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Optimization on Methylene Blue and Congo Red Dye Adsorption onto Cassava Leaf using Response Surface Methodology

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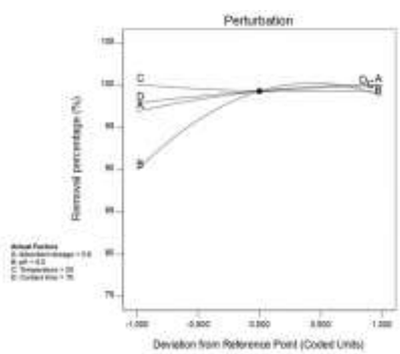
GRAPHICAL ABSTRACT



ABSTRACT

In this work, the operating parameters for removal of Methylene blue (MB) and Congo red (CR) dye via adsorption onto Cassava leaf (CL) powder was optimized using Response Surface Methodology (RSM). The range of study for contact time was between 20 to 120 minutes while the adsorbent dosage range was 0.2 to 1.0 g. As for the pH, the range was from pH 2.0-11.0. Lastly, the temperature of the solution was set from 25 ˚C to 75 ˚C. The trend of the dye removal was found to be best fitted into quadratic model. It was found that pH played a significant role in the MB and CR dye removal. Alkaline condition was more favourable for MB dye removal while CR dye can be adsorbed better on CL in acidic solution. Optimum MB removal at 99.9% could be obtained at minimum contact time of 20 min and room temperature under neutral pH and 0.83 g of CL powder. Meanwhile, 93.24% of CR dye removal could be achieved under optimized condition of 0.86 g of CL powder and acidic condition of pH 2.0 at minimum contact time of 20 min as well as room temperature. This indicates that CL powder has the potential for dye removal under mild condition of room temperature and within short period of time.

Keywords: Methylene blue, Congo red, adsorption, cassava leaf.

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1. INTRODUCTION

Textile industry plays a key role in the world of industrialization as it caters to one of the basic needs of mankind. As a diverse industry, textile industry not only limited to final product range, but also in terms of raw material, processes, products, equipment, and extremely complex supply chain [1-2]. Due to its wide application, the main concerns arise as the textile wet processing utilized more than 2000 different chemicals which can cause harmful effects to human and animal health [1]. From the lists of chemicals that presence in textile wastewater, dyes are the major pollutants among the other chemicals [3].

Different types of textiles requires different chemical properties of dyes. Thus, there are more than 10,000 various dyes and pigments were widely used in industry and specifically the synthetic dyes that generated worldwide annually had reached about 7 x 10^5 tons [4]. The distribution of world consumption of dyes as illustrated in Fig. 1. Based on Fig.1, more than 50% of total global synthetic dye consumption accounts to Asia country [5]. From this statement, the increasing amount of dye consumptions will directly reflect the presence of dye in the effluent as certain amount of dyes might escape from each of the processes and eventually contribute to highly dye concentration in the wastewater.

Fig. 1 World consumption of synthetic dye in year 2017 [5]

Among the synthetic dyes, there are several dyes were commonly used in industrial processes that can cause negative impacts towards human and environment, especially Methylene blue (MB) and Congo red (CR) dye. MB dye was selected as a target contaminant due to its wide utilization in most of the industries such as textile and furniture industries [6]. Due to its wide application, highly concentrated MB dye was expected and proper treatment are required as overdosed of MB dye will cause negative impact towards human health. For instance, it was reported that frequent exposure of MB will harm the human eyes and the ingestion might cause nausea, vomiting and diarrhoea [7, 8].

Based on the dye wastewater generation from various industries worldwide, azo dyes are the main group of dyes, which accounts for 60–70% of total dye effluents [9]. CR dye is one of the examples of azo dyes where it is also well-known of its water soluble properties due to the presence of sulfonic group that make it behave like anionic nature [10]. This made CR dye difficult to degrade and potentially toxic compound [11]. It is considered as doubted carcinogen and mutagen dye where small amount of concentration might bring toxicity to most of the living organisms, especially aquatic life as well as human health [12].

