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# Ammonium-Based Ionic Liquid Modified Bentonite for the Removal of Anionic Dye: Process Optimization Using Box-Behnken Design Approach

Brahim Guezzen[#1], Rachida Berrezouk*[2], Baghdad Medjahed[#3]

[#]*Laboratory of Separation and Purification Technology, Department of Chemistry, Faculty of Sciences, Tlemcen University, Box 119, Algeria*
[1]b_guezzen@yahoo.fr

[3]medjahedbaghdad@yahoo.fr

**Laboratory of Physico-chemical Studies, Department of Chemistry, Faculty of Sciences, Saida University, Algeria*
[2]rachachimie@yahoo.com

***Abstract*— Trioctylmethylammonium chloride (TOMACl) ionic liquid-modified bentonite (TOMA-B) was prepared via a cationic exchange reaction and applied to adsorb Congo Red (CR) dye from aqueous solution. The structure of the prepared adsorbent was characterized mainly using X-ray diffraction (XRD), infrared spectrum (IR), and scanning electron microscope (SEM). The optimum experimental conditions, including temperature (T, 20–60 °C), adsorbent dosage (m/v, 0.1–1 g $L^{-1}$), and initial dye concentration ($C_0$, 50-500 mg $L^{-1}$) at three levels were studied using Box-Behnken design (BBD) based on the response surface methodology (RSM). Prediction models and response surfaces were confirmed by the level values optimized by the desirability function. At the optimized condition, the maximum CR adsorption was found to be 91.44 %. The results represented the considerable potential of ionic liquid-modified bentonite as a promising approach for dye removal.**

***Keywords*— Ionic liquid; Organo-Bentonite; Congo red; Adsorption; Design of experiment.**

## Introduction

Discharge of wastewater containing dyes into water bodies due to their toxic properties can have adverse consequences on living organisms as well as human beings. Most synthetic dyes are toxic, carcinogenic, and mutagenic [1]. They are also almost stable against most chemical and biological degradation. Therefore, it is necessary to remove these dyes before discharging them into water bodies. Nowadays, interest is focused on using low-cost clay adsorbents such as bentonite to capture dyes from aqueous solutions.

Clays have a low affinity for hydrophobic organic compounds due to their hydrophilic surface [2]. However, clays can be activated for hydrophobic adsorption by simple ion exchange reactions with organic cations, thereby converting them into organoclays [3]. Organically modified clays have a stronger adsorption capacity for nonionic and ionic organic compounds than unmodified clays, and the molecular structure of organic cations affects the adsorption capacity and its mechanism [4, 5].

Ionic liquids (Ils) have attracted interest as green solvents for chemical processes because they minimize solvent waste, reduce exposure to hazardous fumes, and are considered environmentally friendly (low toxicity) [6]. Adsorption of anionic dye from aqueous samples by organo-clay using ionic liquids as modifiers have been recently investigated [7-9]. It was demonstrated that the insertion of ILs not only changed the surface properties of clay from hydrophilic to hydrophobic but also significantly increased the basal distance between clay layers [10].

The aim of the current work was to investigate the removal of anionic diazo textile dye CR from an aqueous solution using trioctylmethylammonium chloride ionic liquid modified bentonite (TOMA-B). The optimization of sorption parameters on dye removal was carried out using response surface methodology based on Box-Behnken design.

## I. MATERIALS AND METHODS


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### *A. Chemicals and materials*

Trioctylmethylammonium chloride ($TOMA^+ Cl^-$) was provided by Biochem and was used without further purification. Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, FW: 696.66 g $mol^{-1}$, 99.9 % purity, Biochem) dye was used as adsorbate. The natural Bentonite used in the experiments was supplied from deposits in the area of Maghnia, Algeria. It was converted to a sodium Bentonite (Na-B) according to the method published in a previous study [11]**.** Its chemical composition was as follows: 62.48% $SiO_2$, 17.53% $Al_2O_3$, 1.23% $Fe_2O_3$, 3.59% MgO, 0.82% $K_2O$, 0.87% CaO, 0.22% $TiO_2$, 0.39% $Na_2O$, 0.04% As, 13.0% loss on ignition at 950 °C [12].

### *B. Preparation of TOMA-B sample and characterization techniques*

The organophilic Bentonite sample were obtained by dispersing quantities of 5 g of sodium bentonite (Na-B) in 500 mL of solution and stirred for an hour. A stoichiometric amount of TOMACl corresponding to 100%% CEC of Na-B was dissolved in ethanol and then added dropwise to the Bentonite suspension. The mixture was agitated for 24 h at room temperature and then centrifuged at 3000 rpm for 15 min. Next the product was filtered, washed several times with ethanol and deionized water (until negative chloride test with 0.1 M $AgNO_3$ was obtained) and then dried at 70°C for 24 h. The resulting sample was designated as TOMA-B. The crystalline structure of the organo-modified bentonite sample was compared to that of the sodium bentonite using a Philips X-Pert diffractometer. With a Perkin Elmer FT-IR Spectrophotometer, FTIR spectra in the range 4000-500 $cm^{-1}$ were acquired.

