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Optimization of Fabrication Conditions of KOH-Activated Carbon from Durian Peel for Pb^{2+}Removal by Response Surface Methodology

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Abstract

The present study focuses on optimizing the fabrication conditions of durian peel activated carbon (DPAC) for high carbon yield and efficient removal of Pb^{2+} from theaqueous environment using response surface methodology (RSM) involving central composite design (CCD). Potassium hydroxide (KOH) was used as the chemical activating agent for theformation of DPAC. Individual and interactive effects of influential factors including activation temperature (*T*), impregnation ratio (*IR*) and activation time (*t*) were investigated. The obtained high regression coefficients (R^2) and *p*-values < 0.0001 from the second-order polynomial regression equations indicated the statistical significance of models and excellent expression of experimental data. The combination of two responses including AC yield and Pb^{2+} removal predicted the optimized fabrication conditions, i.e. T = 592 °C, IR = 0.26 and t = 37.5 min, thereby supporting 32.0% of AC yield and 99.5% of Pb^{2+} removal. The results show that the DPAC fabricated using the optimized conditions is an excellent adsorbent for remediation of severely Pb^{2+} contaminated water.

Introduction

Contamination of lead in groundwater is considered as a serious environmental problem because of its high cumulative toxicity [1]. This hazardous metal is not only harmful to aquatic life but also can cause adverse effects on human health, such as neurological damage, convulsions, renal failure, chromosome breakage and birth defect [2]. The concentration of lead in drinking water is permitted at very low level, 15 ppb, by the US Environmental Protection Agency (2002). Traditionally, some methods have been commonly used for the elimination of toxic metal ions like Pb^{2+} from aqueous solutions including ion exchange, chemical precipitation, ultra filtration, electrochemical deposition and adsorption [3]. As reported in the literature, adsorption using activated carbon (AC) is promising as an efficient treatment pathway owing to efficient metal adsorption and recovery, selectivity and cost-effectiveness[4]. However, the main obstacle is the high cost of synthetic activated carbon available in the commercial market, and hence, its potential applications are restricted regarding some economical aspects. It has been reported that such challenge can be solved by using abundant, locally available biomass source as a precursor for AC fabrication.

Durian is widely planted and consumed in tropical regions like Southeast Asia. The significant disposal of nearly zero-cost durian peel from durian processing industries may cause undesirable effect on living environment [5]. On the other hand, it was reported that durian peel could be a very efficient source for fabrication of activated carbon. Note that property and adsorption capacity of activated carbons depend strongly on their fabrication conditions, thus determining optimal parameters for synthesis process appears as a very important task. In this article, we reported the successful application of RSM involving CCD to optimize the fabrication conditions of durian peel activated carbon (DPAC) for high carbon yield and efficient removal of Pb^{2+} from thewater media. The fitness of the obtained models and the significance of influential variables were assessed through the analysis of variance (ANOVA) and coefficients of regression (R^2).

Experimental

Chemicals

All reagents and starting materials were purchased commercially from Merck and were used as received without any further purification unless otherwise noted.

Fabrication of AC from durian peel

Durian fruit peels were collected from the local market, washed with distilled water for several times before dried under sunshine and ground to the diameters of approximately 1.0 mm. The dried raw material was first pyrolyzed at 500 °C for 1 h under anitrogen atmosphere with a heating rate of 10 °C/min. The resulting char was then soaked with KOH solution for 24h. Impregnation ratio (IR) between KOH and the char was calculated as follows:

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

wherew$_{KOH}$ 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 tempertures (T) for different activation time (t). Finally, the as-received KOH-activated carbon was repeatedly washed with deionized water until

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approaching a neutral solution, then dried at 105 °C for 24 h. The formation yields of AC were quantified by the following equation:

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

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

Batch adsorption experiments

The samples of the synthesized ACs were poured into the Erlenmeyer flasks containing 50 mL of aqueous solution of Pb^{2+} 50 ppm. The mixtures were continuously stirred until obtaining the adsorption equilibrium. The AC was then removed from the mixture using filter paper. The residual Pb^{2+} concentrations were determined by AAS and percentage of removal was calculated as:

$$Pb^{2+}removal\,(\%) = \frac{C_O - C_f}{C_O}.100 \qquad (3)$$

where, $C_O$and $C_f$are initial and equilibrium Pb^{2+} concentrations (ppm), respectively.

