

Sorption of Congo Red from Aqueous Solution by Surfactant-Modified Bentonite: Kinetic and Factorial Design Study

B. Guezzen, M. A. Didi, B. Medjahed

Abstract—An organoclay (HDTMA-B) was prepared from sodium bentonite (Na-B). The starting material was modified using the hexadecyltrimethylammonium ion (HDTMA⁺) in the amounts corresponding to 100 % of the CEC value. Batch experiments were carried out in order to model and optimize the sorption of Congo red dye from aqueous solution. The pseudo-first order and pseudo-second order kinetic models have been developed to predict the rate constant and the sorption capacity at equilibrium with the effect of temperature, the solid/solution ratio and the initial dye concentration. The equilibrium time was reached within 60 min. At room temperature (20 °C), optimum dye sorption of 49.4 mg/g (98.9%) was achieved at pH 6.6, sorbent dosage of 1g/L and initial dye concentration of 50 mg/L, using surfactant modified bentonite. The optimization of adsorption parameters mentioned above on dye removal was carried out using Box-Behnken design. The sorption parameters were analyzed statistically by means of variance analysis by using the Statgraphics Centurion XVI software.

Keywords—Adsorption, dye, factorial design, kinetic, organo-bentonite

I. INTRODUCTION

SYNTHETIC dyes have a relatively large group of organic compounds encountered in the spheres of our everyday life automotive, chemical, paper mills, and more specifically the textile sector or all dye ranges are estimated, and chemical families are presented. Currently, waste from the textile industry is heavily laden of dyes. These are often used in excess to improve dyeing; as a result, the waste water is highly concentrated of dyes whose low biodegradability renders the different treatments difficult to apply, which constitutes a source of environmental degradation.

The azo dyes are characterized by the presence within the molecule of an azo group ($-N=N-$) connecting two benzene rings. This category of dye is currently the most widespread in terms of application, since it represents more than 50% of the world production of coloring matter [1], [2]. Studies have shown that several azo dyes including Congo red (CR) dyes

are toxic and mutagenic. As early as 1895, the increase in the number of bladder cancers observed in workers in the textile industry is related to their long exposure to azo dyes [3].

The works done on these azo dyes has shown that these chemical compounds have carcinogenic effects for humans and animals [4]-[6]. According to the DEPA (2000), the estimation of the risks of cancer imposes to set a limit concentration of $3.1 \mu\text{g. L}^{-1}$ of azo dye in the drinking water.

Liquid effluents containing azo dye can be treated using various physical, chemical, and biological treatment methods such as, coagulation/flocculation [7], electrocoagulation, [8], adsorption [9], membrane filtration [10], advanced oxidation [11], photocatalysis [12] and aerobic/anaerobic degradation [13], [14]. However, adsorption is one of the most promising techniques for removal of various dyes including CR [15], [16].

The materials of natural origin including clays are considered to be a good adsorbent because of its large surface area; high cations exchange capacity, chemical and mechanical stability, and layered structure [17]. Bentonite clay represents a low cost and highly effective adsorbent for cationic dyes due to their natural negative charged. However, modifications to the surface of clay using cationic surfactants can change the surface charge of clay from negative to positive [18]. The modification of bentonite clay surface is called as organoclay to cause to transform organophobic to strongly organophilic, and therefore, the adsorbent becomes very efficient in the removal of organic pollutants [19].

The aim of the current work was to investigate the adsorption removal of benzidine-based anionic diazo textile dye CR from an aqueous solution using hexadecyltrimethylammonium modified bentonite (HDTMA-B). The performance of HDTMA-B as an adsorbent for CR removal under different operating conditions was investigated, and the experimental results were analyzed using the pseudo-first order and pseudo-second order kinetic models. The main effects and interactive effects of process variables on percentage removal of dye were analyzed by statistical experiment design according to Box-Behnken matrix.

II. EXPERIMENTAL

A. Chemicals and Reagents

Natural raw bentonite used in this study was obtained from deposits in the area of Maghnia, Algeria. It contained about 86 wt.% montmorillonite, 10% quartz, 3.0% cristobalite and less

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than 1% beidellite. Its chemical composition was as follows: 62.48% SiO₂, 17.53% Al₂O₃, 1.23% Fe₂O₃, 3.59% MgO, 0.82% K₂O, 0.87% CaO, 0.22% TiO₂, 0.39% Na₂O, 0.04% As, 13.0% loss on ignition at 950 °C [20].

