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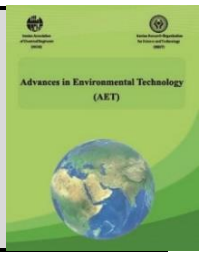

Response surface methodology for optimizing adsorption process parameters of reactive blue 21 onto modified Kaolin

Azam Nojavan, Parvin Gharbani*

Department of Chemistry, Ahar Branch, Islamic Azad University, Ahar, Iran

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ABSTRACT

In this research, Kaolin modified by Cetyltrimethylammonium bromide is used as an adsorbent for the removal of Reactive Blue 21 from aqueous solutions. Response surface methodology was used to study the effect of independent variables, such as Reactive Blue 21 dye concentration (20, 40, 60, 80 and 100 mg/L), time (10, 20, 30, 40 and 50 min), initial pH (2, 4, 6, 8 and 10) and modified Kaolin dosage (0.05, 0.1, 0.15, 0.2 and 0.25 g/50 mL) on dye removal efficiency from aqueous solutions. At the optimum conditions, predicted removal of Reactive Blue 21 by modified Kaolin was 98.26%. The confirmatory experiment was conducted, which confirmed the results by 94.42 % dye removal. Thus, the experimental investigation and statistical approach enabled us to predict Reactive Blue 21 removal by modified Kaolin. Also, the kinetics and isotherm adsorption of Reactive Blue 21 onto modified Kaolin was obeyed pseudo-second order kinetics and Langmuir isotherm.

1. Introduction

The wastewater of textile industries due to presence of a large number of contaminants is causing major hazards to the environment [1]. These colored compounds are inhibiting sunlight and reducing the photosynthetic reaction [2]. Since many organic dyes are harmful to human beings, the removal of color from waste effluents is important [3]. Nowadays, consumption of organic dyes in textile industry is being increased and discharge of dye effluents in environment will lead to damage of environment [4]. Dyes are organic compounds that are resistant to degradation and due to contain aromatic rings in their chemical structure, their biodegradability is low [5-7]. They are toxic and cancerous and may disrupt of kidneys, brain and central neural system in human [8,9]. Dyes are used extensively in textile, paper, plastic, food and cosmetic industries [10]. Presence of dye wastes in environment causes extensive pollution and production of byproducts via oxidation, hydrolysis and other chemical reactions [11]. Different physical (membrane filtration, microfiltration, ultrafiltration, adsorption, coagulation and sediment) and chemical (biological methods and advanced oxidation processes) methods have been used to remove of days [12]. Among these methods, adsorption is mostly used due to cost-effectiveness and simplicity [13-15]. Activated carbon is a high capacity adsorbent for the removal of pollutants [16], but it is expensive. So, the attention is focused to finding a non-expensive and efficiencies adsorbents such as clays (bentonite, sepiolite montmorillonite, alunite, and kaolinite) [17,18]. Clays have been widely studied because they are cheaper than other sorbents such as activated carbons and resins [19]. To improvement of clays efficiency, modification of them is down by various organic/inorganic compounds [20]. Results showed that modification of the clay increased the adsorption capacity [21].Modification is carried out using adsorption of a cationic surfactant onto the external surface and into the interlayer spacing of the clays [22], so the surface of clay changes from hydrophilic to hydrophobic and from negatively to positively charge. The sorption of a cationic surfactant onto the surface of the natural clay is mainly governed by cation exchange and hydrophobic interactions [23]. Kaolin clays were modified with tri-polyphosphate [24,25], and 2-

*Corresponding author. Tel: +98 4144228211
E-mail address: p-gharabani@iau-ahar.ac.ir
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mercaptobenzothiazole [26]. Cetyl trimethylammonium bromide (CTAB) has been used as surfactant for modifying the surface of natural clays and zeolites [27]. Surfactants are surface active compounds and capable of reducing surface and interfacial tension between liquids, solids and gases [27]. It was found that very few studies have been devoted to modify the surface properties of kaolin with surfactants. Phthalocyanine reactive dyes are mostly used in dye & textile industries. They are metal complexes that are used in creations of blue and green colors [28]. Such dyes are mostly derivatives of copper Phthalocyanine (such as Reactive Blue 21) and they are toxic and dangerous due to presence of copper in their structure. Thus low concentration of these dyes is harmful for health of organisms especially human [28]. Therefore, it is necessary to remove such compounds from aqueous environments. Reactive Blue 21 (RB21) is a dye that widely used for coloring cotton, wool, silk and polyamide textiles and contains copper phthalocyanine chromophore vinyl-sulfonic acid, which is toxic even in low concentrations [29-31]. The mean IC50 value for the blue dye was 278mg/L and the mean IC20 value was112 mg/L [32].RB21 has been removed from wastewater by various methods such as turnip peroxidase [28], adsorption onto clinoptilolite [33] and Sorption and Solubilization in Micellar Media [34]. In present research, reactive blue 21 (RB21) has been chosen as a pollutant dye (Figure 1) and its removal by modified Kaolin with Cetyl trimethylammonium bromide (CTAB) will be studied by Response surface methodology.

