REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING IRAQI PORCELLANITE ROCKS

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ABSTRACT

Industrial wastewater and other polluted water need to be treated to make it possible to discharge into rivers and reuse them. Adsorption takes the importance of ways to remove organic and inorganic pollutants in water. The search for materials that are locally available and cheap to use as adsorbent surfaces. The Iraqi porcellanite powder can be used to remove the dye of Methylene Blue in batch method. The effect of various experimental parameters such as contact time, temperature, solution pH, weight of adsorbent, initial dye concentration, ionic strength were investigated. The adsorption studies included both equilibrium adsorption isotherms and kinetics. The applicability of Langmuir and Freundlich equations was investigated at different temperature, and the Freundlich isotherm exhibited the best fit with experimental data. The thermodynamic parameters indicated that the adsorption was a spontaneous process (ΔG was negative), the negative value of ΔH indicate endothermic and ΔS was positive value (random), the kinetic data well described by Pseudo-second order kinetic model with intra particle diffusion as one of the rate limiting steps.

KEYWORDS: Adsorption, Methylene Blue, Thermodynamic and Kinetic.

INTRODUCTION

Synthetic dyes are one of most important materials that are widely used in many industries such as textiles, cosmetics, leather, wool, paper, printing, pharmaceutical and food industries, and may generate large amounts of aqueous colored effluents and causes an important environmental proplems faced the human in last century.[1]

The presence of very small amounts of dye in water (< 1ppm for some dyes) causes aesthetic worsening and decrease the solubility of dissolved oxygen, water transparency, and sunlight permeability, affecting aquatic life and the food chain.[2] As one of the common dyes, methylene blue (MB) is widely used as the coloring agent and disinfected in rubbers, pharmaceuticals, pesticides, varnishes, and dyestuffs and so on[3], it has been reported that cationic dyes like MB are more toxic than anionic dyes.[4] Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade, due to this a conventional biological waste water treatment process is not very efficient in treating dye waste water.

The removal of color from waste water can be accomplished by filtration, microbiological decomposition, ion exchange, chemical coagulation, chemical oxidation and adsorption.[5] The adsorption process provides an attractive and alternative treatment especially if the adsorbent is, inexpensive and readily available.[6]

Therefore the development of efficient, low cost and eco friendly technologies is needed to reduce the dye content in waste water. Among treatment technologies adsorption It is the most efficient method for the removal of synthetic dyes from aqueous effluents.[7,8] In this present study, we studied the adsorption of methylene blue dye on the surface of Iraqi porcellanite. The system variables studied include sorbent dose, contact time, initial concentration of the dye, pH, FTIR analysis, ionic strength and temperature.

MATERIALS AND METHODS

The cationic dye methylene blue (MB) was used as an adsorbate in this work. Molecular formula **:**($C_{16}H_{18}N_3CIS$) was procured from B.D.H and the molecular weight of 319.85 gmol−1. The chemical structure of MB is shown in Fig. 1.

MB dye solution was prepared by dissolving 0.1 g of dye in 1 L the 100 mg/L then dilution to required concentration. wavelength at maximum absorbance (λmax) was determined by scanning the wavelength and found to be 663.5.
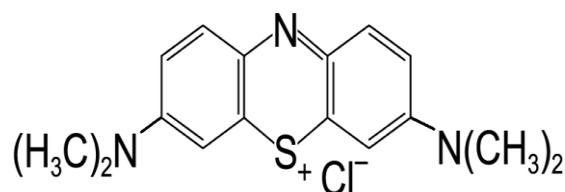

Fig. 1: Chemical Structure of Methylene Blue.

EXPERIMENTAL

Adsorbent materiel

Natural porcellanite samples were obtained from the Ministry of Industry and Minerals (The general company for Geological survey and mining), the clay in powder forms were washed with distilled water to remove impurities and dispose of disposable materials, water soluble salts and other, dried samples for three hours in the oven (at 600°C) and then crushed and sieved to a particle size of 75 μm and then used for experimental work.

