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Adsorption of Methyl Violet Dye from Aqueous Solution by Iraqi Bentonite and Surfactant – Modified Iraqi Bentonite

Suhad Shaker Mohammed **Dhafir T.A. Al-Heetimi**

Department of Chemistry, College of Education for Pure Science Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq.

dhafir1973@gmail.com

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Abstract

Natural bentonite (B) mineral clay was modified by anionic surfactant sodium dodecyl sulfate (SDS) and characterized using different techniques such as: FTIR spectroscopy, scanning electron microscopy (SEM) and X-Ray diffraction (XRD). The bentonite and modified bentonite were used as adsorbents for the adsorption of methyl violet (MV) from aqueous solutions. The adsorption study was carried out at different conditions such as: contact time, pH value and adsorbent weight. The adsorption kinetic described by pseudo–first order and pseudo – second order equilibrium experimental data described by Langmuir, Freundlich and Temkin isotherm models. The thermodynamic parameters standard free energy (ΔG°), standard entropy (ΔS°) standard enthalpy (ΔH°) were investigated and determined.

Keywords: Adsorption, Natural Bentonite, anionic surfactant, Methyl Violet, Isotherm, Thermodynamic.

1. Introduction

Environmental pollution has been become a large problem [1]. A large number of dyes flow into the rivers by many industries such as plastics, paper, rubber, cosmetics, pharmaceutical and food- stuff [2]. 12% of synthetic textile dyes used each year is lost during manufacturing process and 20% of these dyes go into the environment through effluents [3]. Methyl violet is popular dye due to its various purposes such as biological stain, dermatological agent, and veterinary industrial products [4].

Methyl violet is a mutagen and mitotic poison which may cause cancer and can cause severe eye irritation through ingestion or skin contact [5]. There are different physical and chemical techniques to remove methyl violet from their aqueous solution such as oxidation [6]. adsorption [7]. and ion exchange [8].

Adsorption is one of the most active treatment processes to remove methyl violet from waste water by using different kinds of adsorbents such as zeolite [9]. Carbon nanotubes [10].

sepiolite [11]. and bentonite [12]. Modified bentonite also shows efficient to remove of methyl violet from aqueous solution.

Al-Dujaili et al., [13]. used surfactant – modified bentonite and kaolinite clays to remove and appear to be more efficient than unmodified samples.

Bentonite is yellow solid clay mineral, very hard and high porosity [14]. It consists of aluminum oxide and silica with small amounts of impurities such as CaO, MgO, Fe_2O_3 , SO_3 and Na_2O . The chemical structure of bentonite is $Al_2O_3 . 4SiO_2 . H_2O$ Minerals clays have low content of organic carbon and hydrophilic character due to the nature of the interlayer spaces of the minerals [15].

The ion – exchange with surfactant due to the mineral's clays can convert from organophilic to organphobic and increases the minerals clays interlayer [16]. In this study, a negative surfactant sodium dodecyl sulfate (SDS) was used to modify the bentonite clay. Isotherm, dynamics and thermodynamic functions to removal the methyl violet dye from its aqueous solution on the surface of bentonite clay and on the modified bentonite surface were studied. The modified clay was diagnosed by (FTIR), (XRD) and (SEM).

2. Material and Methods

2.1 Adsorbate and Adsorbent

The adsorbate methyl violet (MV) used in this research was obtained by Sigma-Aldrich $\geq 98\%$, $C_{24}H_{28}N_3Cl$, M.Wt = 393.5 g/mol and the used surface was bentonite clay obtained by general Company for Geological Survey.

The chemical analysis of the clay is listed in **Table1.** The anionic surfactant sodium dodecyl sulfate (SDS $> 98\%$) was purchased from the Romil company. A stock solution (1000 mg/L) was prepared by dissolving of 1g of methyl violet in 1L of deionized water.

Table1. The chemical analysis of Bentonite (B).

SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	Na_2O	L.O.I	Total%
54.66	14.65	4.77	6.00	4.88	1.20	0.65	12.56	99.37

2.2 Preparation of Surfactant Impregnated Mineral Clay

The clay, which is in the form of powder was washed several times with deionized water and then dried the clay at 90°C for 6 hours and then left to cool at room temperature. The B-SDS was attended by dissolving 3.5g of SDS in 1L of deionized water and mixed with 50g of bentonite with stirring for 24 hours. The suspension washed several times by deionized water, then dried at 100°c for 7 hours. The B and B-SDS used in this research were sieved ($\leq 75\mu m$).