The surfactant hexadecyltrimethylammonium bromide HDTMA (C₁₉H₄₂Br N) (purity of >99%) and the CR dye (C₃₂H₂₂N₆Na₂O₆S₂) (purity of >99%) were purchased from Biochem.

B. Preparation of HDTMA-B and Characterization Methods

The natural bentonite used in this study was converted to sodium bentonite (Na-B), following the method described by Makhoukhi et al. [21].

The HDTMA-B was prepared by adding 10 g of sodium bentonite to HDTMA solution in amounts equivalent to the CEC of sodium bentonite (93 meq/100 g), and stirring for 24h at room temperature. The suspensions were then centrifuged at 3000 rpm for 15 min, washed with distilled water several times until no Br⁻ was detected in the supernatant by the use of AgNO₃, and the mixture was then dried at 70 °C.

The organo-bentonite sample was compared to the sodium bentonite with Fourier transform infrared (FTIR) and Thermogravimetric analyses (TGA).

The FTIR spectra were recorded over the range 4000-500 cm⁻¹ with a Perkin Elmer FT-IR Spectrophotometer. Thermogravimetric analysis was obtained by using a PerkinElmer TGA-7 thermogravimetric analyzer. Approximately 20-30 mg of finely dried ground samples were heated from 30 to 900 °C at 20 °C/min in an open platinum crucible under nitrogen atmosphere.

C. Adsorption Experiments

Adsorption experiments were conducted in a batch mode using aqueous of CR solutions to obtain equilibrium data. A stock solution of the dye with a concentration of 1000 mg/L was prepared in distilled water. From the stock solution, various concentrations were prepared by dilution.

Batch adsorption experiments were carried out in a 100 mL Erlenmeyer flask by adding a known mass of sorbent to 25 mL CR solution (known concentration) at natural pH 6.6 on a thermostatic shaker with a shaking speed of 250 rpm.

Samples of the supernatant were centrifuged, and analyzed through UV-vis at 498 nm (Analytik Jena SPECORD 210 Double Beam UV-VIS was used for the absorbance measurements). The amount (mg) of dye adsorbed per gram of adsorbent at time 't' (q_t), the amount adsorbed per mass unit of adsorbent at equilibrium (q_e) and percentage removal (% removal) were calculated using the following equations:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (2)$$

$$\% \text{ Removal} = \left(1 - \frac{C_t}{C_0}\right) 100 \quad (3)$$

where C₀ (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of CR, respectively. m (g) is the amount of adsorbent, and V (L) is the volume of the aqueous solution.

D. Adsorption Kinetics of CR

The effects of experimental parameters such as temperature, adsorbent dosage and CR initial concentration on the kinetics of the sorption process were investigated. Equilibrium studies were carried out for 180 min to determine the equilibrium time.

Effect of temperature on the kinetics of the adsorption of CR was studied by adding a 25 mg of adsorbent to each 25-mL volume of dye aqueous solutions (m/v=1g/L) having an initial concentration 50 mg/L. The experiments were carried out at 20, 40, and 60 °C.

The effect of the initial dye concentrations on the sorption capacity was examined at temperature (20±2 °C) by varying the initial dye concentrations (20, 50, 100, and 500 mg/L) to a constant sorbent dosage (1 g/L).

To study the effect of sorbent dosage on the sorption kinetics of dye, adsorption experiments were carried out with 50 mg/L of anionic dye at temperature (20±2 °C) by varying the range of m/v ratio from 0.1 to 1 g/L.

A pseudo-first-order and pseudo-second-order models were applied to fit the experimental data and evaluate the adsorption kinetics of CR on modified bentonite [22], [23]. These models can be generally expressed in linearized form by the following equations:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k₁ and k₂ are the equilibrium rate constants of pseudo-first-order (min⁻¹) and pseudo-second-order model (g.mg⁻¹.min⁻¹), respectively.