Adsorbent Characterization

In order to elucidate the particle properties (e.g., surface morphology and particle size) of the resulting porceiianite powders the powder texture was observed by the scanning electron microscope (SEM).

Chemical functional groups were examined by FT-IR apparatus type Shimadzu using KBr pellet method of room temperature. The spectra were retrieved in the wave number range from 400 to 4000 cm^{-1}.

Adsorption studies

Batch equilibrium experiments had been carried out to find the optimum pH, contact time and equilibrium isotherms. A series of 100 ml stopper conical flasks were used by adding 0.5 gm of Porcellanite particle size of (75 μm) to 50 ml of 100 mg/l of dye.

The experiments were done at room temperature, after gentle shaking for desired time at 120 rpm. The mixture was then centrifuged and the concentration of the dye determines using UV-Vis spectrophotometer (UV-1200 Spectrophotometer). The removal efficiency and the equilibrium uptake of MB dye were calculated according to the equations:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \, 100 \quad \ldots\ldots.1$$

$$Qe = \frac{Vsol.(C_o - C_e)}{m} \quad \ldots\ldots.2$$

Where **Co** is concentration of dye before the adsorption (mg/l), **Ce** is equilibrium concentration (mg/l), **m** (g) adsorbent weight and **V** solution volume in liter, **Qe** is the equilibrium adsorption capacity (mg/g).

Kinetic study

Kinetic of methylene Blue on Porcellanite was carried out with (0.5 g) of the porcellanite powder transferred into 100 ml screw cupped conical flask containing 50 ml of 100 mg/l of tested dye, different samples were shaken at (120 rpm) for (10, 20, 30 and 40°C) by using isothermal water-bath shaker then the mixture solution was taken out at different periods of time. The mixture was centrifuged then measure the amount of the adsorbed dye spectrophotometrically at 663.5 nm, and estimated by eq.(2).

RESULTS AND DISCUSSION

Characterization of the adsorbent

The FT-IR spectrum as show in figure (2) and Chemical functional in the porcellanite characteristic bands.
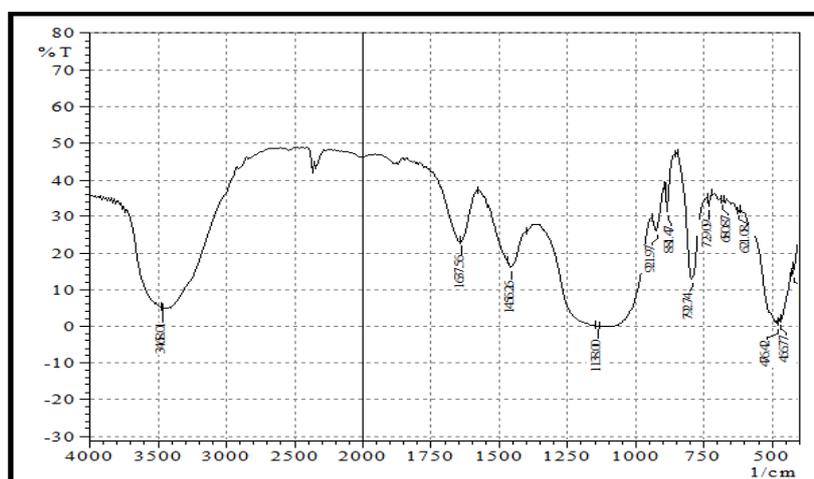

Fig. (2): FT-IR of porcellanite powder.

