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Response Surface Methodology Optimization of Methylene Blue Removal by Activated Carbon Derived from Foxtail Palm Tree Empty Fruit Bunch

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Abstract

The release of dyes in form of wastewater causes serious environmental problems such as retards photosynthesis, inhibit growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen. In this study, activated carbon derived from foxtail palm (*Wodyetia bifurcata*) empty fruit bunch (EFB) was used as an adsorbent to remove methylene blue in aqueous solution. The preparation process of activated carbon consisted of H_2SO_4 impregnation followed by carbonization at 300ºC for 24 hours. The optimization adsorption process was carried out using Response Surface Methodology (RSM) via Box-Behnken design. Three important operating variables namely dye concentration, contact time and adsorbent dosage were studied. The optimum conditions obtained were 100 ppm of methylene blue, 13 h of contact time and 2 g of activated carbon with the highest percentage of methylene blue removal of 99.9%. Based on the study, activated carbon derived from foxtail palm EFB showed good potential as an adsorbing agent.

1. Introduction

Dyes are broadly used in the leather and textile dyeing, food technology, pharmaceutical and cosmetic industries (Wu, et al., 2014). One of the greatest contributors of water pollutant after agriculture is the textile industry (Fabon, et al., 2013). Textile industry is among the chemical industries involved in water pollution wherein degree of pollution is characterized by its high water consumption and chemical usage (Fabon, et al., 2013). Dyeing process requires some amount of water. Wastewater from printing and dyeing units is often rich in colors, containing residues of reactive dyes and chemicals (Adinew, 2012). Often, the wastewater is discharged without any further treatment. The release of dyes in form of wastewater produces serious environmental problems. Dye being one of the recalcitrant; persist for long distances in flowing water, retards photosynthesis, inhibit growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen (Patil, et al., 2011). Dyes also can be harmful to humans as it may cause allergic dermatitis, skin irritation and cancer.

Nowadays, many industries are using activated carbon as adsorbing agent for dye removal in wastewater. However, because of the high cost of activated carbon and rising related problems has forced new researches in order to find alternative low cost adsorbing agents. As time passes, numerous counts of adsorbing agents-activated carbons based on agricultural by-products or wastes, such as coconut shell, sugarcane bagasse, rice husk, orange peel etc, had successfully been produced. Nevertheless, adsorption capabilities of those agents are still not satisfying enough (Lokman, 2006). Mohamed, et al., (2014) conclude a successful methodology for removal of all types of dyes at low cost has not been established due to the high cost of adsorbent preparation. Thus, new adsorbent agents which are more economically cheap and available, and highly adsorptive are still needed. In this study, a new adsorbent agent derived from foxtail palm empty fruit bunch (EFB) was used.

2. Materials and Methods

2.1. Reagents

Analytical grade reagents and deionized water were used in all sample preparations and experiments.

2.2. Preparation of Activated Carbon from Foxtail Palm EFB

The foxtail palm tree empty fruit bunch (EFB) was collected from Jeli district, Kelantan. After collecting, it was then washed and oven dried. After that, part of the dried foxtail was soaked in concentrated sulphuric acid, H_2SO_4 in a sufficient amount to cover the raw materials completely. The mixture was mixed vigorously for 30 min, and was left for 1h. After mixing, the slurry was placed in crucibles and heated to a temperature of 300ºC for 24h. After carbonization, the products were then washed with distilled water to remove residual organic and mineral

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materials and were subjected to dry at 100ºC in an oven for 24h. The preparation of activated carbon was done based on method discussed by Rahman, et al., (2012) and with minor modification.

2.3. Preparation of Dyes

A stock solution (1000 mg/L) of methylene blue ($C_{16}H_{18}C_1N_3S$) was prepared by dissolving 1 g of methylene blue powder with distilled water. Similar procedure was used to prepare congo red dye.

