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Contributed Paper

Modeling and Optimization of Removal of Rhodamine - B from Wastewaters by Adsorption on Modified Clay

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ABSTRACT

The treatments of wastewaters contained dyestuffs are difficult and require special advanced treatment technologies. It is known that the adsorption is one of the effective methods commonly used for treatment of wastewaters. In this study, the removal of Rhodamine-B was studied by using modified clay as an adsorbent reagent. The effects of relevant parameters, namely; reaction time, adsorbent concentration, NaCl concentration and the pH have been investigated on the decolorization efficiency using central composite design. A model has been obtained among removal efficiency and relevant parameters. Then, the obtained model was optimized. The proposed method was applied successfully to remove Rhodamine-B in the real sample.

Keywords: modeling, removal, rhodamine-B, adsorption, modified clay, central composite design

1. INTRODUCTION

The presence of waste products in environment is a worldwide problem and it has been highlighted by various environmentalist groups [1]. The cleaning of wastewater is one of the most serious environmental problems. Discharge of dyeing industry wastewater into natural water bodies is not desirable as the color prevents reoxygenation in receiving waters by cutting off penetration of sunlight [2]. Most of the dyes used as coloring materials are toxic to aquatic organisms and food web [1, 3]. Usually the dyes can also cause allergic dermatitis and skin irritation and also lead to carcinogenic and other disorders [1, 4]. Colored compounds comprising pigments and dyes are used widely in textile, paint, pulp, paper, plastic, food, dyeing, printing, pharmaceutical, cosmetic, rubber and leather industries [1, 4, 5]. Among the various classes of dyes, basic dyes are the brightest class of soluble dyes used by the textile industry, because their tinctorial value is very high [6]. Rhodamine-B is a famous basic red dye and is used to dye paper, bamboo, weed, straw, leather [7], silk [8,9], wool, and tannin mordant

cotton [8]. Besides its application in dyeing industries, combination of Rhodamine-B with auramine-o (a basic dye) is widely used as a biological stain in many biomedical research laboratories [7].

Many different treatment approaches have been suggested to tackle the removal of dyes from aqueous solutions. The advanced oxidation processes, biological degradation, coagulation, electrochemical and adsorptions were widely used [9-18]. Adsorption is by far the most effective and non-destructive technique that is used for the removal of dyes from aqueous solutions. It is attractive because the adsorbed dyes can be recovered with suitable regenerating agents [2]. The most commonly used adsorbents for dye removal from wastewater are activated carbon and clays [17, 19, 20]. Clays have been used as promising low-cost adsorbents. There are several types of clays such as smectites (montmorillonite and saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [21]. The clays are classified based on the differences in their layered structure. Clay materials have high surface areas, layered structures and high porosity. Also, they possess a net negative charge and hence have the capacity to adsorb positively charged materials [22].

To evaluate the capability of the modified clay for removal of Rhodamine-B from waste water samples, the method must be optimized for various parameters. Different variables can affect the removal process, i.e., adsorbent concentration, initial pH, reaction time and NaCl concentration, and in most cases they must be optimized. The classical optimization technique of changing one variable at a time to study the effects of variables on the response is time consuming and expensive, particularly for multivariable systems. In addition it does not represent the effect of interactions between different factors. Statistical design of experiments is a useful technique for obtaining valuable and statistically significant models of a phenomenon by performing a minimum number of experiments. It also considers interactions among the variables and can be used to optimize the operating parameters in multivariable systems. Response surface methodology (RSM) is used for the modeling and analysis of problems in which a response of interest is influenced by several variables, with the objective of optimizing this response. The most common design under RSM is central composite design (CCD); it is efficient and flexible, providing sufficient data on the effects of variables and overall experiment error with a minimum number of experiments. Furthermore, it offers useful data about direct, pair wise interaction and curvilinear variable effects [23-28].

In this study, the use of Modified Clay as an effective adsorbent for the removal of, Rhodamine-B as a basic dye, was proposed and the effect of four experimental parameters on the adsorption were studied. Central composite deign (CCD) and response surface methodology (RSM) were developed as experimental strategies for modeling and optimization of the influence of some variables on the removal of Rhodamine-B.

