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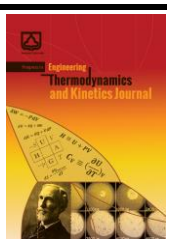

Research Article

Adsorption of methylene blue from aqueous solution on modified gypsum; performance, adsorption kinetic, and thermodynamic

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ABSTRACT

In this work, an attempt has been made to investigate the performance of surface-modified gypsum as an adsorbent for the removal of methylene blue (MB) from aqueous solution. The effect of initial concentration of MB, pH, contact time, temperature, and dose of adsorbent on the adsorption of MB was assessed. To study the structure and morphology of the adsorbents, Fourier transform infrared spectroscopy and scanning electron microscopy analyses were performed. The microstructure study revealed that the gypsum showed a coherent and smooth structure before modification with potassium hydroxide, but after treatment, an adsorbent with a porous structure and regular and finer particles was obtained. Equilibrium data were best described by the Langmuir isothermal model. The monolayer adsorption capacity for gypsum and KOH-modified gypsum at pH=10, an adsorbent dose of 0.1 g, an initial dye concentration of 25 ppm, a contact time of 30 min, and a temperature of 25 °C was found to be 13.35 and 29.24 mg/g, respectively, which is higher than the adsorption capacity of blank gypsum under the same conditions. The adsorption kinetic data were well fitted by the pseudo-second order model. Thermodynamic evaluations indicated that the adsorption process was favorable, spontaneous, and exothermic.

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1. Introduction

A Water pollution is the most unfavorable environmental problem and it requires solutions for appropriate treatment [1]. There are over 100,000 types of commercially-available dyes and their annual production is more than 7×10^5 tons per year [2]. The existence of dyes in effluents is a major concern due to their harmful effects on human life and also for both toxicological and esthetical reasons [3].

Dye removal techniques fall into three categories of physical, biological and chemical methods [4]. Among these three groups, the physical method of adsorption can be an effective method for the treatment of wastewater [5]. The adsorption technique consists of the transfer of adsorbate from the bulk solution to the solid surface [1]. The advantages of this method are its low cost, easy availability, flexibility and simplicity of design, biodegradability, high efficiency, ease of operation, and ability to remove dyes in more concentrated [6].

The activated carbons due to their high adsorption abilities are a favored and popular adsorbent, but because of their high cost, their use is limited. In order to decrease the treatment cost, efforts have been made to find low-cost alternative adsorbents. Gypsum as an abundant, inexpensive and easily available mineral source, can be considered as a low-cost adsorbent. It is often used, to improve the adsorption capacity in chemical modification.

Although it is not highly hazardous, Methylene blue (MB) can cause some adverse effects such as increased heart rate, shock, vomiting, cyanosis, quadriplegia, jaundice and tissue necrosis in humans [6]. Deniz et al. studied the adsorption of Basic Red 46 by gypsum as a low-cost natural adsorbent. They found an adsorption capacity of 39.17 mg/g [7]. Rauf et al. investigated the removal of Toluidine Blue from aqueous solution by adsorption on gypsum. The maximum adsorption capacity was found to be 28 mg/g [8].

The objective of this study was to investigate the adsorption characteristics of modified gypsum by potassium hydroxide solution for the removal of methylene blue from aqueous solution.

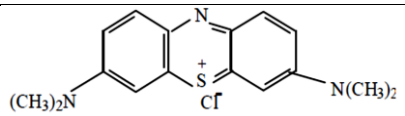
2. Materials and methods

2.1 Adsorbent and dye solution

The cationic dye, methylene blue (M_w: 319.85 g·mol^{-1}, λ_{max}: 665 nm) with a purity of over 98% was purchased from Merck company. The characteristics and molecular structure of this dye are given in Table 1. The dye stock solution was prepared by dissolving a given amount of methylene blue in 500 mL of distilled water. All working solutions were prepared by diluting the stock solution to the determined concentration. The solution pH was adjusted with 1 Molar HNO_3 and NaOH solutions. The gypsum used was prepared from a local market.

The chemical composition of the gypsum used (analyzed by wet chemical method) was mainly composed of $CaSO_4 \cdot 2H_2O$ with 46 wt% of SO_3 along with 19.8% crystal water. The gypsum was then ground and passed through a 60 mesh sieve to prepare a gypsum powder with a particle size of less than 250 micrometers. The gypsum powder was poured into a 1 molar potassium hydroxide solution (KOH) for 3 hours and then washed with deionized water until the pH value reached 7. Finally, the gypsum was kept in an air oven at around 333 K (the limiting temperature to avoid any thermal decomposition of gypsum) for 18 hours to dry completely. The modified gypsum by KOH solution (MGK) was kept in plastic containers to prevent contact with moisture and any contamination.

Table 1. Physical and structural properties of methylene blue

Dye name	methylene Blue
Abbreviation	MB
C.I name	basic blue 9
C.I number	52015
class	phenothiazine
Type of dye	cationic
Molecular weight	319.85 gr/mol
λ_{max}	665 nm
Empirical formula	$C_{16}H_{18}N_3SCl$
Molecular Structure	

2.2 Experimental procedure

The adsorption of methylene blue was carried out in a batch mode at different and specific levels of adsorbent (MGK), dose (0.1, 0.2, 0.3, 0.4 g), dye solution concentration (10, 15, 20 & 25 ppm), pH (4, 6, 8 & 10), temperature (25, 30, 35, 40 °C) and contact time (20, 30, 40 & 50 min). Weighed amounts of MGK were added to 100 mL of dye solution with a determined concentration. Afterwards, the mixture was filtered and the residual dye concentration in the solution was determined by using a UV-Vis spectrophotometer at a wavelength of 665 nm. The adsorption capacity (q) was calculated by the following equation:

$$q = \frac{(C_0 - C_t)}{M} \times V \quad (1)$$

Where C_e and C_0 represent the initial and equilibrium dye concentrations (mg/L), respectively. M and V are the amount of adsorbent used (g) and the volume of the solution (L), respectively.

