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Removal of crystal violet from aquatic environment by surfactant-modified dolomite

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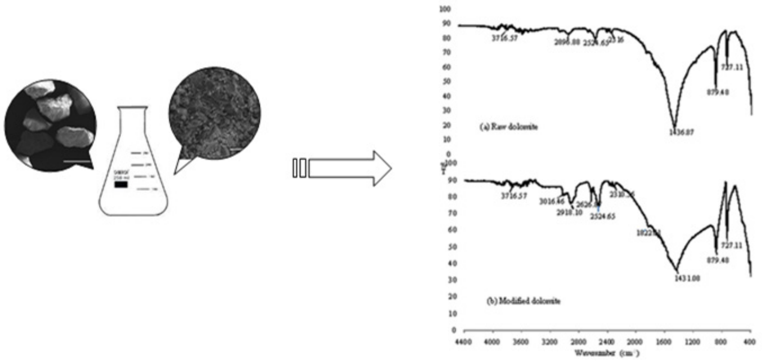
HIGHLIGHTS

- Evaluation of crystal violet removal using dolomite for the first time.
- dolomite modified with SDS shows good adsorption capacity to remove CV ions.
- Adsorption kinetic, isotherm, and thermodynamic were studied in detail.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents the adsorption of crystal violet (CV$^+$) from aqueous solution on surfactant-modified dolomite. Liquid phase batch operations were carried out to observe the effect of various experimental parameters such as initial dye concentration, adsorbent dosage, pH and NaCl concentration. The optimum conditions for these parameters were calculated by Taguchi method. Equilibrium isotherm data were analyzed according to Langmuir, Freundlich and Temkin equations. The experimental data fitted well to Freundlich adsorption model. The maximum adsorption capacities by Langmuir analysis were determined to be 49.261mg/g at 22°C that indicates suitable performance of this adsorbent. Pseudo-first-order and pseudo-second-order kinetics and the intraparticle diffusion models were also evaluated for the adsorption of CV$^+$ onto surfactant-modified dolomite. The positive value of free energy change confirmed the nature of physisorption of dye onto adsorbent.

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1. Introduction

Many industries use cationic dyes to color their products [1]. Crystal violet (CV^+) as a cationic dye is belongs to the class of triarylmethane, used for dyeing in varying industries [2]. When these dyes are left in the industrial effluent, could be a hazardous to the environmental. Thus, the removal of dyes from wastewater is important [3]. There are several chemical or physical processes to treat dye wastewaters. Adsorption process is one of the efficient physical methods to remove dyes from wastewater [4].

In recent years, low-cost clays have been applied as one of the adsorbents for the removal of dyes from dye effluent [5]. Dolomite as a low cost adsorbent is belong to calcite group and general formula of dolomite is $AB(CO_3)_2$ that A can be calcium, barium and or strontium and the B can be iron, magnesium or manganese [6]. Dolomite was applied in adsorption of many elements including the removal of Cu^{2+}, Pb^{2+}, strontium (II) and barium(II) [7,8], phosphate and ortho-phosphate [9–10], oil [11], fluoride [12] and arsenate [13].

Taguchi method is a powerful technique which can be used as an optimization technique for minimizing experiments number and expense. Taguchi method is a suitable method for analyzing interaction effects when ranking and screening various controllable factors [14].

In the present work, the batch study was undertaken for the removal of CV^+ onto Sodium Dodecyl Sulfate (SDS)-modified dolomite by Taguchi method. The effect of pH, adsorbent mass, NaCl concentration and initial dye concentration has been studied and the obtained experimental data were analyzed using adsorption isotherm models. Kinetic experiments have been also conducted to determine the rate of crystal violet adsorption onto modified dolomite and thermodynamic parameters were determined.

2. Experimental and analytical methods

2.1. Adsorbent

The dolomite used was obtained from Hamedan¸ Iran. The sample identified to be suitable for the chemical and mineralogical analysis, washed in deionized water and dried at 60°C. Dolomite was composed of 31.77% CaO, 20.19% MgO, 0.57% SiO_2, 0.23% Al_2O_3, 0.06% Na_2O, 0.043% P_2O_5, 0.03% K_2O, Fe_2O_3 0.01% (X-ray fluorescence spectroscopy (XRF) instrument (Philips, Netherlands). The ignition loss of the dolomite was also found to be 46.96%.

