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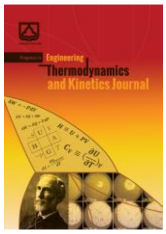

Research Article

Adsorption of methylene blue from aqueous solution on modified gypsum; Performance, Adsorption kinetic, and Thermodynamic

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ABSTRACT

This document gives a template for authors to prepare manuscripts for submission in Progress in Engineering Thermodynamics and Kinetics Journal. The abstract sh In this work an attempt has been done on investigating the performance of surface modified gypsum as an adsorbent for removal of methylene blue (MB) from aqueous solution. The Effect of initial concentration of MB, pH, contact time, temperature, and dose of adsorbent on adsorption of MB were assessed. To study the structure and morphology of adsorbents, Fourier transform infrared spectroscopy and Scanner electronic microscopy analyzes were performed. The microstructure study revealed that the gypsum showed a coherent and smooth structure before modifying with potassium hydroxide, but after treatment an adsorbent with 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 in pH=10, adsorbent dose of 0.1 g, initial dye concentration of 25 ppm, contact time of 30 min and temperature of 25 °C were found as 13.35, 29.24 mg/g, respectively, which is higher than the capacity of adsorption of blank gypsum in the same conditions. The Adsorption kinetic data were well fitted with the pseudo-second order model. Thermodynamic evaluations indicated that the adsorption process was favorable, spontaneous and exothermic.

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1. Introduction

Water pollution is the most unfavorable environmental problem and it requires solutions for appropriate treatment [1]. There are over 100000 types of commercially-available dye and its 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's 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 could be an an effective method for 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 is its low cost, easy availability, flexibility and simplicity of design, biodegradability, high efficiency, ease of operation, and ability to removal of dyes in more concentrate [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 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 on the adsorption of Basic Red 46 by gypsum as a low-cost natural adsorbent. They found with the 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 found adsorption capacity was 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) by purity of over 98% was purchased from Merck company. The characteristics and molecular structure of this dye is given in Table 1. The dye stock solution was prepared by dissolving the given amounts of

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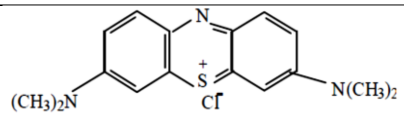
methylene blue in to a 500 mL distilled water. All of working solutions were prepared by diluting the stock solution to the determined concentration.

The solution pH was adjusted with 1 Molar HNO_3 and NaOH solution. The used gypsum was prepared from a local market. The chemical composition of the used gypsum (analyzed by wet chemical method) was mainly composed of $CaSO_4{\cdot}2H_2O$ with 46 wt% of SO_3 along with 19.8 % of crystal water. Then, the gypsum was ground and passed through a 60 mesh sieve so as to prepare the gypsum powder with a particle size of less than 250 micrometers. Gypsum powder was poured in a 1 molar potassium hydroxide Solution (KOH) for 3 hours and then washed with deionized water until pH value reached 7. Finally, the gypsum was kept in an air oven at around 333 K (the limited temperature to avoid any temperature decomposition of gypsum) for 18 hours to be dried 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 gr), 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). Weighted amounts of MG were added to 100 ml of dye solution with determined concentration. Afterwards, the mixture was filtered and the residual dye concentration in solution was determined by using UV-Vis spectrophotometer at a wavelength of 665 nm. The Adsorption capacity (q) was calculated by the following equation:

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

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 (gr) and the volume of the solutions (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 are the concentrations 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 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 standard KBr technique (0.5 mg sample with 250 mg KBr). For SEM studies, the powder of the mentioned specimens were 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) is the equilibrium dye concentration in the solution and amounts of dye adsorbed on adsorbent at equilibrium, respectively. K_L refers to the Langmuir constant (L/mg). From the values of intercept and slope of C_e/q_e versus C_e diagram, isotherm constants were determined. By using the Langmuir isotherm constant dimensionless factor referred to as separation factor or equilibrium parameter can be achieved [7]:

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

Where K_L is the Langmuir constant, 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 as 0.5 indicating that the adsorption process is favorable [10]. Freundlich model can be shown as [13]:

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

Where intercept, K_f, is denoted Freundlich isotherm constant (mg/g) and slope 1/n is the adsorption intensity. C_e (mg/L) and q_e (mg/g) is the equilibrium dye concentration in the solution and 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 intercepts of 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]:

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

B, q_e and q_s are respectively Dubinin–Radushkevich constant (mol^2/kj^2), amounts of dye adsorbed on adsorbent at equilibrium and 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 intercept of Ln (q_s). The parameter ε is also 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.