### *C. Batch adsorption experiments*

All experiments were done in a 100 mL Erlenmeyer containing 25 mL of the aqueous phase containing desired concentrations of CR dye (at natural pH 6) and amount of TOMA-B composite. The flasks were shaken with a magnetic stirrer at 300 rpm for 60 minutes which was sufficient to achieve equilibrium in preliminary experiments.. For all the experiments, after agitation, solid and liquid phases were separated by centrifugation at 3000 rpm for 10 min (model Hettich Zentrifugen EBA 20). The concentrations of CR after adsorption were measured using Analytik Jena (SPECORD210) UV-vis spectrophotometer at $\lambda_{max}$ = 498 nm. The adsorption efficiency (% Removal) was calculated by using the following formula:

$$\%\,\boldsymbol{Removal} = \left(\mathbf{1} - \frac{\boldsymbol{C_e}}{\boldsymbol{C_0}}\right)\mathbf{100} \quad (1)$$

Where $C_0$ is the initial concentration of CR dye (mg $L^{-1}$) and Ce is the dye concentration in solution at equilibrium (mg $L^{-1}$)**.**

### *D. Experimental design*

Adsorption process operating parameters are optimized based on Box-Behnken design (BBD), which can reduce experiment time, total cost, and variability, and improve responsiveness. BBD (3 factors and 3 levels) was not only used to study the individual and interaction effects of process variables but also to obtain the best operating variables for CR sorption. Independent variables were chosen as temperature (A), adsorbent dosages (B), and initial CR dye concentration (C), and the dependent variable was selected as percentage removal (Y). The ranges and levels of the process variables are listed in Table 1. Adsorption experiments were planned according to these variables and their levels in Design-Expert 13® software. The data obtained were fitted with an empirical second-order polynomial model as follows:

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

where $Y$ is the predicted response; $X_i$ and $X_j$ are the independent variables in coded units; $\beta_0$ is the constant coefficient and $\beta_i$, $\beta_{ii}$, and $\beta_{ij}$ are regression coefficients for linear, square, and interaction effects, respectively. n is the number of independent variables.

## II. RESULTS AND DISCUSSION

### *A. Characterization of adsorbent*

Fig.1a shows the FTIR spectra of Na-B, and TOMA-B. The infrared spectra of the samples showed that the shapes of the peaks were very similar, indicating that the clay's structure was not destroyed after modification. The bands appearing at 2850 and 2919 $cm^{-1}$ are ascribed to the TOMA's C–H stretching bond frequency of ethylene groups in TOMA, suggesting that the alkylammonium was successfully introduced into the bentonite. The XRD patterns of Na-B and TOMA-B samples are shown in Fig.1b. A typical diffraction


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peak of Na-B is located at 6.97°, corresponding to a basal spacing of 1.27 nm. After intercalation with ionic liquid at a concentration of 100 percent of cation exchange capacity, the typical diffraction peak of modified Bentonite moves to a lower angle (3.73°), standing for a basal spacing of 2.37 nm. The increase of the basal spacing indicates that the organic cation intercalates into the interlayer space of the clay.

