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Abstract. Batik industry is a growing textile industry in Kelantan. Improper treatment of wastewater from manufacture units leads to water pollution. One of the most abundant and harmful pollutants found in the batik industries effluents is Rhodamine 6G. A nanomagnetic adsorbent composite (NMAC) was used in this study to remove the Rhodamine 6G from aqueous solution. In this study, Box-Behnken Design is applied to obtain a model for optimum conditions for dye removal. A maximal dye removal (99.03%) was attained with optimum conditions; initial dye concentration of 26.12 mg L^{-1}, contact time of 14.33 min, adsorbent dose of 0.05 g, particle size of 190.26 µm and pH of 6.54. A quadratic equation was validated with 99.97 % fit between predicted and experimental outcomes.

INTRODUCTION

Batik industry is well known in Kelantan and dominates by Small Medium Enterprises (SME). The traditional batik manufacturer usually operates at the backyard or nearby river. Accumulation of water discharge containing dyes from small batik manufacture units without proper water treatment is an existing problem [1]. These effluents have considerable negative impacts on the water quality and become a great threat to the people and environment. One of the commercial dyes used in textile industries is Rhodamine 6G which was reported by Material Safety Data Sheet as corrosive, irritant, poses acute toxicity and environmental hazards. Rhodamine 6G dye is a 'Hazardous Chemical' according to the OSHA Hazard Communication Standard [2].

In recent years, numerous water treatment methods involving the physical and chemical treatment for removal of dyes from aqueous solution such as processes of chemical coagulation and precipitation, solvent extraction, membrane filtration and adsorption [3]. Nevertheless, the application of various water treatments is limited by different technological and economical limitations therefore resulted in low efficiency of the removal process.

Currently, magnetic activated carbon has received attention from the researchers because of its unique structural and functional elements resulting in various beneficial usages. Magnetic nanoparticles are biocompatible with low toxicity from the aspect of environmental concerns [4,5]. The magnetic separation techniques of magnetic activated carbon enable it to be cost effective, simplicity and high efficiency in separation of pollutants from aqueous solution. Therefore, low cost and efficient (NMAC) becomes the novel and alternative methodology for removal of dye from aqueous solution. It is microporous and has high specific surface area, porosity and superparamagnetic property which results in magnetic separability. It displays better performance in adsorption if compared with normal activated carbon

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adsorbent or micron sized adsorbent due to high specific surface area [6]. The application of NMAC in removal of dye from aqueous solution is highly encouraged in industries especially in textile industry.

In this research, the application of interest was to evaluate the performance of laboratory developed NMAC for Rhodamine 6G removal from aqueous solution. The challenge of this study to ensure the laboratory developed NMAC able to save time while removing contaminant effectively. To solve the problem, a statistical optimization of different parameters comprises of dye concentration, contact time, adsorbent dose, particle size and pH were tested by adopting the Box-Behnken model of response surface methodology.

PREPARATION OF NANOMAGNETIC ADSORBENT COMPOSITE

A raw coconut shell (CS) was first carbonized by using modified drum method and the carbonized coconut shell were grounded into powder form. The coconut shell powder is then further subjected to activation with KOH at a ratio of 1:3, with slow agitation. The mixture was left to mature for about 5 to 6 hour and then followed by filtration and and rinsing with ddH_2O. The powder is then dried in oven at temperature of 90 °C -100 °C. The dried powder was placed in a muffle furnace (Carbolite ELF 11/6B) and heated to 800-900 °C (10 °C/min), and kept for 15-30 min. The cooled down sample was washed, neutralized with 5% HCl, dried and stored for further modification. The synthesis of CS-NMAC was initiated by acclimatizing the CS activated carbon using nitric acid (HNO_3) solution for 1 h at 80 °C following the method previously described by Wannahari et al [6]. This is to remove any impurities and enhance the active surface of the carbon particle. At the same time, $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ were dissolved with 450 mL of deionized water under mechanical stirring for 30 min at 30 °C. The chemical precipitation was achieved under vigorous stirring by adding 30-60 mL of ammonium hydroxide ($NH_3.H_2O$) solution. The reaction vessel was kept at 70 °C for 1 h. Five grams of modified CS activated carbon powder was added and mixed completely using mechanical stirring. Afterwards, 6 mL of epichlorohydrin was added and stirred at 85 °C for 1 h. The reaction mixture was then sonicated (Q Sonica) at 80 λ for 1 h. The mixture was continuously stirred for another hour at 85 °C. The mixture was then cooled down to room temperature. The precipitate was washed rapidly with deionized water and ethanol, dried at 50 °C, and collected via an external magnetic field.