2.3 Characterization of the Modified Adsorbent

The minerals analysis of B and B-SDS were characterized by using x-ray diffraction (XRD) technique (Shimadzu 6000) powder diffractometer (Japan) using Cuk $\propto$ radiation, $\lambda = 1.5418 A^{\circ}$ at 40KV, 30mA and 2θ range from 10-80°. The Fourier-transform infrared spectroscopy (FTIR) (Shimadzu 8400, Japan) in the wave number range of ($4000\text{-}600 cm^{-1}$) was used to identify the modification of B. Scanning electron microscope (SEM) type –T-Scan, Vega -111 (Czech) was used to identify the surface morphology of the clays.

2.4 Adsorption Isotherm Studies

Adsorption experiments were performed with the addition of 0.1g of B and 0.1g of B-SDS (separately) with 10ml of methyl violet into conical flasks (100mL) at different initial concentrations of (100,150,200,250,300,350 and 400) mg/L. Equilibrium of adsorption, surface weight, acid function, kinetics, temperature effect of various degrees (25,35 and 45)℃ and thermodynamics studied. The concentration of the dye methyl violet was determined by the adsorption measurement using UV-VIS spectrophotometer BG (T80) at 580 nm. The amount of the adsorbent of methyl violet (q_e, mg/g) was calculated by equation (1).

$$q_e = \frac{(C_o - C_e) \times V}{w} \tag{1}$$

Where V is the volume (L), W is the adsorbent weight (g), C_o is the initial concentration (mg/L) and C_e is the residual concentration at the equilibrium (mg/L).

The percentage of methyl violet removal was calculated by using equation (2).

$$\% \text{ Removal } (R\%) = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

3. Result and Discussion

3.1 FTIR Spectra

The FTIR spectra for B and (B-SDS) are shown in **Figures 1a,1b.** respectively. The bands in **Figure 1a.** at 3612.67cm^{-1} and 3541.31cm^{-1} can be attributed to the vibrations for the structural hydroxyl group (OH stretching) and the band at 1647.21cm^{-1} attributed to the group OH deformation. The bands at 1006.84cm^{-1} , 914.26cm^{-1} , 877.61cm^{-1} and 796.60cm^{-1} attributed to Si-O, Al-OH, Fe-O and Mg-O stretching bands respectively. After modification with surfactant SDS **Figure 1b.** The bands at (3612.67, 3541.31, 1006.84, 914.26, 877.61 and 796.60) cm^{-1} were shifted and change in the intensity of all bands. The bands at 2924.09cm^{-1} and 2852.72cm^{-1} in modified B can be attributed to the symmetric and asymmetric stretching vibrations of CH_3 and CH_2 groups of the SDS surfactant respectively [17,18].