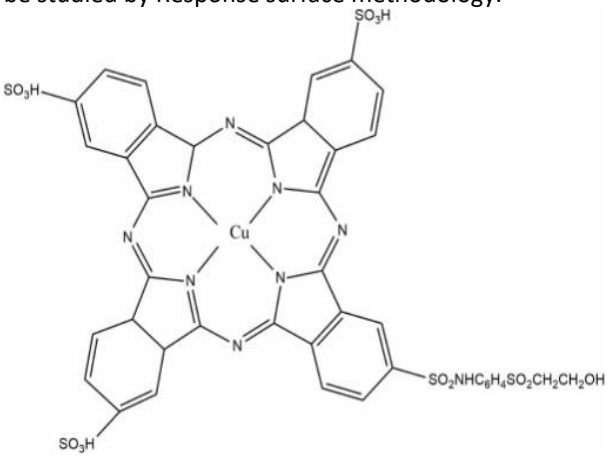

Fig. 1: Chemical structure of RB21 dye

Adsorption isotherms are mathematical equations that are used to determine amount of adsorbed substance on adsorbent in low temperature. Langmuir(1), Freundlich(2) and Temkin(3) isotherms are the most common isotherms and their equations have been stated as follows, respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

$$q_e = K_F C_e^{1/n} \quad (2)$$

$$q_e = B \ln(K_T C_e) \quad (3)$$

where, qe and qm are the amount of absorption per unit mass of adsorbent at equilibrium (mg/g) and for complete coverage or a single layer of absorbent absorption capacity (mg/g), respectively. Ce is the solution equilibrium concentration (mg/l)B and K_L is the adsorption equilibrium constant (L/mg) of Langmuir. K_F and 1/n are Frundlich isotherm constants. B is a constant that depends on the heat of adsorption and K_T is the equilibrium constant of Temkin isotherm (L/g) [12].

One of important studies in adsorption process is to study the adsorption kinetics. Adsorption kinetics depends on physico-chemical properties of adsorbent and it influences on adsorption mechanism. In current research, pseudo first and second-order kinetics have been studied to investigate adsorption kinetics of RB21 onto K-CTAB.

The pseudo-first-order differential form is as follows [13]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

In the above equation, K_1 is the first-order apparent speed constant (min^{-1}), qe and qt are the adsorption capacity in the equilibrium and any time, respectively (mg/g).
The pseudo-second-order differential form is as follows:

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

In the above equation, K_2 is the second-order apparent speed constant (g mg^{-1} min^{-1}) [12].

Design of experiments is a knowledge by which effectiveness of each factor affecting process and output specifications can be stated in form of an equation. Main goals of experimental design are reduction of number of experiments, reduction of costs and determination of variables that are the most effective on the response. Other goals of experimental design are deletion of unnecessary factors, calculation of importance percent of each variable and determination of favorable condition [14]. Response Surface Methodology (RSM) is a set of statistical techniques and it is used for optimization of processes and the response is affected by number of variables. Number of experiments is reduced and all coefficients of second order regression model and effect of factors are calculated by such technique. RSM is a helpful method to find favorable state of factors and to shows the effect of factors on results of experiments [15,16] Central composite designs (CCD) are the mostly used designs in response procedure method. Such designs are produced by combination of a complete two-level factorial design, star design and a central point. Sometimes a number of experiments are repeated in them. Therefore, $N=2^f+2f+1$ experiments are required for testing f factor. When the number of factors is above three factors, this design is cheaper than three-level factorial designs and

requires less time. Points of complete factorial design are located in -1 and +1 surfaces, points of star designs are located on (- α) and (+α) surfaces and central points are located on the surface [17,18].The mathematical relationship between response and variables can be presented in an equation (6) and in the form of a second-order polynomial:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (6)$$

Here, y represents the predicted response for the elimination efficiency, β_0 is constant factor, β_i is coefficient of linear effects, βii is coefficient square effects, β_{ij} is factor interactions, while x_i and x_j are variables. ε is the random error between predicted and measured values [14].

2. Materials and methods

2.1. Materials

Reactive Blue 21 dye (M=159.62 g/mol, λ_{max}= 614 nm) was purchased from Ardabil Arta Tejarat Zarrin Company (Iran) and Kaolin was purchased from Dae Jung Company (Korea). Cetyl trimethylammonium bromide (CTAB), Sodium hydroxide and hydrochloric acid were purchased from Merck Company (Germany).

