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Effect of preparation conditions of activated carbon prepared from rice husk by CO₂ activation for removal of Cu (II) from aqueous solution

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Abstract - The optimal conditions for preparation of rice husk-based activated carbon (RHAC) for the removal of Cu (II) from aqueous solutions were investigated using central composite design (CCD). Based on the CCD, a two-factor-interaction (2FI) and a quadratic models were respectively developed for RHAC yield and percentage of Cu (II) removal. The significant factors on each experimental design response were identified from the analysis of variance (ANOVA). The optimum conditions obtained for preparing RHAC were obtained by using 737°C and 1.82 h for activation temperature and activation time respectively which resulted in 30.22 % of RHAC yield and 11.70 % of Cu (II) removal.

Index Terms - Activated carbon, Cu (II) removal, Central composite design, Optimization, Rice husk

I. INTRODUCTION

Copper is a metal that is used in industries such as plating, mining and smelting, brass manufacture, electroplating and petroleum refining. These industries produce much wastewater and sludge containing Cu (II) ions with various concentrations, which have negative effects on the environment [1]. Copper is also found as a contaminant in food, especially shellfish, liver, mushrooms and nuts [2]. It has been reported that excessive intake of copper by humans may lead to severe mucosal irritation, hepatic and renal damage, widespread capillary damage, capillary damage and central nervous system problems [3]. The World Health Organization recommended a maximum acceptable concentration of Cu (II) in drinking water to be 1.5 mg/l [4]. Therefore, the concentration of this metal must be reduced to a level that satisfies environmental regulations for various water bodies. The most commonly used techniques for removing Cu (II) ion from aqueous solutions include oxidation, reduction, precipitation, membrane filtration, biological process, ion exchange and adsorption. Among those treatment technologies, activated carbon adsorption is preferred used.

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Activated carbon has porous surface structure and high surface area. However, the high cost of commercial activated carbon has led to the development of agricultural waste based activated carbons. Several researchers have studied the production of activated carbon from *Ceiba pentandra* hulls [4], pecan shell [5], hazelnut shell [6], peanut hull [7], almond shell [8], peach stone [9] and sawdust [10].

In this work, an attempt was made to optimize the preparation conditions of activated carbon from rice husk (RH) waste for the removal of Cu (II) ions from aqueous solutions. Utilizing RH in preparing activated carbon will decrease the cost of waste disposal and also convert this waste into value-added products. A standard RSM design called a central composite design (CCD) is suitable in optimizing the effective parameters with a minimum number of experiments, as well as in analyzing the interaction between the variables [11]. The effects of preparation variables; activation temperature and activation time were studied simultaneously to give high responses; RHAC yield and Cu (II) percentage removal from aqueous solution.

II. MATERIALS AND METHODS

A. Materials and RHAC preparation

Rice husk (RH) was obtained from the local rice processing mill in Kepala Batas, Penang, Malaysia. Stock solutions of Cu (II) were prepared by dissolving appropriate amounts of Cu(NO₃)₂·3H₂O (Merck, 99% purity) in deionized distilled water.

RH was washed and dried at 105°C for 24 h to remove the moisture contents. The dried RH was ground and sieved to the size of 1-2 mm before loading in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization step was carried out at 400°C for 30 min under nitrogen (99.99%) flow. The activation step was done using similar reactor as in carbonization step. Once the final activation temperature was reached, the gas flow was switched from nitrogen to CO₂ for different period of time. The sample was then cooled to room temperature under nitrogen flow.

B. Adsorption studies

For batch adsorption studies, 0.3 g of adsorbent were mixed with 100 ml aqueous of Cu (II) solutions with 50 mg/l initial concentration in 13 sets of 250 ml Erlenmeyer flasks. The mixture was agitated at 400 rpm at 30°C until equilibrium

was reached. The concentration of Cu (II) solution was determined using a spectrophotometer (model DR 2010) at wavelength of 560 nm. The percentage removal at equilibrium was calculated as follows:

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

where C_o and C_e are the liquid-phase Cu (II) concentrations at initial state and at equilibrium, respectively.

C. Activated carbon yield

The RHAC yield was calculated as follows :

$$\text{Yield}(\%) = \frac{w_c}{w_o} \times 100 \quad (2)$$

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

D. Design of experiments

The variables studied were activation temperature (x_1) and activation time (x_2). Both variables together with their respective ranges were chosen based on the preliminary studies as given in Table 1.

