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Spent Coffee Ground as Low-Cost Adsorbent for Congo Red Dye Removal from Aqueous Solution

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Abstract. This study represents the utilisation of spent coffee ground to remove Congo red dye from aqueous solution. Congo red dye may cause adverse effect towards human and aquatic organism if present in water. This study investigated three parameters, adsorbent dosage (0.5, 1.25 and 2 g), initial dye concentration (10, 30 and 50 mg/L) and contact time (10, 35 and 60 min). Batch adsorption studies were carried out to study the effect of these parameters towards percentage of Congo red removal. Optimisation study was conducted using Response Surface Methodology (RSM) by employing Central Composite Design (CCD). Quadratic model was selected for the response. The highest percentage of Congo red removal obtained was 88.43% with operating conditions of 2 g adsorbent dosage, 50 mg/L initial dye concentration and 60 minutes contact time. Meanwhile, the percentage of CR removal that predicted by RSM was 89.17% with conditions of 1.87 g adsorbent dosage, 48.18 mg/L initial dye concentration and 57.96 minutes contact time with the desirability of 1. This study indicates that spent coffee ground could be employed as a low cost adsorbent for the removal of Congo red dye.

1. Introduction

Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) is being classified as direct dye was being used in the dyeing of cotton and rayon, paper, leather, and nylon. Congo red dye is a benzidine-based azo dye, contains amines, NH_2 and sulfonate, SO_3 functional groups have an ability to metabolize to benzidine, which carcinogenic to human being [1, 2]. Untreated effluent that contain CR dye will cause disruptions to photosynthetic processes of aquatic plants, drop oxygen levels in water and resulting in the suffocation of aquatic flora and fauna [1] allergic dermatitis, skin irritation, cancer, and mutations [2].

Various method can be used to treat the dye wastewater either physical or chemical method. For example, sonochemical degradation, photochemical degradation, electrochemical removal, electrochemical degradation, coagulation and flocculation, membrane separation, activated carbon adsorption, biodegradation, fenton-biological treatment scheme, photo-fenton processes, oxidation or ozonation [3]. However, all these methods are highly cost for developing country. As alternative, adsorption was found as the most effective method for wastewater treatment. Numerous studies have been done to find out the most efficient adsorbent that able to remove overall dye from wastewater.

Coffee is one of the high demand agricultural products because it is the most preferable brewed drink. In the process of brew coffee production, the solid residue that produce from coffee extraction is pressed and dried [4]. As a result, the production of soluble coffee produce large amount of residue is generated annually. To overcome the problem, comprehensive development of proper wastes management action with the existing national regulations is required. In this study, raw coffee waste ground was used as adsorbent to remove Congo red dye from wastewater. The dripping process of coffee will transform the coffee beans into coffee-ground with micro- or macrospores. Furthermore, the spent coffee waste contains a large amount of organic compounds such as fatty acids, lignin, cellulose, hemicellulose and other polysaccharides [5]. Instead of disposing them, they can be a perfect source of adsorbent and be used to remove dye from wastewater [6].

In this study, the response for RSM model that being used is Congo red removal (%) with three process variables, which are adsorbent dosage, initial concentration and contact time. The adsorption performance of spent coffee ground was studied using Response Surface Methodology (RSM) by employing second-order polynomial model of Central Composite Design (CCD).

2. Materials and Methods

2.1. Chemicals
The chemicals that used are CR dye (Bendosen), distilled water, 0.1M citric acid ($C_6H_8O_7$) (Sigma-Aldrich) and 0.2M disodium hydrogen phosphate (Na_2HPO_4) (HmBG).

2.2. Preparation of spent coffee grounds as adsorbent
The spent coffee grounds collected from a certain coffee shop was washed and rinsed with water until the brown colour of the water turned clear. Then, it was sun dried to remove the water [7]. Then, spent coffee ground was dried at 105°C for 5 hours in the oven. The dried spent coffee ground was grinded and sieved using a sieving machine to get particle size of 300µm. The spent coffee ground adsorbent powder was collected and kept in a desiccator and used for further analysis.

2.3. Batch adsorption studies
A stock solution of Congo red (1000 mg/L) was prepared in distilled water, and the working solutions were prepared from successive dilution of stock solution. Batch adsorption studies were carried out using the prepared spent coffee ground as adsorbent. The constant parameters in this study were agitation speed (150 rpm), temperature (37°C), pH 5, volume of solution (100 mL) and adsorbent size (300 µm). Whereas, the three manipulated variable are initial Congo red dye concentration, contact time and adsorbent dosage. The range of initial Congo red dye concentration was 10 to 50 mg/L. The contact time was varied from 10 to 60 minutes and the adsorbent dosage was 0.5 g to 2 g.