2.2. Analysis

FTIR model BRUKER-TENSOR 27 (Germany), XRD model D5000 (Siemens Co. Germany) and TGA model 1500, Rheometric Scientific were used to identify modified Kaolin. Also, UV-Vis spectrophotometer model DR5000-15V (HACH CO, America) was used to record dye concentration at any time.

2.3. Modification of kaolin by CTAB

In order to prepare modified Kaolin, 10 g Kaolin and 90 ml distilled water was added in 250 ml Erlenmeyer on the stirrer. Then, 1 g CTAB was added gradually and it was stirred for 3h in ambient temperature. Then, precipitate was filtered, washed several times with distilled water and placed in an oven for 3h in 105 ^{o}C.

2.4. Procedure

RSM was used to obtain main effects of independent variables affecting on the response in adsorption process of RB21 dye on K-CTAB. The study is a central composite design with second order model. In this research, effect of four independent factors on response was studied including initial concentration of RB21 dye, adsorbent dosage, time and pH. The levels of such factors have been shown in Table 1.

Table 1. Factors and levels of the operational parameters.

Variables		-2	-1	0	1	2
dosage (g/50 ml)	A	0.05	0.1	0.15	0.2	0.25
Dye conc. (mg/L)	B	20	40	60	80	100
pH	C	2	4	6	8	10
Time (min)	D	10	20	30	40	50

After entering factors and levels in Design-Expert 7 (DX7) software, 30 experiments were suggested in different conditions. At first, solutions were prepared with required concentrations and their pH was adjusted in required ranges. The solution was poured in 100 ml Erlenmeyer and was placed on the stirrer. desired amounts of adsorbent were added to solution and it was Stirred for certain times. Then, samples were filtered and their adsorption was recorded by UV-Vis spectrophotometer. Experiments and their predicted results is shown in Table 2.

Table 2. Designed experiments along with experimental and predicted values.

Trial No	A (g/50ml)	B (mg/L	C (pH	D (min	%R Exp.	% R Pre.
1	0.15	60	6	30	82.7	69.51
2	0.15	100	6	30	24.5	28.42
3	0.2	80	4	40	65.2	72.75
4	0.2	40	4	40	99.0	90.96
5	0.2	80	8	20	99.3	87.31
6	0.25	60	6	30	82.4	68.36
7	0.1	80	4	40	45.4	53.3
8	0.1	40	8	20	72.6	93.66
9	0.1	40	4	40	97.1	87.34
10	0.2	40	8	20	84.0	49.19
11	0.15	60	2	30	84.3	75.42
12	0.05	60	6	30	83.3	96.58
13	0.15	20	6	30	98.6	96
14	0.2	40	8	40	81.3	80
15	0.1	80	8	40	49.5	46.84
16	0.15	60	6	10	99.1	90.14
17	0.2	80	8	40	49.1	52.84
18	0.1	40	4	20	67.8	55.04
19	0.1	80	8	20	32.7	64.94
20	0.2	40	4	20	99.7	78.33
21	0.15	60	6	30	98.3	84.95
22	0.15	60	6	30	99.0	96.3
23	0.15	60	6	30	94.0	73.03
24	0.15	60	6	50	75.6	87.39
25	0.2	80	4	20	98.2	99.3
26	0.1	40	8	40	99.4	99.3
27	0.1	80	4	20	99.4	99.3
28	0.15	60	10	30	99.4	99.3
29	0.15	60	6	30	98.9	99.3
30	0.15	60	6	30	99.4	99.3

In this research, Removal%, qe and qt were obtained via following equations:

$$\%\text{Removal} = \frac{(C_0 - C_t)}{C_0} \quad (7)$$

$$q_e = \frac{(C_{0-}C_e)}{C_0} \times 100 \quad (8)$$

$$q_e = \frac{(C_{0-}C_t)}{C_0} \times 100 \quad (9)$$

where, Removal% is percent of dye removal, C_0 (mg/L) is initial solution concentration, C_e (mg/L) equilibrium concentration, C_t (mg/L) concentration in any time, V is solution volume (L) and M is adsorbent mass (g) [12]. q_e and q_t are the adsorption capacity in the equilibrium and any time, respectively (mg g^{-1}).