2.2. Preparation of surfactant-modified dolomite

200g of raw dolomite and 5g NaCl were immersed in 2L water while 40g SDS was used as a surfactant. Temperature of the reaction mixture was kept at the room condition (25°C) and the pH value was adjusted at 4.4±0.1. The mixture was stirred for 24h and then kept standing overnight. After the clear liquid was decanted off the top, the modified samples were washed several times using tap water and then washed with deionized water. The resulting products were finally dried at 60°C for 24h.

2.3. Characterization methods

In order to demonstrate the dolomite structure, SEM (VEGA-TESCAN Model instrument coating with gold) micrographs of the grain cross-sections were reported. Fourier transform infrared spectrometer spectra were recorded (KBr) on a Shimdzu 8400s FTIR to observe surface modification.

A surface analyzer (PHS-1020, PHSCHINA) was used to measure the nitrogen adsorption isotherm at 77.3 K in the range of relative pressure (P/P_o) 0.0268 to 0.957. The surface areas were calculated by the BET (Brunauer–Emmett–Teller) method. The total pore volume value was $0.472 cm^3/g$, the average pore diameter was 0.698 nm and the BET surface area value was 8.907 (m^2/g).

2.4. Batch adsorption experiments

Adsorption of CV^+ (obtained from Merck) was carried out by a batch technique to obtain equilibrium data. For optimizing the different factors which affect the amount of adsorption, Taguchi method was utilized. To reduce the error rate tests, were performed randomly and each adsorption sample was carried out in twice to avoid any discrepancy between experimental results and for determine the optimal conditions, three levels and four factors with three interactions (A*B, A*C and A*D) were considered (Table 1).

Designed experiments by Taguchi method was shown in Table 1. Adsorption experiments were carried out by adding 0.05, 0.1 and 0.5g of the dolomite sample to varying concentration (5, 20 and

Table 1. Designed experiments by Taguchi method

Num	A) adsorbent dosage (g)	B) initial dye concentration (mg/L)	C) pH	D) NaCl concentration (mg/L)	S/N ratio
1	0.05	5	6	0.1	-0.1225
2	0.05	5	9	10	1.3711
3	0.05	5	4	100	-3.8358
4	0.05	20	6	10	15.0563
5	0.05	20	9	100	19.0462
6	0.05	20	4	0.1	13.4420
7	0.05	50	6	100	24.8259
8	0.05	50	9	0.1	26.5308
9	0.05	50	4	10	15.1388
10	0.1	5	6	0.1	1.3265
11	0.1	5	9	10	1.3711
12	0.1	5	4	100	-5.0829
13	0.1	20	6	10	13.6501
14	0.1	20	9	100	14.3916
15	0.1	20	4	0.1	8.5335
16	0.1	50	6	100	20.0924
17	0.1	50	9	0.1	24.9614
18	0.1	50	4	10	12.7897
19	0.5	5	6	0.1	-11.4050
20	0.5	5	9	10	-10.2572
21	0.5	5	4	100	-18.8619
22	0.5	20	6	10	-2.0475
23	0.5	20	9	100	-0.8192
24	0.5	20	4	0.1	-7.3509
25	0.5	50	6	100	1.6844
26	0.5	50	9	0.1	6.4856
27	0.5	50	4	10	-0.1313

50 mg/L) of CV^+ solution in a series of 100 mL flasks. NaCl concentration was varied in 0.1, 10 and 100 mg/L. Each flask was filled with 50mL aqueous solution of CV^+ and adjusted to desired pH 6.0, 9.0 and 12.0. Temperature was kept in 22±1°C.