2. MATERIALS AND METHODS

2.1 Materials

The granular Modified Clay (MC) used in this work was from Phoslock Water Solutions Ltd (PWS), an Australian public company. The used modified clay is commercial bentonite clay in which the sodium and/or calcium ions are exchanged for lanthanum. It was developed in Australia by the CSIRO in the late 1990's by Dr Grant Douglas (US Patent 6350383). Chemicals used were as follows: Rhodamine-

B (RB) dye, NaCl, HCl and NaOH from Merck Chemicals. The characteristics of Rhodamine-B are given in Table 1 and its structure is given in Figure 1 [1].

Table 1. Characteristics of Rhodamine-B dye.

Color Index No.	45170
Formula	$C_{28}H_{31}N_2O_3Cl$
Formula Weight	479.02
λ_{max}(nm)	554
ε ($dm^3mol^{-1}cm^{-1}$)	60000.0
Solubility	Very high

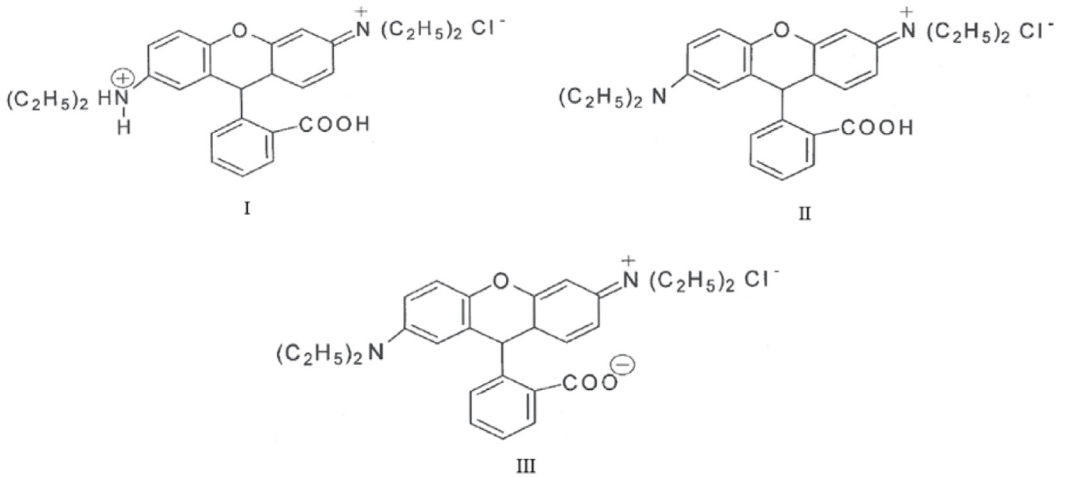

Figure 1. Structure of Rhodamine-B in acidic (I), neutral (II) and alkaline (III) aqueous media.

2.2 Instruments

The spectrophotometric measurements were made with a PG mode T80 UV-Vis double-beam spectrophotometer (Japan) utilizing a 1-cm quartz cell.

2.3 Statistical Software

Essential Regression and Experimental Design for Chemists and Engineers (EREGRESS), as a MS Excel Add-In software [27, 28] was used to design the experiments and to model and analyze the results.

2.4 Method

The dye stock solution was prepared by dissolving accurately weighted dye in known volume of distilled water. The serial dilutions were made by diluting the dye stock solution in accurate proportions to the desired initial concentrations. The pH of each dye solution was adjusted with 0.1M HCl or NaOH using a pH meter.

Adsorption experiments were carried out in a rotary shaker (320 rpm) using 125 ml shaking flasks containing 50 ml of dye solutions at various initial pH values. Various amounts of adsorbent at different conditions were added to each flask and then the flasks were sealed to prevent any change in volume of the solution during experiments. Dye concentrations were determined by measuring absorbance at λ_{max} of dye with UV-Vis spectrophotometer and computing from a calibration curve. The percentage of adsorption was assessed using the Eq. (1):

$$Y(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where Y, C_0 and C are removal efficiency, initial and remained concentrations of dye. The percentage of removal (Y(%)) was used as response in CCD.