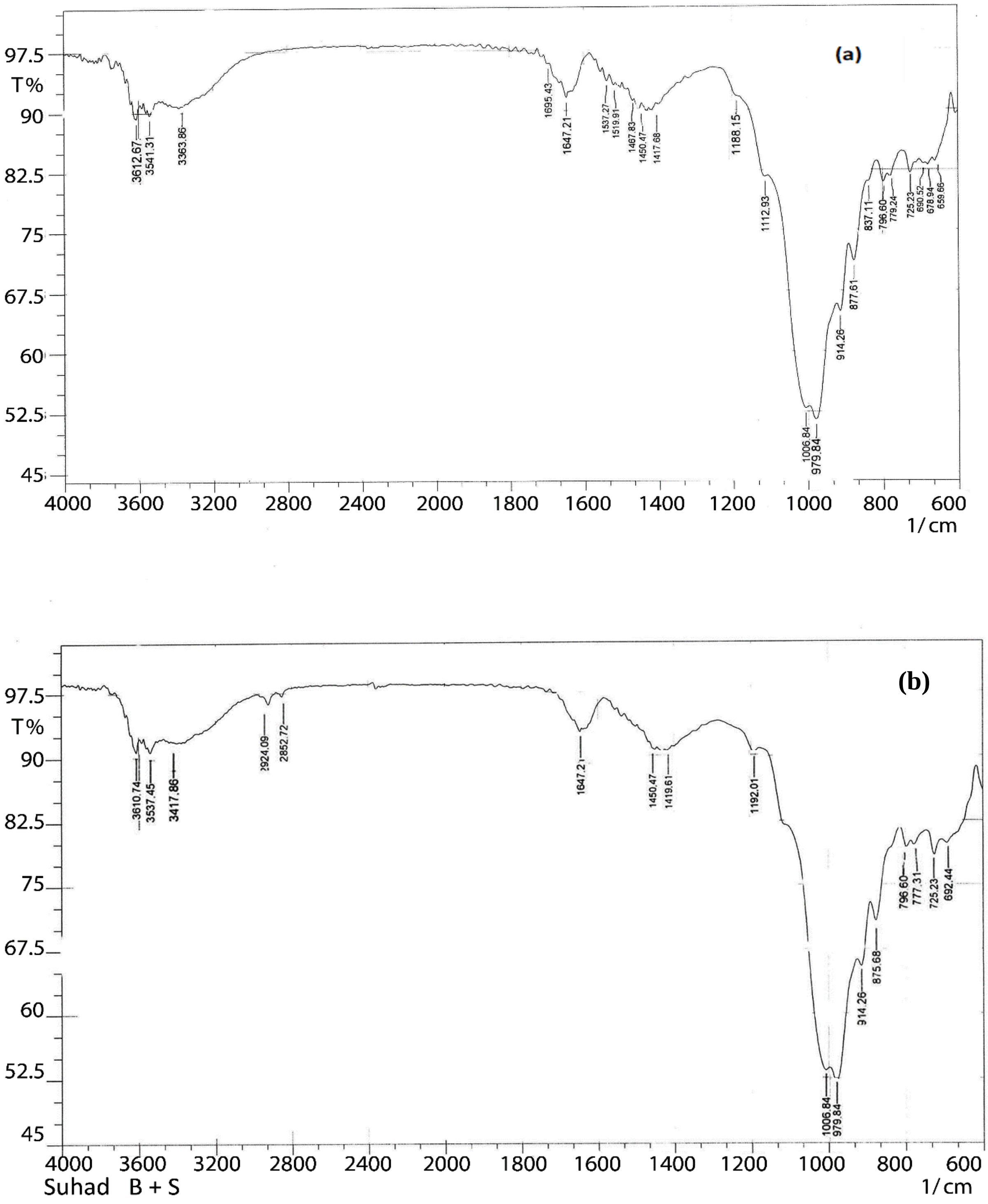

Figure 1. FTIR spectra of (a) B and (b) B-SDS.

3.2 SEM Analysis

The scanning electron microscopic analysis shows crystalline structure, surface texture and porosity of the surface material. The SEM micrograph of B and B-SDS are shown in **Figure 2.** With a magnification force of (5kx). The micrograph in **Figure 2a.** Shows that the B outer shape contains a number of similar conglomerates and hillside or plateau forms containing a number of pores. In **Figure 2b.** Shows that the outer shape of the B-SDS was covered with a thin layer of surface-active material and filled with pores on the surface [19].

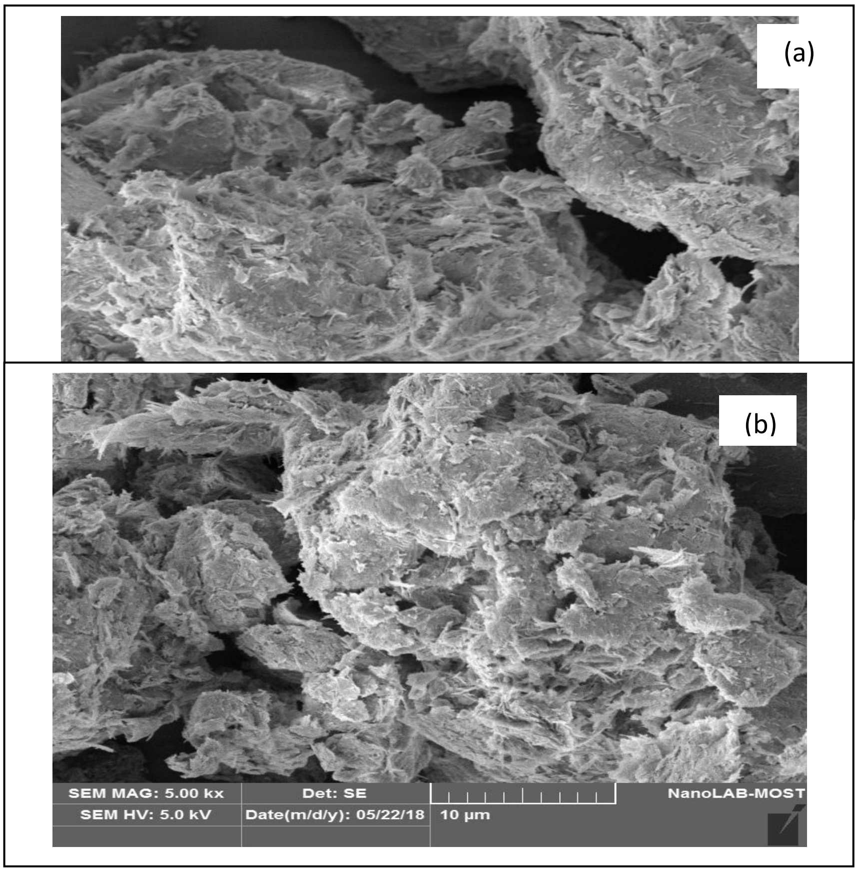

Figure 2. SEM Photomicrographs for B(a) and B-SDS (b).