The NMAC provided were sieved by using different sizes of sieves to classify them into respective sizes. After sieving, the samples were purified by washing with water to remove unwanted impurities and filtered by using Fisher brand filter paper with pore sizes of 90 mm. The washing process was considered complete as the filtrate appeared clear or the pH value of filtrate was approaching 7. The samples were dried in the oven at 80 °C for 3 to 5 days depending on the progress of drying. The purified samples were then kept in containers according to range of sizes for further testing and characterization.

PREPARATION OF RHODAMINE 6G

A Rhodamine 6G stock solution was prepared with concentration 0.005% (w/v). Serial dilution of the stock solution was carried out to prepare working standards prior to equilibrate with different concentrations of dye solution.

BOX-BEHNKEN DESIGN

Box-Behnken experimental design is applied for evaluation of the effects and interactions of the variables and experimental factors optimization. All the parameters which have the strong effects on the response were selected as the variables to be tested in the 46-run experiments of the Box-Behnken design experiment. Therefore, the optimum levels of various parameters were determined. Design Expert version 11 software was used in designing the experiments. In the study, five factors which are dye concentration, contact time, adsorbent dose, particle size and pH were designated as X_1, X_2, X_3, X_4 and X_5 (Table 1). They were coded with +1 and -1 which represent high and low value respectively according to the equation 1:

$$x_i = \frac{Xi - Xo}{\Delta X} \quad i = 1, 2, 3, 4, 5 \tag{1}$$

Where xi is independent variable's coded value, Xi is independent variable's actual value, Xo is independent variable's actual value at center point while ΔX is independent variable's step change value.

TABLE 1. Level of parameters in Box-Behnken experimental design.

Parameters	Minimum (-1)	Maximum (+1)
X_1: Initial dye concentration (mg/L)	1	50
X_2 : Contact time (mins)	15	60
X_3 : Adsorbent dose (g)	0.025	0.25
X_4 : Particle size (µm)	60	225
X_5 : pH	3	10

The mathematical relationship between the independent variables and desire response was modeled by a second-order polynomial equation 2 calculated from the result obtained and was shown as follow:

$$Y=\beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \quad (2)$$

Where Y is response (percentage of dye adsorbed), β_0 is offset term, x_1, x_2, and x_3 are independent variables, β_1, β_2, and β_3 are linear coefficients, β_{12}, β_{13} and β_{23} are cross-product coefficients / coefficients of the linear-by-linear interaction effect between independent variables and β_{11}, β_{22}, β_{33} are quadratic coefficients.

Coefficient of regression (R^2) and analysis of variance (ANOVA) were used to assess the goodness of fit of the polynomial model [7].

PREPARATION OF RHODAMINE 6G

The adsorption capacity of adsorbents was observed by adding the adsorbents into the Rhodamine 6G dye solution at different parameters and then mixed. The solution was then shaken thoroughly using a mechanical shaker under speed of 150 rpm. The commercial activated carbon adsorbent was separated through filtration while external magnetic field was used to separate the NMAC adsorbent from the solution with the help of a magnet. The concentration of Rhodamine 6G in solution after removal was analyzed using Thermo Scientific Genesys 20 UV-Visible spectrophotometer.

The percentage of adsorption or percentage of Rhodamine 6G dye removal was calculated from the equation 3:

$$\% \text{ Adsorption or } \% \text{ Dye Removal} = \left[\frac{Co - Ce}{Co} \right] \times 100\% \quad (3)$$

Where Co and Ce are the initial concentration and equilibrium concentration of the Rhodamine 6G dye, respectively.

RESULTS AND DISCUSSIONS

Results

Five independent variables were prescribed into three levels and selected for each of experiments in Box-Behnken Design. The percentage of Rhodamine 6G dye removal measured in different runs presented wide variation in which the percentage ranged from a minimum of 6.040% to a maximum of 99% (Table 2). The percentage of Rhodamine 6G dye removal is highly influenced by the variables selected in the study.