TABLE I
BBD MATRIX OF REAL AND CODED VALUES ALONG WITH EXPERIMENTAL AND PREDICTED VALUES

| Run Order | Actual and Coded Values | | | Removal Efficiency (%) | | |
|---|---|---|---|---|---|---|
| | T ($X_1$) | m/v ($X_2$) | $C_0$ ($X_3$) | Experimental | Predicted | Residual |
| 1 | 20(-1) | 0.55(0) | 50(-1) | 71.75 | 70.94 | 0.81 |
| 2 | 20(-1) | 0.1(-1) | 275(0) | 17.54 | 15.92 | 1.62 |
| 3 | 20(-1) | 1(1) | 275(0) | 42.42 | 43.58 | -1.16 |
| 4 | 20(-1) | 0.55(0) | 500(1) | 15.04 | 16.31 | -1.27 |
| 5 | 40(0) | 1(1) | 50(-1) | 91.19 | 90.84 | 0.35 |
| 6 | 40(0) | 1(1) | 500(1) | 14.67 | 12.24 | 2.43 |
| 7 | 40(0) | 0.1(-1) | 500(1) | 11.94 | 12.29 | -0.35 |
| 8 | 40(0) | 0.1(-1) | 50(-1) | 35.73 | 38.16 | -2.43 |
| 9 | 60(1) | 0.55(0) | 50(-1) | 83.87 | 82.60 | 1.27 |
| 10 | 60(1) | 0.1(-1) | 275(0) | 32.47 | 31.31 | 1.16 |
| 11 | 60(1) | 0.55(0) | 500(1) | 31.95 | 32.76 | -0.81 |
| 12 | 60(1) | 1(1) | 275(0) | 54.69 | 56.30 | -1.61 |
| 13[a] | 40(0) | 0.55(0) | 275(0) | 20.63 | 19.50 | 1.13 |
| 14[a] | 40(0) | 0.55(0) | 275(0) | 19.08 | 19.50 | -0.42 |
| 15[a] | 40(0) | 0.55(0) | 275(0) | 18.79 | 19.50 | -0.71 |

**Note:** a, three additional tests at the central point (0, 0, 0) for the calculation of the Student and Fisher's tests.

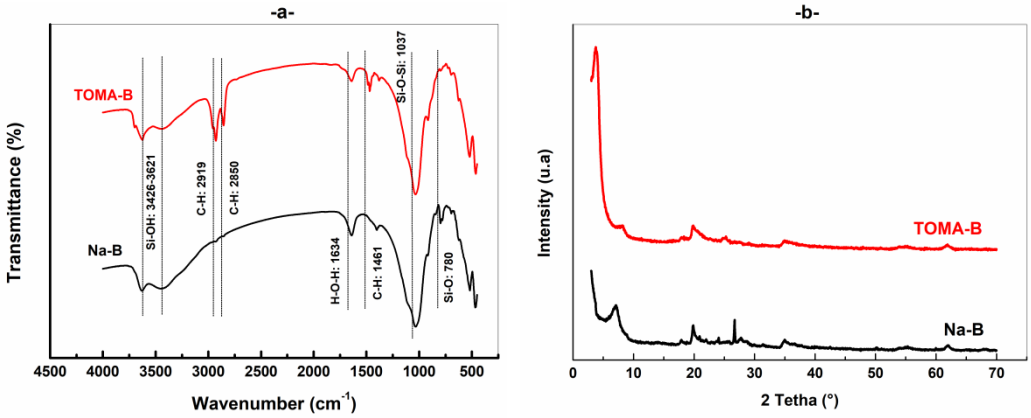


**Fig.1** FTIR spectra (a) and XRD diffractograms (b) for Na-B, and TOMA-B.

*B. Process optimization*

The optimum conditions for adsorption of CR azo dye onto surface of TOMA-B were determined by means of the BBD under RSM.

*1) Model fitting and statistical analysis:*

Analysis of Variance (ANOVA) of the quadratic polynomial model for modeling adsorption efficiency is listed in Table 2. The model F-values of 202.21 demonstrated the significant model, with a very low probability value of P< 0.0001. Based on the obtained data, the adsorbent dosage and initial dye concentration are the more significant factor. In addition, quadratic term effects were observed to be significant for the quadratic models. Table 2 also presents the fit statistics for the model of the adsorption efficiency by adsorbent. The coefficient of variance (C.V. %) measures the model's reproducibility; it is the ratio of the standard error to the mean value of the observed response as a


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percentage. As a general rule, if the C.V. value is less than 10% the model can be assumed to be reasonably reproducible [13]. Its value was 6.14, which justifies the reproducibility of the model. The value of the correlation coefficient ($R^2$) exceeds 0.99, proving the suitability of the existing model.

TABLE II
ANOVA FOR RESPONSE SURFACE REDUCED QUADRATIC MODEL

| Source | Sum of Squares | Df | Mean Square | F-value | P value | |
|---|---|---|---|---|---|---|
| **Model** | 9609.69 | 9 | 1067.74 | 202.21 | < 0.0001 | Significant |
| **Residual fit** | 26.40 | 5 | 5.28 | | | |
| Lack of Fit | 24.44 | 3 | 8.15 | 8.33 | 0.1091 | Not Significant |
| Pure Error | 1.96 | 2 | 0.9787 | | | |
| **Fit Statistics** | | | | | | |
| $R^2$ | 0.9973 | | Standard. Deviation | 2.30 | Adeq Precision | 41.8921 |
| Adjusted $R^2$ | 0.9923 | | C.V. % | 6.14 | | |

