THE OPTIMIZATION OF DIRECT RED 81 AND METHYLENE BLUE ADSORPTION ON NAOH-MODIFIED RICE HUSK

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ABSTRACT

The objectives of this investigation are to obtain optimal adsorption conditions for direct red 81 (DR81) and methylene blue (MB) from aqueous solution on NaOH modified rice husk (NaOH-RH) using Response Surface Methodology (RSM). A Box–Behnken Design (BBD) statistical experimental design was used to investigate the adsorption of DR81 and MB on NaOH-RH. For DR81, pH (4-7), initial concentration of dye (25-125 mg/l), adsorbent dose (2–6 g/l), and for MB pH (7-10), initial concentration of dye (25-125 mg/l) and adsorbent dose (0.25-0.75 g/l) were selected as independent variables. The results showed that the predicted values for both dye adsorptions were close to the experimental values and were in a good agreement, on the other hand, the R-Square values for DR81 (R^2=0.9685) and MB (R^2=0.9832) indicated that the regression is able to give a good predict of response for the adsorption process in the range studied. From the BBD predictions, the optimal conditions in the adsorption process for removing 54.04% of DR81 were found to be 25 mg/l initial dye concentration and 6 g/l adsorbent dose at pH 4. Also, removing 97.66% of MB was found to be 25 mg/l initial dye concentration and 0.595 g/l adsorbent dosage at pH 8.89.

Keywords: NaOH-modified rice husk, Direct red 81, Methylene blue, Adsorption.

1. Introduction

Many industries generate effluent that may have a large amount of different types of dyes and enter into the environment. For example some of these dyes like DR81 and MB may cause adverse effects such as aesthetic, carcinogenic and toxicity consequently can harmful on human beings, animals and plants (Mahvi et al. 2009, Mahvi and Heibati 2012, Ashrafi et al. 2013). A lot of methods and techniques such as precipitation, filtration, reverse osmosis, coagulation, adsorption, chemical degradation, biological and enzymatic treatment have been used in wastewater treatment (Gholami-Borujeni et al. 2011, Gholami-Borujeni et al. 2011). Among these methods, dye adsorption is comparatively a cost-effective method (Sadaf and Bhatti 2014, Ashrafi et al. 2015). Many uses of rice husk and rice husk ash have been suggested in the papers for adsorption of pollutants, such as: oil or oil product (Angelova et al. 2011), humic acids (Imyim and Prapalimrungsi 2010), dyes (Safa and Bhatti 2011). NaOH modify chemical and mechanical properties of rice husk and clean natural dirties such as fats and waxes from the surfaces and consequently revealing functional groups like –OH. Therefore, this modifying technique can be useful for the surface modification of rice husk for increasing the capacity of adsorption (Sharma et al. 2010, Chakraborty et al. 2011). The objective of this work was to study the potential of NaOH modified rice husk for the adsorption of DR81 and MB from aqueous solutions. To find the optimum conditions, RSM based on Box–Behnken Design (BBD) had been used.

2. Material and method

2.1. Preparation of NaOH-RH adsorbent

After washing the rice husk, it was dried in oven 60 ºC. Then it was immersed in the 5 % NaOH solution and was autoclaved at 121 ºC for 15 min at 10 psi. Then it kept in 25 ºC for 24 h. After this time, it was filtered and washed many times with distilled water until clear water with neutral pH obtained in the effluent. Then, it was dried at 40 ºC for 24 h.

2.2. Box–Behnken factorial design of experiments

To investigate the effect of three factors on removal efficiency of dyes, Box–Behnken factorial design method was used. As shown in Table 1, three factors at three different levels (-1, 0, +1), selected for the determination of optimal conditions was designated as A, B, and C, corresponding to pH, initial concentration of dyes, and adsorbent dose. The coded mathematical model for these designs can be given by the following quadratic (Eq. 1):

$$R = X_0 + X_1A + X_2B + X_3C + X_4AB + X_5AC + X_6BC + X_7AA + X_8BB + X_9CC \quad (1)$$

where *R* is the predicted percentage removal of each dye, X_0 is the intercept, $X_{1\text{-}9}$ are the estimated regression coefficients of the linear, square and interaction effects and *A, B and C* are the coded factors (Table 1).

Table 1. Experimental ranges and levels of variables for DR81 and MB adsorption.