2.4. Comparative Biosorption Study

In the adsorption experiments, a set of conical flasks containing 25 mL of samples were taken. Methylene blue and congo red solutions were used to compare the activity of the activated carbon. The percentage of removal of the dyes was calculated as Eq. 1.

$$\text{Percentage of removal} = \frac{(C_i - C_f)}{C_i} \times 100\% \qquad \text{(Eq. 1)}$$

C_i is the initial concentration and C_f is the final concentration

2.5. Effect of pH

In this experiment, a series of conical flasks containing, 25 mL of 25 ppm dyes (methylene blue and congo red) with different pH of 4, 6 and 8 with 1.0 g of activated carbon made from foxtail palm EFB was added. The conical flasks were then shaken in an orbital shaker at 150 rpm. After 1h, the samples were withdrawn and filtered. Percentage of dye removal was determined by an UV-Visible spectrophotometer (DR-5000) at 663 nm-669 nm wavelength. Each experiment was repeated twice and mean value was taken.

2.6. Optimization of Biosorption Parameters using Response Surface Methodology (RSM)

In this study, optimization is done to discover the conditions at which to apply a procedure that produces the best possible response. According to Bezerra, et al., (2008), the most pertinent multivariate techniques used in analytical optimization is the response surface methodology (RSM). Response surface methodology is a collection of mathematical and statistical techniques based on the fit of a polynomial equation to the experimental data (Bezerra, et al., 2008). The experimental design used in this study is the Box-Behnken design. This experimental design uses three variables and a total of 17 reactions to study the response pattern and to determine the optimum combination of variables. According to Box & Behnken (1960), 17 experiments were sufficient to find the best response pattern. The effects of A (dye concentration, ppm), B (contact time, h) and C (adsorbent dosage, g) at three variables' levels (-1, 0, +1) in the reaction process were evaluated. The software Design Expert 6.0.8 was used in analysing the experimental data. The independent variables and their levels were coded by Box-Behnken design model as given in Table 1.

Table 1: The actual and coded independent variables in the Box-Behnken design for the percentage removal of methylene blue

Variables	Symbols	Levels		
		-1	0	+1
Dye concentration (ppm)	*A*	25	162.5	300
Contact time (h)	*B*	1	12.5	24
Adsorbent dosage (g)	*C*	1	2	3

The quadratic equation model discussed by Marzuki, et al., (2015) was used to estimate the optimum value and consequently, to describe the interaction between the factors. The quadratic equation model is as in Eq. 2.

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_{j2} + \sum_{i=1}^{j-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad \text{(Eq. 2)}$$

Y is the response, i and j are the linear and quadratic coefficients, respectively, X_i and X_j are the uncoded independent variables and regression coefficients, k is the number of studied and optimized factors in the experiment, β_0 is a constant coefficient, β_j, β_{jj}, and β_{ij} are the interaction coefficients of linear, quadratic and second order terms, respectively, k is the number of studied factors and ε is the error. The value of correlation coefficient (R^2) was used as a tool to express the quality of the fit of the polynomial model. The significance of a model was represented by a p-value < 0.05. Analysis of variance (ANOVA) was also carried out. The stated statistical analysis discussed by Marzuki, et al., (2015) to illustrate the removal of dye is suitably characterized by the quadratic model.

3. Results and Discussion

3.1. Comparative Adsorption

3.1.1. Effect of pH

The comparative adsorption of both methylene blue and congo red onto activated carbon has been investigated from pH of 4, 6 and 8. It was found that the percentage removal of methylene blue is higher than congo red as shown in Figure 1, with 93.89%, 94.64% and 92.32% respectively. Interestingly, there was no significant difference in terms of percentage removal for methylene blue. As for congo red, there was no significant different in percentage removal between pH 6 and 8. However, at pH 4, the percentage removal was found to be the lowest with 53.25%. The result showed that the effect of pH in methylene blue is insignificant. Meanwhile, the percentage of removal for congo red is influenced by the increasing pH of solution. According to Alqaragully (2014), increase in adsorption capacity of congo red dye with increase of pH of solution caused by attractive forces of functional group of dye and adsorbent force. Thus, based on the obtained result, methylene blue was chosen as an adsorbent agent for subsequent experiments.