3.3 XRD Analysis

The XRD analysis of B and B-SDS are shown in **Figure 3a, b.** The difference between B and B-SDS is only in the intensity of the XRD peak, while there is no change in the B metal clay. This indicates that the crystalline structure of the B remains intact and has not been destroyed after the surface has been modified by the surface-active materials as noted in the **Figure 3.** This is corresponding with that mentioned in the literature [20, 21].

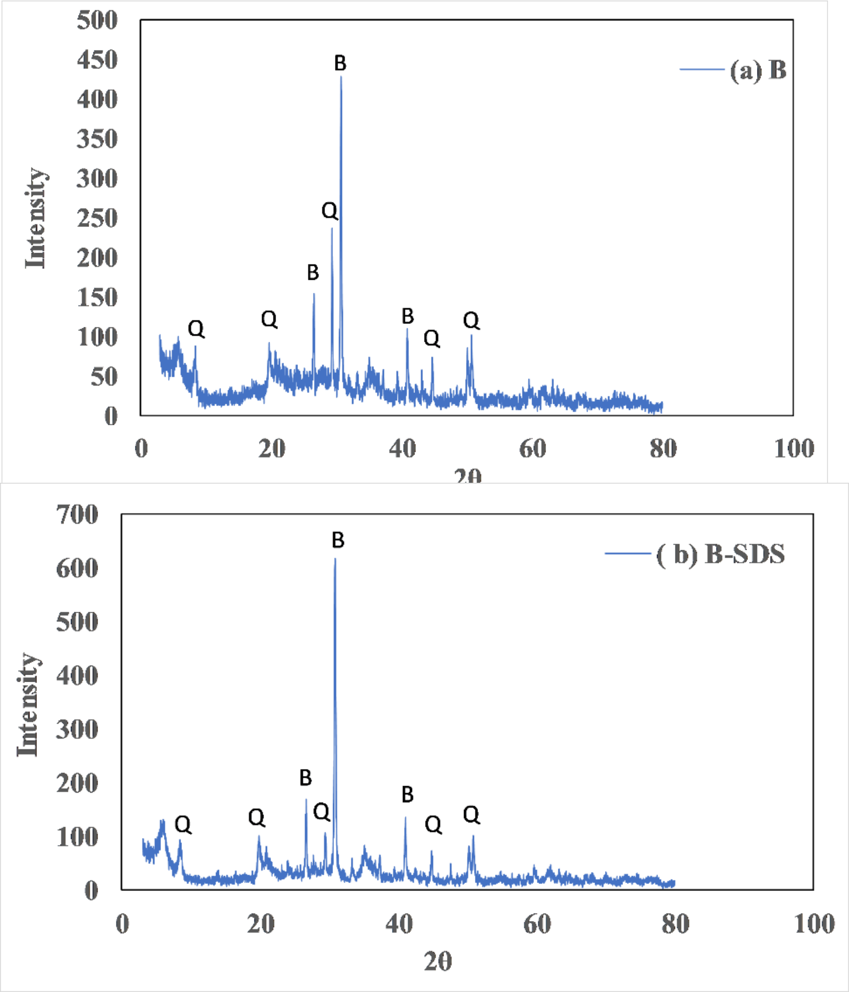

Figure 3. XRD analysis of the B(a) and B-SDS (b).

3.4 Adsorbent Weight Effect

The effect of the weight of B and B-SDS to remove of the MV dye were studied at 25℃ and an initial concentration of 250 mg/L is shown in **Figure 4.** The increasing in the extent of the removal ratio (R %) of the dye MV on the B after 0.1g of the surface was not removed and the adsorption proves approximately (99%). On the other hand, the removal ratio of the dye MV increases by increasing in the weight of B-SDS, and this increase can be explained by the abundance of adsorption sites free and insert the high concentration between the solution and the surface of the solid surface [22]. In addition, increasing of removal ratio (99.59%) can be attributed to the high surface area of the B-SDS because of the increase in the particle space of the B-SDS, which increases the removal capacity of the surface [23].