Experimental design with RSM

To optimize the fabrication conditions of DPAC, RSM technique was used to derive mathematical correlation between three independent variables including activation temperature (T), impregnation ratio (IR) and activation time (t) and the response (carbon yield, removal efficiency for Pb^{2+}) via the following second order polynomial regression equation:

$$y = f(x) = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k}\sum_{j=1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 \qquad (4)$$

where, y is the predicted response; x_i and x_j are the independent variables (i,j=1, 2, 3, 4….k). The parameter β_o is the model constant; β_i is the linear coefficient; β_{ii} is the second–order coefficient and β_{ij} is the interaction coefficient [6]. As presented in Table 1, Central composite design (CCD) was used to establish the experiment matrix involving center variables (encoded 0), low (encoded -1), high (encoded +1) and rotatable (encoded ±α) levels. The total number of experiments (N) for three independent variables (k = 3) containing 2^k factorial experiments, 2k axial experiments and six replications at centers is 20. Analysis of variance (ANOVA) was calculated using Design–Expert version 9.0.5.1 (DX9).

Table 1: Independent variables and their encoded levels for CCD

No	Independent factors	Code	Levels				
			–α	-1	0	+1	+α
1	Activation temperature (^{o}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

Development of Regression Model Equation

The experimental and predicted results of AC yield and Pb^{2+} removal efficiency are presented in Table 2. The DPAC appeared as a very efficient adsorbent for Pb^{2+} with up to 99.8 % removal. 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 were studied as input parameters. Accordingly, the quadratic equations describing the correlation between the responses and independent variables were given as:

$$y_{AC\,yeild} = 28.2 + 1.78x_1 - 0.05x_2 + 1.22x_3 - 1.26x_1x_2 + 1.76x_1x_3 + 2.64x_2x_3 - 0.27x_1^2 + 0.26x_2^2 - 1.41x_3^2 \qquad (5)$$

$$y_{Pb^{2+}removal} = 99.7 - 0.47x_1 - 2.07x_2 - 0.06x_3 - 1.18x_1x_2 - 0.43x_1x_3 + 0.15x_2x_3 - 1.69x_1^2 - 1.43x_2^2 - 0.08x_3^2 \qquad (6)$$

Table 2: Matrix of observed and predicted values

No	Input factors			Actual (%)		Predicted (%)	
	x_1	x_2	x_3	$y_{AC\,yeild}$	$y_{Pb^{2+}removal}$	$y_{AC\,yeild}$	$y_{Pb^{2+}removal}$
1	400	0.5	30	28.7	97.8	26.9	97.6
2	600	0.5	30	28.0	99.2	29.5	99.9
3	400	1.5	30	22.7	96.0	24.1	95.5
4	600	1.5	30	23.1	93.1	21.6	93.1
5	400	0.5	90	19.3	97.9	20.6	98.1
6	600	0.5	90	31.8	98.0	31.2	98.6
7	400	1.5	90	30.0	97.1	28.3	96.6
8	600	1.5	90	31.3	92.1	32.8	92.4
9	332	1.0	60	24.0	95.0	24.4	95.7
10	668	1.0	60	30.4	95.0	30.4	94.1
11	500	0.16	60	28.7	99.8	29.0	99.1
12	500	1.84	60	28.7	91.7	28.8	92.2
13	500	1.0	9.5	22.0	99.5	20.1	99.5
14	500	1.0	110.5	26.0	99.6	26.2	99.3
15	500	1.0	60	28.2	99.6	28.2	99.7
16	500	1.0	60	28.0	99.8	28.2	99.7
17	500	1.0	60	28.5	99.7	28.2	99.7
18	500	1.0	60	27.9	99.8	28.2	99.7
19	500	1.0	60	28.3	99.5	28.2	99.7
20	500	1.0	60	28.1	99.6	28.2	99.7