UV spectrophotometer Genesys 20 was used to measure the absorbance reading of Congo red solution. The maximum wavelength of 498 nm was used throughout the experiment to obtain standard calibration curve and to determine absorbance reading of CR solution after adsorption process. The percentage of Congo red removal was calculated using Equation 1. The data was then inserted in Design Expert software version 10 for analysis.

$$\text{Percentage of Congo red removal, Y (\%)} = \left(\frac{C_o - C_f}{C_o} \times 100\%\right) \tag{1}$$

2.4. Experimental design using response surface methodology (RSM)
In the setting of CCD in Design Expert software (version 10.0), the independent variables were A (initial concentration), B (adsorbent dosage) and C (contact time), while the response variables were % (Congo red removal). CCD allowed each independent variable to range in three levels: the low level (-1), the centre level (0) and the superior level (+1), which are shown in Table 1. A total of 20 experimental runs were performed. Statistical analysis was carried out to check the significant effect for the parameters. Analysis of the results involved the effect of parameters on both responses using 3D response surface graph and contour plot.

Table 1. Variables with their respective coded values.

Variable	Code	Unit	Real values			Coded values		
			Low	Centre	High	Low	Centre	High
Initial dye concentration	A	mg/L	10	30	50	-1	0	+1
Adsorbent dosage	B	g	0.5	1.25	2	-1	0	+1
Contact time	C	min	10	35	60	-1	0	+1

3. Results and Discussion

3.1. Response surface Methodology

Table 2 shows the experimental responses using CCD model. The maximum percentage of Congo red removal was 88.43% with operating conditions of 2 g adsorbent dosage, 50 mg/L initial dye concentration and 60 minutes of contact time. The minimum percentage of CR removal was 44.37% with operating conditions of 0.50 g adsorbent dosage, 50 mg/L initial dye concentration and contact time of 10 minutes. To determine the relationship between the independent variables and its corresponding response, several types of model, namely, linear, 2FI, quadratic and cubic model have been tested. The program recommends quadratic model for Congo red removal (%) with adjusted R-squared 0.9416. Regression analysis was performed to fit the response function of Congo red removal (%). The final empirical model for Congo red removal, Y (%) is shown in Equation 2.

$$Y=80.55+6.6\,A-0.57\,B+1.25\,C+9.54\,AB-4.43\,AC+6.16\,BC\;-5.57\,A^2-1.54\,B^2-1.58\,C^2 \quad (2)$$

From the model, negative signs in front of the terms indicate antagonistic effect, whereas the positive sign indicate synergistic effects. Equation 2 was used to predict Congo red removal (%) in combination with the experimental data, which are given in Figure 1. The predicted value generated by CCD model was indicated by the straight line and the actual values from the experimental data were represented by the point. Some of the actual values overlap with the predicted value. Overall, the placement of actual value was near with the predicted values which imply the actual value was best fit with the predicted value. The F-test analysis of variance (ANOVA) was used to evaluate the statistical significance of the quadratic model equation between adsorbent dosage, contact time, and initial concentration shown in Table 3. The determination coefficient (R^2) shown was significant at a confidence level of 97% for Congo red removal. The stability of the model was further justified through analysis of variance (ANOVA).

In the experimental design, the significance of every source of variation was determined by p-value. If the value of p-value is less than 0.0500, it indicates that the result data is not random and the model terms are statistically significant [8, 9]. From Table 3, based on p-values of each model term, the independent variables (A), interactive coefficients (AB, AC and BC), quadratic terms (A^2) significantly affected the percentage of Congo red removal.

Table 2. Experimental design matrix with coded value and response values.

Run	Adsorbent dosage (g), (A)	Initial concentration (mg/L), (B)	Contact time (min), (C)	Removal of Congo red (%)
1	-1	0	0	64.24
2	0	0	0	81.16
3	0	0	0	80.20
4	0	0	0	81.71
5	-1	-1	+1	75.71
6	+1	+1	+1	88.43
7	+1	0	0	85.07
8	+1	-1	-1	79.00
9	+1	-1	+1	59.25
10	0	0	0	80.84
11	0	0	0	80.29
12	-1	-1	-1	77.97
13	0	0	0	80.38
14	0	0	+1	82.25
15	0	+1	0	80.02
16	+1	+1	-1	83.77
17	0	-1	0	77.35
18	0	0	-1	75.03
19	-1	+1	-1	44.37
20	-1	+1	+1	66.98

Table 3. Analysis of variance (ANOVA) for response surface quadratic model.