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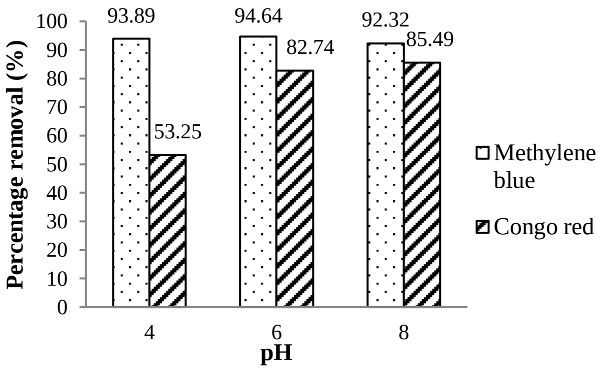

Figure 1: Effect of pH on adsorption of dye solution

3.2. Optimization of Biosorption Parameters using Response Surface Methodology (RSM)

3.2.1. RSM Design Table

The actual experimental design matrix which consisted of 17 experiments has been designed by Box-Behnken design is given in Table 2. The percentage removal of methylene blue was found to be in the range of 64.62% - 99.87%.

3.2.2. Regression Model and Analysis of Variance (ANOVA)

A best fitting model was established by a regression analysis based on the experiment data and using Design Expert 6.0.8 software (Eq. 3). Fitting of the data to various models and their subsequent ANOVA illustrated that the percentage removal of methylene blue was suitably characterized by a quadratic polynomial model. The significant terms and the equation, in terms of coded factors are showed in Eq. 3.

$$Y (\%) = 99.81 – 8.53A + 6.97B + 7.52C – 5.41A2 – 3.13B2 – 3.45C2 + 8.29AB + 8.77AC – 5.13BC \quad \text{(Eq. 3)}$$

where Y is the percentage removal of methylene blue (%), A is the dye concentration (ppm), B is the contact time (h) and C is the adsorbent dose (g). Synergistic effect between mutual interacting or individual parameters is represented by a positive sign in front of the term, whereas the negative sign represents the antagonistic effects (Marzuki, et al., 2015). Contact time (A), adsorbent dose (B), interaction between dye concentration and contact time (AB), and interaction between dye concentration and adsorbent dose (AC) represent synergistic effect in this study.

The statistical significance of ratio of mean square due to regression and mean square residual error was tested using ANOVA. ANOVA is a statistical method that subdivides the total variation in a set of data into component parts linked with specific sources of variation for the purpose of testing hypotheses on the parameter of the model (Rusly, et al., 2010). The ANOVA result for the removal of methylene blue using activated carbon is shown in Table 3.

Table 2: Experimental design and results of the response surface design

Run no.	A: Dye concentration (ppm)	B: Contact time (h)	C: Adsorbent dose (g)	Percentage removal (%)
1	162.5	24	1	97.75
2	25	12.5	1	99.59
3	300	1	2	66.3
4	162.5	1	3	98.98
5	300	24	2	99.58
6	162.5	12.5	2	99.85
7	300	12.5	3	99.85
8	162.5	12.5	2	99.82
9	25	24	2	99.67
10	162.5	12.5	2	99.82
11	162.5	24	3	99.87
12	25	1	2	99.82
13	162.5	1	1	76.33
14	162.5	12.5	2	99.8
15	300	12.5	1	64.62
16	162.5	12.4	2	99.75
17	25	12.5	3	99.75

Table 3: Analysis of variance (ANOVA) and coefficients of the model

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	Prob > F	
Model	2346.92	9	260.77	61.25	< 0.0001	significant
A	581.41	1	581.41	136.6	< 0.0001	
B	388.09	1	388.09	91.16	< 0.0001	
C	452.40	1	452.40	106.3	< 0.0001	
A2	123.13	1	123.13	28.92	0.0010	
B2	41.19	1	41.19	9.675	0.0171	
C2	50.05	1	50.05	11.76	0.0110	
AB	274.73	1	274.73	64.53	< 0.0001	
AC	307.48	1	307.48	72.22	< 0.0001	
BC	105.37	1	105.37	24.75	0.0016	
Residual	29.80	7	4.26		< 0.0001	
Lack of Fit	29.80	3	9.93	7249.57		significant
Pure Error	0.00548	4	0.0014			
Cor Total	2376.72	16				
R^2	0.9875					
Predicted R^2	0.7944					
Adjusted R^2	0.9713					

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The Model F-value of 61.25 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, A^2, B^2, C^2, AB, AC and BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 7249.57 suggests that the Lack of Fit is significant. There is only 0.01% chance that a "Lack of Fit F-value" this large could occur due to noise.