TABLE 1
INDEPENDENT VARIABLES AND THEIR CODED LEVELS

Variables (factors)	Code	Coded variable levels				
		-α	-1	0	+1	+α
Activation temperature, °C	x_1	537.9	600.0	750.0	900.0	962.1
Activation time, h	x_2	2.00	1.00	2.00	1.00	2.00

The CCD consists of 2^n factorial runs, $2(n)$ axial runs and five center runs, where n is the number of factors. For two variables, 4 factorial points, 4 axial points and 5 replicates at the center points were employed, indicating that altogether 13 experiments for this procedure for the precursor calculated as shown below:

$$N = 2^n + 2n + n_c = 2^2 + 2(2) + 5 = 13 \quad (3)$$

where N is the total number of experiments required. The center points are used to determine the experimental error and the reproducibility of the data. The axial points are located at $(\pm\alpha, 0, 0)$, $(0, \pm\alpha, 0)$ and $(0, 0, \pm\alpha)$ where α (1.414) is the distance of the axial point from center and makes the design rotatable. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factor. The two responses were RHAC yield (Y_1) and Cu (II) removal (Y_2). Each response was used to develop an empirical model which correlated the response to the two preparation variables using a second-degree polynomial equation as given by (4):

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

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

E. Model fitting and statistical analysis

The experimental data were analyzed using a statistical software Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) for regression analysis to fit the second-degree polynomial equation and also for the evaluation of the statistical significance of the equations developed.

F. Characterization of RHAC

Proximate analysis was carried out using thermo gravimetric analyzer (Perkin Elmer TGA7, USA) and elemental analysis was performed using Elemental Analyzer (Perkin Elmer Series II 2400, USA). The surface area, pore volume and average pore diameter of the RHAC were determined by using Micromeritics ASAP 2020 volumetric adsorption analyzer. A 21-point analysis was carried out at 77 K to obtain the nitrogen adsorption isotherm. The surface area of the sample was determined using Brunauer-Emmett-Teller (BET) equation. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the samples was examined using a scanning electron microscope (JEOL, JSM-6460 LV, Japan).

III. RESULTS AND DISCUSSION

A. Development of regression model equation

Table 2 shows the complete design matrixes together with both the response values obtained from the experimental work. Run 9-13 at the center point were conducted to determine the experimental error and the reproducibility of the data.

TABLE 2
DESIGN MATRIX FOR CMS MEMBRANES PREPARATION

Run	Variables		Response	
	Activation temp, x_1 (°C)	Activation time, x_2 (h)	RHAC yield, Y_1 (%)	Cu (II) removal, Y_2 (%)
1	600.00	1.00	26.58	6.90
2	900.00	1.00	18.25	9.85
3	600.00	3.00	24.51	7.50
4	900.00	3.00	15.27	10.27
5	537.87	2.00	31.27	4.50
6	962.13	2.00	15.21	11.90
7	750.00	0.59	23.27	12.10
8	750.00	3.41	19.15	10.28
9	750.00	2.00	21.24	11.29
10	750.00	2.00	20.23	11.10
11	750.00	2.00	21.00	11.32
12	750.00	2.00	20.90	11.21
13	750.00	2.00	21.16	11.30

The RHAC yield and the percentage of Cu (II) removal were found to range from 15.21 to 31.27% and 6.90 to 12.10%, respectively. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant. For response of RHAC yield, two factor interaction (2FI) model was selected as suggested by the software. On the other

hand, for Cu (II) removal, the quadratic model was the best model to correlate the data to the response. The final empirical formula models for the RHAC yield (Y_1) and Cu (II) removal (Y_2) in terms of coded factors are represented by (5) and (6), respectively.

$$Y_1 = 21.39 - 5.04x_1 - 1.36x_2 \quad (5)$$

$$Y_2 = 11.24 + 2.02x_1 - 0.19x_2 - 1.79x_1^2 - 0.29x_2^2 - 0.045x_1x_2 \quad (6)$$

The quality of the model developed was evaluated based on the correlation coefficient (R^2) value. The closer the R^2 value to unity, the better the model as this will give predicted values which are closer to the actual values for the response. The R^2 values for (5) and (6) are 0.982 and 0.945 respectively. These values indicated that 98.2 and 94.5% of the total variation in the RHAC yield and Cu (II) removal respectively were attributed to the experimental variables studied. The R^2 value of 0.982 and 0.945 for (5) and (6) were considered very high, indicating that there was a good agreement between the experimental and the predicted values for carbon yield and the removal of pollutant as suggested by the model.

B. Analysis of variance

F-value from the model implied the significance of the model similarly, the value of Prob > F less than 0.05 indicated that the model terms were significant [12]. Table 3 shows the ANOVA values for linear model for RHAC yield. The prediction of the model is significant with F-value of 86.80 and Prob > F less than 0.0001. In this case, the activation temperature (x_1) and activation time (x_2) were significant to the response. However, the effect of activation temperature was greater than activation time as shown by high F value. The ANOVA data for Cu (II) removal is presented in Table 4.