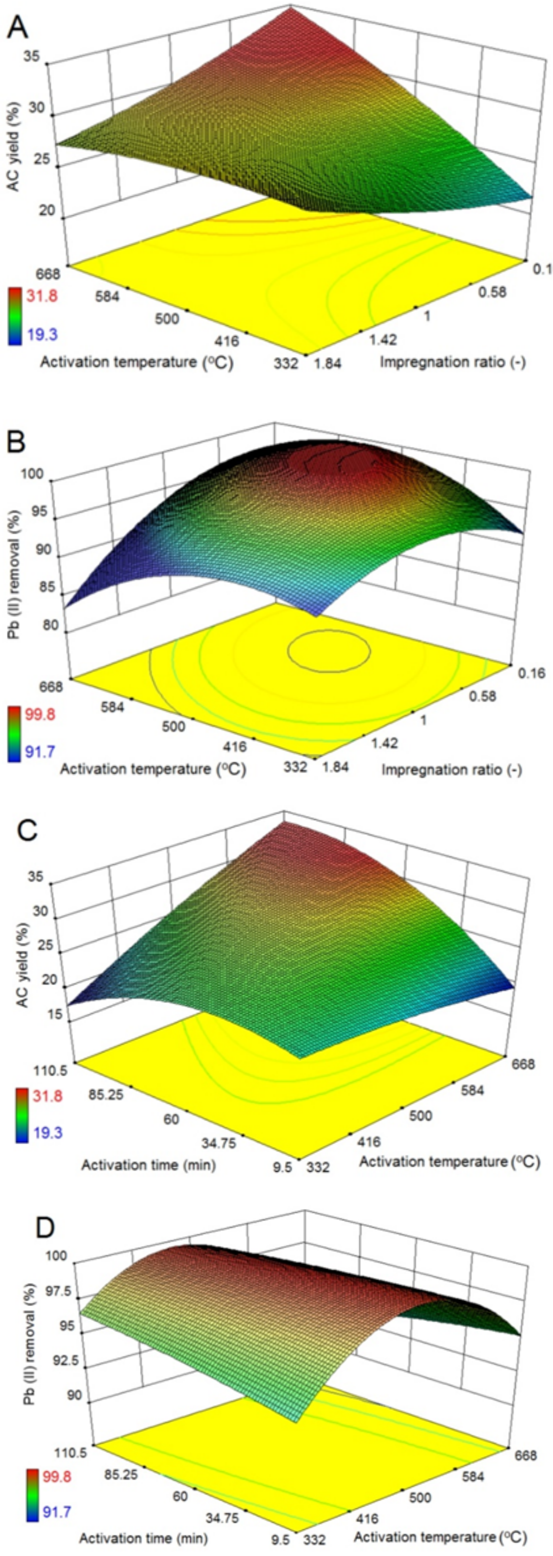
The data of the ANOVA for regression equations was shown in Table 3. In general, the P-values < 0.05 and the R^2 more approaching to 1.0 are desirable since they indicate that the derived quadratic models are statistically significant at 95% confidence level [7]. Regarding these standards, both quadratic regression models developed for AC yield and removal efficiency of Pb^{2+} were statistically significant because their P-values were obviously less than 0.0005 and the R^2 obtained higher than 0.9. The regression model for Pb^{2+} removal has better compatibility with a high R^2 value of 0.9747. Moreover, the goodness of fit of the models was further confirmed by the adequate precision (AP) ratios greater than 4.0 [8].

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	187.80	9	20.87	10.61	0.0005	Mean = 27.18
	x_1	43.11	1	43.11	21.92	0.0009	R^2 = 0.9052
	x_3	20.24	1	20.24	10.30	0.0094	AP = 12.355
	x_2^2	24.85	1	24.85	12.64	0.0052	
	x_3^2	55.65	1	55.65	28.30	0.0003	
	x_2x_3	28.45	1	28.45	14.47	0.0035	
Pb^{2+}removal (%)	Model	138.80	9	15.42	42.88	<0.0001	Mean = 97.49
	x_2	58.32	1	58.32	162.17	<0.0001	R^2 = 0.9747
	x_1^2	11.04	1	11.04	30.71	0.0002	AP = 18.201
	x_1x_2	41.17	1	41.17	114.47	<0.0001	
	x_1x_3	29.26	1	29.26	81.37	<0.0001	

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

The dimensional response surface plots in Figures 1 describe the interactive influence of two variables on two responses while one factor is maintained at zero level. According to the observation in Figure 1, at the constant activation time of 60 minutes, both activation temperature (332 °C – 668 °C) and IR (0.16 – 1.84) strongly affect the AC yield and Cu (II) removal. Obviously, higher values of activation temperature and lower values of IR promote higher AC yield. Meanwhile, the removal of Pb^{2+} is more favored in the intermediate temperature range and moderate IR; the optimized temperature and IR ratio for Pb^{2+} removal, in this case, are determined at 500 °C and 1.0, respectively. Figure 1 (C,D) presents the effect of activation time (9.5 min – 110.5 min) and activation temperature (332 °C – 668 °C) at IR = 1.0. Generally, the AC yield increases with increasing activation time and temperature.