By using the Dubinin–Radushkevich constant, the mean free energy factor can be calculated (j/mol), which was computed by the relationship [11]:

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

Pseudo first order equation is a kinetic model that is widely used for physical adsorption and its linear form of equation is as follows [18]:

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

Where k_1 (g/mg.min) is represented as the constant rate of adsorption. q_e and q_t (mg/g) are the amount of dye adsorbed onto adsorbent surface at equilibrium and at t, respectively (mg/g). The parameters of model determined by 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 model can be determined from slope and the intercept of the plot of t/q_t versus t which is shows in Figure 7.

One of the most useful models for describing the chemical adsorption is the Elovich equation, which is given by the following equation [18]:

$$q_t = \frac{\text{Ln}\ (\alpha\beta)}{\beta} + \frac{\text{Ln}\ (t)}{\beta} \qquad (12)$$

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 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]:

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

Where k_{id} represents intraparticle diffusion rate constant ($mg/g.min^{0.5}$) and I is a constant and intercept of 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, maximum adsorption of MB was obtained at the pH 10. Generally, due to the increased concentration of H^+ ions at the low amounts of pH and compete with dye ions for adsorption sites on the adsorbent surface, the adsorption of cationic dyes was reduced in the acidic PH. But, on increasing the pH values more than 10, the adsorption value goes down. This could be due to the fact that the excess OH^- ions compete with active sites of the adsorbent to adsorb cationic groups of dye. A similar result was reported previously [6,7].

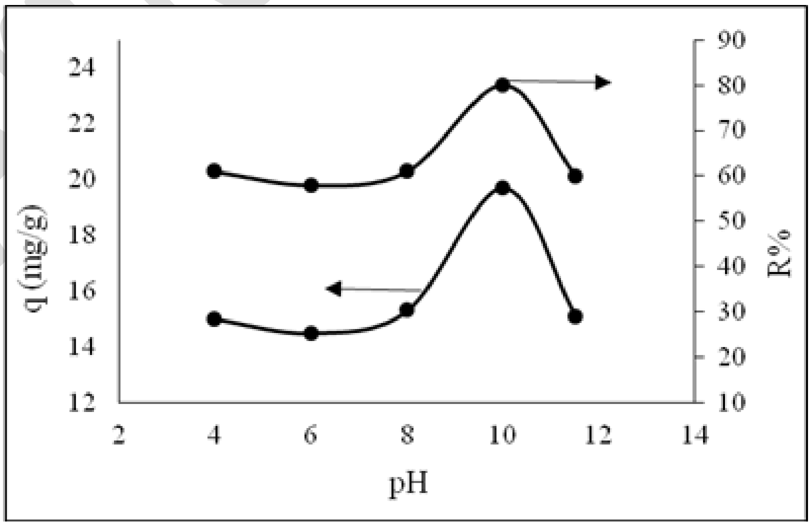


Figure 1. Effect of pH on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, temperature of 25 °C, adsorbent dose of 0.1 g and contact time of 30 min)

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].

