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Optimization of *Areca catechu* Fronds as Adsorbent for Decolorization and COD Removal of Wastewater through the Adsorption Process

(Pengoptimuman Pelepah *Areca catechu* sebagai Penjerap untuk Penyingkiran Warna dan COD Air Sisa melalui Proses Penjerapan)

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ABSTRACT

Areca catechu *fronds show higher capability for removal of color and COD and were utilized as an adsorbent for adsorption process.* Areca catechu *fronds activated carbon (AC) undergoes activation process after carbonization under purified carbon dioxide and turned as activated carbon. Three variables were chosen for the preparation optimization which consists of temperature, activation time and impregnation ratio in order to study the effect toward the removal of color and COD from cotton textile mill wastewater. For this study, the response surface methodology (RSM) was employed. Quadratic model were develop based on three variables and responses of color and COD. High values of the coefficient determination, R^2 were obtained from analysis of variance (ANOVA) for both responses. The optimum* Areca catechu *fronds activated carbon (AC) preparation condition was established at temperature 797 °C for 1.57 hour of activation time and 2.75 impregnation ratios, corresponding to the removal of color and COD with 78.83 and 62.41%, respectively.*

Keywords: Activated carbon; adsorption; Areca catechu*; COD; color*

ABSTRAK

Pelepah Areca catechu *mempunyai kebolehan yang tinggi untuk menyingkirkan warna dan COD serta digunakan sebagai bahan penyerap untuk proses penyerapan. Karbon aktif (AC)* Areca catechu *melalui proses pengaktifan selepas karbonisasi dibawah karbon dioksida bersih untuk dijadikan karbon aktif (AC). Tiga pemboleh ubah dipilih untuk penyediaan optimum yang terdiri daripada suhu, masa pengaktifan dan nisbah pemadatan untuk mengkaji kesan terhadap penyingkiran warna dan COD daripada air sisa kilang tekstil kapas. Dalam kajian ini, kaedah gerak balas permukaan (RSM) telah digunakan. Model kuadratik dibangunkan berdasarkan kepada tiga pemboleh ubah serta tindak balas warna dan COD. Nilai pekali penentu, R^2 diperoleh daripada analisis varians (ANOVA) untuk kedua-dua tindak balas. Keadaan penyediaan optimum karbon aktif (AC) pelepah* Areca catechu *pada suhu 797*°C selama 1.57 jam masa pengaktifan dan nisbah *pemadatan 2.75, sepadan dengan penyingkiran warna dan COD masing-masing sebanyak 78.83 dan 62.41%.*

Kata kunci: Areca catechu; *COD; karbon aktif; penjerapan; warna*

INTRODUCTION

The treatments of industrial wastewater containing dyes are very challenging. This is because the presences of dyes in water body can avoid the penetration of sunlight which is required by the aqueous plant for photosynthesis (Robinson et al. 2002). Moreover, dyes effluent are able to cause skin allergy and even promote cancer towards human (Manu & Chaudhari 2002). Dyes were utilized by different industries such as textile, paper printing, food and cosmetics. Among industries, textile wastewater has the highest potential to cause serious environmental problems due to several characteristics (Sayan 2006). For example, highly recalcitrant chemical oxygen demand (COD), strong effluent color, high suspended solids, fluctuated pH and high temperature (Ahmad & Hameed 2009; Anouzla et al. 2009; Sayan 2006). Typically, the dye wastewater for COD range from 150 to 1200 mg/L and for BOD range from 80 to 6000 mg/L leading to the BOD/COD ratio around 0.25 (Oller et al. 2011). This indicated that the wastewater contains large amount of non-biodegradable organic matter. Moreover, the treatment of dye wastewater is insufficient with the conventional treatment.