Independent variables	Coded symbol	Code levels					
		DR81			MB		
		-1	0	1	-1	0	1
pH	A	4	5.5	7	7	8.5	10
Initial concentration of dye (mg L^{-1})	B	25	75	125	25	75	125
Adsorbent dose (g L^{-1})	C	2	4	6	0.25	0.5	0.75

2.3. Batch adsorption studies

The adsorption study conducted by shaking 50 ml of each dye solution in a 100 ml Erlenmeyer flask. After keeping the solution flask under agitation rate 150 rpm for 3h, the adsorbent was separated by keeping the solution under settling condition for 15 min and the samples were analyzed for dye concentration using UV–Vis spectrophotometer.

3. Results and discussion

3.1. Normal probability

The normal probability plot of the residuals with a 95% confidence for DR81 and MB was shown in Fig. 1(a) and (b) respectively. It can be seen from these figures that for both dye, the points fall fairly close to the straight line. Consequently, we can say that the data from the experiments comes from a normally distributed population and they were reliable (Yi et al. 2011).

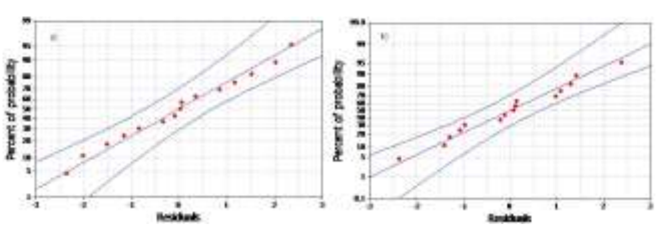

Figure 1. Normal plots of residuals for a) DR81 and b) MB.

3.2. Analysis of variance (ANOVA)

The following simplified second-order polynomial equations have been given from the ANOVA output by substituting the coefficients Xi in (Eq. 1) by their values for each dye:

$$(\%)\ R_{DR81} = +25.64 - 7.15\ A - 4.12\ B + 4.56\ C - 3.12\ AC + 4.85\ B^2 \quad (2)$$

$$(\%)\ R_{MB} = +85.42 + 5.30\ A - 8.61\ B + 5.53\ C - 2.89\ AC - 5.64\ A^2 - 5.17\ C^2 \quad (3)$$

Where *R* is the percent adsorption efficiency of DR81 and MB; *A*, *B* and *C* are the coded values of the operational variables pH, initial dye concentration and adsorbent dose, respectively.

As shown in Table 2, the results revealed that the second-order polynomial model, Eqs. 2-3, were statistically significant and sufficient to represent the actual relationship between the efficiency of adsorption and the significant variables, with satisfactory coefficient of determination R^2 =0.9685 and R^2 =0.832 for DR81 and MB respectively.

Table 2 Analysis of variance for experimental responses of DR81 and MB adsorption.

Source	DR81					MB				
	DF	Sum of squares	Mean square	F value	Prob. > F	DF	Sum of squares	Mean square	F value	Prob. > F
A	1	408.6	408.6	73.06	0.0004	1	225.1	225.1	49.06	0.0009
B	1	135.6	135.6	24.25	0.0044	1	593.4	593.4	129.3	< 0.0001
C	1	166.2	166.2	29.72	0.0028	1	244.4	244.4	53.26	0.0008
AB	1	7.1	7.1	1.28	0.3088	1	6.7	6.7	1.47	0.2791
AC	1	38.9	38.9	6.95	0.0461	1	33.4	33.4	7.28	0.0429
BC	1	0.0	0.07	0.013	0.9151	1	2.8	2.8	0.61	0.4709
A^2	1	4.4	4.4	0.79	0.4139	1	117.3	117.3	25.57	0.0039
B^2	1	86.9	86.9	15.54	0.0109	1	18.1	18.1	3.96	0.1034
C^2	1	19.6	19.6	3.51	0.1200	1	98.7	98.8	21.53	0.0056
Model	9	858.7	95.4	17.06	0.0030	9	1340.0	148.9	32.44	0.0007
Lac of fit	3	27.9	9.3	1489	0.0007	3	22.87	7.62	204.9	0.0049
Total	14	886.6				14	1363			

DR81: R^2 =0.9685 , MB: R^2 =0.9832

3.3. Main and interaction effects of variables

Table 2 for DR81 shows that, the main effect of all three variables is significant, and the pH of solution was found to have the greatest effect on the response. According to Table 2, the interaction effects between pH and adsorbent dose is significant. The response surfaces graphs in Figs. 2a b and c show the effects of the all variables on the adsorption efficiency of DR81. According to the Fig. 2a and b, it has been found that the pH has negative effect on the adsorption efficiency of DR81. This observation is in agreement with those reported previously by other researchers for adsorption of DR81 by chitosan that have amino functional groups (Chiou et al. 2004). It has been found that (Fig. 2a and c) with the increases of the initial concentration of DR81, the adsorption percentage decreases, while the amount of dye removed at equilibrium (14.77 mg/g) is more than when the initial concentration of DR81 is low. This is in agreement with our previous study of DR81 adsorption on pumice (Mahvi and Heibati 2012).

