ecoss 30 European Conference on Surface Science
31 August - 5 September 2014 Antalya, Turkey

Central composite design optimization of textile dye adsorption onto nanoclay

Aydin Hassani[a], Alireza Khataee[b,*] Semra Karaca [a], Murat Kıranşan [a]

[a] *Department of Chemistry, Faculty of Science, Atatürk University, 25240 Erzurum, Turkey*
[b] *Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*
**E-mail address: a_khataee@tabrizu.ac.ir (ar_khataee@yahoo.com)*

1. Introduction

The presence of organic dyes in aqueous environments such as livers and lakes can cause detrimental effects on such environments due to the reduction in light penetration and photosynthesis [1]. Moreover, the presence of dyes in aqueous environments adversely affects their aesthetic nature [2]. There are many technologies to remove organic dyes from industrial effluents including biological, adsorption, membrane, coagulation–flocculation, ozonation and advanced oxidation processes. Because of low biodegradability of organic dyes, conventional biological treatments are not efficient enough to degrade organic dyes and treat colored wastewaters; thus, organic dyes in aqueous solutions are degraded or removed through physicochemical processes [3]. Among physicochemical treatment methods, the adsorption process using solid adsorbent has been found to be an efficient and economic method [3]. Montmorillonite is one type of clay materials, which exists in most soils abundantly [4]. In recent years, the application of montmorillonite for treating polluted aqueous environments has been widely investigated by many researchers [5,6]. According to above-mentioned statements, we studied the capability of montmorillonite for the adsorption of Basic Yellow 2 (BY2) dye.

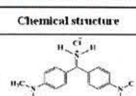
To vigorously evaluate the efficacy of the montmorillonite for the adsorption of BY2, response surface methodology (RSM) based on central composite design (CCD) was used to investigate the effect of different operational parameters including initial dye concentration, adsorbent dosage, temperature and reaction time on decolorization in batch flow mode reactors due to its advantages in comparison with conventional statistical approach.

2. Experimental

2.1. Reagents

The inorganic clay, used in this study, was K-10 grade montmorillonite purchased from Sigma–Aldrich Co. (USA) with a surface area of 279.27 m^2/g. The chemical composition (wt%) of the clay sample (main elements) was determined by Rigaku RIX-3000 X-ray fluorescence spectrometry (Rigaku Corporation, Japan). The cation-exchange capacity (CEC) of the clay is determined by the ammonium acetate method [7] as 120 meq/100 g. The montmorillonite clay with above-mentioned specifications was utilized to remove BY2 from aqueous solutions. The dye was purchased from Shimi Boyakhsaz Company, Iran and used without any purification. The characteristics of the dye are shown in Table 1. All chemicals used in the present investigation were of analytical grade purchased from Merck, Germany.

Table 1. Characteristics of C.I. Basic Yellow 2.

Color index name	Chemical structure	Molecular formula	M_w (g/mol)	λ_{max} (nm)	Class
Basic Yellow 2 (BY2)		$C_{17}H_{22}ClN_3$	303.83	432	Diarylmethane

2.2. General procedure

To carry out the adsorption experiments, 100-mL glass-stoppered round-bottom flasks immersed in a thermostatic shaker bath were used. The initial pH was adjusted with concentrated HCl and NaOH solution and measured by a WTW inoLab pH meter (WTW Inc., Weilheim, Germany). The pH meter was standardized with buffers before every measurement. At the end of each experimental run, the supernatant was withdrawn and centrifuged for 5 min at 6,000 min-1. The residual BY2 in the solution was measured with a Varian Cary 100 UV spectrophotometer at λ_{max} of 432 nm. The color removal (%) by adsorption onto montmorillonite was estimated through Eq. (1):

$$\text{Color removal (CR (\%))} = [1-(C/C_o)] \times 100 \quad (1)$$

where C_o and C are the dye concentrations at time 0 and t, respectively.

2.3. Experimental design

RSM based on CCD was used to optimize the removal of BY2 by the adsorption onto montmorillonite nanoclay. In recent decade, RSM has been utilized to assess interactive effects of different operational variables in various biochemical and chemical processes. For this reason, RSM method is very practical than the conventional one-factor-at-a-time strategy . To analyze the efficacy of the process for removing BY2 through RSM, Design-Expert software was applied. The effect of four main variables influencing the color removal was evaluated: the initial dye concentration (mg/L), the adsorbent dosage (g/L), temperature (°C) and reaction time (min). The number of experiments was calculated through Eq. (2):

$$N = 2^k + 2k + x_0 \quad (2)$$

where N, k and x_0 are the number of experiments, the number of variables and the number of central points, respectively. According to Eq. (2), the total number of experiments was obtained to be 31 (k =4, x_0 = 7). The selected variables (X_i) were coded as x_i according to Eq. (3):

$$x_i = (x_i - x_0)/\delta x \quad (3)$$

where x0 and δx are the values of xi at the center point and step change, respectively . The ranges and levels of the selected variables are represented in Table 2.

Table 2. Ranges and levels of variables for the adsorption of BY2 by central composite design (CCD).