2.5 Central Composite Design

The experimental conditions were optimized using central composite design (CCD). Four independent factors, namely the time (F_1), adsorbent dose (F_2), concentration of NaCl (F_3) and initial pH (F_4) were studied at five levels with four repeats at the central point, using a central composite design. For each of the studied variables, high (coded value: +2) and low (coded value: -2) set points were selected as shown in Table 2. In addition, the 4-factor CCD matrix and experimental results obtained in the decolorization runs are presented in Table 3, which was designed using EREGRESS software.

For an experimental design with four factors, the model including linear, quadratic and cross-terms can be expressed as Eq. (2):

$$\text{Response} = b_0 + b_1F_1 + b_2F_2 + b_3F_3 + b_4F_4 + b_5F_1F_2 + b_6F_2F_2 + b_7F_3F_3 + b_8F_4F_4 + b_9F_1F_2 + b_{10}F_1F_3 + b_{11}F_1F_4 + b_{12}F_2F_3 + b_{13}F_2F_4 + b_{14}F_3F_4 \quad (2)$$

where, F_1-F_4 are the variables, and b_0-b_{14} are the coefficient values obtained by multiple linear regression (MLR). The response surface plots are obtained by a statistical process described in the design and the modeled CCD data. Response surface methodologies graphically illustrate relationship between the parameters and the response and also they are the way to obtain an exact optimum [29, 30].

Table 2. The factors, their coded and real experimental values used in central composite.

Variable	Name	-2 (low)	-1	0	+1	+2 (high)
F1	Time (min)	5	26	47	69	90
F2	$C_{Adsorbent}$(g/L)	0.10	0.20	0.30	0.40	0.50
F3	C_{NaCl}(g/L)	0.00	5.00	10.00	15.00	20.00
F4	pH	7.00	8.25	9.50	10.75	12.00

Table 3. The four-factor central composite design matrix and the value of the response function (Y(%)).

Exp#	F_1	F_2	F_3	F_4	Y(%)
1	1	-1	-1	1	19.94
2	-1	-1	1	-1	48.74
3	2	0	0	0	60.38
4	1	1	-1	1	30.86
5	1	1	-1	-1	84.52
6	-1	-1	-1	-1	41.89
7	-1	1	1	-1	44.29
8	0	0	2	0	60.58
9	1	-1	1	1	22.47
10	1	-1	1	-1	38.81
11	1	1	1	1	32.69
12	-1	1	-1	1	38.57

Table 3. Continued.

Exp#	F_1	F_2	F_3	F_4	Y(%)
13	-1	1	1	1	28.15
14	-1	-1	-1	1	23.58
15	0	2	0	0	66.56
16_a	0	0	0	0	63.10
17_a	0	0	0	0	64.57
18	0	0	0	-2	77.67
19	0	0	0	2	16.42
20_a	0	0	0	0	67.29
21	0	0	-2	0	63.39
22	-1	1	-1	-1	61.60
23	-2	0	0	0	23.69
24_a	0	0	0	0	64.15
25	1	-1	-1	-1	57.43
26	1	1	1	-1	58.63
27	-1	-1	1	1	21.44
28	0	-2	0	0	44.23

a indicates 4 repeat of center points.

3. RESULTS AND DISCUSSION

The percentage of removal were collected as response in order to optimize four independent factors, namely the reaction time (F_1), adsorbent dose (F_2), concentration of NaCl (F_3) and initial pH (F_4). Table 2 and 3 present the levels of coded and actual experimental variables examined. In addition Table 3 presents the corresponding response of each run.

In order to find the important factors and build a model to optimize the procedure, the model was constructed using a full quadratic model including all terms of Eq. (2). Table 4 shows the estimated values of 15 parameters in Eq. (2) which were obtained by the least squares matrix.

To obtain a simple and a realistic model, the insignificant terms ($p > 0.05$) were eliminated from the model through a backward elimination process.

The reduced model was obtained using significant linear, quadratic and interaction parameters that is shown in Eq. (3):

$$Y(\%) = b_0 + b_1 \times \text{time} + b_2 \times C_{\text{adsorbent}} + b_3 \times \text{pH} + b_4 \times \text{time} \times \text{time} + b_5 \times C_{\text{adsorbent}} \times C_{\text{adsorbent}} + b_6 \times C_{\text{NaCl}} \times C_{\text{NaCl}} + b_7 \times \text{pH} \times \text{pH} \quad (3)$$

Table 4. Coefficient, their values and p-value for all variables represented in Eq. 2.