E. Experimental Design

The experimental design method consists to highlight and quantify the influence existing between two types of variables:

- The factor: a variable, which acts on the system studied,
- The response: the measured quantity in order to know the effects of the factors on the system.

In recent years, it is being adopted to the sorption process of dye from distinct matrixes (e.g., references [24], [25]).

In this work, based on the data and the results of the adsorption kinetics study of the RC carried out previously, it was studied the influence of temperature (20-60 °C), solid/solution ratio (0.1-1 g/L) and initial dye concentration (50-500 mg/L) upon the percentage removal. The remaining independent variables (pH and adsorption time) were kept constant during the experimental procedures.

The range and level of experimental variables investigated in this study are shown in Table I. Each of the parameters was coded at three levels: -1, 0, and +1.

The optimization process was carried out using Box-Behnken designs (BBD) that can reduce experimentation time,

overall cost, and variability with improved reaction output [26].

The correlation between response and the selected variables can be described by a quadratic equation that is given as [27]:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^n \beta_{ij} X_i X_j \quad (6)$$

where Y is the predicted response (predicted percentage removal), X_i and X_j are the input variables which affect the response, n is the number of independent variables. β_0 is a constant, β_i , β_{ii} , and β_{ij} are the coefficients estimated from regression and they represent the linear, quadratic, and cross products of variables on response. The experimental data were processed by using the Statgraphics Centurion XVI software.

TABLE I
CODIFICATION AND LEVELS OF THE THREE INDEPENDENT VARIABLES
CONSIDERED FOR THE SORPTION OF CR

Variable	Range and levels		
	Low (-1)	Medium (0)	High (+1)
Temperature, X_1 (°C)	20	40	60
Solid/solution ratio, X_2 (g/L)	0.1	0.55	1
Initial dye concentration, X_3 (mg/L)	50	275	500

III. RESULTS AND DISCUSSION

A. Characterization of the Adsorbent

The FTIR spectra of sodic bentonite and organo-modified bentonite containing HDTMA were shown in Fig. 1.

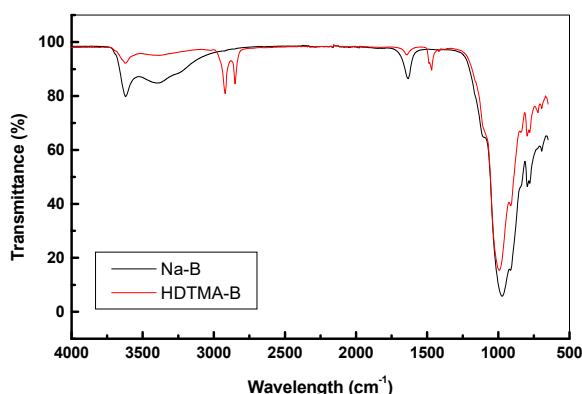


Fig. 1 FTIR spectra for sodic bentonite and HDTMA modified bentonite

The characteristic bands at 3623 cm^{-1} and 1634 cm^{-1} are assigned respectively to the OH bending vibrations of valence and deformation of water present in the bentonite, whereas a broad band between 3425 and 3375 cm^{-1} was recorded to the OH stretching vibration [28].

The band around 995 cm^{-1} was attributed to asymmetric stretching vibration of Si–O–Si tetrahedral and a doublet at 780 and 795 cm^{-1} indicated the presence of quartz in the bentonite [29]. The bands coming from the ammonium

surfactant for the intercalated clay are also observed. Two bands at 2923 and 2849 cm^{-1} in HDTMA modified bentonite was assigned to the symmetric and asymmetric C–H stretching vibrations of methyl and methylene groups and suggested the presence of cationic surfactants in the bentonite. Also, the band at 1467 cm^{-1} was assigned to the C–H bending vibration.

Thermal stability of Na-B and HDTMA-B was determined by TGA (Fig. 2). From the ATG curve of Na-B, two weight loss steps are observed. The first at 99°C (6.2 %) due to the dehydration of the materials which is attributed to the removal of the physisorbed and interlayered water [30] and the other between 400 and 670°C (2.2 %) was caused by dehydroxylation of the montmorillonite [31]. These two mass losses (3.4 and 6.9 %) were also observed for the organo-modified bentonite. The weight loss of 16.5 % in the temperature range of 200 – 500°C , which is due to the decomposition of the alkyl chain on HDTMA. Similar results have been reported by other researchers [32], [33].