The validity of the model was also confirmed by the high value of the adjusted R^2 (0.9713) compared to the value of predicted R^2 (0.7944), which suggested that there was a total variation of 97% percentage removal to the independent variables. On the contrary, only 3% of the total variation could not be explained by the model. According to Marzuki, et al., (2015), the experimental and predicted values share good correlation when the value of correlation coefficient (R) approaches 1. Based on the obtained result, the high value of R^2 (0.9875) proved the good relation between experimental and predicted values of the response. Thus, the relationships, represented by the model were well within the chosen range.

3.2.3. Effect of Dye Concentration and Contact Time

As illustrated in Figure 2, the response surface curve is shows the effect of dye concentration and contact time with adsorbent dose of 2.00 g as its constant factor. At concentration of 25 ppm, it was found that the percentage removal of methylene blue at 1h and 24 h produces significant difference with 99.54% and 99.67% respectively.

Meanwhile, at concentration of 300 ppm, at 1 h, the percentage removal was found to be the lowest with 66.30%, whereas at 24 h the removal was as high as 99.58%. It can be seen that highest percentage removal can be achieved during longer contact time as well as higher dye concentration. As for the dye concentration of 162.50 ppm with contact time of 12.50 h, the obtained percentage removal was almost constant (in the range of 99.75% to 99.85%). It was established from the study that, as the dye concentration and contact time increases, the percentage removal also increases. This is because, in the process of dye adsorption, before the methylene blue molecules diffuses into the porous structure of the adsorbent, the molecules have to first come across the boundary layer film onto adsorbent surface (Tan & Hameed, 2001). Therefore, the higher concentration of methylene blue solutions will take relatively longer time to be adsorbed due to higher amount of molecules.

3.2.4. Effect of Dye Concentration and Adsorbent Dose

Figure 3 is showing the effect of dye concentration and adsorbent dose with constant contact time of 12.50 h. Maximum percentage removal was obtained from all the variables except for experiment number 15 (Table 2) with only 64.62%. Percentage removal decreased with increase in concentration. This is due to the increase in availability of surface active sites resulting from the increased dose and accumulation of the adsorbent (Patil, et al., 2011). However, increase in adsorbent dose lead to increase in dye removal. This is primarily because higher adsorbent dose provides large excess of adsorption sites (Wu, et al., 2014).

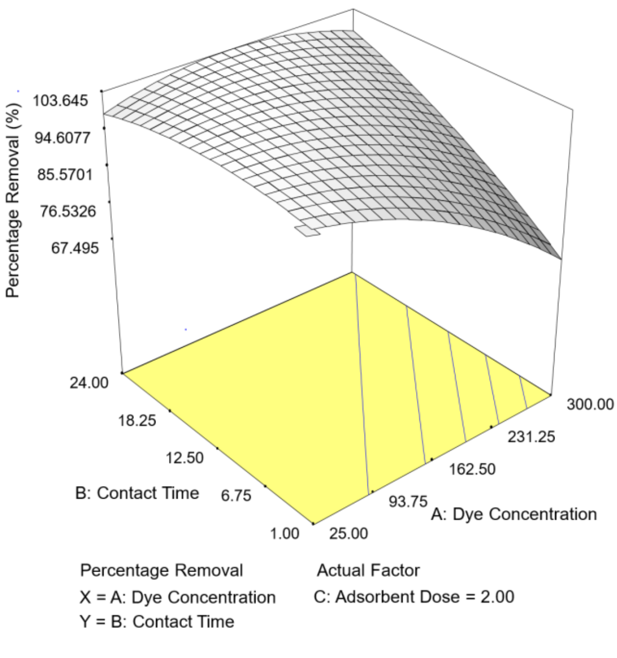

Figure 2: Response surface curve showing the effect of dye concentration (A) and contact time (B)