TABLE 3
ANOVA FOR RESPONSE SURFACE LINEAR MODEL FOR RHAC YIELD

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	217.62	2	108.81	86.80	<0.0001
x_1	202.83	1	202.83	161.80	<0.0001
x_2	14.79	1	14.79	11.80	0.0064
Residual	12.54	10	1.25	-	-

TABLE 4
ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR CU (II) REMOVAL OF RHAC

Source	Sum of squares	Degree of freedom	Mean square	F value	Prob > F
Model	55.33	5	11.07	11.51	0.0029
x_1	32.75	1	32.75	34.06	0.0006
x_2	0.30	1	0.30	0.31	0.5928
x_1^2	22.25	1	22.25	23.14	0.0019
x_2^2	0.60	1	0.60	0.62	0.4561
x_1x_2	0.0081	1	0.0081	0.00842	0.9294
Residual	6.73	7	0.96	-	-

The model F-value of 11.51 and Prob > F of 0.0029 again confirmed that the model was significant. In this case, x_1 , x_1^2 were significant model terms and x_2 , x_2^2 and x_1x_2 were insignificant to the response. From the statistical results obtained, the two models above were found to be adequate to

predict the responses for preparation of RHAC within the range of the variables studied.

C. Activated carbon yield and Cu (II) removal

Figs. 1 and 2 shows the three-dimensional response surface which were constructed to show the effects of variables on the RHAC and Cu (II) removal respectively.

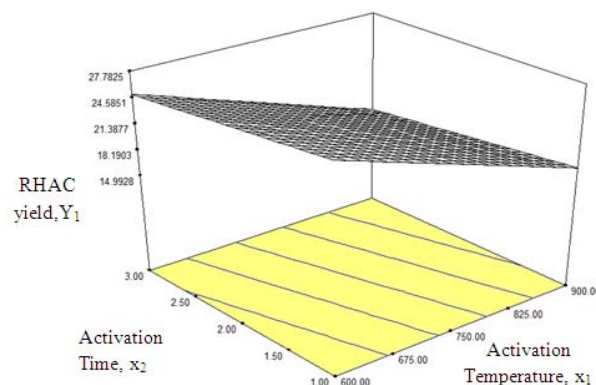


Fig. 1. Three dimensional response surface plot for RHAC yield

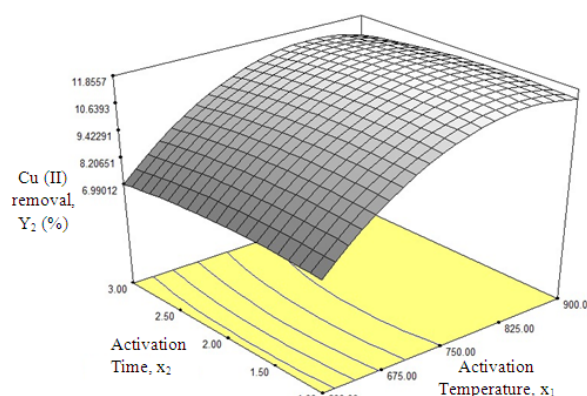


Fig. 2. Three dimensional response surface plot for percentage of Cu (II) removal

Activation temperature imposed greater effect on carbon yield and Cu (II) removal than activation time. The activation temperature is an important parameter in shaping the pore structure of activated carbon. At higher activation temperatures, the removal of volatile matters becomes more extensive, resulting in a lower solid yield [13]. The results obtained agreed with the findings of Hameed et al. [14] and Tan et al. [15] that produced activated carbon from oil palm empty fruit bunches and coconut, respectively. It was observed that Cu (II) removal increases with increases in activation temperature. The highest Cu (II) removal was obtained at the maximum activation temperature within the range of study. By increasing activation temperature, more pores are developed which favors Cu (II) removal [16].

D. Process optimization

One of the main aims of this study was to find the optimum process parameters at which RHAC produced will have a high

carbon yield and a high Cu (II) removal. However, it is difficult to optimize these responses under the same condition because the interest regions of factors are different. When adsorption performance increases, RHAC yield will decrease and vice versa. Therefore, the function of desirability was applied using Design-Expert software in order to reach a compromise between these two responses. In optimization analysis, the target criteria was to set as maximum values for all responses while the values of the variables were set within the ranges being studied. As shown in Table 5, the experimental conditions with the highest desirability were selected and applied to prepare the optimum activated carbon.