The removal percentage of the dye (%R) was also calculated by:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

In the above equation, C_t is the concentration of dye at any time t (mg/L).

2.3 Characteristic Test

The Fourier transform infrared spectroscopy (FTIR; Shimadzu 8400s) and scanning electron microscopy (SEM; Tescan/VEGAII) were used to investigate the molecular structure and microstructure of the modified gypsum before and after the adsorption process. The FTIR spectra were collected using a Shimadzu 8400s FTIR spectrometer in transmittance mode from 400 to 4000 cm^{-1} using the standard KBr technique (0.5 mg sample with 250 mg KBr). For SEM studies, the powder of the mentioned specimens was coated with carbon.

The Langmuir isotherm is an empirical model and in its formulation assumes monolayer and homogeneous adsorption. The linear form of Langmuir model [9-11]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (3)$$

Where q_{max} is the maximum adsorption capacity (mg/g); C_e (mg/L) and q_e (mg/g) are the equilibrium dye concentration in the solution and the amount of dye adsorbed on the adsorbent at equilibrium, respectively. K_L refers to the Langmuir constant (L/mg). From the values of the intercept and slope of the C_e/q_e versus C_e diagram, isotherm constants were determined. Using the Langmuir isotherm constant, a dimensionless factor referred to as the separation factor or equilibrium parameter can be obtained [7]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

Where K_L is the Langmuir constant. The R_L value indicates the adsorption nature to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1), or unfavorable (R_L>1) [13]. From the data calculated in Table 2, the R_L value was found to be 0.5, indicating that the adsorption process is favorable [10]. The Freundlich model can be shown as [13]:

$$\text{Log}(q_e) = \text{Log}(K_F) + (1/n)\,\text{Log}(C_e) \quad (5)$$

Where the intercept, K_f, denotes the Freundlich isotherm constant (mg/g) and the slope, 1/n, is the adsorption intensity. C_e (mg/L) and q_e (mg/g) are the equilibrium dye concentration in the solution and the equilibrium adsorption capacity, respectively.

Temkin and Pyzhev for the adsorption isotherm assumed that the heat of adsorption of molecules decrease linearly with coverage adsorbent surface during the adsorption process [14]. The linear form of Temkin model can be expressed as [15]:

$$q_e = \frac{RT}{b_T} Ln(A_T) + \frac{RT}{b_T} Ln(C_e) \quad (6)$$

Where A_T (L/g) and b_T (J/mol) are Temkin constants determined from the slope and intercept of the q_e versus $ln(C_e)$ plot.

The adsorption data was also analyzed by using the Dubinin–Radushkevich isotherm model. This model is usually used to express the adsorption mechanism with a distribution of gaussian energy onto a heterogeneous surface [9]. Its linear form can be expressed as [12]:

$$Ln\ (q_e) = Ln\ (q_s) - \beta\varepsilon^2 \quad (7)$$

β, q_e, and q_s are respectively the Dubinin–Radushkevich constant (mol^2/kJ^2), the amount of dye adsorbed on the adsorbent at equilibrium, and the maximum adsorption capacity (mg/g). The plot of $ln(q_e)$ versus ε^2 (Figure 6 (d)) should give a straight line with a slope of β and an intercept of $ln(q_s)$. The parameter ε is also a Dubinin–Radushkevich constant (J/mol) and can be calculated as [12]:

$$\varepsilon = RT\ Ln(1 + \frac{1}{C_e}) \quad (8)$$

Where R, T, and C_e represent the gas constant (8.314 J/mol.K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

Using the Dubinin–Radushkevich constant, the mean free energy factor can be calculated (J/mol), which is computed by the relationship [11]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The pseudo-first order equation is a kinetic model that is widely used for physical adsorption, and its linear form is as follows [18]:

$$Ln\ (q_e - q_t) = ln\ (q_e) - k_1 t \quad (10)$$

Where k_1 (g/mg·min) is the rate constant of adsorption. q_e and q_t (mg/g) are the amount of dye adsorbed onto the adsorbent surface at equilibrium and at time t, respectively. The parameters of the model are determined by the plot of $ln(q_e - q_t)$ versus time.

The experimental data often corresponded to the pseudo second order kinetic model. The pseudo second order model is expressed as [17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

Where k_2 (g/mg·min) is the pseudo-second order rate constant. The constants of the model can be determined from the slope and the intercept of the plot of t/q_t versus t, which is shown in Figure 7. One of the most useful models for describing chemical adsorption is the Elovich equation, which is given by the following equation [18]:

$$q_t = \frac{\mathrm{Ln}\,(\alpha\beta)}{\beta} + \frac{\mathrm{Ln}\,(t)}{\beta} \quad (12)$$

Where β and α represent the desorption constant (g/mg) and initial adsorption rate (mg/g·min), respectively. The plot of q_t versus Ln(t) provides a line with a slope of 1/β and an intercept of Ln(αβ)/β.