The results of the FTIR spectrum of the porcellanite rock powder, Fig(2) showed the presence of the main absorption bands. We observe a strong band confined between 3460 - 3620 cm^{-1} resulting from the stretching vibration of the hydroxyl groups. The absorption band at (1138.00 cm^{-1}) belongs to Si-O group. The spectrum also showed peak at (467 cm^{-1}) represent Absorption of the group (Fe-O). The spectrum shows an absorption band at (792.7cm^{-1}) and represents the absorption of the group (Al-O). These chemical groups represent effective sites where the adsorption process occurs because of its negative charge, which gives these groups the ability to form chemical bonds or physical bonds because they contain an electronic pair or an electrostatic charge that you can share to form a physical link.[9]

Scanning Electron Microscope (SEM)

The morphology of porcellanite were investigated using SUPRA 55VP analytical Scanning Electron Microscope SEM, in figure(3) Scanning Electron Microscope photograph before adsorption revealed the surface morphology and the different level of porosity in porcellanite. The surface after MB adsorption shown in figure (4) however shows that porcellanite is loaded with MB dye.
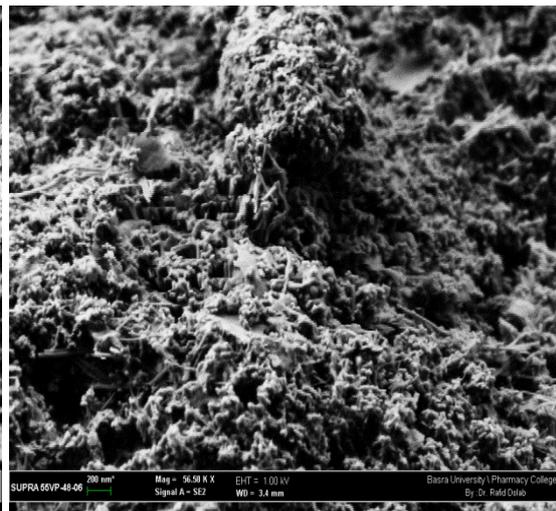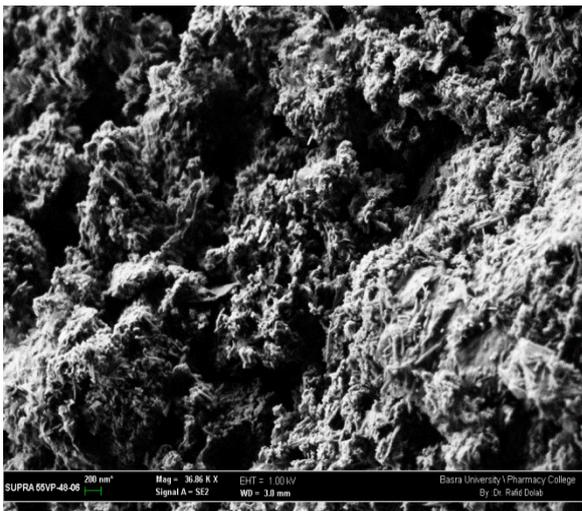

Fig (3): SEM image of porcellanite before MB adsorption.

Fig (4): SEM image of porcellanite after MB adsorption.

Effect of contact time

The effect of contact time on the removal of MB by adsorption on porcellanite roks was studied as function of time at fixed initial concentration (100 mg/l) at different times(5-360 min). Figure (5), showed that the adsorption rate of MB onto Porcellante which is fast at the beginning and optimum contact times was (60) min The removal percentage of dye on porcellante was found to be 99.9%.
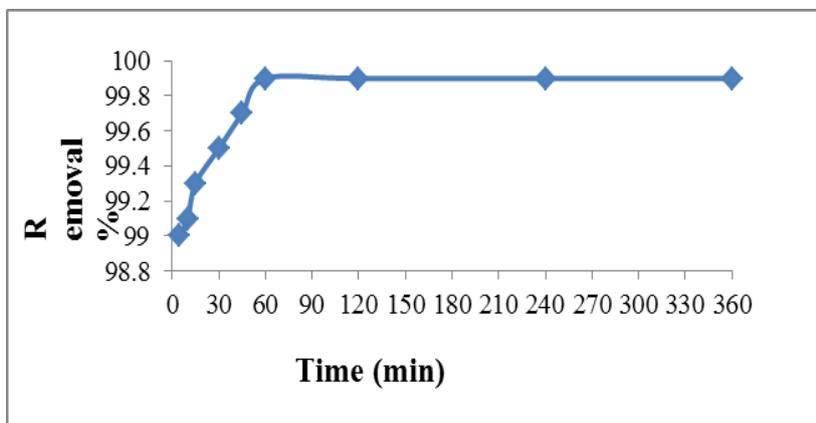

Fig (5): The effect of contact time on adsorption of MB dye onto porcellanite.