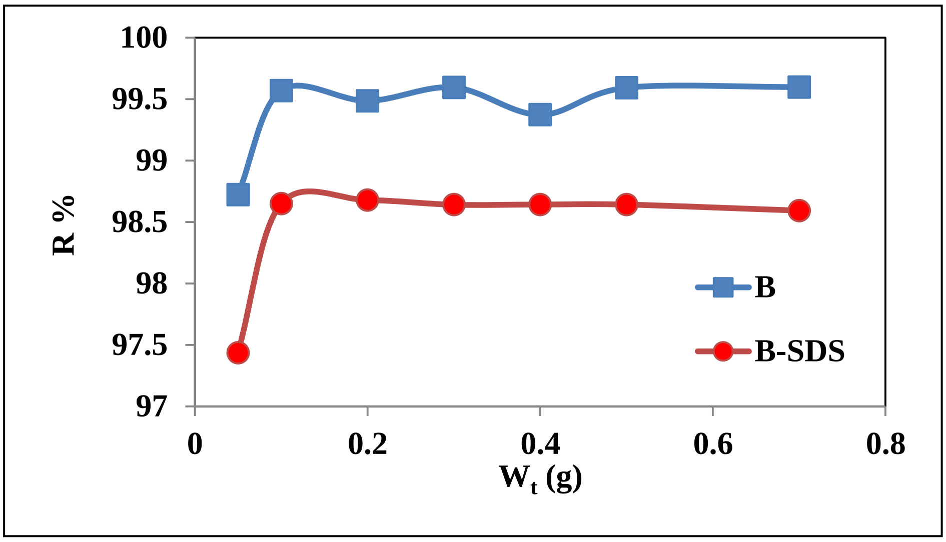

Figure 4. Effect of adsorbent dosage on the removal of MV onto B and B-SDS at 25℃.

3.5 Effect of Contact Time

The effect of contact time on dye adsorption on both B and B-SDS was studied at an initial concentration 250 mg/L, 25℃ , pH=4.45 and 0.1g of B and 0.1 g B-SDS respectively. The capacitance of the MV increased over time and reach affixed value at a specified time. It found that the time needed to reach equilibrium is 8min and 1.5min for B and B-SDS respectively, **Figure 5.** The adsorption speed in the primary stage was high because of the availability of vacant positions on the surfaces of the mezza and after a certain period of time, the adsorption capacity remains constant due to the lack of effective adsorption sites available. The MV dye absorbed on the surface of B-SDS was faster than the surface of B due to the higher affinity on the B-SDS surface [24]. In addition, the surface of B changed from hydrophilic to hydrophobic after modification of SDS [25,26].

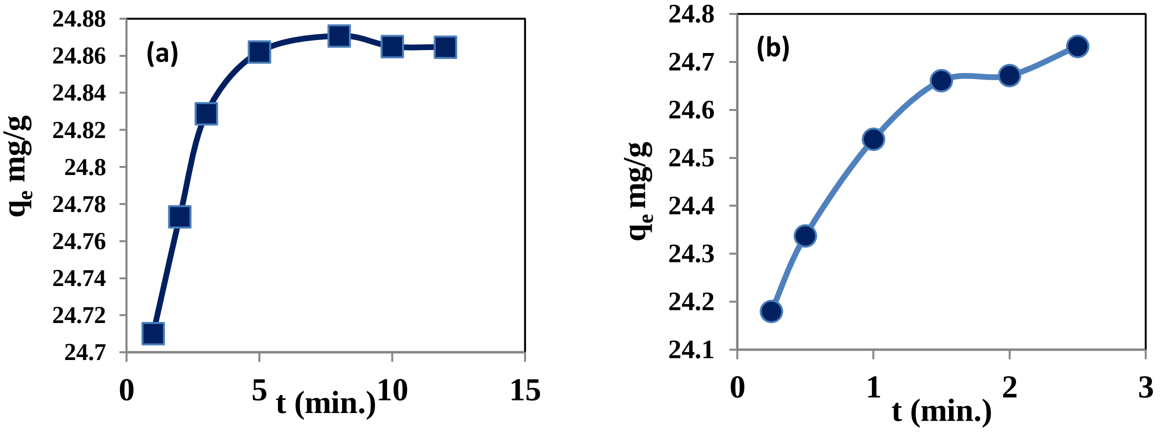

Figure 5. Effect of contact time on adsorption of MV onto (a) B and (b) B-SDS at 25^{o}C.

3.6 Influence of pH

The effect of pH on the removal of (MV) on B and B-SDS was studied using concentration of 250mg/L at 25°C and absorbent weight of 0.1g for both B and B-SDS. The results are explained in **Figure 6.** The removal of (MV) onto B and B-SDS decreased with increasing the pH of a solution. Cationic dye produces molecular cations (N^+) dissolution in water and depends on the water pH. At low pH, the surface of the adsorbent become protonated results at lower adsorption of the protonated dye [27].

