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Removal of Cu^{2+} from Aqueous Water by Adsorption onto the Efficient and Recyclable Durian Shell-Derived Activated Carbon

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Abstract. We investigated the use of durian shell-derived activated carbon (DSAC) for the removal of Cu^{2+}. To determine the optimal condition for Cu^{2+} removal, the response surface methodology (RSM) was used to establish a second-order polynomial model with variables such as Cu^{2+} concentration (C_i), adsorbent dosage (d_{DSAC}) and pH. With $R^2 = 0.9847$ and P-value < 0.0001, the model was proved to be statistically significant. The RSM based confirmation test revealed that the removal of Cu^{2+} was maximum (99.6%) at optimal conditions: $C_i = 61.6$ mg/L, $d_{DSAC} = 5.0$ g/L and pH = 5.2. Based on calculated R^2, data fitness for adsorption isotherms were positioned as follows: Langmuir > Tempkin > Freundlich. In other words, monolayer adsorption was the most favorable behavior with maximum capacity of 76.92 mg/g from Langmuir model. Interestingly, DSAC was reused at least five times without a considerable decrease of Cu^{2+} removal efficiency. Therefore, durian shell can be used as a highly effective, reusable and promising raw material to fabricate the activated carbon.

Introduction

Copper is a carcinogenic and non-biodegradable transition metal, which its pollution is originated from fertilizer manufacture, mineral processing industrial effluent, chemical pollutants leaking and tan–house. Some endangered risks such as neurological disorders, respiratory failure, and birth defects are attributable to the long-term accumulative effects of copper pollution. Adsorption is recognized as one of the most effective and promising means of treatment for the removal of copper from contaminated pristine water because of its high performance and outstanding recyclability [1-3].

Among the emergent microcrystalline and non-graphitic substrates, which own a wide range of crucial properties linking with adsorption capacity, such as surface area, and micro–porous structure, activated carbon (AC) has been evaluated as a highly effective adsorbent. Thus, many studies focused on its potential applications for the removal of heavy metals or hazardous synthetic dyes via the adsorption route. However, the structural and chemical characteristics of ACs were proved to be strongly dependent on the carbonaceous resources because the raw materials contain various molecule components, which refer to the functional groups essential for adsorption [4]. Durian is mainly cultivated in the tropical countries and a large amount of its waste shell is directly discarded from manufacturing factories without pre-treatment, which can lead some environmental pollution problems [6]. Admittedly, the strategies aim to take advantage of the locally available durian shell bioresource for the fabrication of energy- and cost-effective AC has been paid much attention of environmental scientists. To obtain the high porosity, durian shell-derived activated carbon (DSAC) can be commonly synthesized by several methods including physical and chemical activation [7]. In physical route, the raw material was carbonized at high temperature under N_2 atmosphere followed by controlled gasification in the presence of CO_2 or steam [4-6]. In chemical activation, strong dehydrating reagents were used to soak with raw materials or its char source.

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Then, chemical-impregnated precursors were pyrolyzed to develop new pores through violent reactions between carbonaceous components and reagent molecules. KOH is considered as an effective and green reagent for activation of raw materials compared with several activation chemicals because of its eco-friendly properties and commercial cost-effectiveness [7].

Herein, we investigated fundamental parameters to optimize the model of Cu^{2+} removal by adsorption onto DSAC. The response surface methodology (RSM) is available on the statistical program Design–Expert 9, allowing to design independent variables matrix and to predict the optimal conditions based on polynomial regression equations. The experimental input consists of variables: initial Cu^{2+} concentration (C_i), the dosage of AC (d_{DSAC}), pH of the solution and the output is the optimized condition, which reveals the maximum percentage of Cu^{2+} removal. Moreover, the synthesized AC was characterized and used to perform the adsorption equilibrium via Langmuir, Freundlich, and Temkin isotherm models. The adsorbent recyclability was also conducted to prove the potential removal of Cu^{2+}.

Experimental Section

Production of Activated Carbon from Durian Shell (DSAC). The durian shell was carbonized at 500 ^{0}C under an N_2 atmosphere. The char was soaked with KOH solution (the weight ratio of the char and KOH was 1:1) for 1 day, then KOH–impregnated char was heated to 600 ^{0}C under an N_2 atmosphere. The sample was repeatedly washed with de-ionized water until filtered water obtained a neutral solution, before slowly dried at 105^{0}C.