Intra-particle diffusion model is proposed to describe the mechanism of diffusion. This model is expressed by the following equation [19]:

$$q_t = k_{id}\, t^{0.5} + I \quad (13)$$

Where k_{id} represents the intraparticle diffusion rate constant (mg/g·min$^{0.5}$), and I is a constant representing the intercept of the q_t versus $t^{0.5}$ plot.

3. Results and discussion

3.1. Effect of pH

The pH is an important factor affecting the adsorption process. Figure 1 shows the effect of pH on the adsorption of methylene blue on MGK. As seen, the maximum adsorption of MB was obtained at pH 10. Generally, due to the increased concentration of H^+ ions at low pH values and their competition with dye ions for adsorption sites on the adsorbent surface, the adsorption of cationic dyes is reduced in acidic pH. However, on increasing the pH values beyond 10, the adsorption value goes down. This could be due to the fact that the excess OH^- ions compete with the active sites of the adsorbent to adsorb the cationic groups of the dye. A similar result was reported previously [6,7].

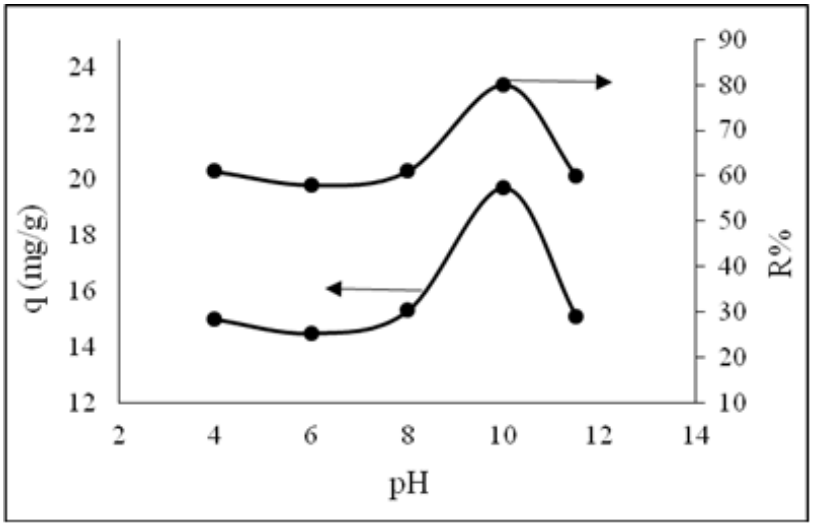


Figure 1. Effect of pH on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, temperature of 25 °C, adsorbent dose of 0.1 g and contact time of 30 min)

3.2 Effect of adsorbent dosage

One of the important parameters in the determination of adsorption capacity is the used dosage of adsorbent for a given initial concentration of the adsorbate. Figure 2 shows the q versus the dose of adsorbent. As seen in Figure 2, any increase in the amount of adsorbent causes the removal percentage of MB, which could be due to increased active sites of adsorbent. Nonetheless, the adsorption capacity decreased. The decrease in adsorption capacity along with increasing dose of adsorbent is due to some adsorption sites remaining unsaturated during the adsorption process [6,9,10].

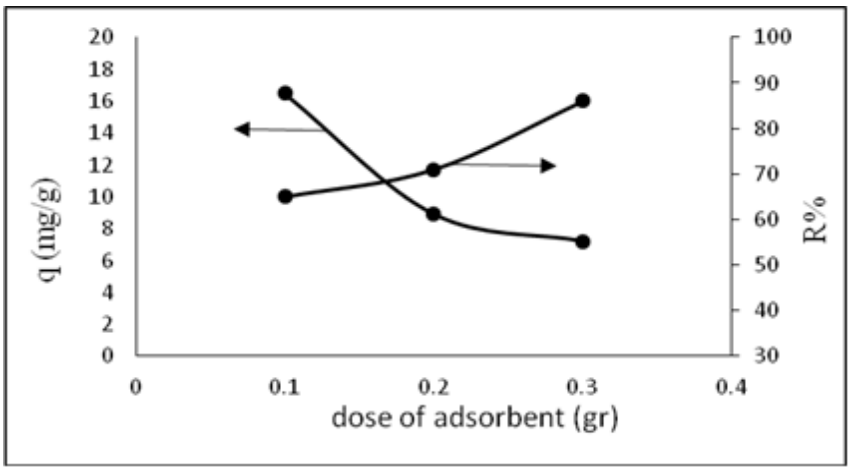


Figure 2. Effect of adsorbent dosage on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, temperature of 25 °C, pH 10 and contact time of 30 min)

3.3 Effect of initial dye concentration

The initial dye concentration creates a significant driving force to overcome mass transfer resistances of dyes from the aqueous bulk to solid surface [7]. The effect of initial dye concentration on methylene blue adsorption is shown in Figure 3. Dye adsorption increases with increase in initial concentration of methylene blue solution. The increase in loading capacity of the adsorbent is probably due to a high driving force for mass transfer [6].