According to Table 2, in the case of MB, the main effect of all three variables is significant. In the case of interaction effects, the interaction effects between pH and adsorbent dose is significant. Nevertheless, the other variables interactions were insignificant. The response surfaces graphs in Figs. 3a b and c show the effects of the all variables on the adsorption efficiency of MB. According to results, it revealed that the pH has positive effect on the adsorption efficiency of MB. This observation is similar to other studies results (Sharma et al. 2010, Deng et al. 2011). It has been found that (Fig. 3a and c) with the increases in concentration of the initial concentration of MB, the adsorption efficiency decreases, while the amount of dye removed at equilibrium (342.3 mg/g) is more than when the initial concentration of MB is low. This is in agreement with other studies of dye adsorption (Sharma et al. 2010, Chakraborty et al. 2011). Fig. 3b and c shows the adsorption efficiency of MB increases with increasing adsorbent dose.

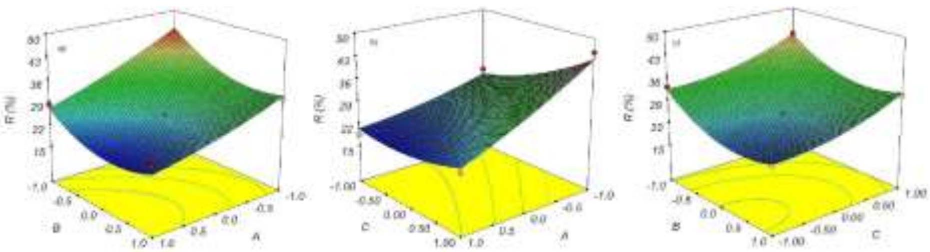

Figure 2. Surface plots showing the effects of a) pH and Initial concentration of dye, b) pH and Adsorbent dose, c) Initial concentration of dye and Adsorbent dose on adsorption of DR81.

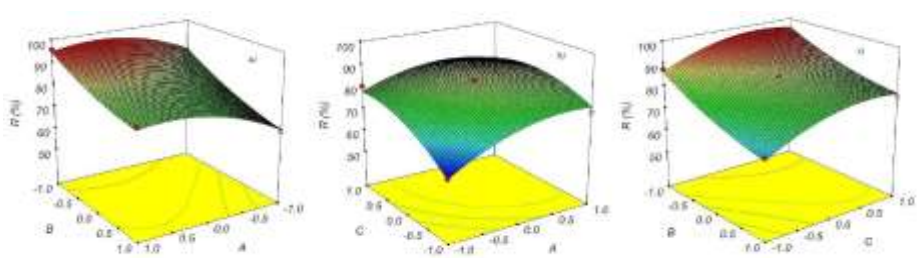

Figure 3. Surface plots showing the effects of a) pH and Initial concentration of dye, b) pH and Adsorbent dose, c) Initial concentration of dye and Adsorbent dose on adsorption of MB.

3.4. Optimization

To be aware of the optimum values of variables for dye adsorption, the accurate optimal values of the variables were obtained to find the specific point that maximizes the efficiency. The results showed that the optimal pH, initial concentration of dye and adsorbent dosage for DR81 adsorption, are 4, 25 mg/l and 6g/l respectively, which results to the highest efficiency (54.04 %) of adsorption. While in the case of MB the optimal pH, initial concentration of dye and adsorbent dosage are 8.89, 25 mg/l and 0.595g/l respectively, which results to the highest efficiency (97.66 %) of adsorption.

4. Conclusion

The optimal conditions for the maximum adsorption of DR81 (54.04% from prediction) were 25 mg/l initial dye concentration and 6 g/l adsorbent dosage at pH 4. In the case of MB the optimal conditions for the maximum adsorption (97.66% from prediction) were 25 mg/l initial dye concentration and 0.595 g/l adsorbent dosage at pH 8.89.

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