The pH values were adjusted by adding a few drops of dilute NaOH or HCl, and were measured by a digital pH meter (PL-500, EZODO). The pH-meter was calibrated using buffer solutions of pH 4.0 and 9.0 before use. The suspensions were stirred in shaker at 170 rpm for 1h, Then suspensions were centrifuged at 4000 rpm for 15 min at the end of the adsorption process. The concentration of the dye in the solution was analyzed using a (T80 +UV/VIS) Spectrophotometer. The measurements were made at the wavelength λ_{max}= 583nm, which corresponds to maximum absorbance. The amount of CV^+ adsorbed (mg/g), (q_e), onto modified dolomite was calculated from the mass balance equation (1).

$$q_e = (C_0 - C_e) \times {}^{V}\!/_{W} \tag{1}$$

where, C_0 the initial concentration of the dye solution (mg/L), C_e the equilibrium concentration of the dye solution (mg/L), V the volume of dye solution (L), and W the mass of adsorbent sample used (g).

3. Results and discussion

3.1. SEM analysis

The scanning electron microscopy results of the raw dolomite obtained by SEM (VEGA-TESCAN Model instrument coating with gold) were given in Fig. 1. The sample a (Fig. 1a) shows the presence of discrete grains with some grains having sharp edges and the images illustrate that the raw dolomite has significant amounts of calcite impurities. The sample b (Fig. 1b)

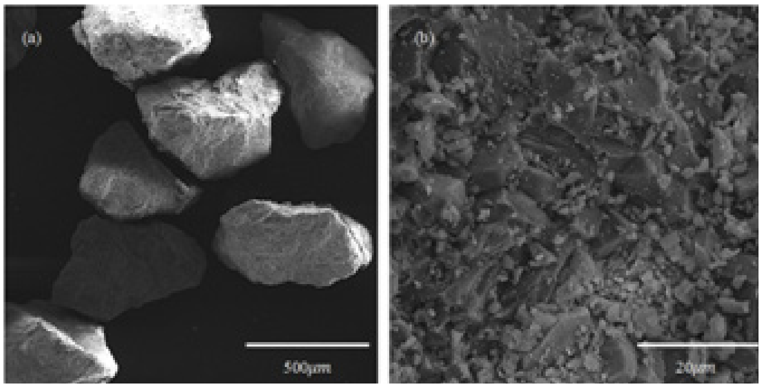

Fig. 1. SEM image of a) dolomite grains, b) raw dolomite surface.

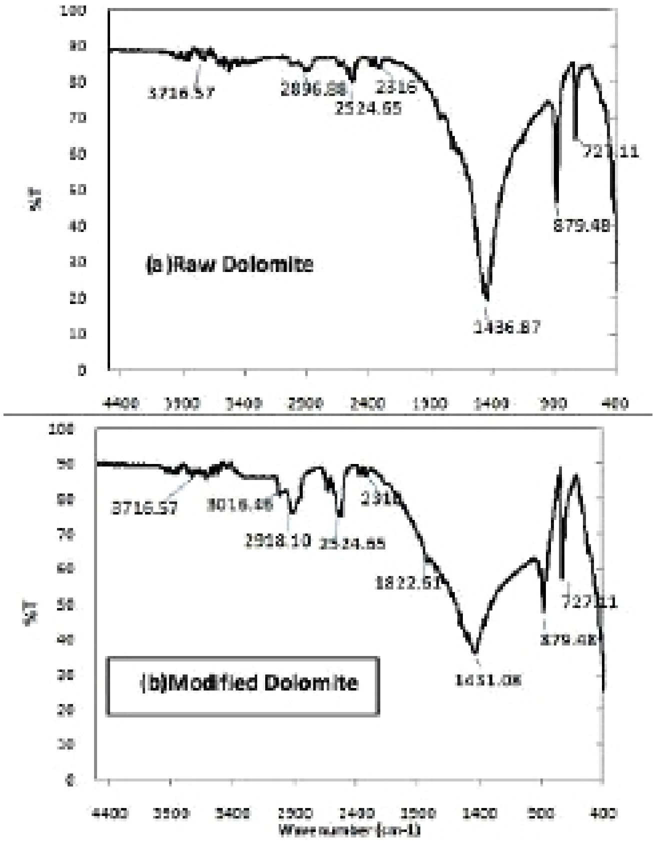

Fig. 2. FTIR spectrum of a) raw dolomite, b) modified dolomite.

shows the dolomite structure consists of rough and uneven surface with suitable sites for adsorption of dye molecule.