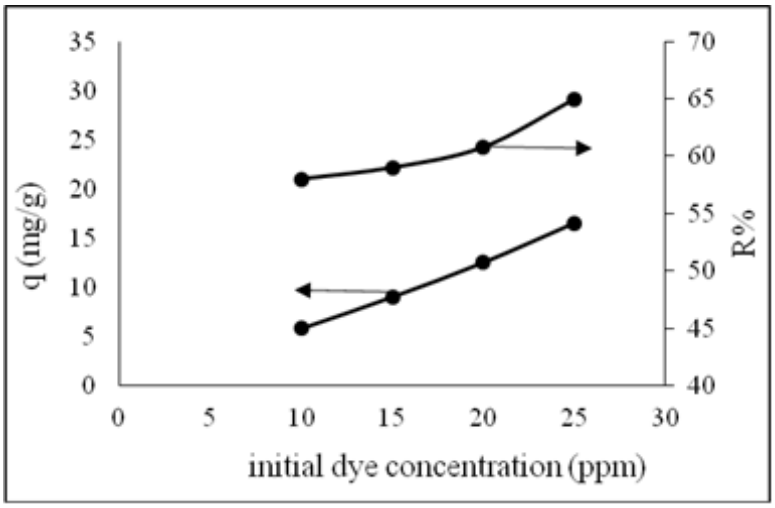


Figure 3. Effect of initial dye concentration on MB adsorption by modified gypsum (adsorbent dose of 0.1 g, temperature of 25 °C, pH 10 and contact time of 30 min)

3.4 Effect of temperature

Figure 4 shows the effect of temperature on the adsorption of methylene blue. As seen, temperature changes have little effect on the adsorption process and q decreases with increasing temperature. The maximum adsorption of MB was obtained at ambient temperature (25 °C).

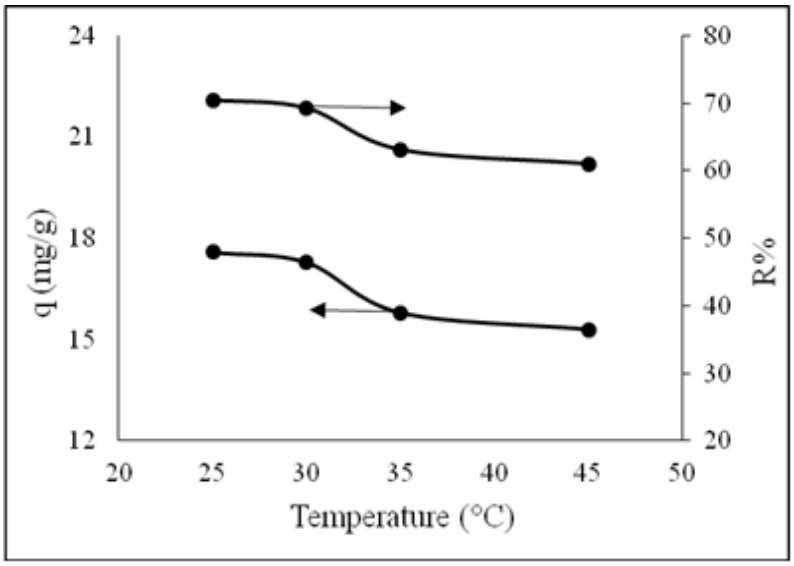


Figure 4. Effect of temperature on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, pH 10, adsorbent dose of 0.1 g and contact time of 30 min)

3.5 Effect of contact time

The contact time required to reach an equilibrium state in the dye adsorption process is an important economic factor [7]. In Figure 5, the effect of contact time on MB adsorption by modified gypsum in the range of 20-50 minutes was investigated. The adsorption of MB was rapid during the first 20 to 30 minutes, which could be due to the existence of unsaturated sites on the adsorbent surface in the initial stages of the adsorption process. However, later, because of the saturation of the adsorbent, the amount of adsorption becomes constant.

According to the studied adsorption parameters, the obtained optimum conditions here for modified gypsum are pH = 10, initial dye concentration = 25 mg L^{-1}, adsorbent dose = 0.1 g, contact time = 30 min and temperature = 25 °C. In this condition, the maximum removal percentage (%R) and adsorption capacity are obtained as 80% and 29.24 mg/g, respectively. According to our previous work [10], the R and q for blank gypsum in the same condition were obtained as 46.5% and 13.35 mg/g.

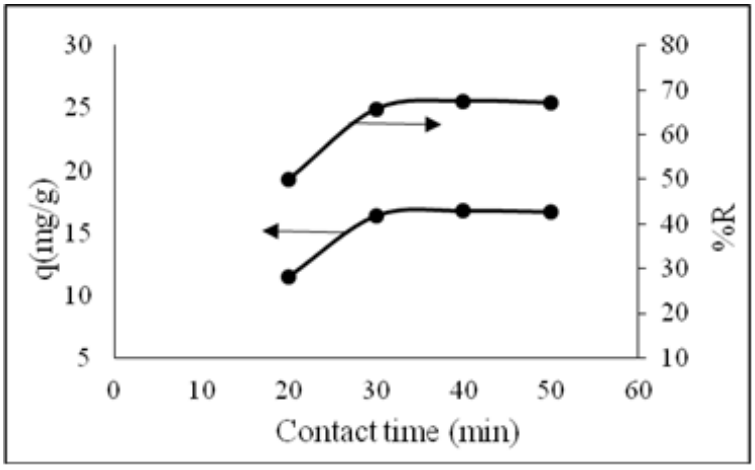


Figure 5. Effect of contact time on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, pH 10, adsorbent dose of 0.1 g and temperature of 25 °C)

3.6 Analysis of equilibrium data using adsorption isotherm

The adsorption isotherm curve is an important and fundamental issue in the study and design of adsorption systems. The adsorption isotherm model describes the relation between the concentration of adsorbate on the adsorbent surface and that remaining in the bulk solution at an equilibrium state and at constant temperature and pH. In the present study, the equilibrium data were determined at pH 10, a contact time of 30 min, a dye concentration of 25 mg L^{-1}, an adsorbent dose of 0.1 g, and a temperature of 25 °C, and the isotherm models of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich were investigated.