B. Kinetics Studies

1. Effect of Temperature

The effect of the contact time on the adsorption of CR dye was examined at different temperature (Fig. 3). The removal of CR by HDTMA-B increased with increasing contact time, and equilibrium was reached within 60 min.

The prolonged shaking had no positive effect on the sorption of CR. Temperature affected sorption to a lesser extent within the range of 20 – 60°C . The adsorption of CR decreased from 98.92 to 63.00% with increasing temperature from 20 to 60°C . These results indicate the exothermic nature of sorption process of the dye on HDTMA modified bentonite. Similar behaviour on CR dye removal has been found using distinct adsorbent [34], [35].

2. Effect of Adsorbent Dosage

The influence of adsorbent dosage on the removal efficiency was investigated for three various amounts in the range of 0.1 – 1 g/L at initial pH of 6.6 at different time intervals (Fig. 5). Fig. 5 indicates that the adsorption of CR on the adsorbent increased with time and reached equilibrium in less than 60 min. At equilibrium time, when the solid/solution ratio was increased from 0.1 to 1 g/L , the CR removal efficiency was increased from 52.30% to 98.92%. This result can be explained that increasing the adsorbent dose increases the surface area of the adsorbent and consequently more number of sites available for adsorption.

3. Effect of Initial Dye Concentration

The sorption of CR by HDTMA-B was investigated by varying its initial concentrations (20 , 50 , 100 , and 500 mg/L) at initial pH of 6.6 for different time intervals. As can be seen from Fig. 7, when the equilibrium time was increased, the adsorption efficiency was not drastically increased. The removal of CR dye by HDTMA-B occurred very quickly from the beginning of the experiments and the maximum adsorption of CR was sequestered within 40–60 min for all tests. When the initial dye concentration was increased from 20 to 500

mg/L, the CR removal efficiency was decreased from 98.53% to 54.62%. Thus, the equilibrium adsorption capacity increased from 19.71 to 273.10 mg/g. However, increasing the initial concentration of CR from 20 to 100 mg/L had little

influence on the adsorption percentage. One can affirm that the sorption of CR by HDTMA-B depends on the initial dye concentration until saturation.

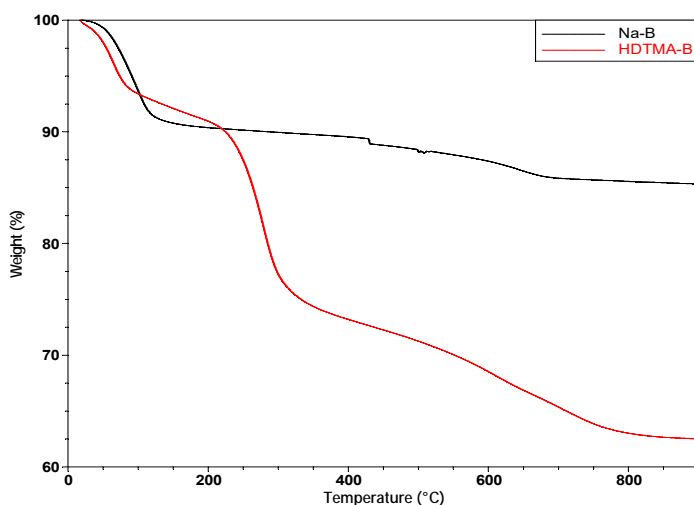


Fig. 2 TGA thermograms of sodic bentonite and HDTMA modified bentonite

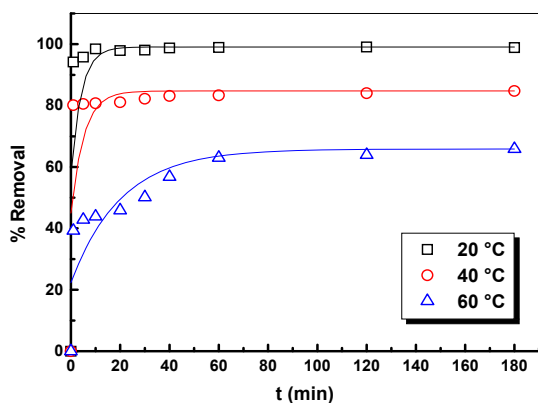


Fig. 3 The effect of temperature on the removal of CR by HDTMA-B for different time intervals $C_0 = 50$ mg/L, $m/v = 1$ g/L, $pH = 6.6$