3. Results and discussion

3.1. Characterization of modified Kaolin

Modified Kaolin was identified using FTIR, XRD and TGA. FTIR Spectra of Kaoline and K-CTAB have been shown in Figure 2. Figure. 2a shows FT-IR of Kaolin. The peak observed in 3674 cm^{-1} associates with OH attraction of internal crystalline hydroxyls, in 3374 cm^{-1} related to H-O-H vibration of adsorbed water and the peak of 2925 cm^{-1} associates with attraction of C-H group. Peak of 1670 cm^{-1} associate with H-O-H bonds of water. 1016 cm^{-1} and 632 cm^{-1} peaks associate with functional groups related to Si-O and Al-OH. Peak of 844-949 cm^{-1} shows bond vibrations of Al-OH group in Kaolin and peak of 791 cm^{-1} associates with internal poly-tetrahedral bonds of Si-O-Si in SiO_2 [35]. Fig. 2b shows Kaolin modified with CTAB. According to Fig. 2b, a pair of peaks has been created in areas of 2850 cm^{-1} and 2921 cm^{-1} and they associate with symmetrical and unsymmetrical stretching vibrations of methyl and methylene groups [36]. Figure 3a shows XRD pattern of Kaolin. It shows diffraction content of crystalline layered network of Kaolin with impurities of quartz (Q) and muscovite (M). Peaks observed in 2θ= 10, 26, 36, 38, 50° associate with Kaolin, 2θ= 19.31° associates with muscovite and 2θ= 20.91, 29.12° associates with quartz. Fig. 3b shows XRD pattern of Kaolin modified with CTAB. As shown, the intensity of Kaolin peaks has changed after modification.

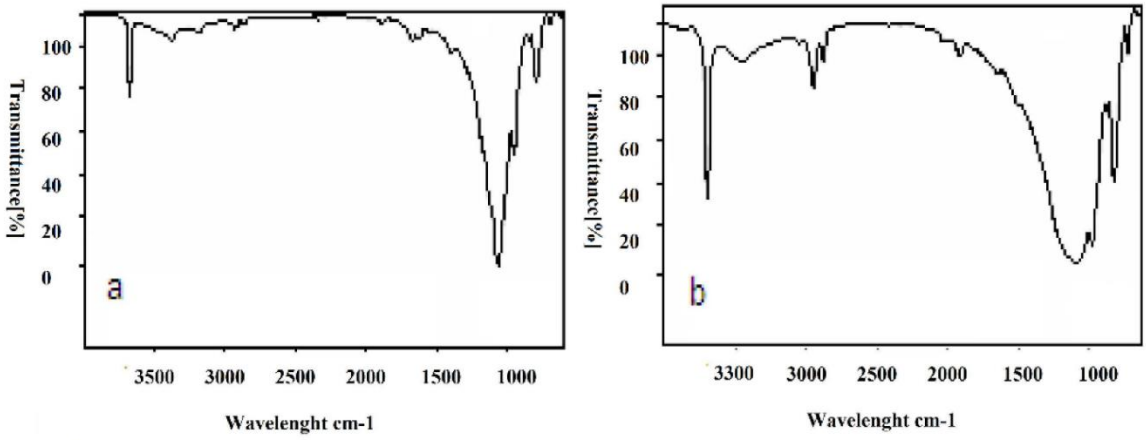

Fig. 2. FTIR of: a) Kaolin; b)K-CTAB

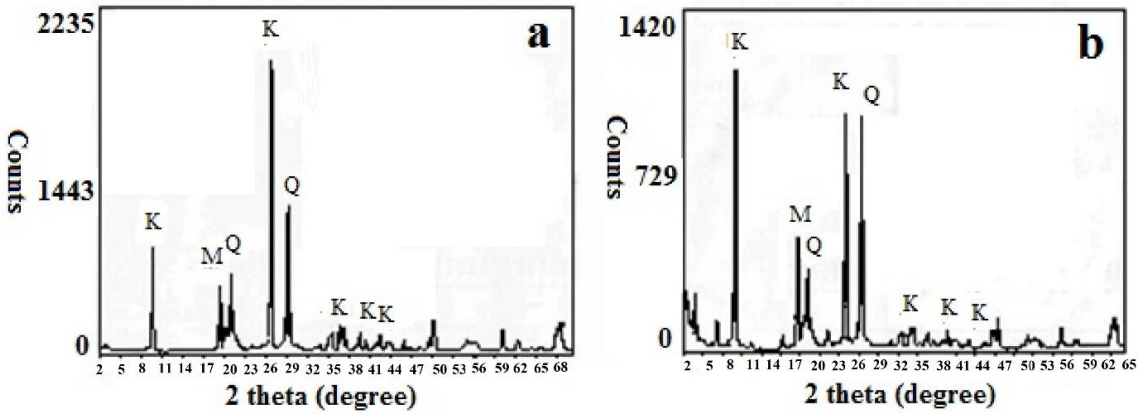

Fig. 3. XRD of a) K, b: K-CTAB

The thermal Gravity of Kaolin (K) and Kaolin-CTAB (K-CTAB) is presented in Figure 4 As shown, three stages is observed in thermal decomposition of K-CTAB . The first stage that was occurred over 130˚C - 200˚C related to adsorbed water. The second stage was down in the range of 300°C - 500°C due to the coordinated water and the partial loss of organic

moieties. The third loss was occurred due to the elimination of the organic groups and the dehydroxylation of the silanol groups on the clay surface over a temperature range of 550°C - 900°C. The typical hydrophilic character of K, which was evident by the strong difference between the percentages of the first mass loss stage. An additional change was the increase inthe total mass loss, which values were 11.49% and 13.79% for K and K-CTAB respectively.