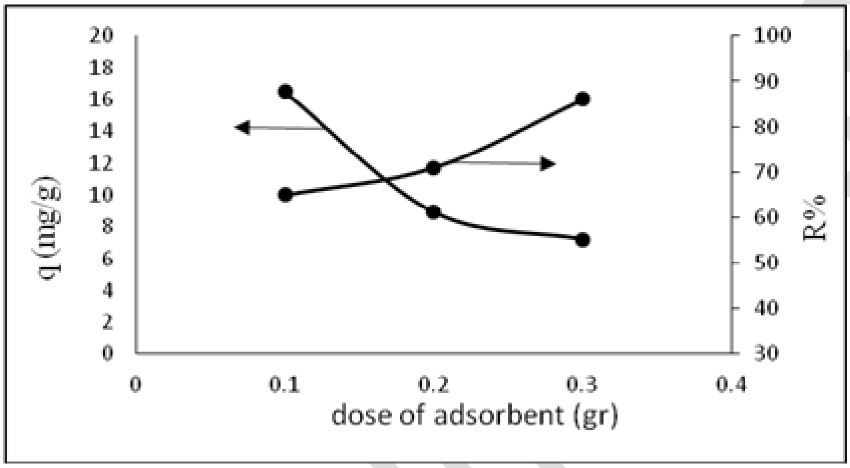


Figure 2. Effect of adsorbent dosage on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, temperature of 25 °C, pH 10 and contact time of 30 min)

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].

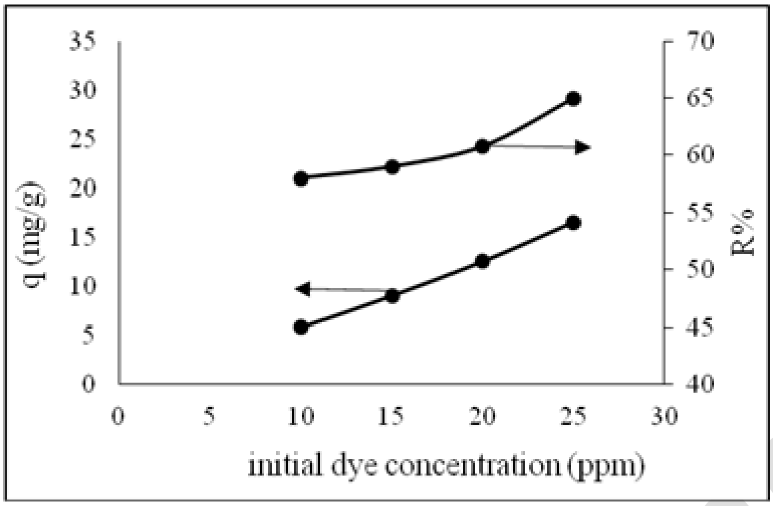


Figure 3. Effect of initial dye concentration on MB adsorption by modified gypsum (adsorbent dose of 0.1 g, temperature of 25 °C, pH 10 and contact time of 30 min)

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 adsorption process and q decreases with increasing temperature. Maximum adsorption of MB was obtained at the ambient temperature (25 °C).

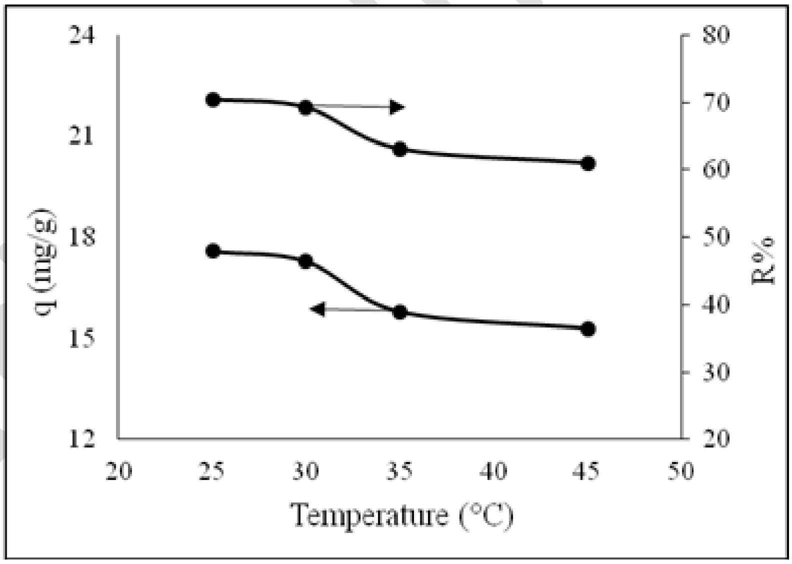


Figure 4. Effect of temperature on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, pH 10, adsorbent dose of 0.1 g and contact time of 30 min)

3.5 Effect of contact time

The contact time required to reach equilibrium state in dye adsorption process is an important factor economically [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 times of adsorption process. But, later because of the saturation of 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.