Analysis of Variance (ANOVA) for Box-Behnken Design

From the analysis of variance (ANOVA) (Table 2), the quadratic model is highly significant (p<0.05) with adequate signal (adequate precision; 37.417). The lack of fit test for the model is not significant (p<0.05) indicated that the model generated from Box-Behnken Design fits well.

The analysis shows significant interaction effects (p<0.05) of dye concentration (A^2), dye concentration and contact time (AB), dye concentration and adsorbent dose (AC). Based on individual parameter, the initial dye concentration (A) is a significant variable (p<0.05) compares to other individual process variables.

TABLE 2. Analysis of variance (ANOVA) for the response surface quadratic model.

Source	Sum of square	Degree of Freedom (DF)	Mean square	*F* value	*P* value	Remarks
Model	14447.73	20	722.39	77.58	< 0.0001	Significant
A – Dye concentration	6975.57	1	6975.57	749.17	**< 0.0001**	
B – Contact time	0.32	1	0.32	0.04	0.8543	
C- Adsorbent dose	12.01	1	12.01	1.29	0.2702	
D – Particle size	1.25	1	1.25	0.13	0.7176	
E - pH	1.01	1	1.01	0.11	0.7459	
A^2	6585.12	1	6585.12	707.24	**< 0.0001**	
B^2	0.86	1	0.86	0.092	0.7652	
C^2	9.00	1	9.00	0.97	0.3379	
D^2	1.12	1	1.12	0.12	0.7325	
E^2	0.54	1	0.54	0.06	0.8117	
AB	128.29	1	128.29	13.78	**0.0015**	
AC	1473.07	1	1473.07	158.21	**< 0.0001**	
AD	4.25	1	4.25	0.46	0.5074	
AE	7.736E-003	1	7.736E-003	8.309E-004	0.9773	
BC	2.22	1	2.22	0.24	0.6310	
BD	4.74	1	4.74	0.51	0.4844	
BE	1.92	1	1.92	0.21	0.6549	
CD	1.55	1	1.55	0.17	0.6883	
CE	4.79	1	4.79	0.51	0.4818	
DE	9.61	1	9.61	1.03	0.3225	
Residual	176.91	19	9.31			
Lack of fit	163.85	14	11.70	4.48	**0.0536**	**Not significant**
Pure Error	13.06	5	2.61			
Cor Total	14624.64	39				

Quadratic Model for Rhodamine 6G Removal By NMAC

From ANOVA analysis, the quadratic model with statistical significance was obtained, which in terms of actual variables is given as (equation 4):

$$\text{Percentage of Dye Removal} = +\,40.529 + 3.299*\text{Dye concentration} + 0.383*\text{Contact time} - 295.091*\text{Adsorbent dose} + 0.102*\text{Particle size} + 0.532*\text{pH} \quad (4)$$

Interactive Effect of Dye Concentration And Contact Time

The interactive effect between the dye concentration (1 - 50 mg L^{-1}) and contact time (15 – 60 min) on the percentage of Rhodamine 6G dye removal indicated that the removal percentage increases with the increase of contact time Fig. 1. At a specific dye concentration, the longer the contact time, the higher the removal efficiency. The adsorption process is considered complete when the contact time is longer [8]. Meanwhile, when the dye concentration increased, the percentage of Rhodamine 6G dye removal also increased with the condition of increase of contact time. Nevertheless, as the dye concentration reached the maximum point in the study which was 50 mg L^{-1}, the percentage of dye removal showed a slightly decrease trend due to the adsorption process has reached an equilibrium and the dye removal percentage has achieved its maximum point even a longer contact time has been applied [9]. The decrease in the removal of dye after reach the maximum point is the reduction in the available sorption sites contributed to the retarded decrease of dye removal.