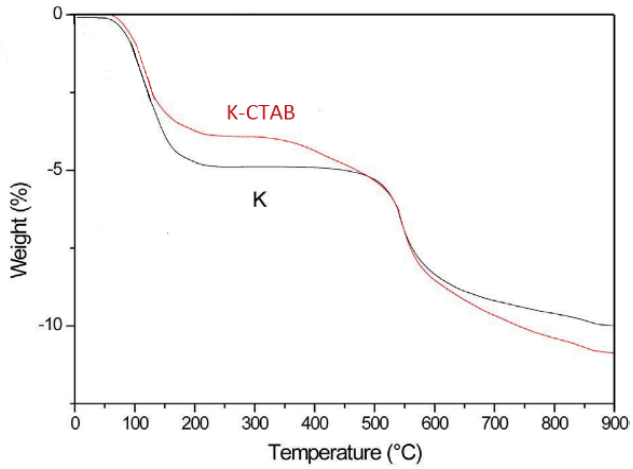

Fig. 4. TGA analysis of kaolin (K) and Kaolin-CTAB (K-CTAB)

3.2. Contact time

In order to study equilibrium time, 50 ml of dye solution with certain concentration was poured in Erlenmeyer. Then, 0.15 g of K-CTAB was added in Erlenmeyer and the stirrer. Sampling was down each 10 minute until 120 minutes. After filtration of samples, adsorption of all samples was recorded using UV-Vis spectrophotometer. Figure 5 shows removal percent of RB12 dye on K-CTAB in different times. According to Figure 5, removal percent was reached to equilibrium after 30 minutes.

3.3. Adsorption isotherms

In order to study adsorption isotherms of RB21 dye on k-CTAB, solutions with different initial concentrations were prepared in constant pH (6.2) and adsorbent and removal% were recorded at equilibrium time (30 minutes). Results of non-linear diagrams of adsorption of RB21 onto k-CTAB have been shown in Figure 6.

According to Figure 5, adsorption of RB21 onto K-CTAB is obeyed of Langmuir isotherm. So, it can be concluded the adsorption of RB21 dye onto k-CTAB is occurred as a mono-layer [17].

3.4. Kinetics

Kinetics results of RB21 adsorption onto K-CTAB has been shown in Figure 7.

As shown in Figure 7, experimental data are best fitted by pseudo second order kinetics. Therefore, adsorption kinetics of RB21 onto K-CTAB is pseudo second order.

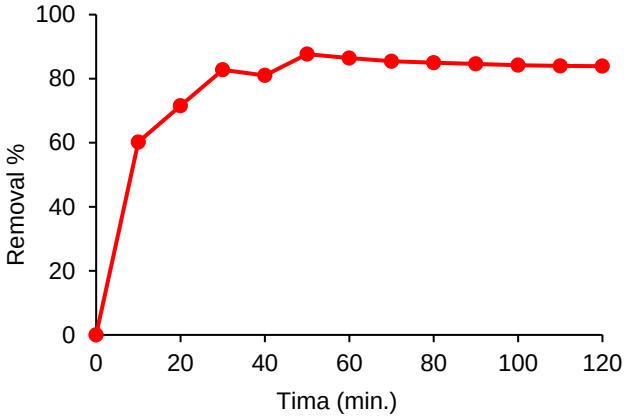

Fig. 5. Effect of contact time on removal of of RB21 on K-CTAB. [RB21]0=60 mg/L; K-CTAB=0.15 g/50ml, pH=6.21.3.