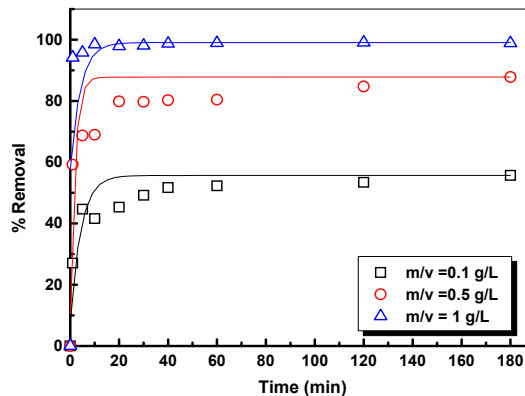


Fig. 5 The effect of adsorbent dosage on the removal of CR by HDTMA-B for different time intervals. $C_0 = 50$ mg/L, $T = 20 \pm 2$ °C, $pH = 6.6$

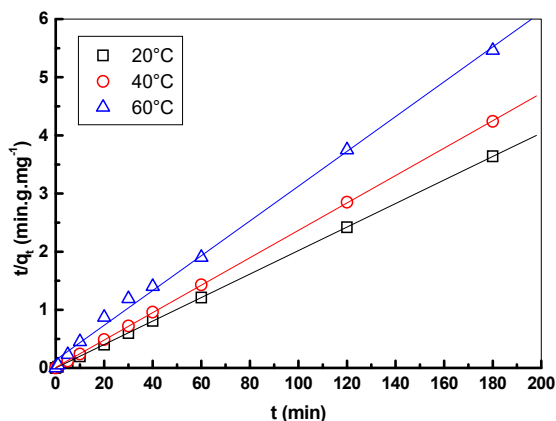


Fig. 4 Pseudo-second order kinetic plot for adsorption of CR on HDTMA-B under different conditions of temperature

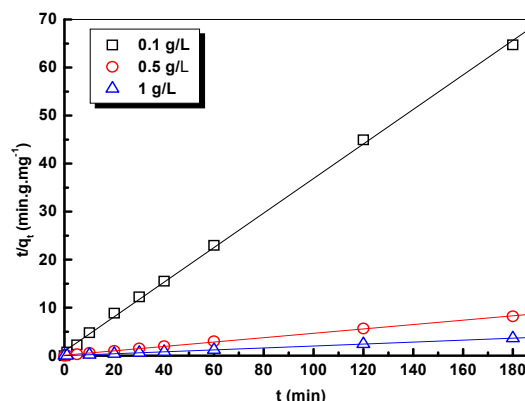


Fig. 6 Pseudo-second order kinetic plot for adsorption of CR on HDTMA-B under different conditions of sorbent dosage

The decrease of the yield of adsorption with an increase of initial dye concentration was related with a high mass gradient pressure between the solution and adsorbent, which provides a driving force to overcome the resistance to mass transfer between the aqueous and solid phase [36], [37].

The adsorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions [38]. The applicability of the pseudo-first order and pseudo-second order model was examined for the adsorption of CR onto HDTMA-B. These models have been fitted with experimental data at various physicochemical conditions.