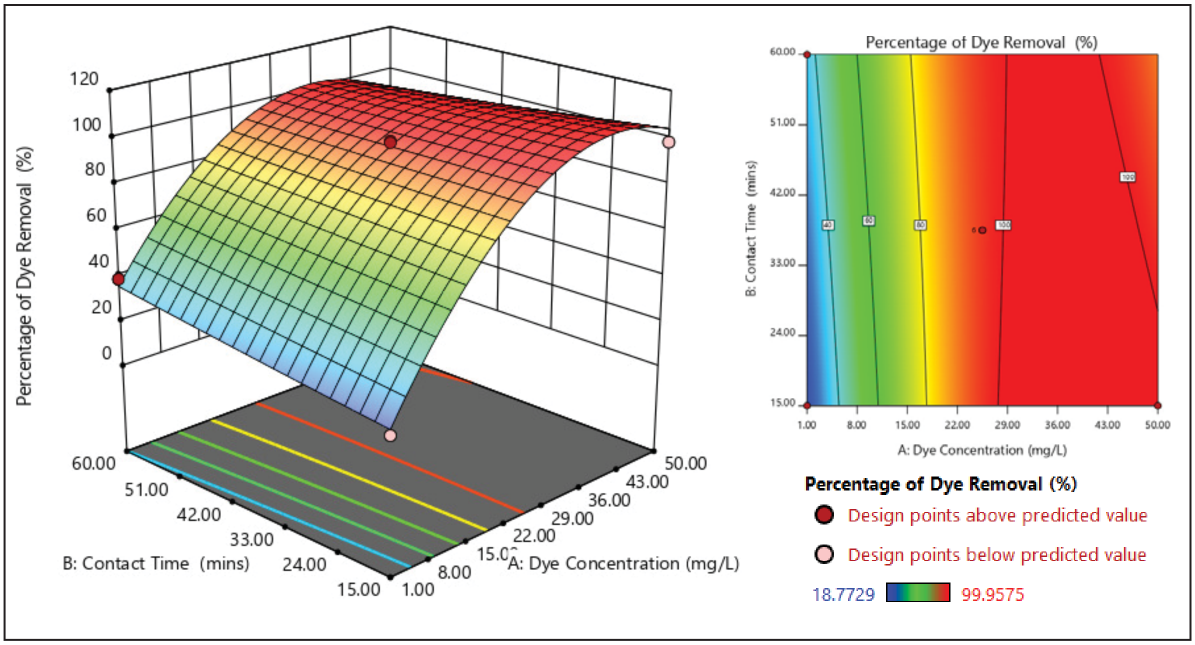

FIGURE 1. (a) Surface graph and (b) contour for interactive effect of dye concentration and contact time.

Interactive Effect of Dye Concentration and Adsorbent Dosage

The interactive effect between the dye concentration (1 - 50 mg L^{-1}) and adsorbent dose (0.03 g - 0.25 g) on the percentage of Rhodamine 6G dye removal indicated that the increase of adsorbent dose increased the percentage of dye removal as shown in Fig. 2. Increase of adsorbent dose contributed to increase of sorption sites for adsorption and subsequently increases the percentage of dye removal. When the dye concentration and adsorbent dose increase, the percentage of dye removal increases until a maximum point was achieved. After the maximum point of dye removal percentage, as the dye concentration and adsorbent dose continued increases, the percentage of dye removal started to show a decreasing trend. When the adsorbent dose was further increased above the optimal amount, the adsorptive capacity showed a decreasing trend due to high adsorbent dose caused particle interaction, aggregation which then decreased the total surface area of adsorbent and increased the diffusional path length at the same time [10]. Rapid dye removal in the initial stage of the experiment at different concentration of dyes however the removal become constant after reach the equilibrium stage and this could be due to large number of active centers at the beginning of adsorption and saturation at the centers on the surface of the adsorbent after reach equilibrium. Increasing amount of the adsorbents increases the contact surface area and exchangeable sites, and then increases the percent removal of dye however when it's reached saturation level the percentage of dye removal become constant [11].