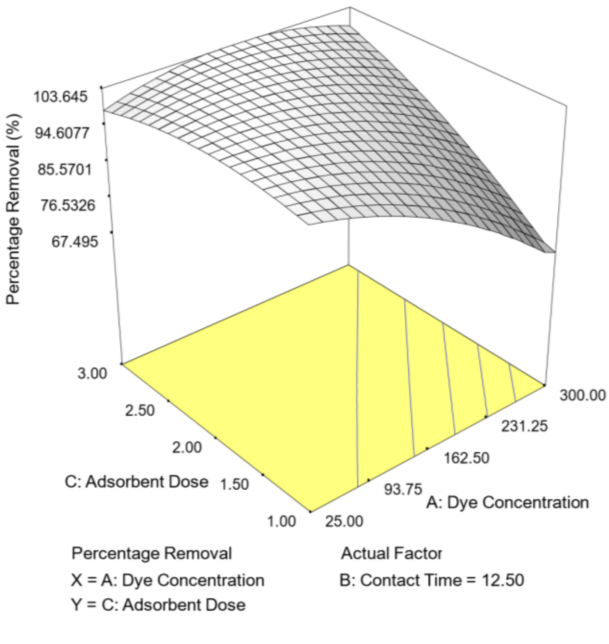

Figure 3: Response surface curve showing the effect of dye concentration (A) and adsorbent dose (C)

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3.2.5. Effect of Contact Time and Adsorbent Dose

As displayed in Figure 4, the response surface curve is showing the effect of contact time and adsorbent dose with dye concentration of 162.50 ppm as its constant variable.

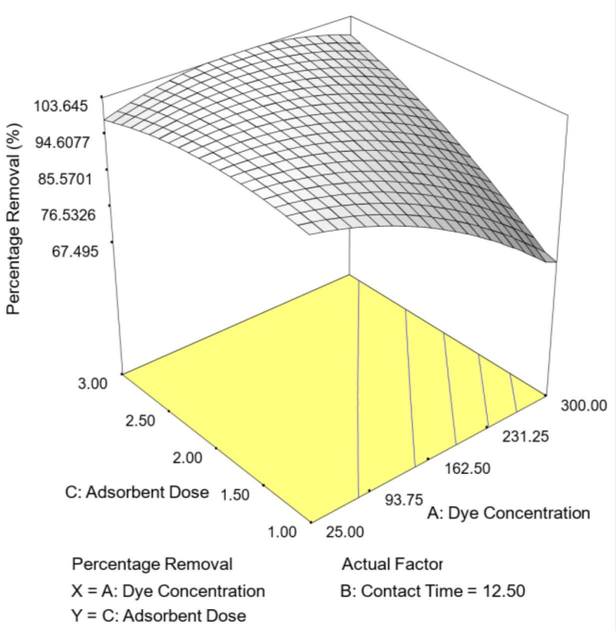

Figure 4: Response surface curve showing the effect of contact time (B) and adsorbent dose (C)

The percentage removal was found to be high with only slight differences between them. It ranges from 97.75% to 99.87%. Although, only experiment number 13 (Table 2) was found to be the lowest with only 76.33% percentage removal. Percentage removal decreased with minimum adsorbent dose and contact time. It is clear that from this study, an increase in the percentage of dye removal related to increase in adsorbent dose and contact time. The increase in removal of methylene blue with adsorbent dose is due to the introduction of more binding sites for adsorption (Alqaragully, 2014). As more adsorbent dose is introduced, more adsorption sites are available for adsorption reaction to take place. And as the contact time increases with the adsorbent dose, the chances of total dye removal are definite.

3.2.6 Suggested Optimum Conditions

The highest percentage removal from various run was 99.87% at 162.50 ppm dye concentration, 24 h contact time and 3 g of adsorbent dose. Optimization adsorption process is necessary to obtain highest percentage removal. Therefore, optimized function of Design Expert 6.0.8 is used to seek the optimum point on response surface. The determined optimum point designated the required optimal combination of variables to achieve the highest percentage removal (Marzuki, et al., 2015). By using the optimized function in Design Expert 6.0.8, one maximum percentage removal was selected. The optimization was run under the conditions of 100 ppm dye concentration, 13 h contact time and 2.00 g of adsorbent dose. The result is shown in Table 4.

4. Conclusion

The current study on removal of methylene blue from aqueous solution by foxtail palm EFB activated carbon has been successfully proven. Adsorption reactions were carried out as the dye concentration, contact time and adsorbent dose were taken as its variables. The highest percentage of methylene blue removal was found under the optimized conditions with 99.90% removal. The adsorption capability was well described using RSM. Based on the findings, activated carbon derived foxtail palm tree EFB showed potential as an adsorbing agent.

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Table 4: The obtained optimum conditions for removal of methylene blue

Experiment	Dye concentration (ppm)	Contact time (h)	Adsorbent dose (g)	Predicted yield (%)	Actual yield (%)	Deviation (%)
1	100	13	2	102.98	99.9	3.08

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