Thus, the advanced treatment technologies such as adsorption are highly demanded. Adsorption is an effective method to decolorize and lowering the COD of dyes wastewater compared to other types of treatments such as chemical oxidation and biological method. This is due to the economically reliable and time consuming of the treatment process. Besides that, the adsorption process are able to completely removed the dyes without producing any sludge. The adsorption process utilized activated carbon as adsorbent is a widespread technology for dyes removal. The term adsorption itself refers to a process where material is concentrated at a solid surface from its liquid or gaseous surroundings (Gupta & Suhas 2009). Nowadays, the productions of low economic adsorbent materials are the main focus. Various alternatives material has been studied and agro waste such as orange peels, coconut shell and maize cob (Okeola & Odebunmi 2010), orange peel (Arami et al. 2005; Sivaraj et al. 2001), natural source such as bamboo (Hameed et al. 2007), guava leaf (Ponnusami et al. 2008) spent tea leaves (Hameed 2009) and zeolites (Benkli et al. 2005; Ozdemir et al. 2004) were used as activated carbon.

The activated carbon itself can be prepared via two activation process which is chemical and physical (Gupta & Suhas 2009). The chemical activation involved the usage of chemical agents in low temperature which will aid the formation of pore onto the surface of the adsorbent. Meanwhile, through physical activation the carbonaceous material will turn into char by carbonization process. The char were activated by the activating agents such as carbon dioxide and steam for a complete formation of activated carbon. The objective of the present study were to determine the optimize condition for preparation of *Areca catechu* fronds AC as adsorbent for removal of color and COD from real mill wastewater. The effect of three variables which is activation temperature, activation time and chemical impregnation ratio were selected for the removal of color and COD in wastewater.

Materials and Methods

Sampling

Wastewater samples were collected from the outlet point of settling tank of activated sludge treatment plant of a nearby cotton textile mill wastewater in Penang, Malaysia. The samples were collected in plastic containers and stored at <5°C to avoid any changes in their physicochemical characteristics before use. The wastewater samples were characterized for COD and color in a laboratory according to the methods prescribed in APHA (1992).

Activated Carbon Preparation and Characterization

The raw materials of *Areca catechu* fronds was washed and consequently dried at 378 K (105°C) for 24 h to remove the moisture content. The raw materials was ground and sieved to the size of 1-2 mm and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. The activation step was carried out after the carbonization step at 993K (720°C) for 1 h under purified carbon dioxide at flowrate of 300 mL/min for 1 h. The sample was then cooled to room temperature under nitrogen flow. The surface morphology of the samples was examined using a scanning electron microscope (JEOL, JSM-6460 LV, Japan).

Batch Equilibrium Studies

The batch adsorption studies were conducted with textile mill wastewater with initial color 552 Pt/C_o and COD 256 mg/L. A total of 20 samples of 200 mL each were placed in different Erlenmeyer flask. For each preparation method of activated carbon, 0.30 g activated carbon was suspended into the solution in each flask. The solution was then kept in an isothermal shaker of 120 rpm at constant temperature of 30°C until it reaches the equilibrium adsorption time. The supernatant sample was withdrawn from each flask and analyze for the color and COD. The color was analyzed through DR2800 spectrophotometer (CECIL 1000 series, Cambridge, UK) at a wavelength of 455 nm based on standard method for DR2800 Method 8025 Platinum-Cobalt Standard. The COD was tested on based on the Standard Method 52220D-Closed Reflux, Colorimetric Method.

Results and Disscusion

Model Development

Table 1 indicated the experimental factors both in coded units and experimental responses. For the analysis, the quadratic model was selected for both responses of color and COD. Based on multiple regression analysis, the three variables and the responses were correlated to each other using the second polynomial equation. X_1, X_2 and X_3 represent a coded value for the process variables of temperatures, activation time and chemical impregnation ratio. While, Y_1 and Y_2 is for color and COD, respectively. Based on the second degree polynomial equation, the empirical model which correlated to the responses was developed. In the equation of the quadratic regression, the synergistic effect were indicates by the positive sign and the antagonist effect were shown through negative sign. The quadratic regression model for the color and COD removal are given by (1) and (2).