Effect of pH on adsorption of MB dye

The pH is one of the most important factors controlling the adsorption of dye onto adsorbent. Adsorption f MB onto porcellanite was carried out for the examination of influence of pH on the dye adsorption, while the initial dye concentration, contact time, temperature, and amount of porcellanite were fixed**.** (50mg/l),4hr, (25°C),(0.5g) respectively. at a rangeof (2 -11) The pH was adjusted by adding a small amount of 0.1M HCl and/or 0.1M NaOH; and it was found that the removal percentage increased with increase in pH (Figure 6) Figure showed that at low pH value, the adsorption was decreased. When solution pH increased from 2 to 11, the adsorption increased. The maximum dye uptake was observed in the pH range of (11).

The basic dyes give positively charged ions when dissolved in water. Thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species. When the pH of dye solution is increased the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent.[10] As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because of adsorption onto charged sites of protons from the solution with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationics.[11]
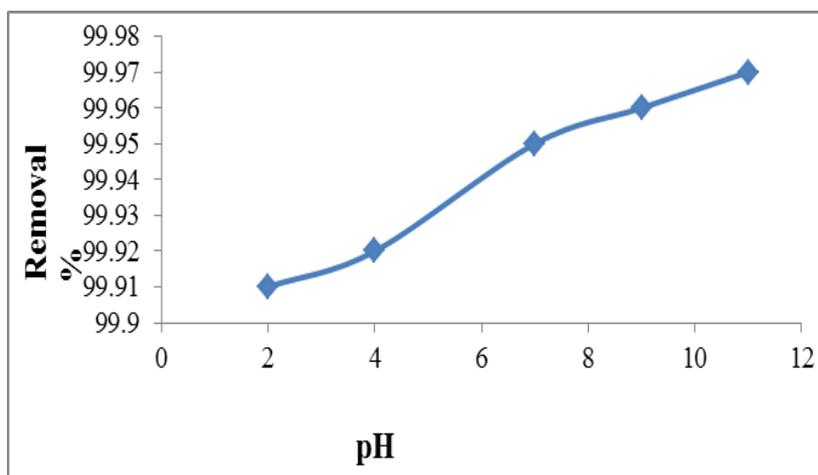

Fig (6): Effect of pH on adsorption of MB dye onto porcellanite surface.

Effect of initial dye concentration

The effect of initial concentration of dye solution on the adsorption was carried out for different concentration of dye solution in the range of (60-200 mg/l) at (25°C). The result revealed that the percentage adsorption of dye was decreases with increases in initial

concentration. The available of free adsorption sites reduced by increasing the initial concentration of dye therefore the removal percentage decreasing.[12,13]

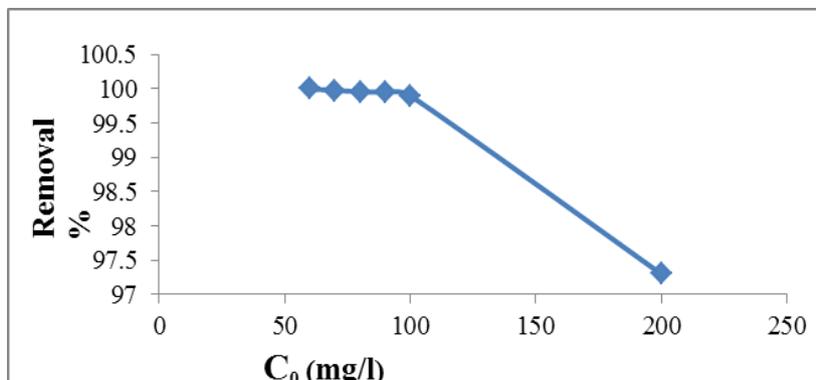Figure. (7) reveal that 100 mg/l is the ideal initial concentration of MB.