Source	Sum of squares	df	Mean of square	F-value	p-value	Remarks
Model	1944.13	9	216.01	35.03	<0.0001	Significant
A-Adsorbent dosage	438.85	1	438.85	71.17	<0.0001	Significant
B-Contact time	3.24	1	3.24	0.53	0.4851	Not significant
C-Initial concentration	15.57	1	15.57	2.53	0.1431	Not significant
AB	727.38	1	727.38	117.96	<0.0001	Significant
AC	156.93	1	156.93	25.45	0.0005	Significant
BC	303.65	1	303.65	49.24	<0.0001	Significant
A^2	85.40	1	85.40	13.85	0.0040	Significant
B^2	6.49	1	6.49	1.05	0.3290	Not significant
C^2	6.89	1	6.89	1.12	0.3153	Not significant
R-squared	0.9693					

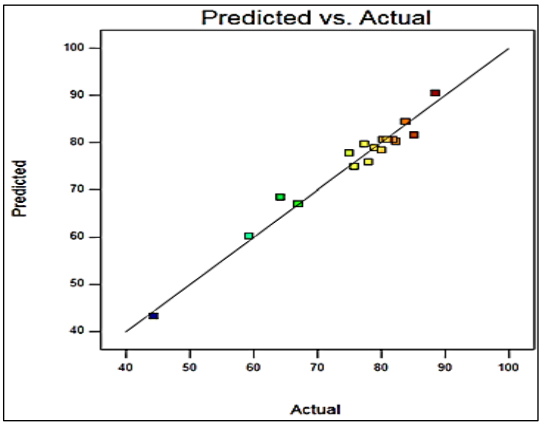

Figure 1. Predicted values vs. experiment values of Congo red removal (%).

Figure 2 shows the three dimensional surface responses for two factors maintained a third at its superior level. The figure indicates that by increasing the adsorbent dosage or contact time and decreasing the initial concentration, the Congo red removal (%) will increase. These results are similar with the classical experiment, study of effect adsorbent dosage, contact time and initial concentration.

Percentage of Congo red removal increases gradually from 65.85% at 0.5 g to 79.92% at 1.25 g then decrease slightly to 79.10% at 2.0 g. This could be explained as the increase of percentage of Congo red removal was rapid initially and then slightly slow down because it almost attained equilibrium [10, 11]. The 3D surface plots gradually increase from 73.85% at 10 mg/L to 79.12% at 30 mg/L then decrease gently to 72.72% at 50 mg/L. For initial concentration 10 mg/L to 30 mg/L, the removal of dye was so efficient due to the availability of many vacant sites for adsorption of dye particles but the percentage of dye removal decreases with an increase in the initial Congo red dye concentration at 50 mg/L, due to the saturation of adsorption sites on the adsorbent surface [12, 13].

The result revealed that there was gradually increase of Congo red percentage removal from 72.03% to 79.12% in contact time condition from 10 to 35 minutes and begin to drop slightly to 74.52% at 60 minutes. The increase of percentage of Congo red removal was rapid initially and then slightly slow down because it almost attained equilibrium. Initially, the rate of adsorption is very high due to large and highly available surface area of adsorbent. After the dye molecules attached to the adsorption site of the adsorbent, longer time was needed for dye to be diffused into the interior active adsorption sites of the adsorbent. Therefore, increase of contact time allowed the whole adsorption process to occur, the rate of adsorption was increasing in this stage until it reached equilibrium [10, 11].

The optimisation process was conducted by the desirability function from Response Surface Methodology (RSM). The desirability helps to determine the factor settings that optimise a single response or a set of responses. It is useful in determining the most efficient operating condition to yield maximum outcome [13]. In this study, the optimum removal of Congo red was 89.17% with operating conditions of 1.87 g of adsorbent dosage, 48.18 mg/L of initial dye concentration and 57.96 minute of contact time with desirability of 1.