No.	Variable	Name	Variable level				
			-2 (α)	-1	0	+1	+2 (α)
1	X_1	Dye (mg/L)	20	40	60	80	100
2	X_2	Adsorbent dosage (g/L)	0.1	0.45	0.8	1.15	1.5
3	X_3	Temperature (° C)	20	30	40	50	60
4	X_4	Time (min)	5	15	25	35	45

3. Results and Discussion

3.1. Model results for the removal of BY2 by montmorillonite

An empirical mutual relationship between the response (CR (%)) and independent studied variables was obtained using Design-Expert software and is shown through Eq. (4):

$$Y\,(CR\,(\%)) = 98.78 - 0.82x_1 + 1.68x_2 - 0.063x_3 + 0.047x_4 + 1.13x_1x_2 + 0.023x_1x_3 - 0.015x_1x_4 - 0.18x_2x_3 - 0.085x_2x_4 + 0.026x_3x_4 - 0.44x_1^2 - 0.91x_2^2 + 0.022x_3^2 - 0.043x_4^2 \quad (4)$$

One of the most important approaches to test the adequacy and reliability of the statistical model is performing analysis of variance (ANOVA). Thus, ANOVA was performed for the adsorption of BY2 onto nanoclay and its results are provided in Table 3. In this manner, the significance and suitability of the model was controlled by the obtained correlation coefficient (R^2) and adjusted R^2 between the experimental and predicted values of the CR (%). The closer the correlation coefficient value is to 1, the better it predicts the determined response. An obtained correlation coefficient of 0.972 indicates that 97.2% of the variations for BY2 removal (%) are explained by the applied model and the model does not explain only 2.8% of the variations. Adjusted R^2 is also a good tool to check the adjustment of the experimental results to the predicted values. According to Table 3, the value of adjusted R^2 was found to be 0.949. Therefore, it seems that there is not a significant difference between R^2 and corresponding adjusted R^2. This indicates a good fitness between the predicted results by the models and corresponding experimental results.

Table 3. Analysis of variance (ANOVA) for the adsorption of BY2 onto montmorillonite.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Regression	133.08	14	9.51	40.73	<0.0001
Residuals	3.73	16	0.23		
Pure error	0.081		0.013		
Total	136.81	30			

R^2 = 0.972, adjusted R^2 = 0.949

In addition, the significance and adequacy of the model can be checked by F-value and p-value. The larger F-value together with smaller p-value indicates the suitability of the models. The F-value of 40.73 and the p-value of <0.0001 demonstrated the adequacy of the model for predicting the BY2 removal (%) as response (Table 3).

3.2. Interactive effects of the studied variables

Response surface and contour plots can be used to assess CR (%) according to a polynomial function. In this approach, two variables were constant and the other two variables would be varied. Three-dimensional surface and contour plots are graphical representation of regression equation for the optimization of reaction conditions and are the most useful approach in revealing the conditions of the reaction system. The results of the relation between independent variables and dependent variable (response) are shown in Fig.1.

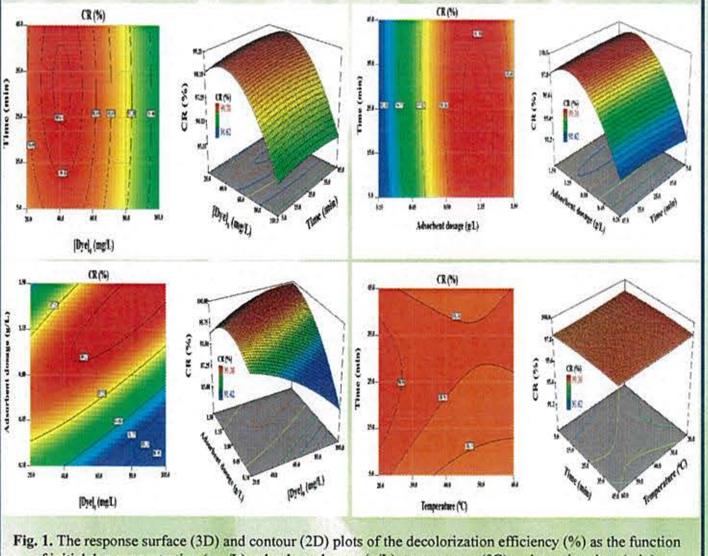


Fig. 1. The response surface (3D) and contour (2D) plots of the decolorization efficiency (%) as the function of initial dye concentration (mg/L), adsorbent dosage (g/L), temperature (°C) and reaction time (min).

References

[1] A.R. Khataee, M.B. Kasiri, L. Alidokht, Environ. Technol. 32 (2011) 1669-1684.
[2] S. Karaca, A. Gürses, R. Bayrak, Energy Convers. Manage. 45 (2004) 1693-1704.
[3] S. Karaca, A. Gürses, M. Açıkyıldız, M. Ejder, Micropor. Mesopor. Mater. 115 (2008) 376-382.
[4] M.-Y. Teng, S.-H. Lin, Desalination 201(2006) 71-81.
[5] L. Wang, A. Wang, J. Hazard. Mater. 160 (2008) 173-180.
[6] R. Wibulswas, Sep. Purif. Technol. 39 (2004) 3-12.
[7] A. Czímerová, J. Bujdák, R. Dohrmann, Appl. Clay Sci. 34 (2006) 2-13.