Fig.(7): Effect of initial dye concentration on adsorption of MB dye onto porcellanite.

Effect of adsorbent dose

The effect porcellanite dose on the adsorption was carried out for different amount of the adsorbent in the range of (0.1-1 g) at (25°C). As shown in figure (8) the results demonstrated increased the removal rate for MB. With the increase in porcellanite dose from 0.1 to 1.0g, the MB removal efficiency increased rapidly from 88.8 to 99.9%. The reason for such behavior might be attributed to greater surface area and large number of vacant adsorption sites thus favoring more MB adsorption. In this study, the optimized adsorbent dose was fixed at 0.5 g for further experiments.[14]
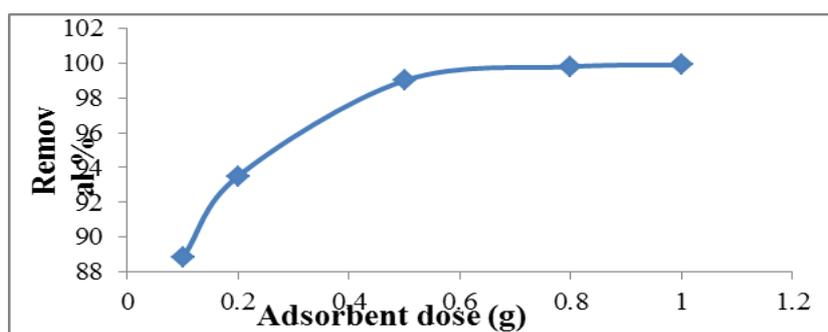

Fig. (8): Effect of adsorbent dose on adsorption of MB dye onto porcellanite.

Effect of the ionic strength on the adsorption of Methylene Blue on porcellanite

The effect of ionic strength on adsorption of the dye was studied by the addition various concentrations of sodium chloride to the solution. The concentration of the salts were kept in the range of 0 to 0.08 M.

As shown in Fig. 9, increasing the ionic strength of the solution caused decrease in adsorption capacity of the dye. This could be attributed to the competition phenomenon between the dye molecules and the ions for the same sites of the adsorbent. On the other hand, "ionic atmosphere may be progressively formed around MB molecules with increased NaCl concentration and result in the reduction of MB adsorption onto porcellante.[15]
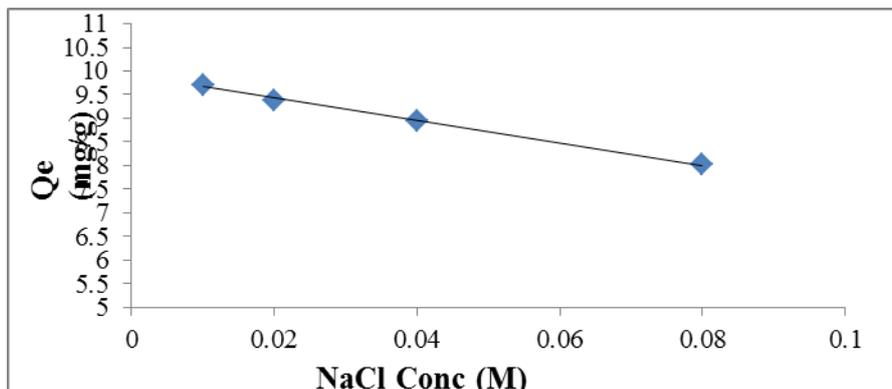

Fig. (9): Effect of ionic strength on adsorption of MB dye onto porcellanite.