The plots of the isotherms are shown in Figure 6, and the results of the parameters and correlation coefficients of the isotherms are summarized in Table 2.

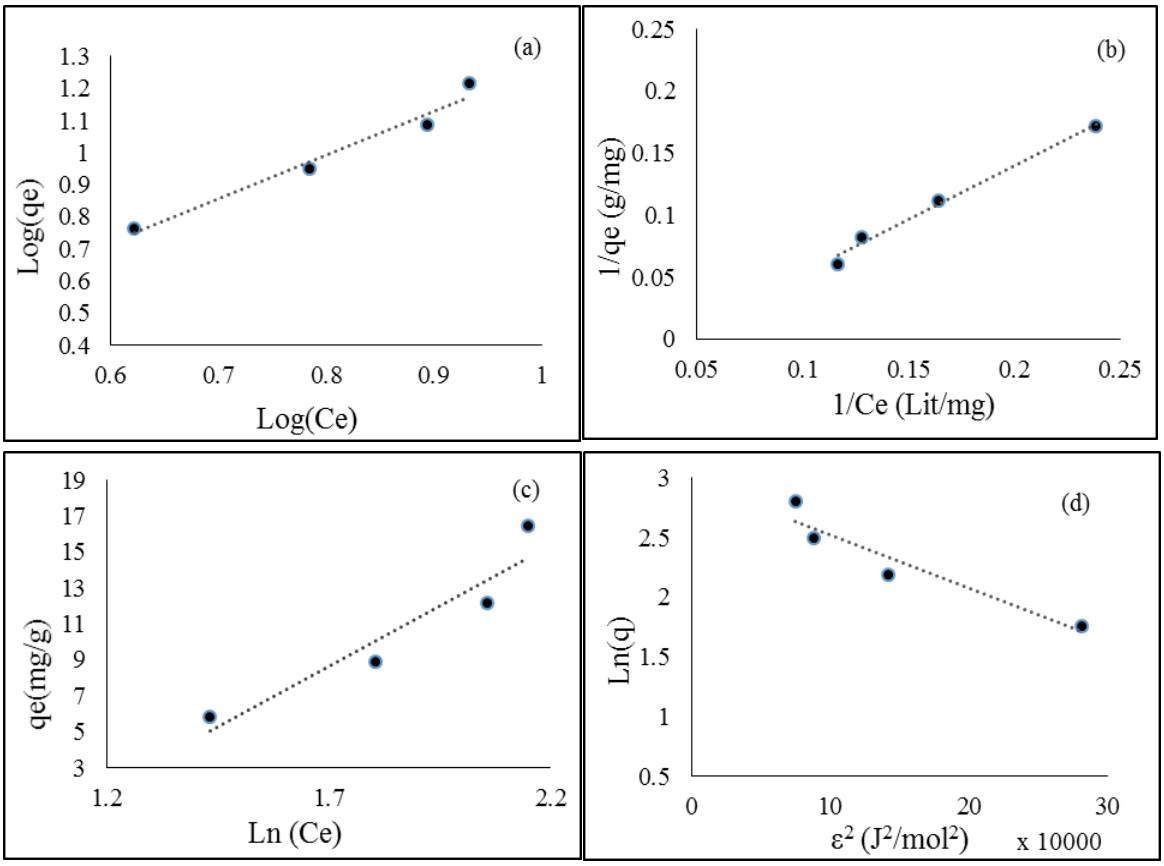


Figure 6. Adsorption isotherm of a) Freundlich b) Langmuir c) Temkin d) Dubinin-Radushkevich for MB-modified gypsum system

Table 2.parameters and correlation coefficients of Isotherms for adsorption of MB on modified gypsum by KOH

Isotherm model	**Parameters**			**R^2**
Langmuir	R_L	)Lit/mg(k_L	)mg/g(q_{max}	0.988
	0.5	0.04	29.24	
Freundlich	n		k_F	0.967
	0.73		0.79	
Temkin and Pyzhev	)Lit/g(A_T		)j/mol(b_T	0.89
	0.35		184.81	
Dubinin–Radushkevich	)kj/mol (E	)mol^2/j^2β (	)mg/g (q_s	0.90
	0.35	4×10^{-6}	19.47	

3.7 Kinetic study of adsorption data

Kinetic models provide useful information about the mechanism and the rate-controlling steps of the overall adsorption process. In this study, the pseudo-first order, pseudo-second order, intraparticle diffusion, and Elovich models have been used to describe the mechanism of adsorption of methylene blue. The experimental data for the kinetic study were determined at pH 10, an initial dye concentration of 25 ppm, an adsorbent dosage of 0.1 g, a temperature of 25 °C, and a contact time of 30 min.

The kinetic model plots are presented in Figure 7, and the parameters and correlation coefficients of the kinetic models are summarized in Table 3.