The program's derived model equation (at a 95% confidence level) is proposed for CR removal in relation to coded values, as shown in Eq. (3):

$$\% \text{ Removal} = 19.50 + 7.03A + 13.16B - 26.12C - 0.66AB + 1.20AC - 13.18BC + 14.77A^2 + 2.50B^2 + 16.38C^2 \quad (3)$$

*2) Optimization of independent variables and validation of model:*

Optimum values of adsorption parameters (temperature, adsorbent dosage, and initial dye concentration) at a fixed pH of 6 were evaluated through numerical optimization. Optimization techniques aim to achieve the maximum desirability index (D). The D value varies between 0 (least desirable) and 1 (most desirable). By targeting the obtaining of a maximum yield in CR (%) and keeping the parameters in their ranges, the suggested optimum conditions (with overall desirability =1) were 43°C, 0.99 g $L^{-1}$ of adsorbent and 51 mg $L^{-1}$ concentration dye, with maximum 91.44 % CR removal. In the case of targeting to minimize the temperature and adsorbent dosage, the numerically optimized parameters of CR removal by TOMA-B suggested by RSM were 0.45 g $L^{-1}$ of adsorbent and initial dye concentration of 51 mg $L^{-1}$ at a temperature of 20°C, with a maximum removal 64.84%, and an overall desirability of 0.729 (Fig.2). The removal efficiency remains remarkably high even though we used about half the mass of adsorbent and at a lower temperature. It is foreseen that the removal of CR in aqueous media at low temperatures and with a minimal adsorbent dosage will save a considerable amount of energy and raw material, thereby minimizing process costs.

TABLE III
EXPERIMENTAL RESULTS AND PREDICTED RESULTS AT THE OPTIMAL CONDITION

| Parameter or Response | Importance | Goal | Range | Predicted Results | Experimental Result | Error (%) | Overall Desirability |
|---|---|---|---|---|---|---|---|
| Temperature (°C) | 3 | In range | 20-60 | 43.04 | 43.0 | 0.09 | |
| Adsorbent dosage (g/L) | 3 | In range | 0.1-1 | 0.99 | 1.0 | 1.0 | **1.000** |
| Initial concentration (mg/L) | 3 | In range | 50-500 | 51.06 | 50.0 | 2.12 | |
| Removal (%) | 5 | Maximize | - | **91.44** | **90.31** | 1.25 | |
| Temperature (°C) | 3 | Minimize | 20-60 | 20.00 | 21.0 | 4.76 | |
| Adsorbent dosage (g/L) | 3 | Minimize | 0.1-1 | 0.45 | 0.45 | 0.0 | **0.729** |
| Initial concentration (mg/L) | 3 | In range | 50-500 | 50.00 | 50.0 | 0.0 | |
| Removal (%) | 5 | Maximize | - | **64.84** | **62.65** | 3.49 | |


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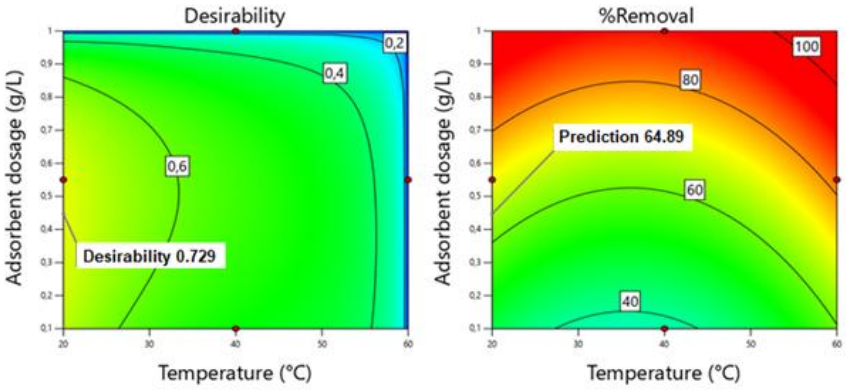


**Fig.2** Desirability and percent removal plots of adsorbent dosage vs. temperature to optimize the adsorption process of CR dye onto TOMA-B

Experiments were conducted under conditions similar to the predicted ones to check whether the predictions were consistent with reality. In this case, the observed experimental results are close to the proposed ones, as shown in Table 3. It can be found that the relative error of each response value is less than 5%, indicating that the model has good consistency and reliability.

## III. CONCLUSIONS

The optimum conditions for the adsorption of CR dye on the TOMA-B were determined through the BBD and RSM. The ANOVA of the quadratic model demonstrates that the model was highly significant. Response surface methodology not only provides valuable information about the interactions among factors but also helps to determine the possible optimal values of the examined factors. On the other hand, Bentonite modified by ionic liquid, is effectively used to remove CR dye with not only cost advantages but also environmental benefits.

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