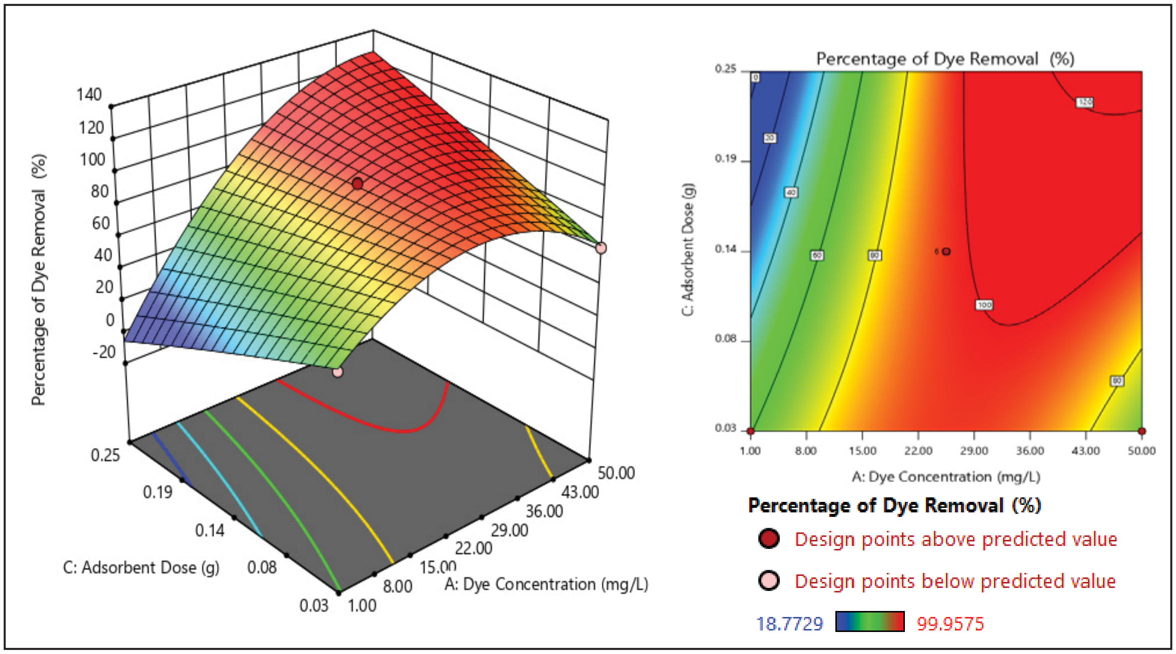

FIGURE 2. (a) Surface graph and (b) contour for interactive of dye concentration and adsorbent dosage.

Model Validation for Removal of Rhodamine 6G Dye

Several sets of validation experiment with different combination of independent variables were performed and the model predicted, and experimental percentage of dye removal were obtained to define and evaluate the validity of the model. The model optimization of variables was carried out based on the best-fitted equation to determine the optimal values of variables which achieve the maximum removal percentage.

From the Box-Behnken experimental design, there were 10 optimized solutions with different parameters which showed the highest predicted percentage of dye removal between 98% to 99% (Table 3). After examined through experiment, the range of differences between predicted and experimental responses was 0.0190% to 3.9630%. The differences occurred were due to some degree of uncertainty and error that may come from variety of sources. It was found out that the maximum optimized conditions for Rhodamine 6G dye removal are dye concentration of 26.12 mg L^{-1}, contact time of 14.33 min, adsorbent dose of 0.05 g, particle size of 190.26 µm and pH of 6.54 with dye removal percentage of 99.0298%.

TABLE 3. Optimized solutions with predicted, experimental responses and their percentage of difference.

Run	A: Dye concentration (mg L^{-1})	B: Contact time (mins)	C: Adsorbent dose (g)	D: Particle size (µm)	E: pH	Percentage of Dye Removal (%)		Percentage of Difference (%)
						Predicted	Experimental	
1	27.33	14.78	0.01	224.99	6.57	99.0002	97.3433	1.6736
2	31.57	10.31	0.05	124.96	6.03	98.9999	98.8154	0.1864
3	32.71	3.03	0.04	106.07	6.17	98.9999	96.4861	2.5392
4	26.12	14.33	0.05	190.26	6.54	99.0001	99.0298	0.0300
5	27.01	13.78	0.01	222.80	6.91	99.000	97.1170	0.0190
6	27.45	8.85	0.01	178.23	6.03	98.9998	95.8143	3.2177
7	23.57	2.87	0.02	210.11	6.06	99.0001	95.0767	3.9630
8	36.27	9.36	0.04	211.09	6.94	98.9998	97.0398	1.9798
9	33.06	9.56	0.04	111.60	6.82	98.9999	97.7385	1.2741
10	29.61	9.97	0.02	174.74	6.38	99.0001	95.5577	3.4772

CONCLUSIONS

Application of Box-Behnken Design is useful to obtain optimum conditions for Rhodamine 6G removal from aqueous solution by NMAC. The outcomes of this study are:

- The Box-Behnken Design able to locate optimum contact time for highest removal efficiency that will be time-effective for cleaning up process.
- The generated quadratic equation model by Box-Behnken Design is valid to predict the removal efficiency by NMAC.

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