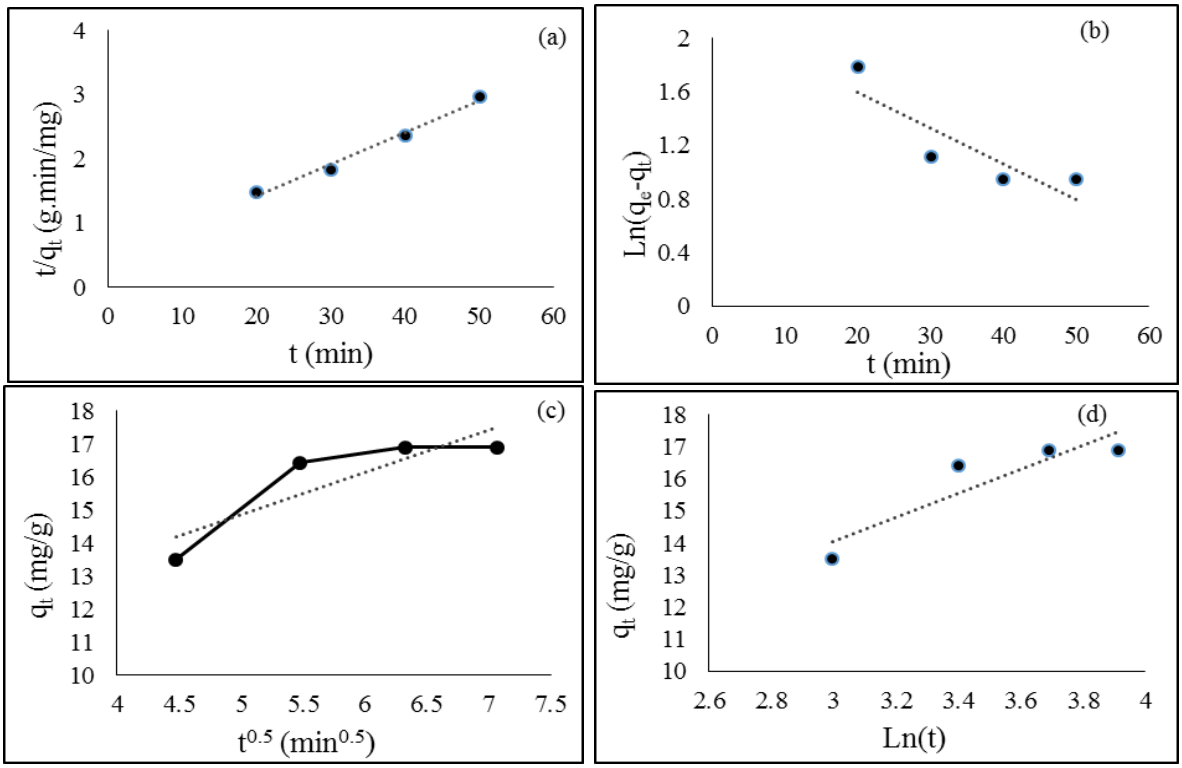


Figure 7. plot of a) pseudo-second order b) pseudo- first order c) Intraparticle diffusion d) Elovich in MB-modified gypsum system

Table 3. parameters and correlation coefficients of kinetic models for adsorption of MB on modified gypsum by KOH

Kinetic Model type	Parameters			R^2
pseudo first order	k_1 (min^{-1})		q_e (mg/g)	0.752
	0.03		8.48	
pseudo second order	h_0 (mg/g.min)	k_2 (g/mg.min)	q_e (mg/g)	0.987
	2.40	0.01	20.08	
Elovich	β (g/min)		α (mg/g.min)	0.820
	0.27		8.06	
intraparticle diffusion	I		k_{id} ($mg/g.min^{0.5}$)	0.766
	8.49		1.28	

3.8 Thermodynamic parameters

Thermodynamic parameters show the effect of temperature on the adsorption process. The thermodynamic parameters such as standard enthalpy change (ΔH°), standard Gibbs free energy (ΔG°), and standard entropy change (ΔS°) associated with the adsorption process can be determined by using the following equations. Standard Gibbs free energy (J/mol) is calculated from the following equation [18]

$$\Delta G^{\circ} = RTLnK_{eq} \quad (14)$$

Where R is the gas constant (R = 8.314 J/mol.K), T is absolute temperature (K) and K_{eq} (= q_e/C_e) is the equilibrium constant. By using the vant Hoff equation [20]:

$$Ln\ K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (15)$$

and plot of Ln K_{eq} versus 1/T (figure 8), can be determined ΔH ° and ΔS ° values.

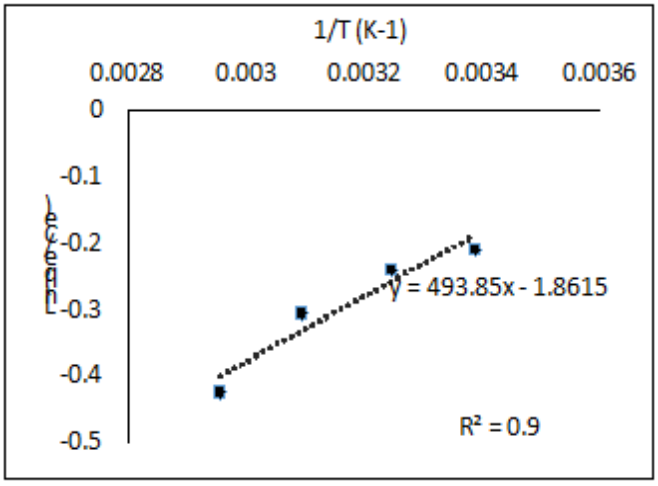


Figure 8. the determined thermodynamic parameters for adsorption of MB on MGK

The thermodynamic parameters are presented in Table 4. The negative values of the parameters ΔG° and ΔH° indicate that the process is spontaneous and exothermic. The negative value of ΔS° also indicates a reduction in the degrees of freedom of the dye ions.