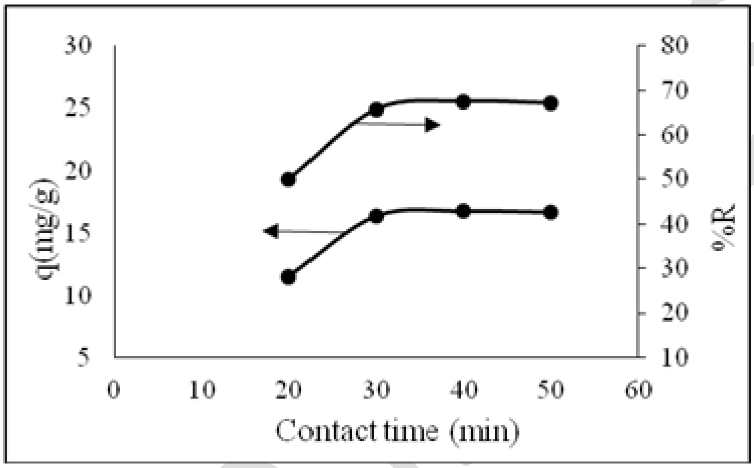


Figure 5. Effect of contact time on MB adsorption by modified gypsum (initial dye concentration of 25 mg L^{-1}, pH 10, adsorbent dose of 0.1 g and temperature of 25 °C)

3.5 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 concentrations of adsorbate in adsorbent surface with the remaining in the bulk solution at equilibrium state and constant temperature and pH. In the present study, the equilibrium data were determined at pH 10, contact time of 30 min, dye concentration of 25 mg L^{-1}, adsorbent dose of 0.1 g and temperature of 25 °C and isotherm models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were investigated.

The plot of isotherms shown in Figure 6 and results of parameters and correlation coefficients of isotherms are given in Table 2 in summary.