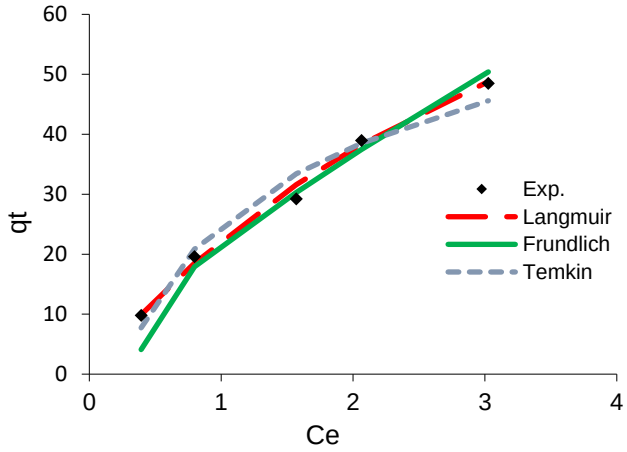

Fig. 6. Langmuir, Frundlich and Temkin adsorption isotherms of RB21 dye onto K-CTAB, K-CTAB =0.15 g/50 mL, pH = 6.2, Time= 30min

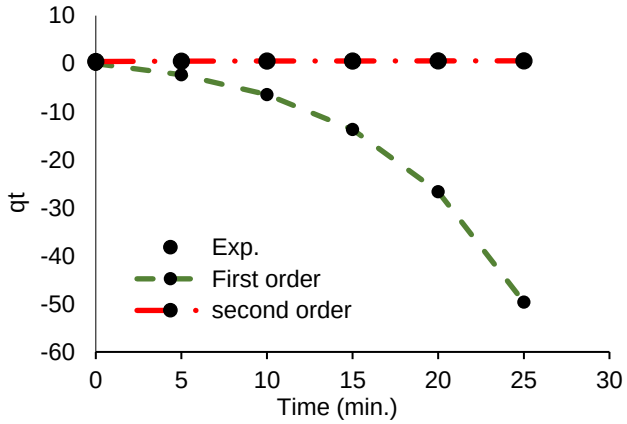

Fig.7. Pseudo first and second order plot of RB21 adsorption onto k-CTAB. Mg/ L 60 = [RB21], pH = 6.2 ،0.15 g/50 mL =K-CTAB

3.5. Response Analysis

To study the significance and adequacy of the model (Table 3), Analysis of Variance (ANOVA) was applied. The results show a high value of coefficient of determination (Pred. R^2

= 0.9320 and Adj R_2=0.9052).The Model F-value of 69.44 confirmed the significant of model and there is only a 0.01% chance that model occurs due to noise. In ANOVA Table, values of "Prob>F" which are less than 0.0500 show the significant of model terms. In this case B, C, D, AB, AC, BC, BD, CD, A2, B2, C2, D2 are significant model terms.

Table 3. ANOVA for response surface quadratic model.

Source	Sum of square	Df	Mean square	F-value	P-value	
Model	109886.37	14	784.74	69.44	< 0.0001	Significant
A: K-CTAB (g/50ml)	7.32	1	7.32	0.65	0.4337	
B: Dye Conc (mg/L)	268.6	1	268.6	23.77	0.0002	
C: pH	193.4	1	193.4	17.11	0.0009	
D:Time (min)	307.09	1	307.09	27.17	0.0001	
AB	3517.38	1	3517.38	311.24	< 0.0001	
AC	490.51	1	490.51	43.4	< 0.0001	
AD	8.66	1	8.66	0.77	0.3952	
BC	1387.38	1	1387.38	122.76	< 0.0001	
BD	299.6	1	299.6	20.32	< 0.0001	
CD	83.4	1	83.4	7.38	0.0004	
AA	3527.65	1	3527.65	312.14	0.0159	
BB	1312.31	1	1312.31	116.12	< 0.0001	
CC	129.1	1	129.1	11.42	< 0.0001	
DD	622.96	1	622.96	55.12	0.0041	
Residual	169.52	15	11.3			
Lack of fit	167.94	10	16.79	53.09	0.0002	Not significant
R^2=0.9320	Adj-R^2=0.9052					

A proper mathematical model between independent variables (initial concentration of RB21, adsorbent dosage, time and pH) and response was obtained. The model by which data were statistically calculated was second order mathematical model. The obtained equation between response (RB21 dye removal %) and independent factors is shown as following:

$$R(\%)=106.92667+105.96667\times Dose+1.98333\times[RB21]+17.01500\times pH+4.81783\times t+14.82687*Dose\times[RB21]+55.36875\times Dose\times pH+1.47125\times Dose\times t-0.23280\times[RB21]\times pH-0.018941\times[RB21]\times t-0.11416\times pH\times t-4536.29167\times Dose^2-0.017292\times[RB21]^2-0.54237\times pH^2-0.047657\times t^2 \quad (7)$$

Coefficients of A, B, C, D parameters were obtained by regression of linear effects, coefficients of mutual effects of parameters (AB, AC, AD, BC, BD, CD) by regression of interaction between parameters and coefficients of A^2, B^2, C^2 and D^2 by regression of power effects of 2. In order to investigate validity of studies, residual values (the difference between experimental and predicted responses) are obtained by frequency percent (normal distribution (8a) and they have been shown in terms of the number of experiments (8b). Linear curve of normal distribution for residual values suggests accuracy of the model and randomization of residual distribution shows precision of the model.