% color removal, Y_1 :

$$81.61 + 8.05X_1 + 2.07X_2 + 10.19X_3 - 11.56X_1^2 - 9.52X_2^2 - 12.44X_3^2 + 4.13X_1X_2 + 5.49X_1X_3 + 2.02X_2X_3 \quad (1)$$

% COD removal, Y_2 :

$$63.44 + 10.11X1 + 2.86X2 + 7.90X3 - 10.20X12 - 7.39X22 - 9.96X32 + 1.32X1X2 + 1.87X1X3 + 2.50X2X3 \quad (2)$$

Table 2 shows the quality evaluation for the develop model which is based on the correlation coefficient R-Squared (R^2), standard deviation values, R^2 adjusted and coefficient of variation (CV). The CV is the ratio of standard error of estimate to the mean value of the observed response and measured the reproducible reasonability of the model. While, the most important is the satisfactory adjustment of the quadratic model to the experimental data which represent by the value of R^2. High R^2 value or value near 1.0 indicated a good agreement between the experimental and predicted value from the models (Anouzla et al. 2009). The R^2 value for color removal is 0.92, while for COD removal is 0.91. According to Jogelekar and May

TABLE 1. Experimental factors in coded units and experimental responses

Run no.	X_1: Temp (°C)	X_2: Time (h)	X_3: IR	Color removal Y_1 (%)	COD removal Y_2 (%)
1	600.00	1.00	0.75	42.58	25.48
2	850.00	1.00	0.75	42.65	38.15
3	600.00	3.00	0.75	33.6	22.82
4	850.00	3.00	0.75	37.6	43.12
5	600.00	1.00	2.75	57.6	32.03
6	850.00	1.00	2.75	67.01	54.51
7	600.0	3.00	2.75	44.1	41.73
8	850.00	3.00	2.75	82.65	67.15
9	514.78	2.00	1.75	27.64	10.93
10	935.22	2.00	1.75	62.1	44.93
11	725.00	0.32	1.75	38.7	31.6
12	725.00	3.68	1.75	62.58	40.15
13	725.00	2.00	0.07	29.23	16.11
14	725.00	2.00	3.43	55.51	41.1
15	725.00	2.00	1.75	84.43	65.6
16	725.00	2.00	1.75	81.1	62.82
17	725.00	2.00	1.75	79.1	59.23
18	725.00	2.00	1.75	83.7	67.15
19	725.00	2.00	1.75	82.54	69.15
20	725.00	2.00	1.75	80.21	59

TABLE 2. Statistical parameters obtained from the ANOVA for reduced model

Variables	*Areca catechu*	
	Color removal (%)	COD removal (%)
Standard deviation, S.D.	7.82	7.35
Mean	58.73	44.64
Coefficient of variation, CV	13.31	16.47
R-squared (R^2)	0.9232	0.9116
R^2 adjusted	0.8541	0.8320

(1987), the determination coefficient R^2 should be at least 0.80 for a good model fit. In this case, the R^2 is fitted to the model. Based on Table 2, the satisfactory adjusted R^2 of the quadratic experimental data are 0.8541 and 0.8320 for color and COD, respectively. It was observed that the removal of color and COD by *Areca catechu* fronds AC has the synergistic effects.

STATISTICAL ANALYSIS

In data analysis, the adequacy and significance of the model were tested through analysis of variance (ANOVA). Tables 3 and 4 summarized the ANOVA for response surface quadratic model for color and COD removal, respectively. The mean squares were obtained by dividing the sum of the squares of each of the two sources of variation, the model and the error variance, by the respective degrees of freedom.

Based on Table 3, analysis of variance (ANOVA) for response surface quadratic model for color removal, the model was significant. This is due to the F-value which is 13.36. In order to evaluate the significant of the model, the value of Prob >F less than 0.05 indicated that the model terms were significant. Contrary, when Prob > F values are greater than 0.10, it indicated that the model term are not significant (Muhammad et al. 2013). From the result, it was observed that X_1, X_3, X_1^2, X_2^2 and X_3^2 were significant while for X_2, X_1X_2, X_1X_3 and X_2X_3 were insignificant to the response.