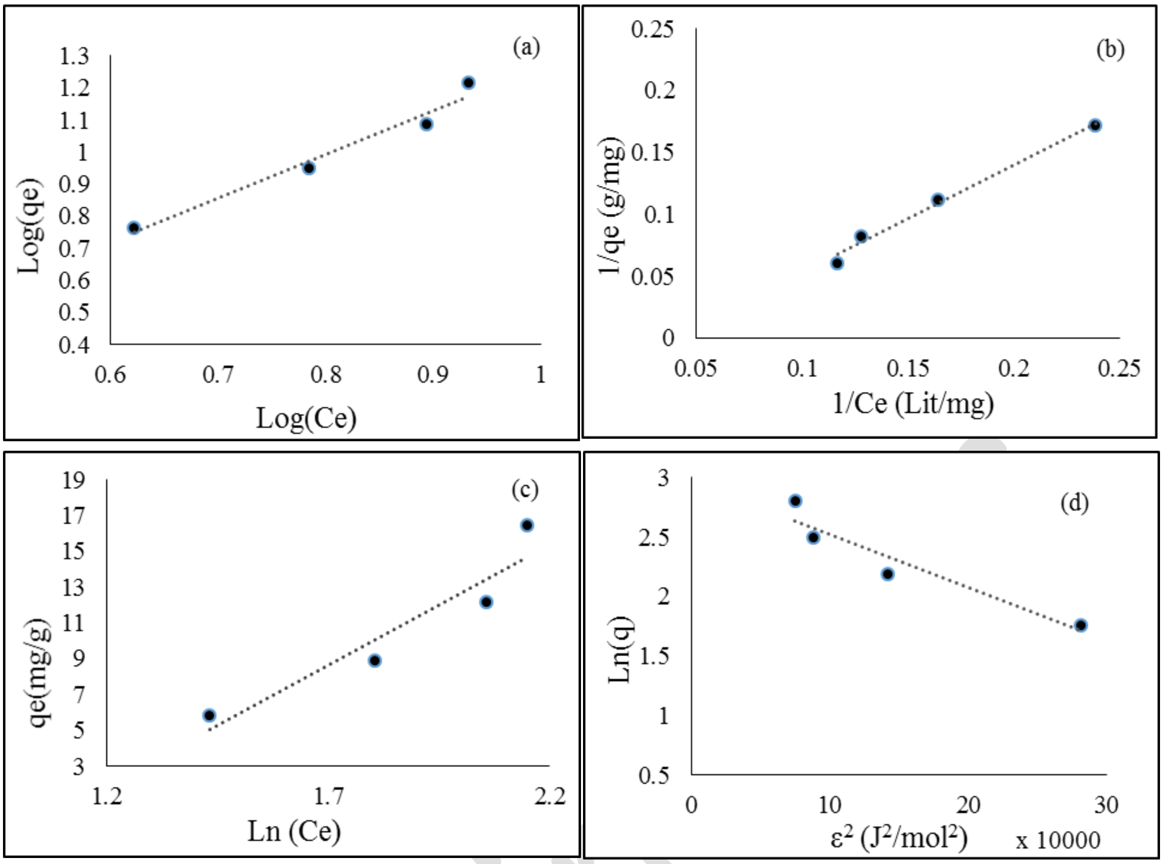


Figure 6. Adsorption isotherm of a) Freundlich b) Langmuir c) Temkin d) Dubinin-Radushkevich for MB-modified gypsum system

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	)mol²/j²β (	)mg/g (q_s	0.90
	0.35	4×10^{-6}	19.47	

3.6 Kinetic study of adsorption data

Kinetic model provides useful information about the mechanism and the rate of controlling steps of overall adsorption process. In this study, the pseudo first order, pseudo second order, intraparticle diffusion and Elovich model have been used to describe the mechanism of adsorption of methylene blue. The experimental data for kinetic study were determined at pH

10, initial dye concentration of 25 ppm, adsorbent dosage of 0.1 gr, temperature of 25 °C and contact time of 30 min.