Table 4. thermodynamic parameters of ΔG°, ΔH° and ΔS°

Temperature (K)	ΔG° (kj/mol)	ΔS° (kj/mol)	ΔH° (kj/mol.K)
298	-2.214	-0.052	-17.713
303	-1.957		
308	-1.697		
318	-1.177		

3.9 FTIR analysis

Figure 9 shows the FTIR spectra of gypsum and modified gypsum by KOH before and after the MB adsorption. The peaks at 609 and 602 cm^{-1} are related to the stretching and bending modes of sulfate (S-O), which are important peaks in the pure gypsum spectrum [19]. There is a main peak in the wavelength range of 1100-1150 cm^{-1}, which is related to the bonds of the compounds of calcium and sulfate (Ca-O, S-O…). This peak is broad and strong in the pure gypsum spectrum but becomes sharper after modification by KOH, which could indicate a decrease in molecular vibrations and their regulation (Figure 9 (a, b)) [22]. The band at 1620 and 1680 cm^{-1} is assigned to O-H vibrations of water in calcium sulfate hemihydrate and calcium sulfate dihydrate, respectively (Figure 9 (a, b)) [23]. The peaks at 2117 and 2239 cm^{-1} were assigned to the chemical water in the gypsum structure (Figure 9 (a)).

The stretching vibrations of the H_2O molecules in the gypsum occur at 3394 and 3546 cm^{-1}, and in the modified gypsum by KOH, they occur at 3404 and 3552 cm^{-1} [21].

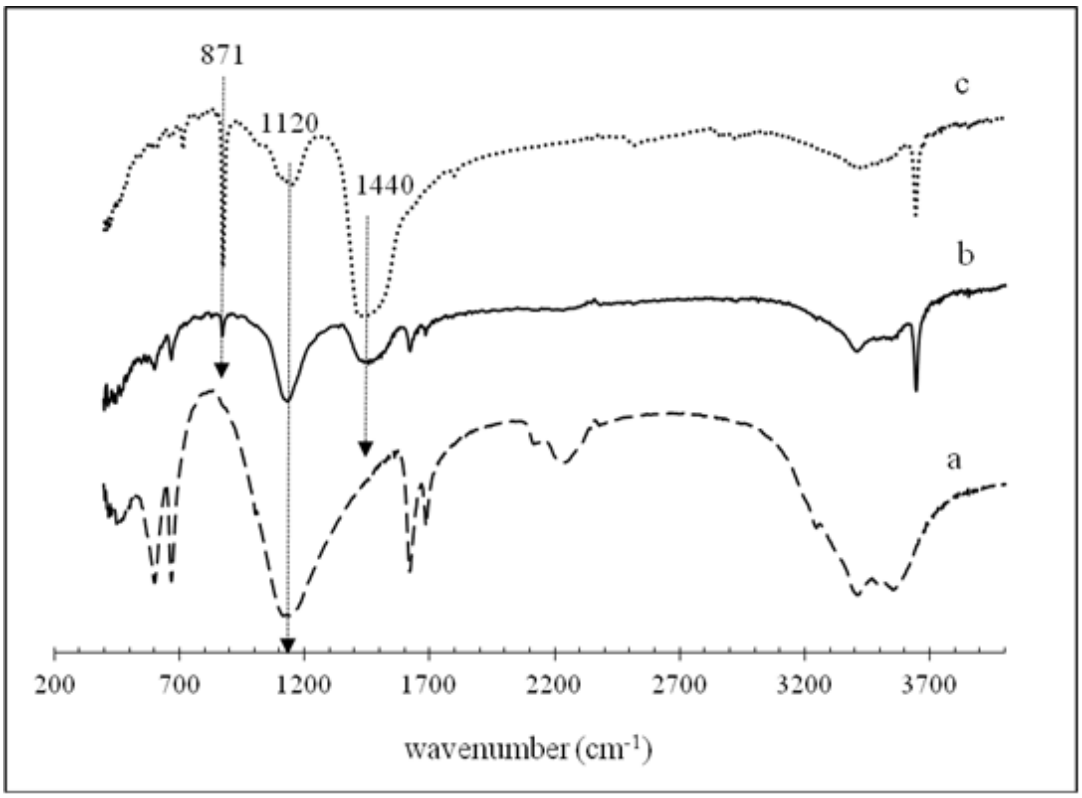


Figure 9. FTIR spectra of a) gypsum, b) modified gypsum before and c) modified gypsum after MB adsorption

In Figure 9 (b, c) the broad and strong peak at 1440 cm^{-1} and the sharp peak at 871 cm^{-1} can be observed, which are characteristic of the C–O stretching mode in compounds caused by the carbonation reaction [21]. Due to the high tendency of carbon dioxide to react with gypsum under alkaline conditions, an interaction may have occurred between gypsum and carbon dioxide gas in the air during the preparation of the modified adsorbent.