The F-value from the analysis of variance for response surface quadratic model COD in Table 4 is 11.45 which implied that the model was significant as well. From the table, X_1, X_3, X_1^2, X_2^2 and X_3^2 were significant while, X_2, X_1X_2, X_1X_3 and X_2X_3 were insignificant. Lack of fit F-test describes the variation of the data around the fitted model. Both of the models indicated a statistically significant lack of fit values which is under 0.05. The value for color removal is 0.0012 and for COD is 0.0483. A significant lack of fit suggested that there maybe some systematic variation encountered for in the hypothesized model as a result of the exact replicate values of the independent variable in the model that provide an estimate of pure error (Bashir et al. 2010).

In addition, the adequate precisions ratios of the model for color and COD removal were 9.465 and 8.819, respectively. Both of the models can be used to navigate

TABLE 3. Analysis of variance (ANOVA) for response surface quadratic model for color removal

Model	Squares	Degree of Freedom (DF)	Mean square	F-value	Prob.>F	Comment
Model	7344.62	9	816.07	13.36	0.0002	significant
X_1	885.75	1	885.75	14.50	0.0034	
X_2	58.52	1	58.52	0.96	0.3508	
X_3	1417.34	1	1417.34	23.20	0.0007	
X_1^2	1924.44	1	1924.44	31.49	0.0002	
X_2^2	1304.96	1	1304.96	21.36	0.0009	
X_3^2	2230.10	1	2230.10	36.50	0.0001	
X_1X_2	136.70	1	136.70	2.24	0.1656	
X_1X_3	32.79	1	240.79	3.94	0.0752	
X_2X_3	32.68	1	32.68	0.53	0.4813	
Residual	611.04	10	61.10			
Lack of Fit	589.67	5	117.93	27.59	0.0012	significant
Pure Error	21.37	5	4.27			

the design space due to the adequate signal when the ratios are greater than 4 (Muhammad et al. 2013).

Figure 1 indicates the adequacy of the model through the relationship between predicted values to the experimental value obtained. The plot data of Y1 and Y2 response were used as the experimental data, meanwhile the predicted data were evaluated from the model in (1) and (2). It is apparent from this figure that the entire model was adequate to predict the color and COD removal and the *Areca catechu* fronds AC yield in the range of preparation variable studied (X_1, X_2 & X_3).

The correlation between the predicted and experimental value were indicated by the value of the correlation coefficient, R^2 which is 0.96 for both color and COD removal. Moreover, the standard deviation values for color and COD is 2.70 and 2.73, respectively, indicated the quality of model was fit. It can be seen from the graph that most of the point are all along the straight line and can be assumed that the data is normally distributed. Taken together, these results suggested that the models develops were able to determine the correlation between the color and COD removal of *Areca catechu* fronds AC based on the preparation variables and the *Areca catechu* fronds AC yield.

The optimum conditions for preparation of *Areca catechu* fronds AC has been successfully optimize through response surface methodology. The verification of experimental and predicted values of prepared activated carbon under the optimum condition for removal of color and COD predicted by RSM were shown in Table 5. The optimum activated carbon was obtained under the

TABLE 4. Analysis of variance (ANOVA) for response surface quadratic model for COD removal