	Coefficient	Values	P
value	b0	-336.61	0.042
	b1	2.705	0.024
	b2	409.68	0.105
	b3	-1.029	0.822
	b4	68.03	0.020
	b5	-0.01657	0.002
	b6	0.914	0.443
	b7	-0.01007	0.671
	b8	-0.115	0.237
	b9	-413.97	0.059
	b10	-5.053	0.323
	b11	-9.667	0.631
	b12	-0.09971	0.236
	b13	0.468	0.255
	b14	-3.985	0.008

Table 5 shows the estimated values of significant parameters. It is always necessary to examine the fitted model and ensure that it provides an adequate expectedness for real system. The model is only validated when it shows a good predictability. The model adequacy can be assessed by the employment of different statistical tools. The most powerful numerical method for model validation is the application of analysis of variance (ANOVA), which is based on the decomposition of total variability in the selected response (Y). It checks the adequacy of the regression model in terms of lack-of-fit test [23-26, 31-33]. The results of ANOVA of the regression for removal of Rhodamine-B are shown in Table 6. The lack-of-fit was meaningless for the regression ($p > 0.05$ at a 95% confidence level). The square of correlation coefficient (R^2) quantitatively measures the correlation between the experimental data and predicted responses that in this work was 0.906. From the graphical point of view, model predictability can also be determined by normal probability plot of residuals and histogram of residuals. The normal probability plot for removal of Rhodamine-B is shown in Figure 2. All these results showed that the proposed model was valid in the prediction of response.

Table 5. Some characteristics of the constructed models according to Eq. 3.

Coefficient	Values	P value
b0	-259.89	0.03456
b1	1.702	0.000464
b2	285.67	0.02185
b3	59.290	0.01797
b4	-0.01564	0.00128
b5	-372.18	0.06257
b6	-0.03285	0.09713
b7	-3.7180	0.00593

Table 6. Analysis of variance (ANOVA) for fit of decolorization efficiency from central composite design.

Source of variance	Sum of squares	*Mean Squares*	*p-Value*	Degree of freedom
Regression	8291.4	1184.5	3.18838E-06	7
Residual	1816.2	90.81		20
LOF Error	1806.6	106.27	0.0728	17
Pure Error	9.581	3.194		3
Total	10107.6			27

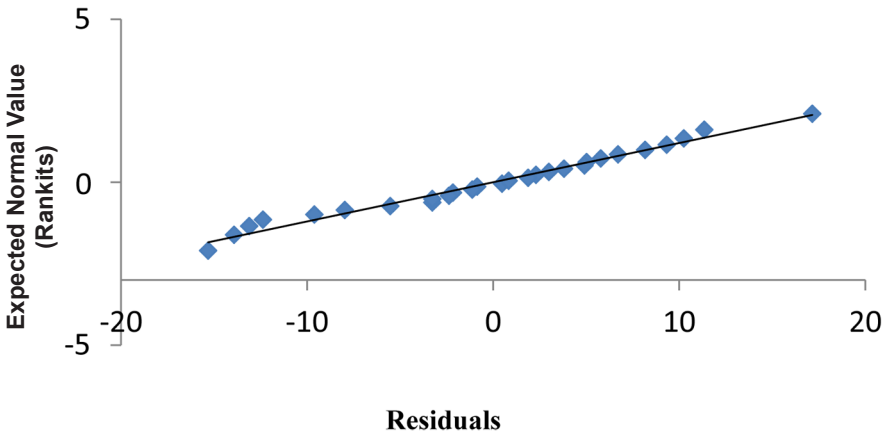

Figure 2. Normal Probability Plot of Rankits vs. Residuals.

3.1 Response Surface and Selection of the Optimum Conditions

In order to gain insight about the effect of each variable, the three-dimensional (3D) plots for the predicted responses were formed based on the model function. Some of the response surface plots are represented in Figure 3, which show the 3D plots of adsorbed dye-percent versus pairs of variables. In plotting response surfaces, two variables kept constant at their code zero level and the other two varying within the experimental ranges.