Figs. 4, 6, and 8 show the pseudo-second-order kinetic model fittings with experimental data for varying temperature, adsorbent dosages and initial dye concentration, respectively (the pseudo first order fitting plots are not presented here). These plots give straight lines with higher linear correlation coefficients. As shown in Table II, the obtained regression coefficients values (R^2) of the pseudo-second order model were better than those of the pseudo-first order model for the sorption of anionic dye at the various systems parameters, suggesting that the pseudo-second order model was more suitable to describe the adsorption kinetics of CR onto HDTMA modified bentonite. Moreover, pseudo-first order kinetic model predicted a significantly lower value of the calculated equilibrium adsorption capacity (q_e , cal) than the experimental value (q_e , exp), indicates the inapplicability of this model. Based on these results, we can say that the pseudo-second order kinetic model provides good correlation for CR adsorption on the HDTMA modified bentonite and the rate limiting step of adsorption process may be chemical sorption. In addition, from Table II, the adsorption capacity increases with the increase in initial dye concentration and but decreases within temperature, and adsorbent dosage respectively. Also, it is noted that the rate constant values, k_2 decrease with the initial dye concentration. This result is similar to that found by other authors, carried in the adsorption of CR from aqueous solution onto Hexadecyltrimethylammonium modified attapulgite [39] and on natural zeolites modified with N,N-dimethyl dehydroabietylamine oxide [35]. Other investigators indicated that this behavior may be due to higher competition

for high concentration sorption sites. At lower concentrations, competition for surface active sites will be low and, as a result, higher sorption rates will be obtained [38].

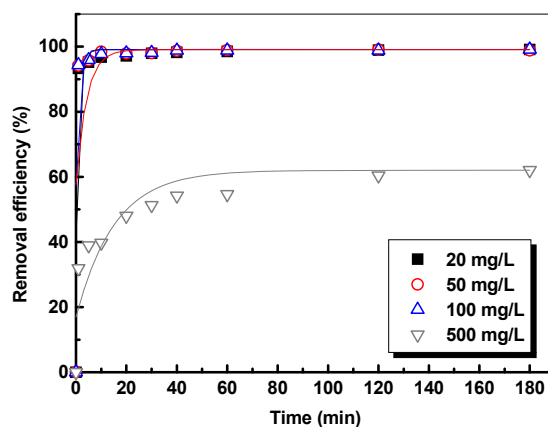


Fig. 7 The effect of initial dye concentration on the removal of CR by HDTMA-B for different time intervals. m/v = 1 g/L, T = 20±2 °C, pH = 6.6

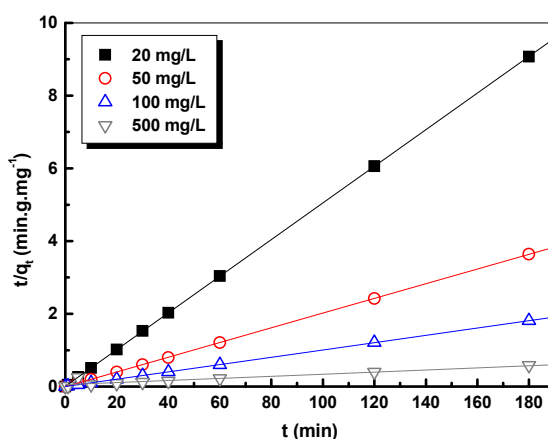


Fig. 8 Pseudo-second order kinetic plot for adsorption of CR on HDTMA-B under different conditions of initial dye concentration

TABLE II
PSEUDO-FIRST- AND PSEUDO-SECOND-ORDER RATE CONSTANTS FOR CR SORPTION ONTO HDTMA-B AT DIFFERENT PHYSICO-CHEMICAL CONDITIONS

Parameters and range	% Removal	q _e , exp (mg.g ⁻¹)	Pseudo-first-order model			Pseudo-second-order model		
			k _i (min ⁻¹)	q _e , cal (mg.g ⁻¹)	R ²	k ₂ .10 ³ (g.mg ⁻¹ .min ⁻¹)	q _e , cal (mg.g ⁻¹)	R ²
T (°C)								
20	98.92	49.46	0.092	4.53	0.63	0.0017	49.52	1.00
40	83.34	41.67	0.05	1.78	0.70	0.0089	43.47	0.99
60	63.00	31.50	0.0023	5.90	0.75	0.22	34.48	0.99
C ₀ (mg/L)								
20	98.53	19.71	0.07	0.96	0.99	0.044	19.88	1.00
50	98.92	49.46	0.092	4.53	0.63	0.0017	49.52	1.00
100	98.85	98.85	0.07	2.81	0.70	0.0002	100	1.00
500	54.62	273.10	0.04	33.26	0.09	0.00082	344.88	0.86
m/v (g/L)								
0.1	52.30	1.06	0.07	1.06	0.88	0.23	2.78	0.99
0.5	80.42	3.30	0.10	3.30	0.81	0.39	22.2	0.99
1	98.92	49.46	0.092	4.53	0.63	0.0017	49.52	1.00

C. Factorial Design Study

The effect of process variables like temperature, adsorbent dosage and initial dye concentration on the sorption of CR was investigated using response surface methodology according to Box-Behnken design.

