm^{-1} was attributed to hydroxyl groups (O–H). The existence of the C=O groups in the structure of aldehydes/ketones and O–N asymmetric stretch could be confirmed by shape peaks, which appeared around 1684 cm^{-1} and 1546 cm^{-1}, respectively [12]. Otherwise, the unsaturated bonds such as C=C and C≡C were confirmed by the presence of shape peaks at 1618 cm^{-1} and 2340 cm^{-1}, respectively, while a narrow stretching at around 1712 cm^{-1} could be attributable to C–O stretching vibration on the structure of esters and ethers [13-14]. On the other hand, diagnostic image via SEM analysis provided the data of surface morphology and was presented in Figure 4. It is obvious that the as-synthesized activated carbon has a porous and

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defect structure. This phenomenon can be explained due to the removal of non-carbon elements such as hydrogen, oxygen, and nitrogen released from the surface of char during pyrolysis process resulted in the formation of rigid carbon skeleton with rudimentary pore structure [15].

Conclusions

The highly porous banana peel–derived *KOH*–activated carbon was successfully synthesized and structurally characterized with emergent properties: porous and defect surface, various kind of functional groups essential for the capture of Cu^{2+} ions in aqueous solution. By the use of the *RSM*–based quadratic regression equations, several variables including activation temperature, impregnation ratio and activation time were investigated and the results revealed that both responses including AC yield and removal efficiency Cu^{2+} were strongly influenced by the initial parameters. Moreover, the maximum value of AC yield and Cu^{2+} removal was obtained 31.1% and 99.6%, respectively at T = 519^{o}C, $IR = 1.8$ and t = 43 min. Based on experimental results, a treatment process can be easily designed using banana peel for the fabrication of activated carbon to remove toxic metal ions from the polluted water.

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