3.10 SEM analysis

SEM images presented in Figure 10 show the microstructure of gypsum before and after modification by potassium hydroxide. As seen in Figure 10 (a, b), it can be seen that the gypsum had a coherent and smooth structure before modification with potassium hydroxide, but after treatment with KOH solution, an adsorbent with a porous structure and regular and finer particles was obtained.

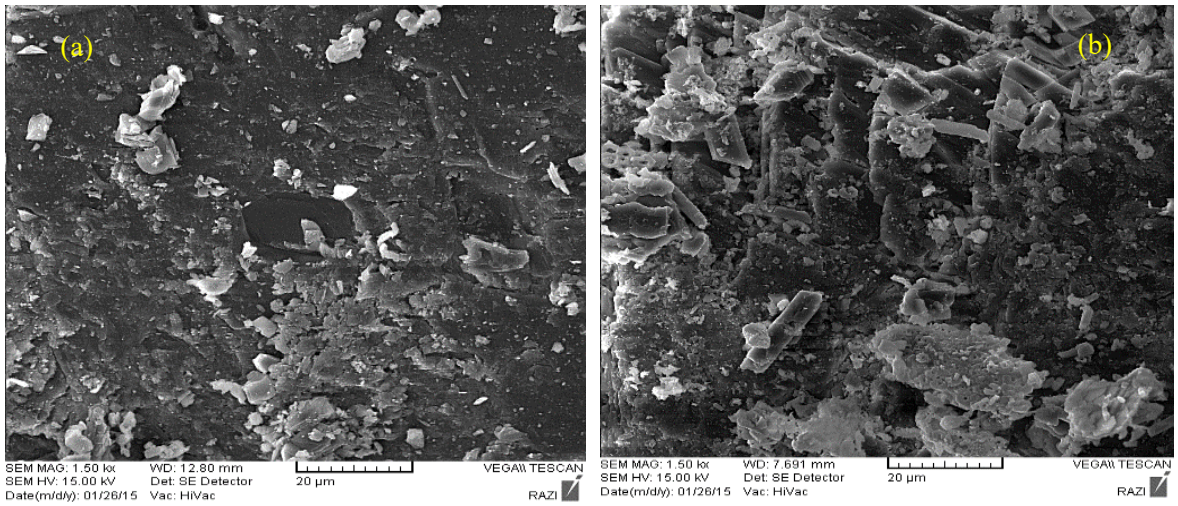


Figure 10. SEM images of a) pure gypsum b) modified gypsum by KOH

Figure 11 shows the microstructure of modified gypsum before and after adsorption of methylene blue. According to the images in Figure 11, the filling of the adsorbent surface after dye adsorption can be clearly seen.

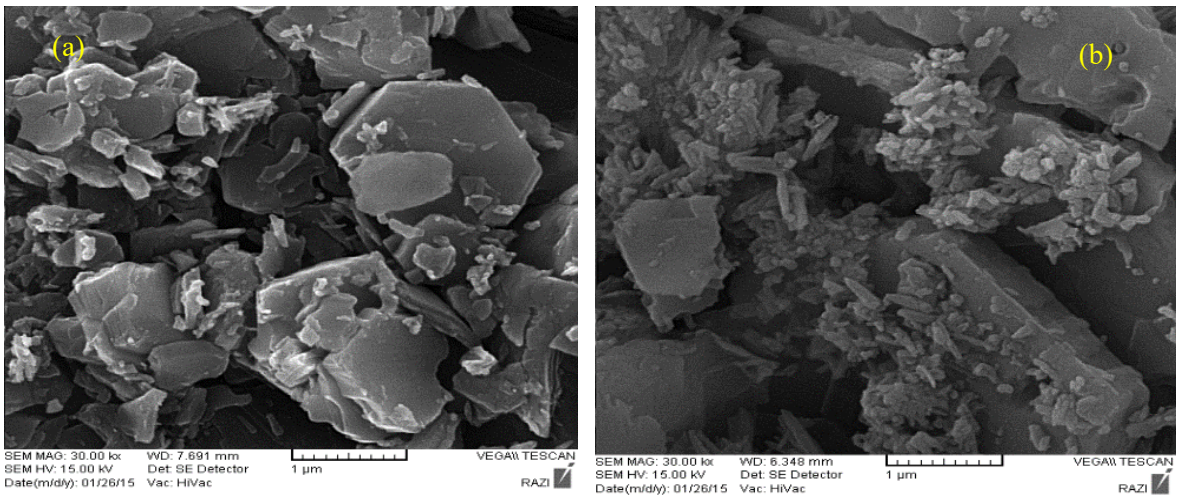


Figure 11. SEM images of modified gypsum a) before, b) after methylene blue adsorption

4. Conclusion

In this study, in order to improve the adsorption capacity of gypsum, treatment with a 1 molar KOH solution was applied, and then the modified adsorbent was used for the removal of methylene blue from aqueous solution. According to the obtained results, the optimum determined conditions were pH 10, a contact time of 30 min, a temperature of 25 °C, an adsorbent dosage of 0.1 g, and an initial dye concentration of 25 ppm. The maximum adsorption capacity was obtained as 29.24 mg/g for modified gypsum under optimum conditions, which is higher than the adsorption capacity of blank gypsum under the same conditions. The experimental data were well fitted with the Langmuir isotherm and the pseudo-second order kinetic model. The thermodynamic study shows that the adsorption of MB on MGK is spontaneous and exothermic.

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

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