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

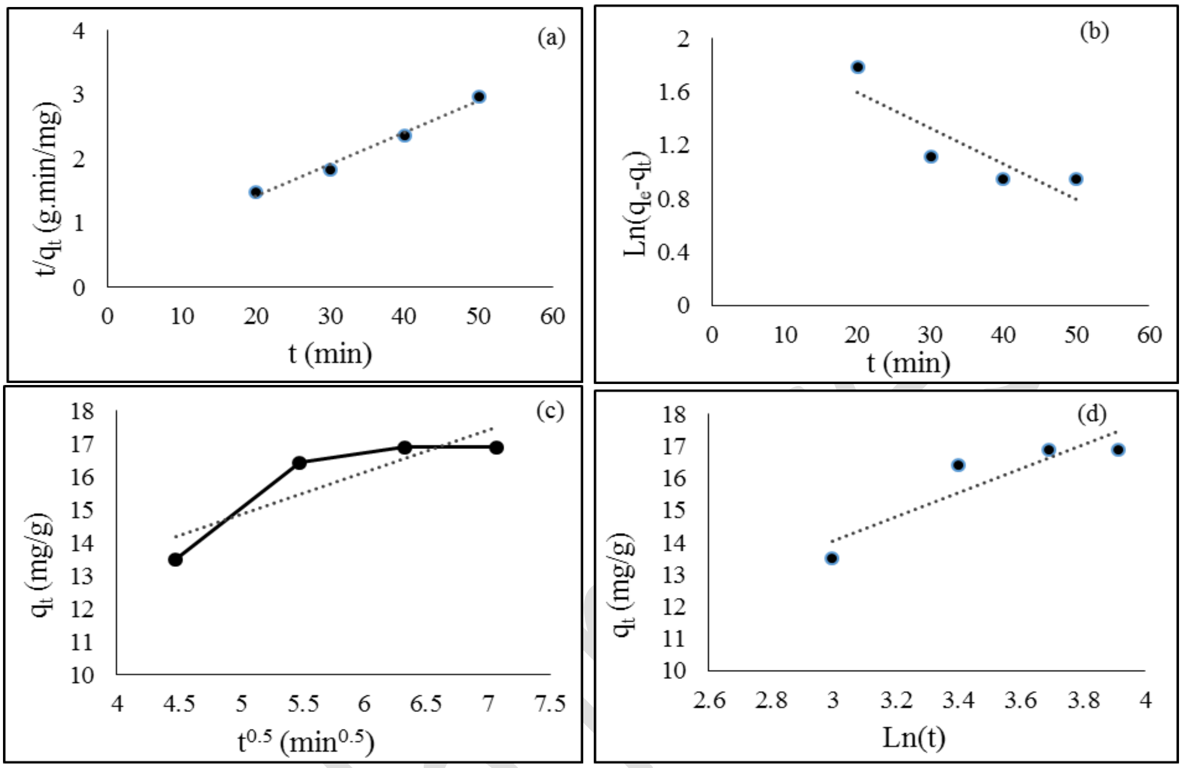


Figure 7. plot of a) pseudo-second order b) pseudo- first order c) Intraparticle diffusion d) Elovich in MB-modified gypsum system

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

3.7 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°), standard entropy changes (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]:

$$\Delta G^{\circ} = RTLnK_{eq} \tag{14}$$

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]:

$$\text{Ln } K_{eq} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{15}$$

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

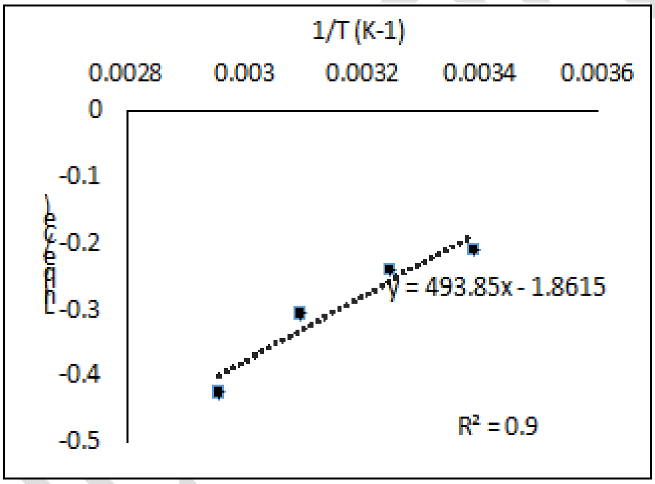


Figure 8. the determined thermodynamic parameters for adsorption of MB on MGK

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

3.8 FTIR analysis

Fig. 9 shows the FTIR spectra of gypsum and modified gypsum by KOH before and after the MB adsorption. The peaks of 609 and 602 cm^{-1} are related to the stretching and bending modes of sulphate (S-O), which are important peaks in the pure gypsum spectrum [19]. There is the main peak in the wavelength range of 1100-1150 cm^{-1}, which is the bond of the compounds of calcium and sulfate (Ca-O, S-O ….) This peak is broad and strong in pure gypsum spectrum, but converts to sharper peak after being modified by KOH**,** which could indicate the decrease in the molecular vibrations and regulate them (Figure 9. a,b) [22]. The band at 1620 and 1680 cm^{-1} is assigned to O-H vibrations of water in calcium sulphate hemihydrate and in calcium sulphate dehydrate, respectively (Figure 9. a,b) [23]. The 2117 and 2239 cm^{-1} peaks were assigned to the chemical water in gypsum structure (Figure 9. a). The stretching vibrations of the H_2O molecules in the gypsum occur at 3394 and 3546 cm^{-1}, and the modified gypsum by KOH occur at 3404 and 3552 cm^{-1} [21].