These plots show that there is no significant interaction between the factors. The selection of optimum conditions of the method is possible from response surface plots (Figure 3).

The optimum conditions can be selected from the obtained model, shown in Table 7.

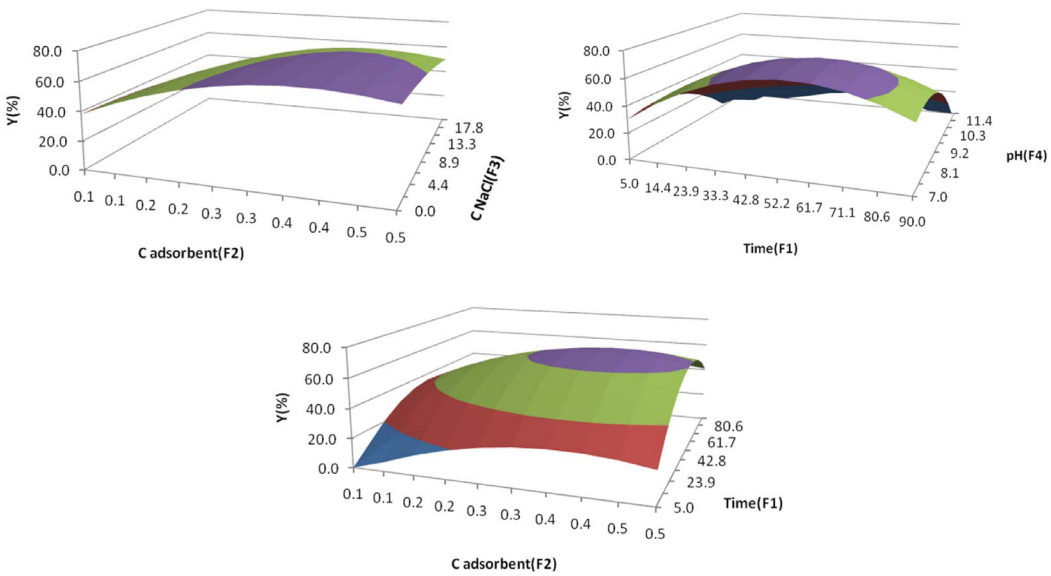

Figure 3. Response surface of full quadratic model between Y(%) and four variables; time (F_1), $C_{adsorbent}$ (F_2), C_{NaCl} (F_3), intial pH(F_4).

Table 7. Optimum conditions obtained by response surface modeling.

Variable name	Optimum values	Selected values
F_1 Time (min)	43-70	57
F_2 $C_{adsorbent}$ (g L-1)	0.32-0.48	0.40
F_3 C_{NaCl} (g L-1)	0.00-7.00	3.50
F_4 pH	7.00-8.50	7.50

3.2 Repeatability Study and Application of the Proposed Method

The repeatability of the proposed method was studied at the optimum conditions by analyzing 5 water samples containing same amount of Rhodamine-B. The percentages of removal of Rhodamine-B from these samples were at the range 89 - 91 % with a relative standard deviation of 0.93%.

Finally, the proposed method was applied for removing of Rhodamine-B from real wastewater. The Real sample was obtained from a dyeing factory (Tabriz, Iran). This solution was treated under the optimum conditions for the removal of Rhodamine-B.

For this purpose the original sample and also several spiked samples were analyzed by monitoring the spectra of samples vs. time. The results showed that the proposed method is capable to remove more than of 70% of Rhodamine-B from the studied wastewaters.

4. Conclusion

In this work the effect of various experimental parameters for the removal of Rhodamine-B were investigated using central composite design and a mathematical model was developed for removal of this compound.

From the foregoing experimental results, it can be concluded that the use of experimental design enables subsequent benefit, in terms of labor time and number of experiments needed to optimize the conditions for modelling the influence of

variables on the removal of Rhodamine-B from aqueous solution. By using central composite design and subsequently response surface methodology: (i) variables that had a high impact on the adsorption were identified; (ii) the optimum conditions of the proposed method were obtained. The repeatability of the proposed method was satisfactory (RSD = 0.89). Finally, the proposed method was applied successfully for removing of Rhodamine-B from a real sample.

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