Batch Adsorption Experiments. The AC (0.8–9.2 g/L) was poured in 50 mL of Cu^{2+} aqueous solution (8–92 mg/L). After absorption equilibrium obtained, the adsorbent was removed from the mixture. The residual concentrations were confirmed by AAS and Cu^{2+} removal was calculated as follows: $Cu^{2+}\ removal = (C_o - C_e).100/C_e$ (1); where, C_o and C_e are initial and equilibrium Cu^{2+} concentrations (mg/L), respectively.

Experimental Design with RSM. We used the RSM as a mathematical method to optimize experimental variables through a second order polynomial regression equation. The central composite design is used to establish given 20 experiments (Table 1) with five levels including the low (–1), high (+1) and rotatable (±α).

Table 1. Independent variables and their encoded levels.

No	Independent factors	Code	Levels				
			–α	-1	0	+1	+α
1	C_i (mg/L)	x_1	8	25	50	75	92
2	d_{DSAC} (g/L)	x_2	0.8	2.5	5.0	7.5	9.2
3	pH (–)	x_3	0.6	2	4	6	7.4

Results and Discussion

The percentage of Cu^{2+} removal is dependent on three parameters including C_i, $d_{DSAC,}$ and pH of the solution. Observed and predicted values of Cu^{2+} removal were shown in Table 2. Moreover, a regression equation was established to describe the correlation between the response and variables as follows: $Cu^{2+}\ removal\,(\%) = 94.6 - 3.1x_1 + 9.7x_2 + 23.3x_3 + 0.3x_1x_2 + 2.5x_1x_3 + 1.3x_2x_3 - 2.9x_1^2 - 7.9x_2^2 - 19.1x_3^2$

The ANOVA results derived from the response surface can be used to assess the significance of quadratic model through correlation coefficients (R^2) and P-values. Overall, the proposed model for Cu^{2+} removal was statistically significant (at 95% confidence level) because the values of probability > F were less than 0.0001 and R^2 value reached to approximately 1.0 (Table 3). Otherwise, lack of fit (LOF) value was statistically insignificant and actual values for regression model of the percentage of Cu^{2+} removal was found to be highly compatible with predicted values. Hence, this indicated the model fitted data well (Fig. 2a).

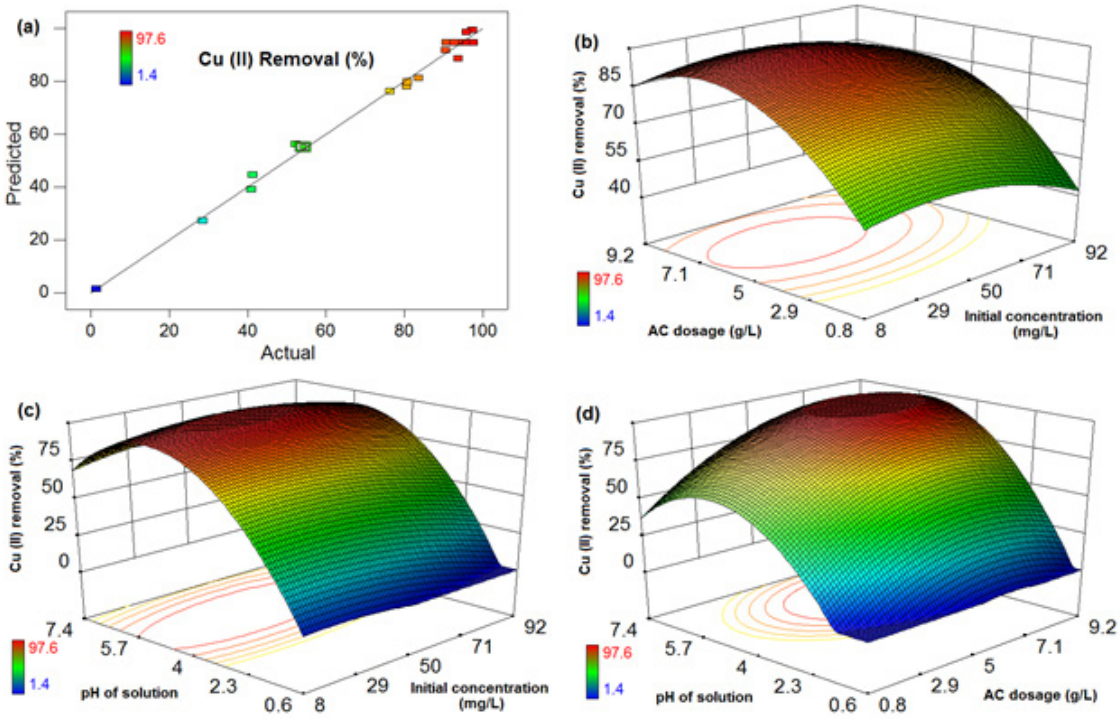

Fig. 1 Actual versus predicted plot (a) and response surfaces (b-d) for regression model of the percentage of Cu^{2+} removal.