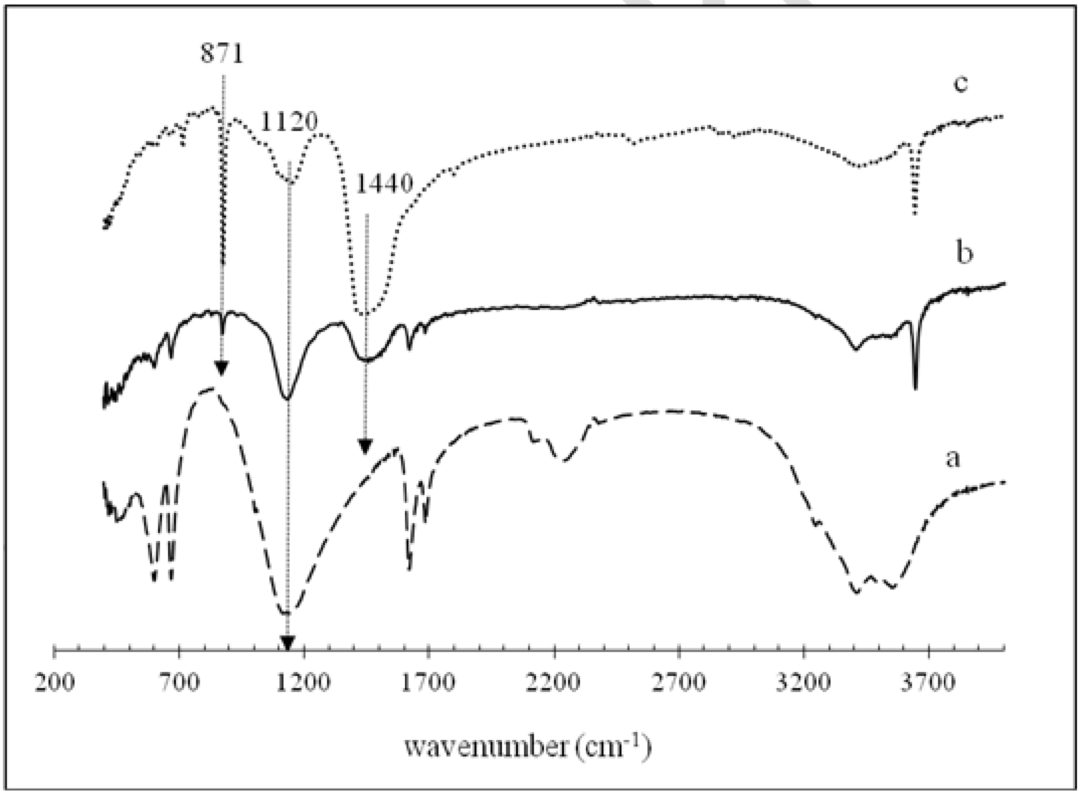


Figure 9. FTIR spectra of a) gypsum, b) modified gypsum before and c) modified gypsum after MB adsorption