3.2. FTIR analysis

FTIR spectra of the raw dolomite and surfactant modified dolomite were recorded in the region 4400–400cm^{-1}. Dolomite FTIR analysis (Fig. 2a) shows main absorption bands of raw dolomite at 2524, 1436, 879 and 727cm^{-1}. The results are in good agreement with the absorption frequencies, indicated by previous researchers [15, 16]. The weak bands at 1040, 799, 525cm^{-1} shows the presence of Si-O vibration of silicate phase [17].

The band at 3716cm^{-1} that corresponds to (OH) vibrations of hydroxyl groups attached to Mg ions (belong to Mg_3OH) located in the natural dolomite and surfactant modified dolomite. Fig. 2b shows the band at 1436cm^{-1} was decreased and shifted to 1431, can be appointed to the intercalation of surfactant molecules between the silica layers [18]. The band intensity at 1822cm^{-1} could be demonstrated characteristics of adsorbed carbonate on the oxide surfaces [19]. The peak at 2316cm^{-1} was decreased and shifted to 2310 which could belong to presence of surfactant molecules and two peaks at 2626 cm^{-1} are illustrated the bending vibration of HCO^{3-} ions both of samples. The strong bands at 2918 and 3016 cm^{-1} was considered with surfactant-modified dolomite can be based the symmetric and asymmetric vibrations of the methylene group (CH_2) [20].

3.3. Taguchi method results

S/N ¬ratio as a summary statistic analysis of recovery is used to find the optimum level of S/N ratio related to recovery (Table 1). By taking the excremental data, the average recovery for the optimum level of the four factors can be received. In optimum conditions (initial concentration of 50 mg/L, initial pH of 9.0, NaCl concentration of 0.1 mg/L, adsorbent dosage of 0.05 g) amount of dye adsorbed (mg/g), (q_e), for CV^+ were calculated 21.21mg/g.

The ANOVA result is reported in Table 2. According to Table 2, the (f) refers to the degrees of freedom of each factor and (S) refers to the factor variation and error variation. The factor variances and the error variance (V), are shown in the fourth column and also (F) in fifth column refers to the variance ratio of each factor variance to the error variance. The data in the sixth column (P) refers to the contribution ratio.

According to the results the optimal conditions are indeed those with most significant contribution to the quality characteristic, in the last column of Table 2 shown by their contribution ratio. Referring to the contribution ratio, the amount of adsorbent and pH has the greatest impact. Uncontrolled or unwanted factors make about 2.26% of significance to the quality characteristic. This pointes show that the factors effect on the quality characteristic have a great influence of about 97.74% on the quality characteristic.

3.4. Adsorption Isotherm

According to the optimal condition Langmuir, Freundlich and Temkin isotherm models were fitted to the experimental data. Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface.

$$C_e/q_e = C_e/q_m + 1/\mathrm{b}q_m \tag{2}$$

The Langmuir equation is commonly expressed as in the linear form [21]:

In this equation, C_e and q_e are the equilibrium concentration of dye (mg/L) and the equilibrium dye concentration on the adsorbent (mg/g), respectively. Where q_m is the amount of the dye adsorbed (mg) per unit of adsorbent (g) and b is the Langmuir adsorption constant (L/mg).

The adsorption equilibrium data was also fitted with the Freundlich model given below [22]:

$$\log q_e = \log K_f + 1/n\, logC_e \tag{3}$$

where K_f and n are Freundlich constants related to adsorption capacity, n is an indicator of how is favorable the adsorption process and K_f (dm^3/g) is the adsorption capacity of the adsorbent. In this equation, C_e is equilibrium concentration of dye (mg/L) and q_e is the amount of the dye adsorbed (mg) per unit of adsorbent (g).

In the Temkin isotherm model, the heat of adsorption of all the molecules in a layer decreases linearly with coverage due to the effects of some indirect sorbate/adsorbate interactions. Adsorption is specified by a similar distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm has been usually used in the following form [23]:

$$q_e = BlnA + BlnC_e \tag{4}$$

Table 2. The ANOVA results in CV^+ removal efficiency with modified dolomite.