There are several technologies which can be used for dye removal application such as membrane separations, oxidation and adsorption. Among the available methods, adsorption method is preferable because of its simplicity in operation, non-toxicity, eco-friendly and lower cost [13]. However, activated carbon (AC) is deemed to be the best sorption materials [14] and the costs of preparing activated carbon have historically been high which cannot be afforded for continuous long-term usage for small and medium industries [15]. Due to its higher cost, various researches have been initiated to focus on developing low-cost adsorbents for wastewater treatment application [16], where a large diversity of low-cost adsorbents is an by-products (wastes) that generated from agriculture and industrial activities which can helps to minimize the pollutant contaminated wastewaters with acceptable cost [17].

Although there are findings on wastes utilization as the adsorbent, most of the adsorbents having the issues on its limited availability. Therefore, Cassava leaf (CL) can considered as an alternative solution to contribute in the era of low-cost adsorbent because of its all year-round availability, flexibility in planting and harvesting time, drought tolerance [18]. Thus far, Adrian et al. [19] found CL to be a potential adsorbent for Cadmium (II) removal. The effectiveness of CL in MB and CR dye removal application was also proven in our previous work [20]. As such, in this work, the potential of CL as dye removal adsorbent is further optimized using Box-Behnken design (BBD) method. The BBD method was selected in this study because it requires fewer runs in order to generate higher order response surface. Hence, it is less time consuming compared to other design methods [21].

2. EXPERIMENTS

In this work, the Box – Behnken design (BBD), which is a subset of method under Response Surface Methodology (RSM), was applied at three levels for the optimization of the adsorption process. Four numerical factors selected were pH of the solution, adsorbent dosage, temperature of the solution and contact time of the adsorption process. The details of the CL powder preparation and dye removal procedure had been detailed out in our previous work [20]. For this work, the range of contact time was between 20 to 120 minutes. In terms of adsorbent dosage, the range was at 0.2 to 1.0 g. As for the pH, the range was from pH 2.0-11.0. Lastly, the temperature was set from a minimum of 25 ˚C to a maximum of 75 ˚C.

Table 1 Experimental design used in this study.

Run no.	A: Adsorbent Dosage (g)	B: pH	C: Temperature (˚C)	D: Contact Time (min)
1	0.6	6.5	50	70
2	0.2	2.0	50	70
3	1.0	2.0	50	70
4	0.2	6.5	75	70
5	0.6	11.0	75	70
6	0.6	2.0	75	70
7	0.6	6.5	50	70
8	0.6	6.5	50	70
9	0.2	11.0	50	70
10	1.0	6.5	25	70
11	0.6	6.5	75	120
12	0.6	6.5	50	70
13	0.6	2.0	50	20
14	0.6	6.5	75	20
15	1.0	6.5	50	120
16	0.6	6.5	50	70
17	1.0	6.5	50	20
18	0.6	6.5	25	120
19	0.6	11.0	25	70
20	0.6	11.0	50	120
21	0.6	11.0	50	20
22	1.0	6.5	75	70
23	0.2	6.5	25	70
24	1.0	11.0	50	70
25	0.2	6.5	50	20
26	0.2	6.5	50	120
27	0.6	2.0	50	120
28	0.6	2.0	25	70
29	0.6	6.5	25	20

This experimental design consisted of 29 runs as tabulated in Table 1. A total of 29 experiment runs were conducted for both MB and CR dye adsorption, respectively. This was to investigate the impacts of each factors on the removal efficiency of the dyes (MB and CR) by using CL as adsorbent as well as to propose the potential optimum conditions for MB and CR dye removal based on ANOVA. A correlation was for each dye removal was obtained using Design Expert software trial version 11 based on the experimental values obtained.