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

3.9 SEM analysis

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

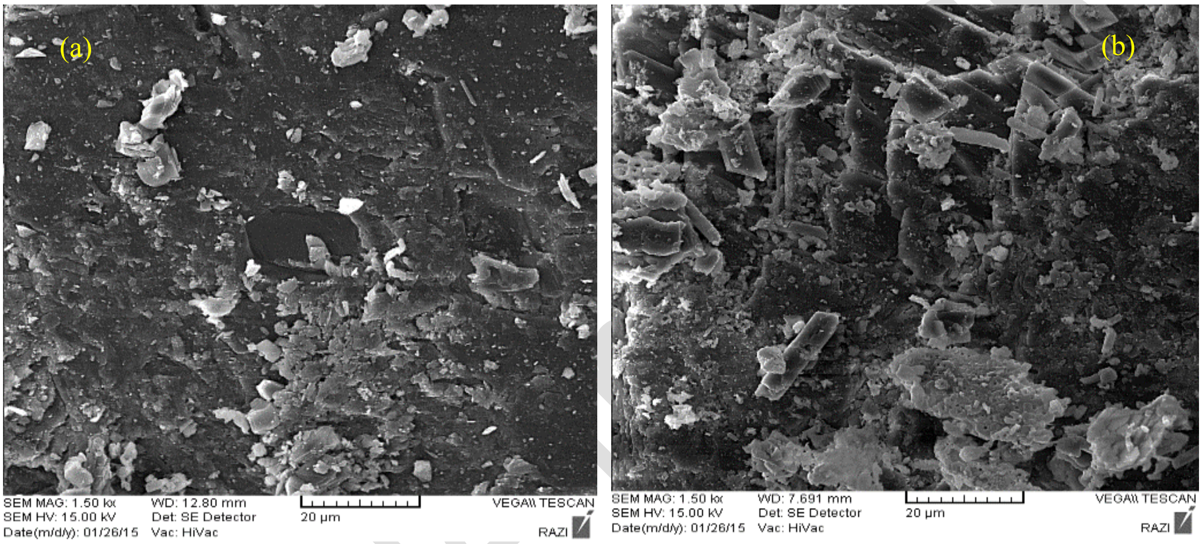


Figure 10. SEM images of a) pure gypsum b) modified gypsum by KOH

Figure 11 shows the micro structure of modified gypsum before and after adsorption of methylene blue. According to the images in Figure 11, the filling of the absorbent surface after dye adsorption could be clearly noticed.

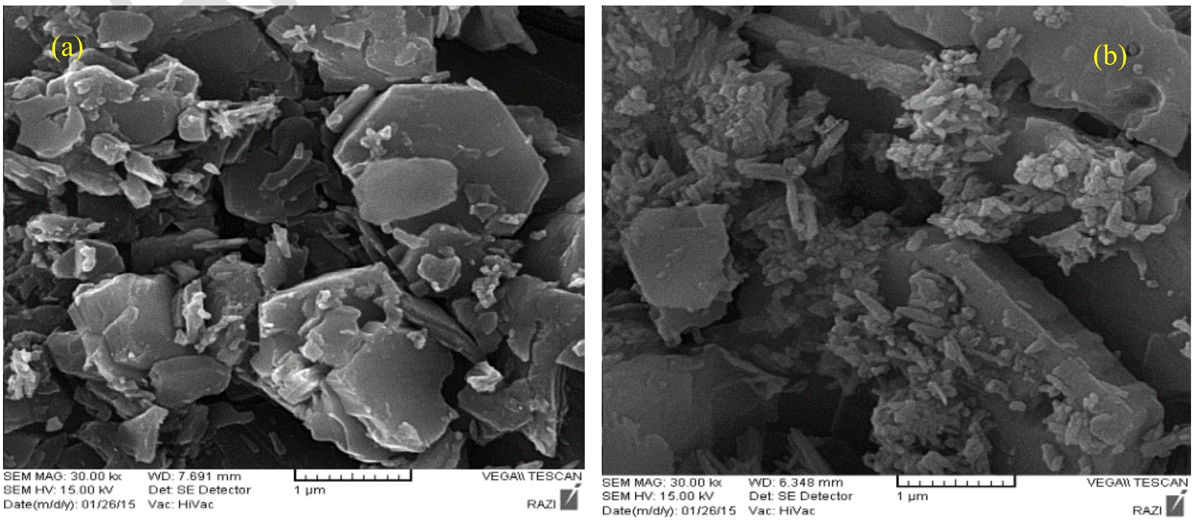


Figure 11. SEM images of modified gypsum a) before, b) after methylene blue adsorption

4. Conclusion

In this study, in order to improve the adsorption capacity of gypsum, treatment by 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, contact time of 30 min, temperature of 25 ° C, adsorbent dosage of 0.1 gr and initial dye concentration of 25 ppm. The maximum adsorption capacity was obtained 29.24 mg/g for modified gypsum in optimum conditions, which is higher than the capacity of adsorption of blank gypsum in the same conditions. The experimental data were well fitted with Langmuir Isotherm and kinetic model of pseudo-second order. 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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