Factor	f	S	V	F	P (%)
A	2	1566.48	783.241	393.71	0
B	2	1826.47	913.236	459.05	0
C	2	275.16	137.581	69.16	0
D	2	14.05	7.026	3.53	0.097
AB	4	46.04	11.511	5.79	0.030
AC	4	1.86	0.466	0.23	0.909
AD	4	17.64	4.409	2.22	0.183
Error	6	11.94	1.989	-	-
Total	26	375965	783.241	-	-

where A (1/g) is the Temkin model constant, corresponding to the maximum binding energy and B is the Temkin constant related to heat of sorption. Therefore, the linear plots of q_e versus $\ln C_e$, enables one to determine the constants A and B.

The calculated constants for Langmuir, Freundlich and Temkin isotherms based on the data collected as shown in Table 3. The results indicate the Freundlich isotherm fits quite well with the experimental data. Based on the results, n value is 1.349 which indicates that effective adsorption intensity.

The isotherm results of the present investigation are comparable with the reported values by previous researchers [24–30]. The value of the maximum adsorption capacity (q_m) for modified-dolomite calculated from the Langmuir isotherm in this study has a higher ability to remove CV from aqueous solution compared to other adsorbents (Table 4).

3.5. Adsorption kinetic considerations

Several kinetic models are available to investigate the behavior of the adsorption process and to test the mechanism of the dye adsorption and also to examine the experimental data. In this study, the adsorption data were analyzed using the pseudo-first-order and pseudo-second-order kinetics and the intraparticle diffusion models.

The pseudo-first-order rate expression of Langergren is given as [31]:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

The pseudo-second-order kinetic model is expressed as [32]:

$$t/q_t = 1/k_2 q_2{}^2 + 1/q_2\, t \tag{6}$$

where qt is the amount of dye adsorbed (mg/g) at various times (t), q_e is the maximum adsorption capacity (mg/g) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_2 is the maximum adsorption capacity (mg/g) for the pseudo-second-order adsorption and k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). Table.5 shows the calculated constants for pseudo-first-order and pseudo-second-order, there is an agreement between q_e experimental and q_2 calculated values for the pseudo-second-order model. The results indicate the pseudo-second-order model better represents the adsorption kinetics. For the pseudo-second-order model with the increase of the temperature the rate constants for surfactant-modified dolomite decrease. The pseudo-second-order plots at different temperature to the adsorption of CV^+ onto modified dolomite are shown in Fig. 3.

The intraparticle diffusion model later is given by the Weber–Morris equation [33]:

$$q_t = k_p t^{1/2} + C \tag{7}$$

where the parameter C is the intercept, k_p is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and q_t is the amount of dye adsorbed (mg/g) at various times (t).

Table 3. Langmuir, Freundlich and Temkin isotherm constants for the adsorption of CV^+.

T (°C)	Freundlich isotherm parameters			Langmuir isotherm parameters			Temkin isotherm parameters		
	K_f	n	r^2	q_m	b	r^2	A	B	r^2
22	1.795	1.349	0.9988	49.261	0.0261	0.90	0.376	8.5237	0.9463

Table 4. Adsorption results of CV+ from the literature by various adsorbents.

Adsorbent	**q_m (mg/g)**	**Ref. nos.**
polymer	12.9	24
jute fiber carbon (JFC)	27.99	25
Activated carbon prepared from waste apricot	32.89	26
NaOH-modified rice husk	44.876	27
Sawdust	37.83	28
Semi-interpenetrated networks hydrogels	35.09	29
Neem Sawdust	4.44	30
Modified dolomite	49.261	In this study

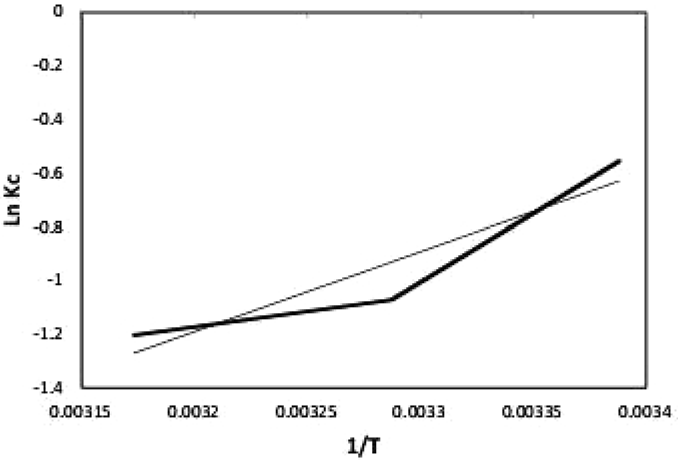

Fig. 3. Pseudo-second-order plots for the adsorption of CV^+ onto modified dolomite.