The dye removal percentage of adsorption is calculated as in Eq. 1 below:

$$\text{Removal percentage} = \frac{(C_0 - C_e)}{C_0} \times 100\% \qquad (1)$$

Where C_0 the initial dye solution concentration (mg/L) and C_e is the dye solution concentration after the designated contact time (mg/L).

3. RESULTS AND DISCUSSION

The trend of the dye removal was found to be best fitted into quadratic model. The standard deviation and coefficient of determination, R^2, are presented in Table 2.

Table 2 Results of model sum of squares.

Source	Std. Dev.	R^2
Model summary statistic for MB		
Quadratic	2.57	0.8613
Model summary statistic for CR		
Quadratic	4.51	0.9070

Fisher's statistical test (F-test) can be used as an indication of the significance of each variable. Table 3 and Table 4 show the analysis of variance (ANOVA) for MB and CR, respectively. The Fisher F-value for MB and CR dye were 6.21 and 9.75, respectively. The large Fisher F-value signifies that the variation in the responses can be explicated by the regression equation. Meanwhile, the P-values of lower than 0.05 indicates the model and the associated terms are statistically significant.

In addition, the coefficient of determination (R^2) was computed where R^2 were 0.8613 and 0.9070 for MB and CR dye, respectively. According to Swamy et al. [22] the R^2 signifies the proportion of the total variation in the response expected by the model. A high R^2 coefficient indicates a satisfactory adjustment of the model to the experimental data.

From this experimental design, the coefficient of variation value obtained from MB and CR dye was 2.65 and 5.38, respectively. The coefficient of variation (CV) is used to show the scattering of the experimental points from the predicted values. Generally, a model with CV of lesser than 10% is preferable [23] as it indicates a high degree of reliability of experiments conducted.

Table 3 ANOVA for MB removal model.

Source	Coefficient estimate	F-value	P-value	Remarks
Model		6.21	0.0008	Significant
A: Adsorbent dosage	1.57	4.51	0.520	
B: pH	4.38	34.90	<0.0001	Significant
C: Temperature	-0.3408	0.2115	0.6527	
D: Contact time	1.02	1.89	0.1911	
AB	-5.03	15.34	0.0016	Significant
AC	-0.1350	0.0111	0.9177	
AD	-0.3150	0.0602	0.8097	
BC	0.2800	0.0476	0.8305	
BD	-2.34	3.32	0.0901	
CD	-0.0925	0.0052	0.9436	
A^2	-0.8302	0.6782	0.4240	
B^2	-4.99	24.54	0.0002	Significant
C^2	0.4523	0.2013	0.6605	
D^2	-0.3964	0.1546	0.7001	
CV.%	2.65			
Adequate precision	10.1877			

Table 4 ANOVA for CR removal model.

Source	Coefficient estimate	F-value	P-value	Remarks
Model		9.75	<0.0001	Significant
A: Adsorbent dosage	-3.02	5.38	0.0360	Significant
B: pH	-8.99	47.55	<0.0001	Significant
C: Temperature	-3.02	5.37	0.0361	Significant
D: Contact time	-0.3008	0.0533	0.8208	
AB	-1.50	0.4402	0.5178	
AC	-7.64	11.46	0.0044	Significant
AD	-1.94	0.7406	04040	
BC	0.5175	0.0526	0.8220	
BD	1.60	0.5025	0.4901	
CD	-6.41	8.06	0.0131	Significant
A^2	-6.02	11.52	0.0044	Significant
B^2	6.36	12.86	0.0030	Significant
C^2	-7.60	18.38	0.0008	Significant
D^2	-5.49	9.60	0.0078	Significant
CV.%	5.38			
Adequate precision	12.0276			