The coded values of the operating variables and the experimental results of percentage adsorption of CR using HDTMA-B are presented in Table III. 12 experiments were carried out to investigate the experimental domain; three experiments at the center point were applied to calculate the pure error and the variance.

TABLE III
BBD MATRIX WITH THREE INDEPENDENT VARIABLES (CODED VALUES) AND CORRESPONDING EXPERIMENTAL DATA

Run	Factor levels			Response function (% removal)	
	X ₁	X ₂	X ₃	Actual	Predicted
1	-1	0	-1	91.95	89.20
2	-1	-1	0	31.51	29.49
3	-1	1	0	68.53	70.42
4	-1	0	1	32.23	35.09
5	0	1	-1	89.77	90.62
6	0	1	1	40.66	35.89
7	0	-1	1	9.58	8.72
8	0	-1	-1	29.49	34.25
9	1	0	-1	57.27	54.40
10	1	-1	0	9.72	7.82
11	1	0	1	25.50	28.24
12	1	1	0	48.43	50.44
13 ^a	0	0	0	37.57	37.52
14 ^a	0	0	0	37.41	37.52
15 ^a	0	0	0	37.60	37.52

a = Three additional tests at the central point (0, 0, 0) for the calculation of the Student and Fisher's tests.

TABLE IV
STATISTICAL PARAMETERS OF BOX-BEHNKEN DESIGN

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
X ₁ : T	867.361	1	867.361	46.28	0.0010 ^b
X ₂ : m/v	3489.88	1	3489.88	186.23	0.0000 ^b
X ₃ : C ₀	3220.43	1	3220.43	171.85	0.0000 ^b
X ₁ ²	119.613	1	119.613	6.38	0.0528
X ₁ X ₂	0.714025	1	0.714025	0.04	0.8529
X ₁ X ₃	195.301	1	195.301	10.42	0.0233 ^b
X ₂ ²	49.7539	1	49.7539	2.65	0.1642
X ₂ X ₃	213.16	1	213.16	11.37	0.0198 ^b
X ₃ ²	267.974	1	267.974	14.30	0.0129 ^b
Total error	93.6994	5	18.7399		
Total (corr.)	8524.71	14			

R² = 98.90 %, R²_{adj} = 96.92 %, b= significant variable

Table IV shows the analysis of variance (ANOVA) model for the percentage removal of CR using HDTMA-B. Based on this analysis, six effects have P-values less than 0.05 (X₁, X₂, X₃, X₁X₃, X₂X₃ and X₃²), indicating that they are significantly different from zero at the 95.0% confidence level. This implies that the linear effects of temperature (P=0.0010), solid/solution ratio (P = 0.0000) and initial dye concentration (P=0.0000) are more significant. The square effects of initial

dye concentration (P=0.0129) and interactive effects of temperature and initial dye concentration (P=0.0233) and adsorbent dosage and initial dye concentration (P=0.0198) were also found to be statistically significant on the adsorption of CR onto HDTMA modified bentonite. Moreover, the determination coefficient (0.989) was very high showing good fitness of statistical model. The coefficient of determination adjusted (R²_{adj}), which is more suitable for comparing models with different numbers of independent variables, is 96.92%.