Table 5. Kinetic parameters for the adsorption of CV^+ onto surfactant-modified dolomite at various temperatures.

T (°C)	k_1 (min^{-1})	q_e(mg/g)	r^2	k_2 (g/mg min)	q_2 (mg/g)	r^2	k_p (mg/g $min^{1/2}$)	C (mg/g)	r^2
22	$1.77*10^{-2}$	9.606	0.809	$3.461*10^{-3}$	23.036	0.94	2.0472	3.78	0.908
31	$1.81*10^{-2}$	5.929	0.918	$2.09*10^{-3}$	22.222	0.932	1.9214	1.98	0.909
42	$1.55*10^{-2}$	2.630	0.850	$1.728*10^{-3}$	21.692	0.941	1.8773	0.87	0.896

Based on the evidence, the adsorption of dye onto surfactant-modified dolomite is a complex process, so the whole process cannot be only described by a single kinetic model. Table.5 shows the calculated intraparticle diffusion constant. The regression of q_t versus $t^{1/2}$ is linear (not shown), but it was not the main rate characterizing step during the whole process.

3.6. Thermodynamic parameters

To study the influence of the temperature on the adsorption capacities of the sample towards CV^+ in optimum conditions, experiments were performed using 50 mg/L dye solutions, 0.1 mg/L NaCl concentration, 0.05 g modified dolomite and pH value 9.0.

The Arrhenius type relationship parameters were determined by the pseudo-second-order rate constant as a function of temperature [34].

$$\ln k_2 = \ln A_1 - {E_a}/{RT} \tag{8}$$

where E_a is the Arrhenius activation energy and A_1 is the Arrhenius factor, which can be evaluated from the slope of the linear plot of $\ln k_2$ versus $1/T$. In this equation R is the gas universal constant which is equal to 8.314 J mol^{-1} K^{-1}, k_2 is the pseudo-second-order rate constant and T is the operating temperature. The other thermodynamic parameters of dye adsorption are expressed by the following equations:

$$lnKc = {\Delta S}/{R} - {\Delta H}/{RT} \tag{9}$$

$$\Delta G = -RT\, lnKc \tag{10}$$

$$\text{Where}: Kc = {C_A}/{C_e} \tag{11}$$

when lnKc is plotted versus $1/T$, ΔS°,ΔH° and ΔG° are the changes of entropy, enthalpy and the Gibbs energy were determined (Fig.4). Where, K_C is the equilibrium constant, C_A is the amount of dye adsorbed on the adsorbent at equilibrium (mg/L) and C_e is the equilibrium concentration of the dye in the solution (mg/L).

The enthalpy change ΔH° for the adsorption process was −24.763 kJ/mol, which did not suggested very strong chemical forces between the CV^+ molecules and surfactant-modified dolomite. On the other hand, the obtained value shows that adsorption process is an exothermic process (Table 6).

Low values of activation energies between 5 to 40 kJ/mol is a specification for physisorption [35] and the result obtained is +26.597 kJ/mol for the adsorption of CV^+ onto surfactant-modified dolomite,