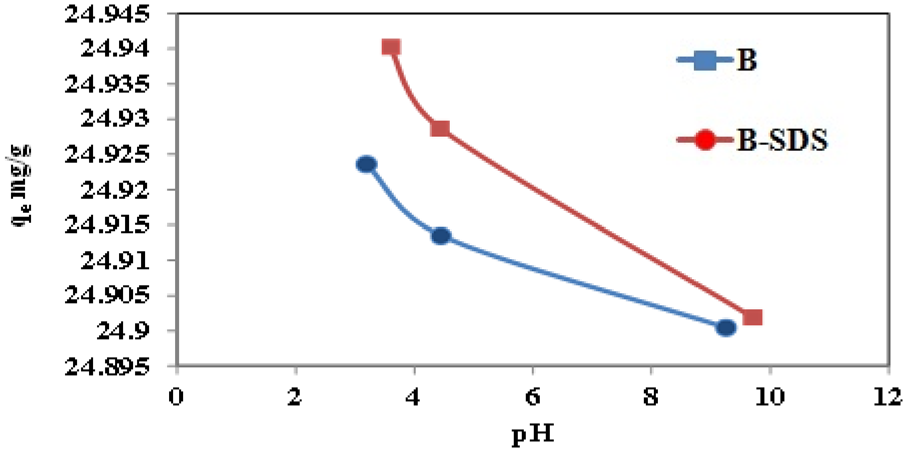

Figure 6. Influence the pH of solution on the removal of (MV) onto B and B-SDS at 25°C.

3.7 Adsorption Isotherm

The adsorption of the (MV) dye from its aqueous solution on the surfaces of B and B-SDS was studied by using three adsorption models: Langmuir, Freundlich and Temkin [28]. The Langmuir isotherm is represented in the following equation [29].

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

Where the C_e and q_e are the concentration at equilibrium (mg/L) and the quantity of (MV) adsorbed onto B and B-SDS (mg/g), respectively q_{max} (mg/g) is the maximum adsorption capacity and K_L is the Langmuir constant in (L/mg). The intercept $\frac{1}{K_L q_{max}}$ and the slope $\frac{1}{q_{max}}$ can find them graphically by drawing $\frac{C_e}{q_e}$ against C_e [30].

The second isotherm model was Freundlich which used for the purpose of description the adsorption of heterogenerous system [31]. The Freundlich isotherm is represented in the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

Where K_F (slope, mg/g) represented adsorption capacity and n (intercept, unit less) represented adsorption intensity. The Freundlich constant (K_F,n) calculated by drawing $\log q_e$ against $\log C_e$. The latest model is the Temkin isotherm can be calculated using the following equation:

$$q_e = B \ln K_T + B \ln C_e \qquad (5)$$

By drawing $\mathrm{g_e}$ vs.$\ln \mathrm{C_e}$ we can determine Temkin constants ($\mathrm{K_T}$and B) [32]. By observing the correlation coefficient R^2 values in **Table 2.** The Langmuir model is not applicable. while observe the applicability Freundlich and Temkin isotherms at all temperatures, it shows the Temkin and Freundlich isotherms are the good fit of experimental date compared that of Langmuir model [33]. On the other hand, $\mathrm{K_F}$values increased by increasing the temperature of all MV adsorption systems on the B and B-SDS surfaces. Temkin isotherm is the good fit of experimental data compared to Freundlich and Langmuir models. **Table 2.** Listed the Langmuir, Freundlich and Temkin isotherms parameters.

3.8 Thermodynamic Parameters

The thermodynamic parameters such as Gibbs free energy ($\Delta G°$), standard entropy changes ($\Delta S°$) and standard enthalpy ($\Delta \mathrm{H}°$) were calculated by using the following equations:

$$\Delta G° = -RT \ln K_{eq} \tag{6}$$

$$K_{eq} = \left({}^{q_e}/_{c_e}\right) * \left({}^{w}/_{V}\right) \tag{7}$$

$$\Delta \mathrm{G}° = \Delta \mathrm{H}° - \mathrm{T}\Delta \mathrm{S}° \tag{8}$$

Where (R) is the universal gas constant, (T) is the absolute temperature. K_{eq} is the equilibrium constant for the adsorption process , q_e (mg/g) is the amount of (MV) adsorbed at equilibrium , C_e(mg/L) is the equilibrium dye concentration in solution , w(g) is the weight of (Band B-SDS) used and V(L) is the volume of (MV) solution used.

$\Delta \mathrm{H}°$ and $\Delta S°$ are standard enthalpy and standard entropy respectively can be calculated by using vent's Hoff equation:

$$\ln \mathrm{K_{eq}} = {}^{\Delta S°}/_{\mathrm{R}} - {}^{\Delta \mathrm{H}°}/_{\mathrm{RT}} \tag{9}$$

The $\Delta \mathrm{H}°$ and $\Delta S°$ can be obtained by drawing $\ln \mathrm{K_{eq}}$ against ${}^{1}/_{\mathrm{T}}$ as the slope and intercept values respectively as shown in **Figure 7. Table 3.** Shows the thermodynamic parameters values at different temperatures. The negative values of ($\Delta \mathrm{G}°$) at all temperatures, which became more negative when the temperature increases. This indicated that the process was more spontaneous at higher temperature. While the positive ($\Delta \mathrm{H}°$) and ($\Delta S°$) an indication that (MV) adsorption on B and B-SDS is a endothermic and randomized process [34].

Table 2. Langmuir, Freundlich and Temkin Isotherm Parameters for the Adsorption of (MV) onto B and B-SDS.