Model	Squares	Degree of Freedom (DF)	Mean square	F-value	Prob.>F	Comment
Model	5568.46	9	618.72	11.45	0.0004	significant
X_1	1395.49	1	1395.49	25.83	0.0005	
X_2	111.54	1	111.54	2.06	0.1813	
X_3	852.15	1	852.15	15.77	0.0026	
X_1^2	1498.10	1	1498.10	27.73	0.0004	
X_2^2	786.34	1	786.34	14.55	0.0034	
X_3^2	1428.79	1	1428.79	26.45	0.0004	
X_1X_2	13.97	1	13.97	0.26	0.6222	
X_1X_3	27.86	1	27.86	0.52	0.4891	
X_2X^3	50.15	1	50.15	0.93	0.3580	
Residual	540.28	10	54.03			
Lack of Fit	452.31	5	90.46	5.14	0.0483	significant
Pure Error	87.97	5	17.59			

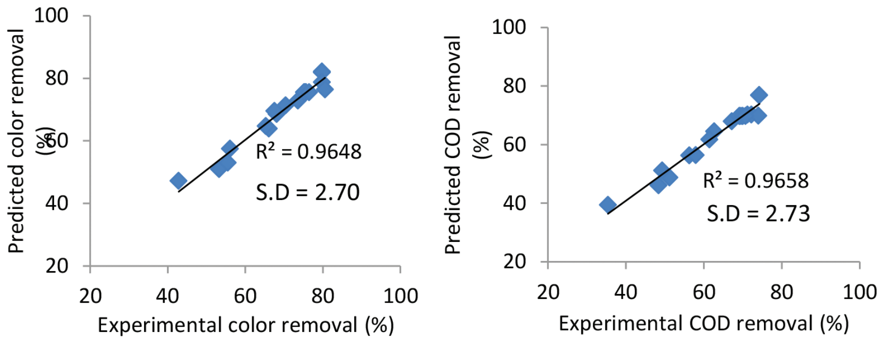

FIGURE 1. Predicted and experimental removal of (a) color (b) COD

TABLE 5. Verification of experimental and predicted values under optimum conditions predicted by RSM

X_1: Temp (°C)	X_2: Time (h)	X_3: IR	Color removal (%)		Error (%)	COD removal (%)		Eror (%)
			Experimental	Predicted		Experimental	Predicted	
797	1.57	2.75	78.83	84.43	6.63	62.41	67.17	7.08

preparation condition of 797°C of activation time in 1.57 h and 2.75 impregnation ratios. The experimental result indicated 78.83 and 84.43% of color and COD removal, respectively. The experimental values obtained were in a good agreement with the values predicted as there were less than 10% of errors recorded. Several studies has reported the similar outcome with this results (Ahmad & Hameed 2009; Amina et al. 2008).

MORPHOLOGY STUDIES

The morphology of the *Areca catechu* fronds AC was observed through scanning electron microscope (SEM) as shown in Figure 2. From the figure, it can be observed that there are several large pores develop on the surface on the *Areca catechu* fronds AC. Based on the direct measurement on the SEM images, the pores diameter size are in the range of 5.6 to 8.2 µm. The size variations were due to the heterogeneous pores that formed. The formation of pores is crucial for the adsorption process (Hameed 2009). Larger pore size will promote the reduction of color and COD of wastewater due to higher adsorption capacity.

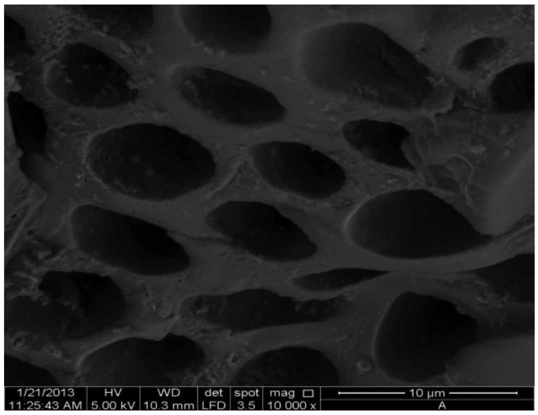

FIGURE 2. SEM images of *Areca catechu fronds* AC

CONCLUSION

The optimization of activated carbon preparation variables consists of temperature, activation time and impregnation ratio was successfully studied through responses surface methodology (RSM). The optimum activated carbon was obtained under the preparation condition of 797°C of activation time in 1.57 h and 2.75 impregnation ratios. The result indicated 78.83 and 84.43% of color and COD removal, respectively, shows a good agreement with the values predicted as there were less than 10% of errors recorded. The *Areca catechu* fronds AC develop heterogeneous pores which enhanced the adsorption capacity onto the surface of the activated carbon.