TABLE 5: MODEL VALIDATION

Act. temp., x_1 (°C)	Act. time, x_2 (h)	RHAC yield (%)			Cu (II) removal (%)		
		Pred.	Act.	Err. (%)	Pred.	Act.	Err. (%)
737	1.82	31.27	30.22	3.33	12.10	11.70	3.31

The optimum RHAC was obtained by using 737°C and 1.82 h of activation temperature and activation time respectively. The optimum RHAC showed 30.22% RHAC yield and 11.70% Cu (II) removal which were only 3.33 % and 3.31% errors for RHAC yield and Cu (II) removal, respectively. It was observed that the experimental values obtained were in good agreement with the values predicted from the models. Relatively small errors between the predicted and the actual values were observed. This indicated that the models were suitable and sufficient to predict the responses from the operating fixed variables.

E. Activated carbon characterization

The results for proximate and ultimate analysis of the samples are tabulated in Tables 6 and 7, respectively. The raw RH was found to be high in volatile matter and moderate carbon content, indicating the suitability of RH to be used as precursor for activated carbon preparation.

TABLE 6
PROXIMATE ANALYSIS

Sample	Proximate analysis (%)			
	Moisture	Volatile	Fixed Carbon	Ash
Raw RH	4.2	58.0	21.7	16.1
RHAC	2.4	20.9	53.5	23.2

TABLE 7
ELEMENTAL ANALYSIS

Sample	Elemental analysis (%)			
	C	H	N	others ^a
Raw RH	38.1	8.3	0.8	52.8
RHAC	73.8	4.9	0.6	20.7

*Estimated by difference

After undergoing activation process, the volatile matter content decreased significantly whereas the fixed carbon content increased in activated sample. Similar trend was observed for the elemental analysis where the carbon content increased up to 73.8% for RHAC. This was due to the pyrolytic effect at high temperature where most of the organic substances have been degraded and discharged both as gas and liquid tars leaving a material with high carbon purity [15].

The BET surface area, total pore volume and average pore diameter of the prepared activated carbon were found to be 370.75m²/g, 0.385cm³/g and 2.61 nm, respectively. The average pore diameter of 2.61 nm indicates that the RHAC prepared was in the mesopores region. During the activation, CO₂ gas molecules diffuse into the carbon structure thus increases the CO₂-carbon reaction, thereby developing more pores on the sample. From the SEM micrograph, the raw RH surface texture was undulating with very little pores as shown in Fig. 3a. After activation process, pores were developed with homogeneous distribution on the RHAC surface (Fig 3b).

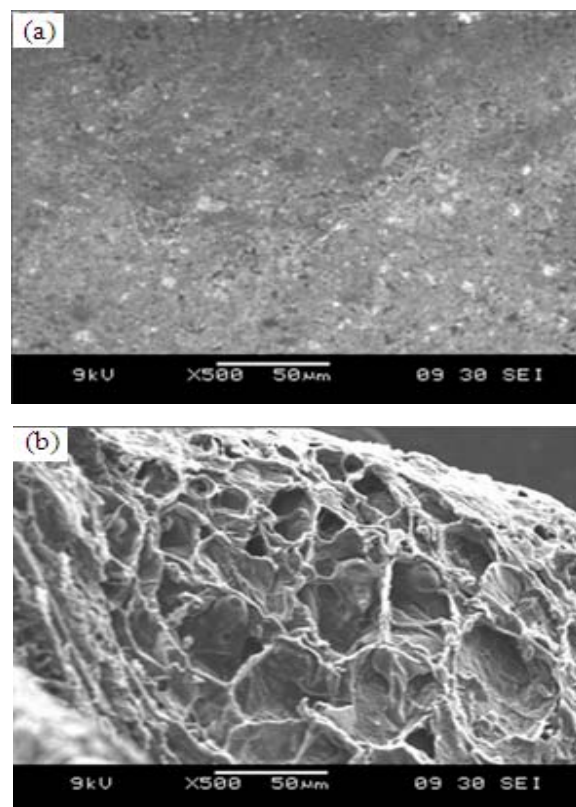


Fig. 3. SEM micrographs; (a) raw RH and (b) RHAC (magnifications: 500x)

IV. CONCLUSIONS

RSM was successfully used to investigate the effects of activation temperature and activation time on the RHAC yield and Cu (II) removal. The optimum RHAC preparation conditions were obtained using 737°C activation temperature and 1.82 h activation time resulting in 30.22% of RHAC yield and 11.70% of Cu (II) removal. Through analysis of the response surface, activation temperature was found to have significant effects on both RHAC yield and Cu (II) removal. The RHAC demonstrated homogeneous type of pores structure with well-developed porosity.

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