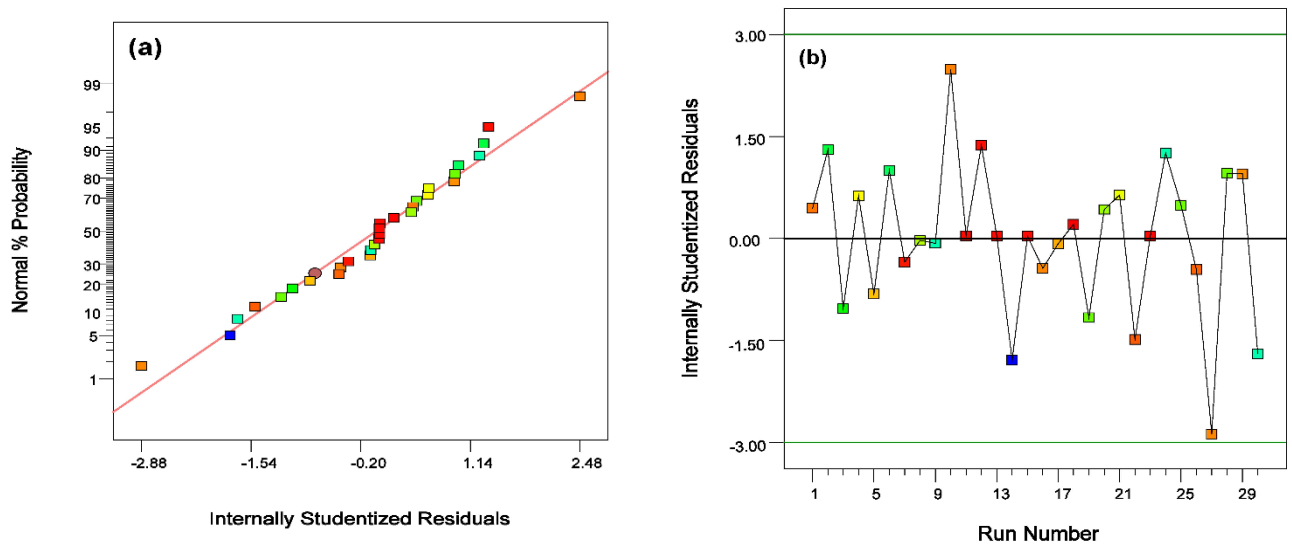

Fig. 8. (a) Normal plot of residuals; (b) Residuals versus run number

In order to investigate the integrated effect of the factors on removal of RB21 by Kaolin, the RSM was used and 3D plots (Figure 9) are shown in Figure 9. According to Figs. 9a, 9b and 9c, removal% is increased by the increasing dosage of adsorbent due to increase of surface area and then decreased. It may be due to agglomeration of K-CTAB particles in larger amounts that resulting in reduction of surface area and so decrease of Removal% [37]. As Figures. 9a, 9d and 9e, removal percent is increased by the increasing concentration of RB21 dye because of forces applied on adsorption sites via dye molecules but in higher concentrations of RB21 dye, removal percent is reduced due to saturation of adsorptions sites [38]. According to Figs. 9b, 9d and 9f, removal percent is increased by increasing of pH. It is known that, pH of solutions is an effective parameter on dye removal. In current research, pHzpc of K-CTAB is obtained about 9.5 (not shown here). In fact, in pH<pHzpc, adsorbent surface has positive charge and in pH>pHzpc, adsorbent surface has negative charge. In strong acidic media, production of protonated species lead to change of RB21 dye structure thus removal percent is reduced. In strong alkaline pHs, repulsion force between anionic dye and negative charge adsorbent leads to repulsion and removal percent is reduced. Therefore, the highest removal percent takes place in weak acidic and alkaline media [39]. According to Figures. 8c, 8d and 8f, increase of contact time has positive effect on dye removal percent and it is due to increasing of contact time between adsorbent and dye molecules that resulting in increasing removal percent of RB21 dye.

3.6. Validation

The results obtained from RSM based experimental trials were validated by carrying out an independent run at a maximum pH of 4 with an initial RB21 concentration of 100 mg/L and 0.24 g/50 ml of adsorbent at half an hour. A maximum removal of 94.42 percent was attained which validated the design.