Isotherm	**Adsorbent**	**298K**			**308K**			**318K**		
		K_L (L/mg)	q_{max} (mg/g)	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2	K_L (L/mg)	q_{max} (mg/g)	R^2
Langmuir	B	0.6430	52.3560	0.9562	0.2253	125.0000	0.1841	0.0810	333.3330	0.0252
	B-SDS	-0.2530	-36.7647	0.2976	-0.2892	-32.8947	0.2538	0.0984	256.4102	0.0340
Freundlich		K_F (mg/g)	n	R^2	K_F (mg/g)	n	R^2	K_F (mg/g)	n	R^2
	B	19.2663	1.8663	0.9047	23.0727	1.2362	0.7791	25.3454	1.0900	0.7936
	B-SDS	12.4680	0.6269	0.7906	13.7943	0.6142	0.7020	23.3991	1.1534	0.7308
Temkin		K_T (L/mg)	B (KJ/mol)	R^2	K_T (L/mg)	B (KJ/mol)	R^2	K_T (L/mg)	B (KJ/mol)	R^2
	B	5.8048	12.0680	0.9702	3.9804	18.3240	0.8394	3.6494	21.2410	0.8929
	B-SDS	1.3438	37.1860	0.9070	1.4099	38.4310	0.8249	3.5240	20.3730	0.8479

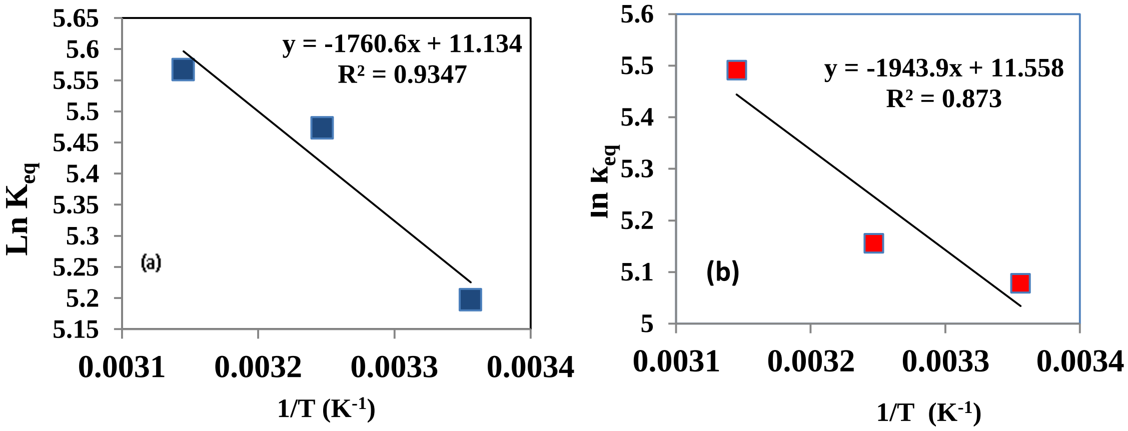

Figure 7. The relationship between $\ln k_{eq}$ and 1/T (a) B and (b) B-SDS.

Table 3. Thermodynamic parameters for the adsorption of (MV) on B and B-SDS.

Adsorbent	T(K)	ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS° (J.K^{-1}.mol^{-1})
B	298	-12.8781	0.0002	+3.0986
	308	-14.0168		
	318	-14.7194		
B-SDS	298	-12.5802	16.1615	+96.0932
	308	-13.2018		
	318	-14.5169		

3.9 Adsorption Kinetics

In order to find the mechanism for the adsorption of (MV) on B and B-SDS two models were applied to study the adsorption kinetics which is the pseudo-first order known as equation (Lagergren) and pseudo – second order known as equation (Ho and Mckay). The adsorption process was carried out at 25,35and 45°C on different times, pH=4.45 and an initial concentration of (MV) of 250mg/L.

The linear formula of the pseudo –first order can be represented by the following formula [35].

$$\ln(q_e - q_t) = \ln q_e - K_1 . t \qquad (10)$$

Where q_e and q_t (mg/g) the amounts of (MV) adsorbed at equilibrium, at t time, $K_1(min^{-1})$ is the rate constant of first order. The amount of K_1 was determined by drawing $\ln(q_e - q_t)$ against t as explain in **Figure 8.**

The linear formula of the pseudo – second order can be represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q^2{}_e} + \frac{t}{q_e} \qquad (11)$$

Where K_2 $(g.mg^{-1}.min^{-1})$ is the rate constant of pseudo – second order calculated from the slope of drawing t/q_t versus time as explain in **Figure 9**. **Table 4.** listed the pseudo – first and second order kinetic parameters. On the other hand, the values of correlation coefficient (R^2) indicate that the adsorption mechanism of (MV) in the B and B-SDS system were more fitted to the pseudo – second order.