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REFERENCES

Ahmad, A.A. & Hameed, B.H. 2009. Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. *Journal Hazardous Materials* 172: 1538-1543.

Amina, A.A., Badie, S.G. & Nady, A.F. 2008. Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch and column studies. *Dyes Pigments* 76: 282-289.

Anouzla, A., Abrouki, Y., Soubi, S., Safi, M. & Rhbal, H. 2009. Colour and COD removal of disperse dye solution by a novel coagulant: Application of statistical design for the optimization and regression analysis. *Journal of Hazardous Material* 166: 1302-1306.

Arami, M., Limaee, N.Y., Mahmoodi, N.M. & Tabrizi, N.S. 2005. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. *Journal of Colloid Interface Science* 288: 371-376.

Bashir, M.J.K., Aziz, H.A., Yusoff, M.S. & Adlan, M.N. 2010. Application of response surface methodology (RSM) for optimization of ammmoniacal nitrogen removal from semi-aerobic landfill leachate using ion-exchange resin. *Desalination* 254: 154-161.

Benkli, Y.E., Can, M.F., Turan, M. & Celik, M.S. 2005. Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed-bed reactors. *Water Resources* 39: 487-493.

Gupta, V.K. & Suhas. 2009. Application of low-cost adsorbent for dye removal-A review. *Journal of Environmental Management* 90: 2313-2342.

Hameed, B.H. 2009. Spent tea leaves: A new non- conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *Journal of Hazardous Materials* 161: 753-759.

Hameed, B.H., Din, A.T.M. & Ahmad, A.I. 2007. Adsorption of Methylene blue onto bamboo-based carbon: Kinetics and equilibrium studies. *Journal of Hazardous Materials* 141: 819-825.

Jogleker, A. & May, A. 1987. Product excellence through design of experiments. *Cereal Foods World* 12: 857-868.

Manu, B. & Chaudhari, S. 2002. Anaerobic decolorisation of simultaned textile wastewater containing azo dyes. *Bioresource Technology* 82: 225-231.

Muhammad, M.H., Abdullah, S.R.S., Mohammd, A.B., Rahman, R.A. & Kadhum, A.A.H. 2013. Application of response surface methodology (RSM) for optimisation of COD, NH3-N and 2,4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBR). *Journal of Environmental Management* 121: 179-190.

Okeola, F.O. & Odebunmi, E.O. 2010. Comparison of Freundlich and Langmuir isotherms for adsorption of methylene blue by agrowaste derived activated carbon. *Advances in Environmental Biology* 4: 329-335.

Oller, I., Malato, S. & Sánchez-Pérez, J.A. 2011. Combination of advanced oxidation process and biological treatments for wastewater decontamination - A review. *Science of the Total Environment* 409: 4141-4166.

Ozdemir, O., Armagan, B., Turan, M. & Celik, M.S. 2004. Comparison of the adsorption characteristic of azo-reactive dyes on mezoporous minerals. *Dyes Pigments* 62: 49-60.

Ponnusami, V., Vikram, S. & Srivastava, S.N. 2008. Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. *Journal of Hazardous Materials* 152: 276-286.

Robinson, T., Chandran, B. & Nigam, P. 2002. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Resources* 36: 2824-2830.

Sayan, E. 2006. Optimization and modelling of decolorization and COD reduction of reactive dye solutions by ultrasound - assisted adsorption. *Chemical Engineering Journal* 119: 175-181.

Sivaraj, R., Namasivayam, C. & Kadirvelu, K. 2001. Orange peels as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste Management* 21: 105-110.

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