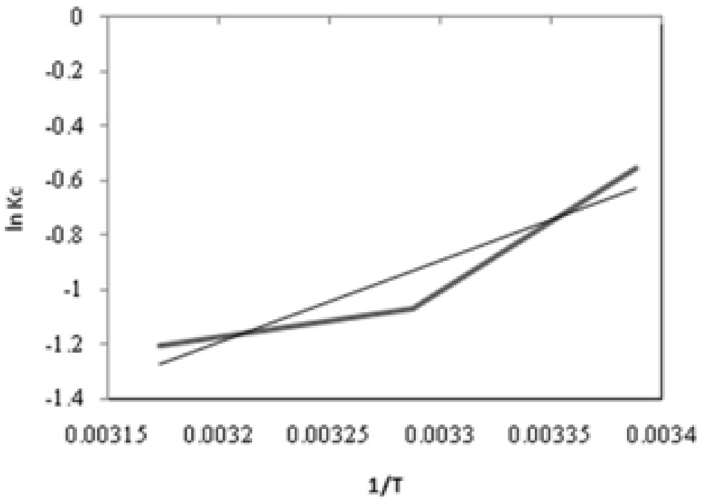

Fig. 4. Plot of lnKc vs. 1/T for estimation of thermodynamic parameter.

Table 6. Thermodynamic parameters calculated with the pseudo-second-order rate constant.

T (K)	1/T	ln k_2	E_a (kJ/mol)	K_c	ln K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K mol)
295.15	0.003388	-5.666	26.597	0.5744	-0.5544	1.36	-24.763	-84.137
304.15	0.003287	-6.171		0.3427	-1.071	2.708		
315.15	0.003173	-6.361		0.3002	-1.2033	3.153		

indicating low potential barrier and corresponding to a physisorption for adsorption process.

The ΔS° obtained is -84.137 J/K mol therefore suggested that no considerable change occurs in the structure of modified dolomite and also there is decreased randomness at the interface of modified dolomite and solution during adsorption process. On the other hand, negative value of ΔS° indicated that reduction of degree of freedom for adsorption species. The ΔG° values were positive therefore reflects that the presence of an energy barrier in the adsorption of CV^+ during adsorption system and need additional energy to complete.

4. Conclusions

This study investigated the adsorption equilibrium and dynamics parameters of crystal violet (CV^+), onto surfactant-modified dolomite. For optimizing the different factors which affect the amount of adsorption, Taguchi method is utilized. In optimum conditions, initial concentration of 50 mg/L, initial pH of 9.0, NaCl concentration of 0.1 mg/L and adsorbent dosage of 0.05 g were chosen. According to the Taguchi results the amount of NaCl concentration has the lowest impact. The most effective parameters for maximizing the capacity of modified dolomite to adsorb CV^+ was found pH of solution and the amount of adsorbent.

The equilibrium data indicate the best fit obtained with Freundlich isotherm model. The maximum adsorption capacities by Langmuir analysis were determined to be 49.261 mg/g. The pseudo-first-order, pseudo-second-order and the intraparticle diffusion models were used to fit the experimental data and the adsorption results indicated that adsorption system was best described by the pseudo-second-order model. The nature of physisorption of CV^+ onto modified dolomite confirms by the positive low value of E_a (+26.597 kJ/mol). The Gibbs energy (ΔG°) values for the adsorption process were positive, which indicates the system achieved energy from an external source and the adsorption was not spontaneous.

The surfactant modified dolomite was shown to be effective as low-cost material in removing CV^+ dye from aqueous solutions.

Symbols

A [1/g]
Temkin adsorption constant
A_1 [-]
Arrhenius factor
b [L/mg]
Langmuir adsorption constant
B [-]
Temkin constant related to heat of sorption

C_e	[mg/L]	dye concentration at equilibrium
C_0	[mg/L]	initial dye concentration
C_A	[mg/L]	amount of dye adsorbed
E_a	[KJ/mol]	Arrhenius energy
k_1	[min^{-1}]	pseudo-first-order adsorption rate constant
k_2	[g /mg min]	pseudo-second-order adsorption rate constant
K_f	[L/g]	Freundlich adsorption constant
k_p	[mg /g (min0.5)]	intraparticle diffusion rate constant
K_C	[-]	equilibrium constant
n	[-]	Freundlich adsorption constant
q_m	[mg/g]	monolayer capacity of the adsorbent
q_t	[mg/g]	adsorbed quantity of dye per g of adsorbent at any time
q_2	[mg/g]	maximum adsorption of pseudo second order
q_e	[mg/g]	adsorbed quantity of dye per g of adsorbent at equilibrium
r^2	[-]	correlation coefficient
t	[min]	time
V	[L]	volume of dye solution
W	[g]	weight of adsorbent used

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