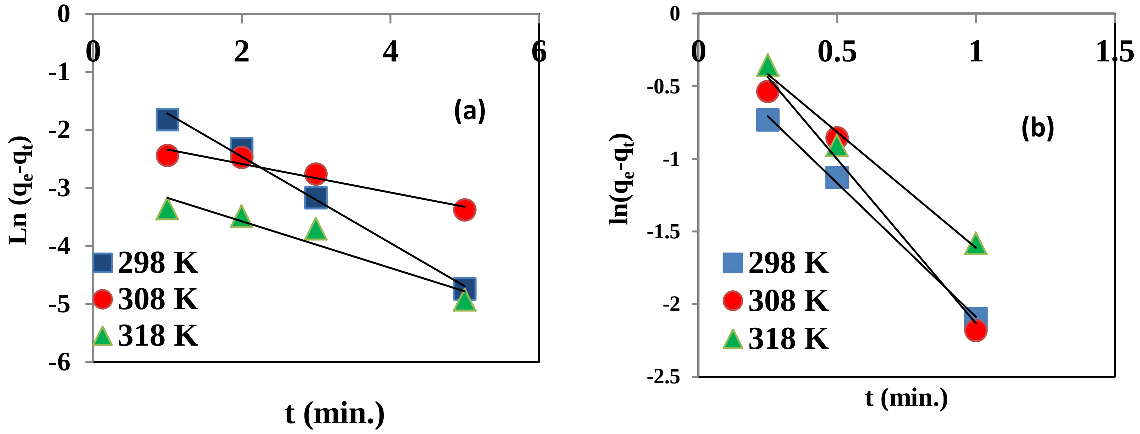

Figure 8. Pseudo-first order plot of (MV) adsorption onto (a) B and (b) B-SDS.

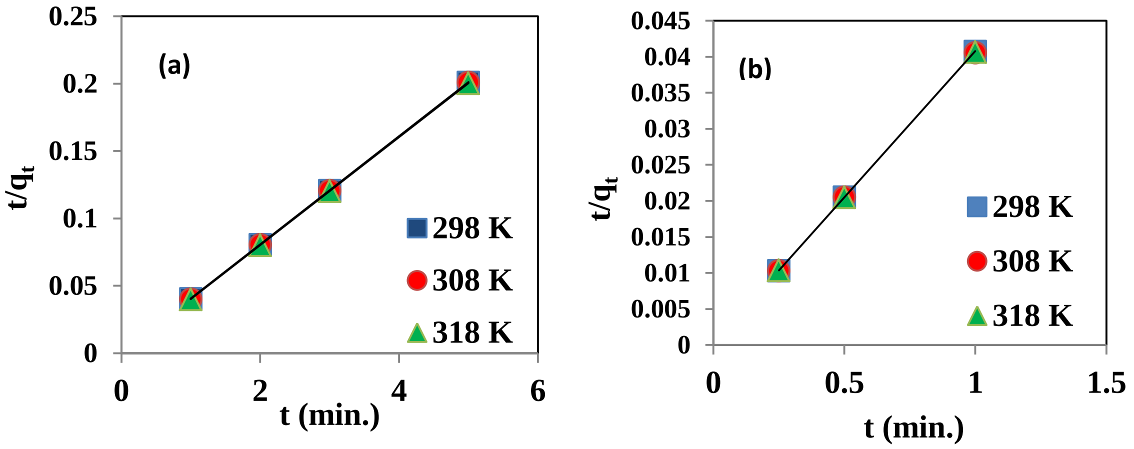

Figure 9. Pseudo-second order plot of (MV) adsorption onto (a) B and (b) B-SDS.

Table 4. kinetic parameters for the adsorption of (MV) on to B and B-SDS.

Adsorbent	**T(K)**	**Pseudo – first order** $K_1(min^{-1})$	R^2	**Pseudo – second order** $K_2(g.mg^{-1}.min^{-1})$	R^2
B	298	0.7456	0.9930	4.0402	1
	308	0.2473	0.9465	8.0808	1
	318	0.4026	0.9109	20.1005	1
B-SDS	298	1.8438	0.9977	8.0000	1
	308	2.2597	0.9781	5.4138	1
	318	1.5939	0.9823	5.4406	1

4. Conclusion

In this study bentonite and modified bentonite were used to remove the (MV) dye from aqueous solutions. The results indicate high adsorption of this dye using both surfaces. Adsorption models have been applied the results showed that model Temkin was the most effective of models Langmuir and Freundlich the adsorption mechanism was studied and the pseudo – second order was the most suitable for both surfaces. The thermodynamic functions of ΔG^o, ΔH^o and ΔS^o were calculated and the process of adsorption of (MV) on both surfaces was found endothermic, spontaneous and randomness.

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