The experimental plots were designed as follows: the two parameters was hold at central level while the others fluctuated from low values from high values (Fig. 2). The experimental factors including C_i, $d_{DSAC,}$ and pH of the solution were found to have strong effects on the percentage of Cu^{2+} removal because P–values of x_1, x_2, x_3, x_1^2, x_2^2, and x_3^2 were statistically significant.

Table 2. Matrix of actual and predicted values.

No	Variables			Response (%)	
	x_1 (mg/L)	x_2 (g/L)	x_3 (-)	Actual	Predicted
1	25	2.5	2	41.0	39.0
2	75	2.5	2	28.5	27.2
3	25	7.5	2	54.2	55.1
4	75	7.5	2	41.3	44.5
5	25	2.5	6	80.6	78.2
6	75	2.5	6	76.3	76.2
7	25	7.5	6	97.3	99.4
8	75	7.5	6	95.8	98.7
9	8	5	4	90.5	91.8
10	92	5	4	83.6	81.2
11	50	0.8	4	52.3	56.2
12	50	9.2	4	93.7	88.7
13	50	5	0.6	1.40	1.30
14	50	5	7.4	80.8	79.8
15	50	5	4	96.8	94.6
16	50	5	4	90.7	94.6
17	50	5	4	95.7	94.6
18	50	5	4	97.6	94.6
19	50	5	4	93.7	94.6
20	50	5	4	92.7	94.6

Table 3. ANOVA for response surface quadratic model.

Source	Sum of squares	DF[1]	Mean square	F-value	Prob. > F	Note
Model	14671	9	1630.2	136.5	< 0.0001[s]	Mean =
x_1	134.1	1	134.16	11.24	0.0073 [s]	74.22
x_2	1272.4	1	1272.4	106.6	< 0.0001[s]	CV =
x_3	7429.5	1	7429.5	622.4	< 0.0001[s]	4.65
$x_1 x_2$	0.72	1	0.72	0.060	0.8110 [n]	R^2 =
$x_1 x_3$	48.02	1	48.02	4.02	0.0727 [n]	0.9919
$x_2 x_3$	13.01	1	13.01	1.09	0.3212 [n]	$R^2_{(adj.)}$ =
x_1^2	117.75	1	117.75	9.86	0.0105 [s]	0.9847
x_2^2	882.6	1	882.61	73.94	< 0.0001[s]	
x_3^2	5259.7	1	5259.7	440.6	< 0.0001[s]	
Residual	119.37	10	11.94			
LOF[2]	84.71	5	16.94	2.44	0.1745 [n]	
PE[3]	34.65	5	6.93			

[1] Degree of freedom, [2]Lack of Fit, [3]Pure Error, [s] significant at $p < 0.05$, [n] insignificant at $p > 0.05$

The Cu^{2+} removal efficiency was significantly dependent on three variables investigated (Figs. 2b-d). At fixed C_i, when d_{DSAC} increased, Cu^{2+} removal efficiency would increase (Fig. 2b). The removal of Cu^{2+} was optimum at the amount of AC from 5 g/L to 7.5 g/L. Effect of C_i and pH of the solution on the percentage of Cu^{2+} removal was revealed in Fig. 2c. Clearly, Cu^{2+} removal was negligibly dependent on C_i while pH of the solution was recognized as a key factor leading to the considerable change of Cu^{2+} removal efficiency. The adsorption of Cu^{2+} onto the AC was negligible at the strongly acidic environment (pH < 2), while this process could be improved clearly if the pH of solution optimized at around 4.0-6.0 and however deducted at pH value more than 6.0. It was found to maximize the Cu^{2+} removal (100%) at pH = 4.0–6.0 and any value of C_i. Fig. 2d showed the effect of d_{DSAC} and pH on the removal of Cu^{2+}. A wide range for the value of pH (4.0–6.0) and d_{DSAC} (5–7.5 g/L) was favorable for the adsorption of Cu^{2+}. Finally, the predicted optimal conditions based model experiment was further conducted to verify the suitability of the proposed models: C_i= 61.6 mg/L, d_{DSAC} = 5.0 g/L and pH = 5.2 (Table 4). Admittedly, the experimental point applied optimal conditions was found to be 99.6% of Cu^{2+} removal, which is nearly closed to the predicted values of 100.2 %. These results demonstrated again the high compatibility of the proposed models with the experimental data.

Table 4. Model confirmation.