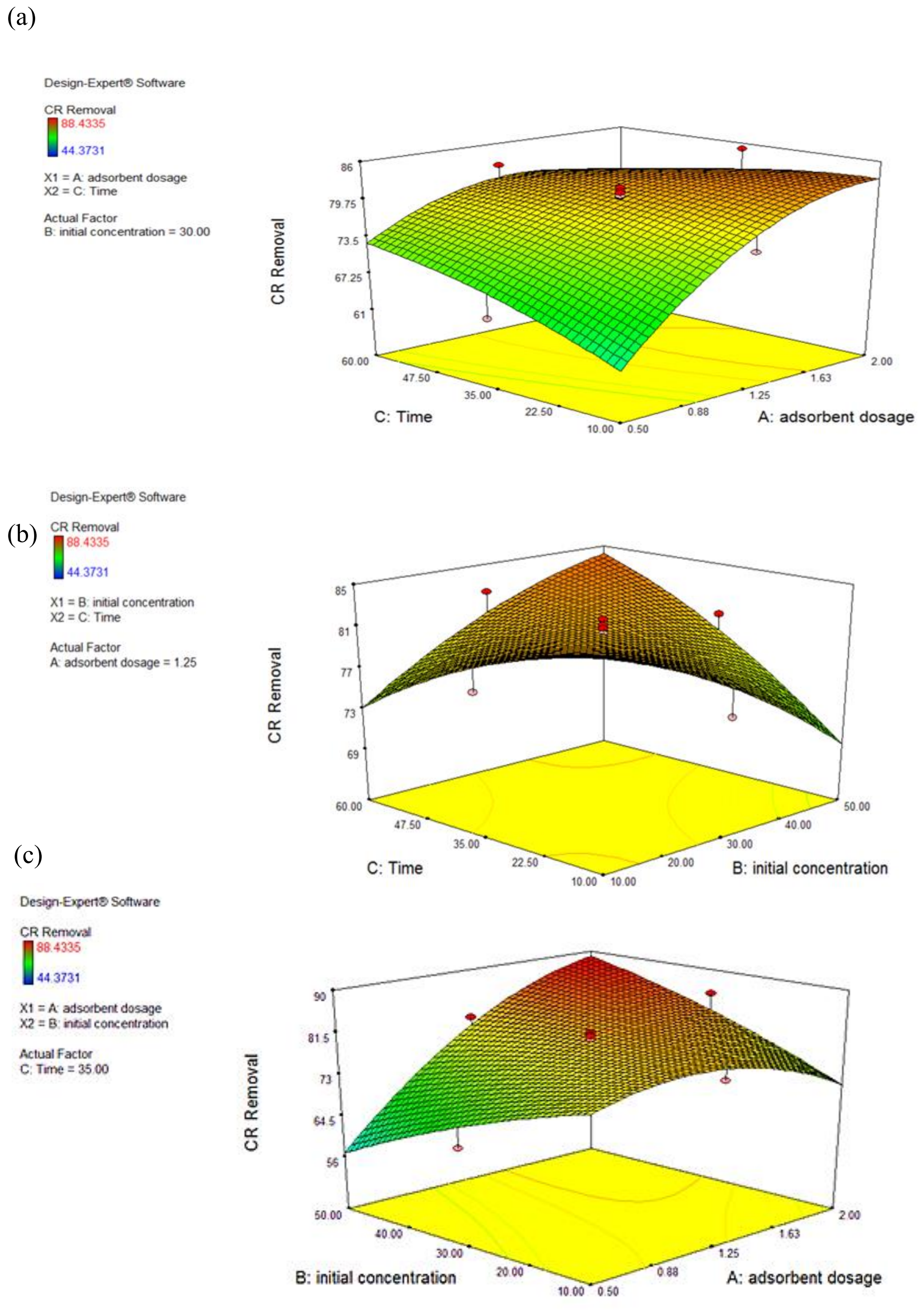

Figure 2. 3D plots: (a) the effect of contact time and adsorbent dosage, (b) the effect of initial concentration and contact time and (c) the effect of initial concentration and adsorbent dosage for Congo red removal (%)

4. Conclusion

Spent coffee ground was successfully used as adsorbent to remove Congo red dye from aqueous solution. Three parameters that investigated, which are adsorbent dosage (0.5 g, 1.25 g and 2 g), initial dye concentration (10 mg/L, 30 mg/L and 50 mg/L), contact time (10 min, 35 min and 60 min) and the response, which is percentage of removal. From the experimental, the percentage of Congo red removal increased with increased adsorbent dosage. Meanwhile, increasing initial dye concentration lead to the decreased for the percentage of Congo red removal and the percentage of Congo red removal increased with longer contact time until it achieved equilibrium point. The statistical analysis revealed the quadratic model was best fit for the response. Optimisation study was performed by employing Central Composite Design (CCD). The optimum conditions for the Congo red removal were found to be at adsorbent dosage of 1.87 g, contact time of 57.96 minutes and initial concentration of 48.18 mg/L. At this optimum condition, the percentage of MB removal was up to 89.17% with desirability of 1.

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