For this work, the empirical correlation between the input variables and experimental results are expressed by Eq. 2 and Eq. 3:

$$\text{Removal rate of MB} = 99.31 + 1.57 * A + 4.38 * B - 0.3408 * C + 1.02 * D - 5.03 * AB - 0.1350 * AC - 0.3150 * AD + 0.28 * BC - 2.34 * BD - 0.0925 * CD - 0.8302 * A^2 - 4.99 * B^2 + 0.4523 * C^2 - 0.3964 * D^2 \quad (2)$$

$$\text{Removal rate of CR} = 89.26 - 3.0225 * A - 8.99 * B - 3.02 * C - 0.3008 * D - 1.50 * AB - 7.64 * AC - 1.94 * AD + 0.5175 * BC + 1.6 * BD - 6.41 * CD - 6.02 * A^2 + 6.36 * B^2 - 7.60 * C^2 - 5.49 * D^2 \quad (3)$$

Fig. 2 shows the perturbation plot for MB dye removal trend with the variation of each parameter, while Fig. 3 shows the perturbation plot for CR dye removal.

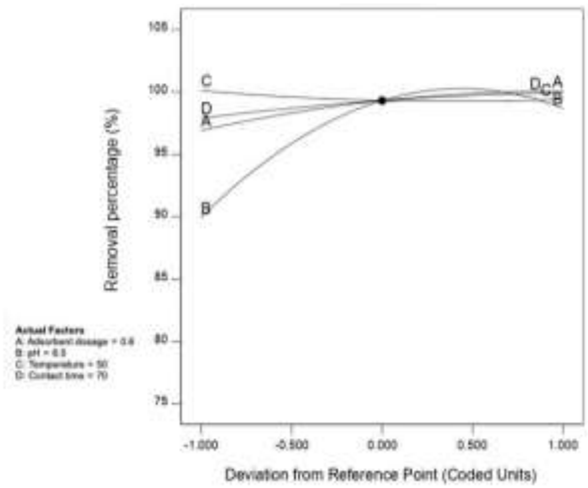

Fig. 2 Perturbation plot for MB dye removal trend

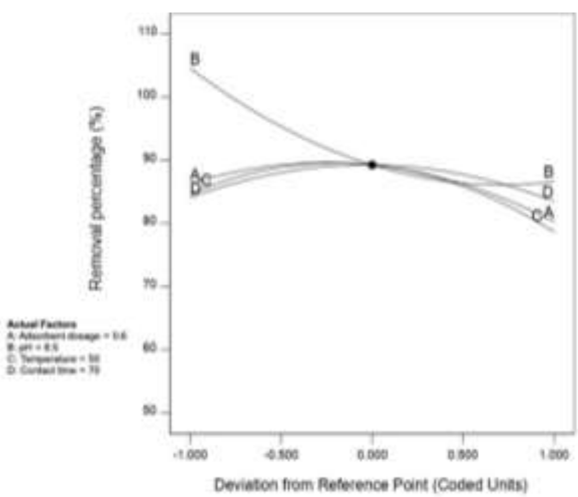

Fig. 3 Perturbation plot for CR dye removal trend

Based on the perturbation plots and ANOVA, it can observed that pH played a significant role in the MB and CR dye removal. MB is a cationic dye which can be adsorbed better by CL in alkaline solution while CR is an anionic dye which can adsorb better on CL in acidic solution. ANOVA for CR removal also identified adsorbent dosage and temperature as significant parameters affecting the dye removal using CL. However, based on the perturbation plot, the amplitude of the effects is not as obvious compared to the effect of pH.

Based on the correlation obtained, optimum conditions for the adsorption process were deduced with the target of obtaining maximum removal rate for CR and MB dye. For this purpose, the Derringer's desirability function method was utilized for optimization of the independent variables [22]. The desirability function scale operates between d = 0 to d = 1 where 0 indicating a completely undesirable response while 1 signifying a fully desired response [24].

In this work, the criteria set was to maximize the removal rate for both dyes at minimum contact time and room temperature for time and energy saving purposes. Therefore, all the parameters were set in the range except contact time was set in target (20 min) and temperature was set at room temperature (25 °C).