Sample	C_i (mg/L)	d_{DSAC} (g/L)	pH (-)	Cu^{2+} removal (%)	
				Predict	*Test*
DSAC	61.6	5.0	5.2	100.2	99.6

Table 5. Isotherm parameters for Cu^{2+} adsorption onto DSAC.

Isotherms	Equations	Parameters	Values
Langmuir	$\frac{1}{q_e}=\frac{1}{q_m K_L}.\frac{1}{C_e}+\frac{1}{q_m}$	K_L (L.mg^{-1})	0.030
		q_m (mg/g)	76.92
		R_L	0.263
		R^2	0.976
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$	K_F [(mg/g).(L/mg)]$^{1/n}$	2.76
		1/n	0.655
		R^2	0.859
Temkin	$q_e = B_1 \ln K_T + B_1 \ln C_e$	K_T (L.mg^{-1})	2.279
		B_1	4.025
		R^2	0.940

To evaluate the crucial data about adsorption behaviors of adsorbent, isotherm parameters could be used to establish several isotherm equations. Accordingly, the isotherm constants of models and the respective correlation R^2 were summarized in Table 5. Values of R^2 for Cu^{2+} adsorption models were observed to be 0.976, 0.859 and 0.940 for Langmuir, Freundlich, and Tempkin, respectively with the data fitness as an order: Langmuir > Tempkin > Freundlich. Therefore, Langmuir model,

which was recognized as the most favorable process for adsorption model, could be used to describe the main monolayer adsorption behavior of Cu^{2+} onto the surface of activated carbon. The maximum adsorption in the present study acquired to be 76.92 mg/g, which was higher than previous studies (Table 6).

Table 6. Comparison of the textural properties of chemical-activated carbon and Cu^{2+} treatment.

Source	Properties of AC		Cu^{2+} treatment				Ref
	Reagent	*Temp.*	*C_o (mg/L)*	*Dosage(g/L)*	*pH*	*q_m (mg/g)*	
Almond husk	H_2SO_4	700	25	5	5	4.87	[9]
Apricot	K_2CO_3	400	10	7	5	17.04	[10]
Palm shell	-	-	0.8	1	5	0.13	[11]
Glucose	H_3PO_4	450	60	0.6	7	48.5	[12]
Sucrose	H_3PO_4	450	60	0.6		42.4	[12]
Starch	H_3PO_4	450	60	0.6		41.1	[12]
Sugarcane fiber	NH_4Cl	500	147	10	7	10.3	[13]
Seed coat	H_3PO_4	300	40	5	7	13.51	[3]
Durian shell	KOH	500	61.6	5.0	5.2	76.92	*This work*

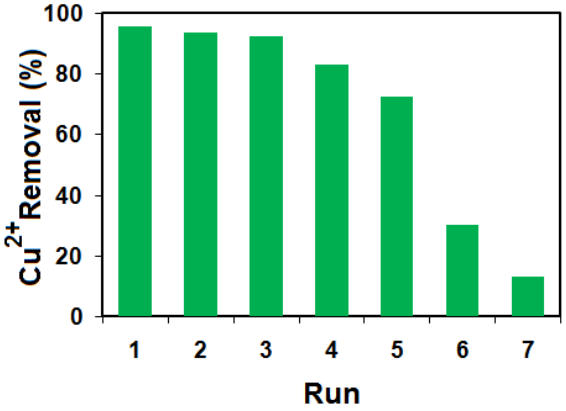

Fig. 2 Reuse test of activated carbon.

The study on the recyclability of DSAC was conducted by the following procedure: 3 x 50 mL HCl (1.4 M) was used to wash Cu^{2+}–adsorbed AC [8]. Then, desorption adsorbent was completely dried at 378 K for 12 h and could be used as an adsorbent for the further study. It is obvious that DSAC exhibited the removal of Cu^{2+} several times from 96 % (1^{st}) to 72 % (5^{th}) (Fig. 2). The present results proposed the durian shell can be used as a promising raw material source for adsorption of Cu^{2+} from wastewater.

Conclusions

The AC synthesized from durian shell source was used as an effective adsorbent for removal of Cu^{2+} ions from aqueous solution. The RSM based quadratic models were statistically significant to assess the influence of independent parameters, including C_i, pH, and d_{DSAC} on the removal of Cu^{2+} and to optimize the adsorption conditions. Under optimal conditions C_i = 61.6 mg/L, d_{DSAC} = 5.0 g/L and pH = 5.2, the excellent result was obtained up to 99.6% of Cu^{2+} removal. Moreover, adsorption isotherm was satisfactory represented by the Langmuir equation with high capacity of monolayer adsorption (76.92 mg/g). The recycling results up to five times proved a great potential for application of low-cost DSAC for removal of environmental pollutants.

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