4. Conclusions

Natural Kaolin is not performance adsorbents to remove of dye containments. To improve of its efficiency, Kaolin was modified by large organic cations, such as cetyl trimethylammonium bromide in a simple way. Results of XRD, TGA and FTIR confirmed modification of Kaolin by CTAB. K- CTAB showed a higher adsorption capacity toward RB21 than kaolin. Results showed that adsorption of RB21 dye onto K-CTAB is obeyed Langmuir isotherm and pseudo second order kinetics. As data, the removal of RB21 dye on K-CTAB is consistent with the percent predicted by the Experimental Design. Therefore, RSM is able to present a proper model to remove RB21 dye by K-CTAB.

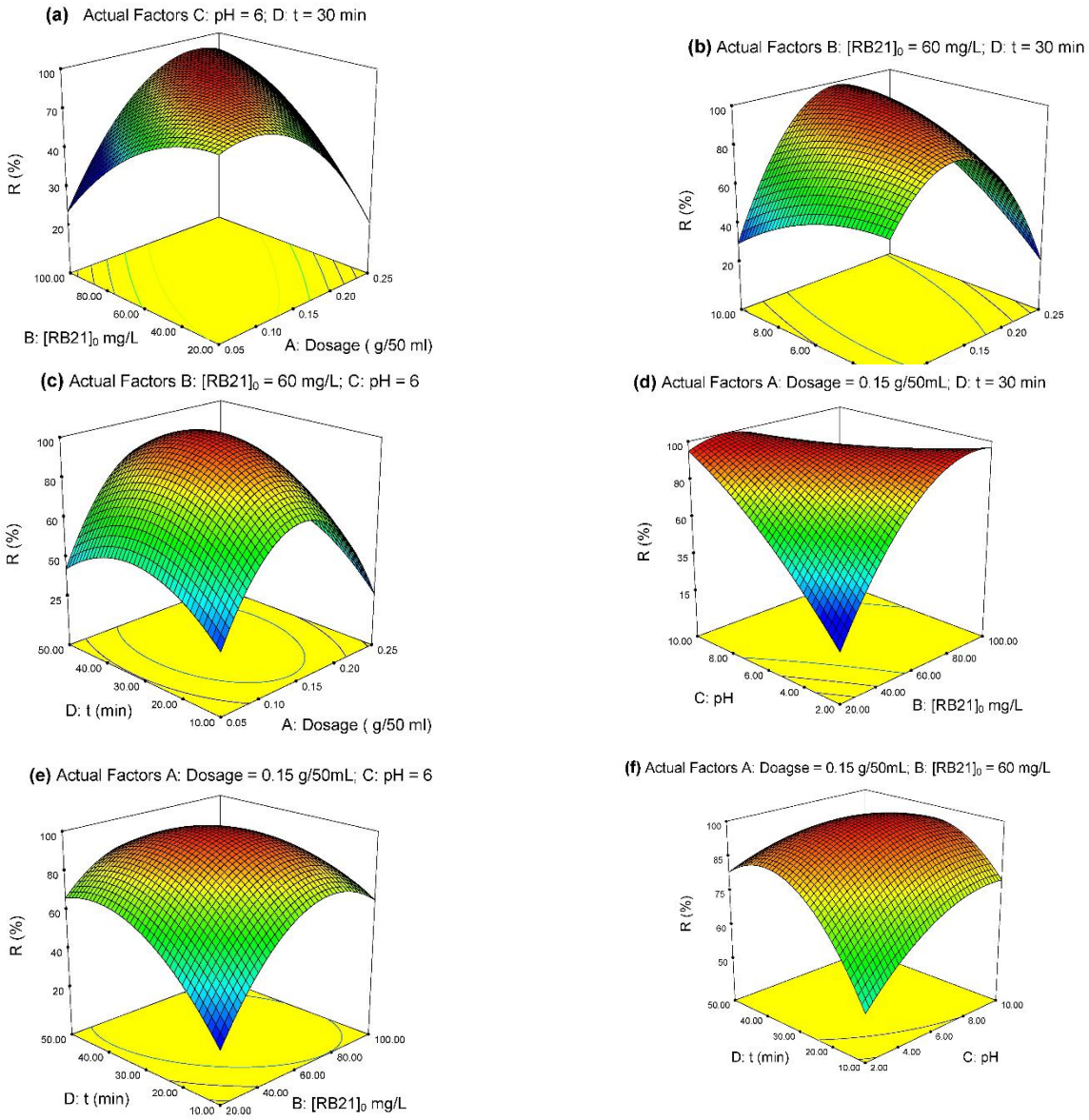

Fig. 9. Counter plots of removal efficiency (%) as a function of (a) initial RB21 concentration and adsorbent dosage; (b) adsorbent dosage and pH; (c) adsorbent dosage and contact time; (d) initial RB21 concentration and pH; (e) initial RB21 concentration and contact time; (f) pH and contact time

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