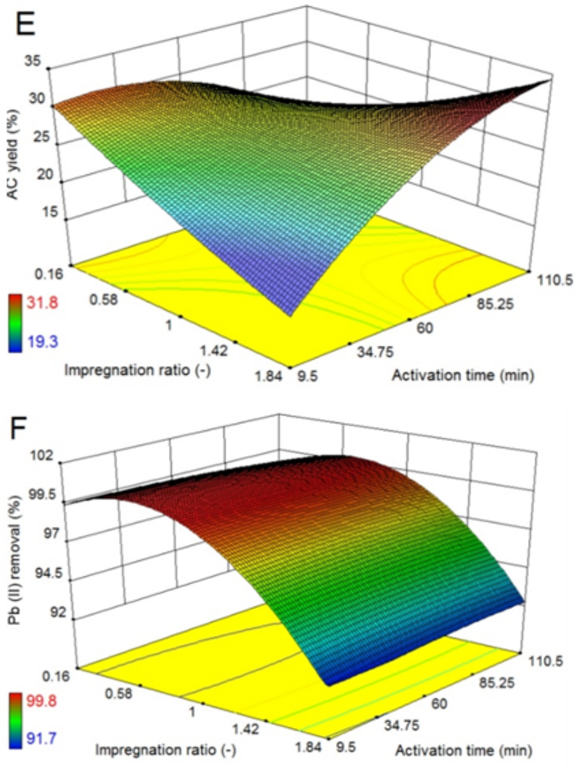


Figure 1: Effect of activation temperature, IR and activation time = 60 min on AC yield (A) and Cu2+removal (B); Effect of activation temperature, activation time and IR=1.0 on AC yield (C) and Cu^{2+}removal (D); Effect of IR, activation time and activation temperature = 500 °C on AC yield (E) and Cu^{2+}removal (F)

In contrast, the negligible influence of activation time on removal of Pb^{2+} is observed on the constant activation temperature line. On the other hand, at a constant activation temperature of 500 °C, the interactive effect of IR (0.16 – 1.84) and activation time (9.5 min – 110.5 min) on the AC yield is quite complicated as observed in Figure 1E. Accordingly, the high AC yield is recorded in the regions of either low values of both time and IR or high values of both factors. For instance, in order to achieve high carbon yields, the low IR of 0.16 requires the activation time lower than 34.75 min and the activation time should be around 85.25-110.50 min if the IR is used at 1.84. The high IR with low temperature is predicted to result in poor carbon yield. In terms of Pb^{2+} removal, the influence of IR appears to much more significant than that of activation time (Figure 1F); the optimum adsorption occurs in the IR range of 0.16-1. The simultaneous optimization of AC yield and Pb^{2+} removal suggests the optimized factors as follows: activation temperature of 592 °C, IR of 0.26 and activation time of 37.5 min. The batch experiments at the optimized parameters were also conducted to verify the suitability of the proposed models. Thereby, the experimental results for AC yield and Cu^{2+} removal were obtained at 32.0% and 99.5% which is almost similar the predicted values of 31.9 % and 99.8 %, respectively (Table 4). These results demonstrate the high compatibility of the proposed models with the experimental data.

Table 4: Model confirmation

Sample	T (°C)	IR (-)	t (min)	Desirability	AC yield (%)		Pb^{2+} removal (%)	
					Predicted	Tested	Predicted	Tested
AC400	592	0.26	37.5	1.0	31.9	32.0	99.8	99.5

Conclusions

The highly porous KOH-activated carbon fabricated from durian peel found to be a very efficient adsorbent for removal of Pb^{2+} from aqueous solution. Response surface methodology was successfully applied to define the optimal regions under theimpact of three independent factors including activation time, temperature and impregnation ratio between the KOH and precursor. The developed quadratic regression equations for both carbon yield and Pb^{2+} were proved to be statistically significant. It was found that the optimal combination of carbon yield and adsorption capacity could be achieved at the activation temperature of 592 °C, *IR of 0.26* and activation time of 37.5 min, producing AC yield and Cu^{2+} removal at 32.0% and 99.5% which were well-confirmed using the batch experiment. These results show that the DPAC fabricated using such optimized conditions is an excellent adsorbent for remediation of severely Pb^{2+} contaminated water.

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References

1. Li YH, Wang S, Wei J, et al (2002) Lead adsorption on carbon nanotubes. Chem Phys Lett 357:263–266.
2. Vuković GD, Marinković AD, Škapin SD, et al (2011) Removal of lead from water by amino modified multi-walled carbon nanotubes. ChemEng J 173:855–865.
3. Flora SJS, Mittal M, Mehta A (2008) Heavy metal induced oxidative stress & its possible reversal by chelation therapy. Indian J Med Res 128:501–23.
4. Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. Arab J Chem 4:361–377.
5. Chandra TC, Mirna MM, Sudaryanto Y, Ismadji S (2007) Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics. ChemEng J 127:121–129.
6. Hameed BH, Tan IAW, Ahmad AL (2008) Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology. J Hazard Mater 158:324–332.
7. Amini M, Younesi H, Bahramifar N, et al (2008) Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillus niger. J Hazard Mater 154:694–702.
8. Esfandiar N, Nasernejad B, Ebadi T (2014) Removal of Mn(II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM). J Ind Eng Chem 20:3726–3736.