Based on Fig. 4, a maximum removal rate for MB can be obtained when adsorbent dosage of 0.83 g, pH of dye solution at pH 7.19 and contact time of 20 min under room temperature will contributed to a maximum removal rate of 99.9% for MB dye adsorption with the overall desirability value of 1.000. On the other hand, for removal of CR, the condition of the parameters where the adsorbent dosage of 0.96 g, dye solution at pH 2.0 and contact time of 20 min under room temperature was expected to contribute to a maximum removal rate of 95.57% with overall desirability value of 0.950 as shown in Fig. 5.

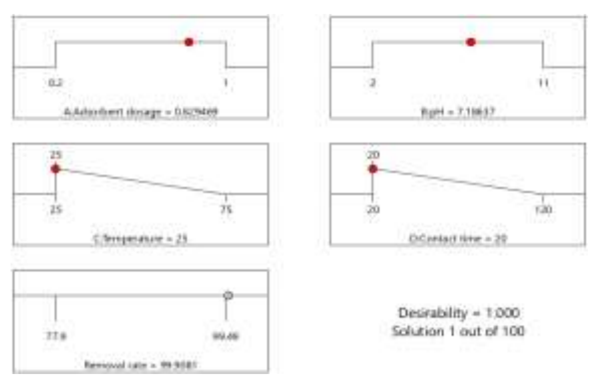

Fig. 4 Desirability ramp for adsorption optimization for MB dye

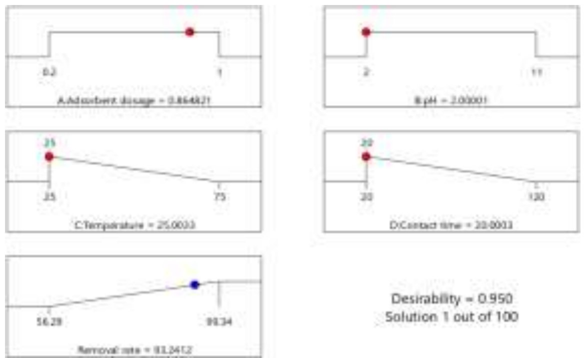

Fig. 5 Desirability ramp for adsorption optimization for CR dye

Physical experimental work was conducted to verify the proposed optimized conditions. Comparison between the predicted value and the actual experimental value at the selected optimum conditions is presented in Table 5 and Table 6 for MB and CR dye adsorption, respectively.

The error between the predicted and actual values was found to be at -1.56% and 2.15% for MB and CR dye adsorption, respectively. This shows that the developed models are well-suited and the optimal values are valid within the specified range of process variables.

Table 5 Comparison between the predicted versus experimental values of the responses at optimum conditions for MB dye adsorption

Optimum condition	Removal percentage (%)		Error (%)
	Predicted value	Experimental value	
Adsorbent dosage = 0.83 g pH = 7.19 Temperature = 25ºC Contact time = 20 min	99.91	98.38	-1.56

Table 6 Comparison between the predicted versus experimental values of the responses at optimum conditions for CR dye adsorption

Optimum condition	Removal percentage (%)		Error (%)
	Predicted value	Experimental value	
Adsorbent dosage = 0.86 g pH = 2.00 Temperature = 25ºC Contact time = 20 min	93.24	95.29	2.15

4. CONCLUSION

In this work, the operating parameters for removal of MB and CR dye via adsorption onto Cassava leaf powder was successfully optimized using RSM. Optimum MB removal at 99.9% could be obtained at minimum contact time of 20 min and room temperature under neutral pH and 0.83 g of CL powder. Meanwhile, 93.24% of CR dye removal could be achieved under optimized condition of 0.86 g of CL powder and acidic condition of pH 2.0 at minimum contact time of 20 min as well as room temperature. This indicates that CL powder has the potential for dye removal under mild condition of room temperature and within short period of time.

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