Individual and interaction effects can be seen in the Pareto chart shown in Fig. 9. These results confirmed that the main effect of test variables was very significant at the 95% confidence level, or the initial dye concentration and temperature have net negative effects on CR removal. On the other hand, their interaction (X₁X₃) has a positive effect upon process efficiency. The sequential quadratic programming in Statgraphics Centurion XVI is used to solve the second-order response model (6); which is valid for coded units is:

$$\% \text{Removal} = 38.681 - 10.412 X_1 + 20.886 X_2 - 20.063 X_3 + 6.987 X_1 X_3 - 7.3 X_2 X_3 + 8.374 X_3^2 \quad (7)$$

Fig. 10 shows the 3D surface plots between every two independent variables on the basis of (7). This is useful to visualize the relationship between the response and the level of each parameter. The response model is mapped against two experimental factors while the third is held constant at its central level. Therefore, the optimum values of operating variables in coded units are X₁ = -0.350, X₂ = 0.955 and X₃ = -0.997. They are converted into uncoded units for the actual values and the optimum values of the test variables were: temperature (33 °C), adsorbent dosage (0.98 g/L) and initial dye concentration (50.68 mg/L). Under the optimal condition, CR dye could be quantitatively removed from aqueous medium solution using HDTMA-B.

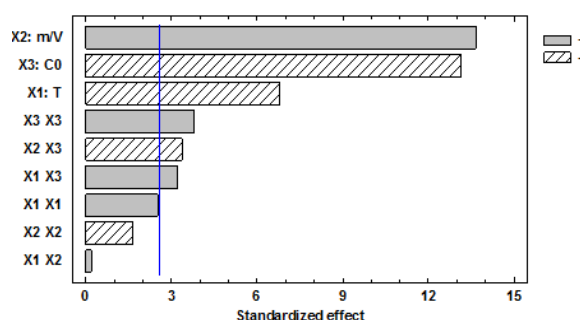


Fig. 9 Pareto chart of standardized effects on the removal efficiency for CR

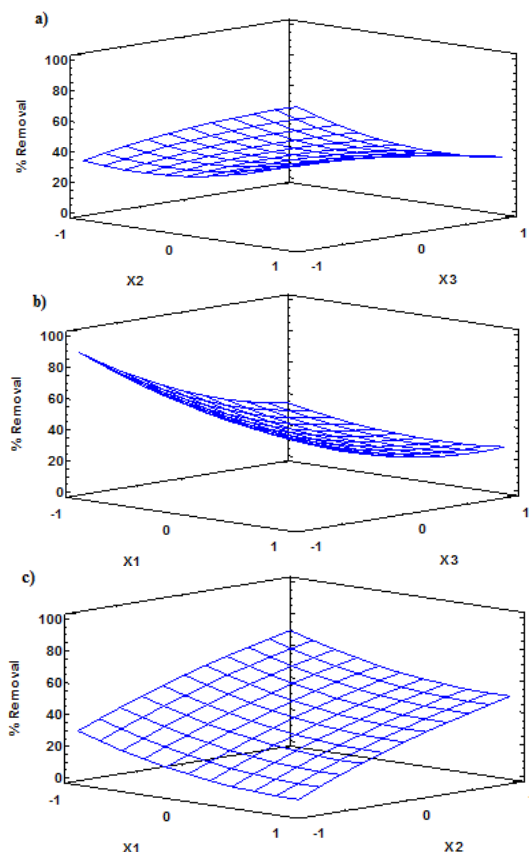


Fig. 10 3D representations of the adsorption efficiency of CR at fixed: a) $X_1=0$, b) $X_2=0$, c) $X_3=0$

IV. CONCLUSION

In the study, HDTMA modified bentonite were used for the removal of CR dye from aqueous solution. The adsorption process of CR depended strongly on the temperature, adsorbent dosage, and the initial dye concentration. Pseudo-second-order model described the adsorption kinetics of CR onto modified bentonite better than first one, and the adsorption was controlled by chemisorptions process. Response surface methodology according to Box-Behnken design was used to find the optimum process conditions for the sorption of CR dye. From the results, all independent factors as well as the square effects of initial dye concentration and interactive effects of temperature and initial dye concentration and adsorbent dosage and initial dye concentration were found to have significant influence on dye adsorption. The optimum conditions for the sorption of CR at the constant pH (6.6) were: temperature (33 °C), adsorbent dosage (0.98 g/L), and initial dye concentration (50.68 mg/L). At the optimized condition, the anionic dye could be quantitatively removed from aqueous media. The study shows that HDTMA modified bentonite seems to be an interesting adsorbent for the removal of CR dye from aqueous media.

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