Adsorption Isotherm

Adsorption isotherm is the relationship between the amount of a substance adsorbed and its concentration in the equilibrium solution at constant temperature. The adsorption isotherm is important from both a theoretical and a practical point of view, because the application of adsorption isotherms facilitates describing the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent.[16] The adsorption of dye from aqueous solution on porcellanite has been studied at different temperatures (10, 20, 30 40°C) the general shape of dye adsorption isotherm are show in figure (10) where the quantities adsorbed on porcellanite (Q_e) are plotted as a function of equilibrium concentration (C_e) at (10, 20, 30 and 40°C).
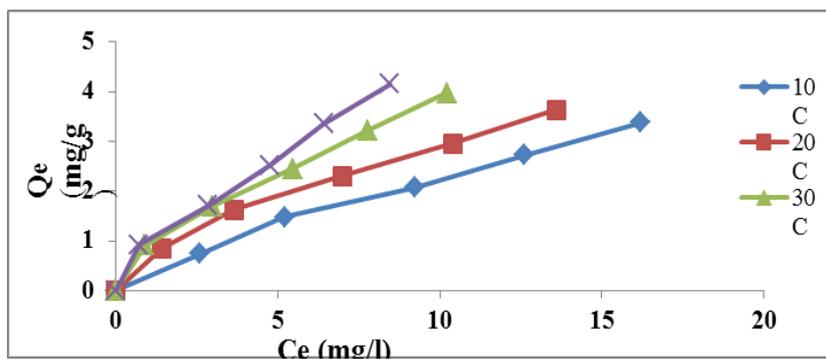

Fig. (10): Adsorption isotherm of dye onto porcellanite at different temperatures.

The shape of the adsorption isotherm of MB dye on porcellanite consistent with (S 3 type) on the Giles classification. This type, indicative of vertical or flat orientation of adsorbed, there is strong inter-molecular attraction within the adsorbed layer, and the adsorbate is monofunctional. In the initial part of an S-curve, the more solute was already adsorbed, the easier it is for additional amounts to become fixed.[17] The experimental adsorption data were applied to both the theoretical Langmuir isotherm equation and empirical Freundlich equation. The results of applying Langmuir e (eq.3) and Freundlich (eq.4).

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \dots\dots 3$$

Where **Qm** is the maximum adsorption capacity (mg/g) and **b** is related to the adsorption energy.

$$\text{Log Qe} = \log Kf + \frac{1}{n} \log Ce \dots\dots 4$$

Where **Kf** is a function of the adsorption capacity and ***n*** is the intensity of adsorption.

Table (1) Results of application of Langmuir & Freundlich isotherm on the system studied.

	Temp(^{o}C)	Langmuir			Freundlich		
		Qm (mg/g)	b (l/g)	R^2	Kf	n	R^2
MB dye	10	10.52	0.79	0.972	4.750	2.525	0.973
	20	14.70	1.41	0.989	4.830	2.109	0.994
	30	14.92	0.56	0.994	5.432	2.074	0.996
	40	14.92	0.41	0.989	7.925	2.386	0.991

The Langmuir and Freundlich isotherms are applied on the experimental data of the adsorption of MB dye on porcellanite by plotting (C_e/q_e) versus (C_e) and ($\log q_e$) versus ($\log C_e$) respectively Langmuir and Fruendlich isotherms Figure 11 & 12). The Langmuir assumes the adsorbent surface is uniform with limit number of active site and no more adsorption take place after formation monolayer.[18,19] Freundlich assumes heterogeneous surface and the concentration of adsorbate affect the adsorption capacity.[20] and (The results of Table (1) show that the value of (Q_m) increased with increasing in the temperature because the adsorption was endothermic, (Kf) is a function of the adsorption capacity and (n) is a function of the strength used adsorption material. Value of n low showed adsorption bond is weak, when the value of n <1 the adsorption coefficient increases with increasing concentration of the solution led to an increase in hydrophobic surface characteristics after monolayer. When the value of n>1 K_f decreases with concentration.[21] The results also show

that the Freundlich isotherm is better fitted on this system than the Langmuir isotherm as show by the linear relationship of (log q_e) versus (log C_e) figure (12).
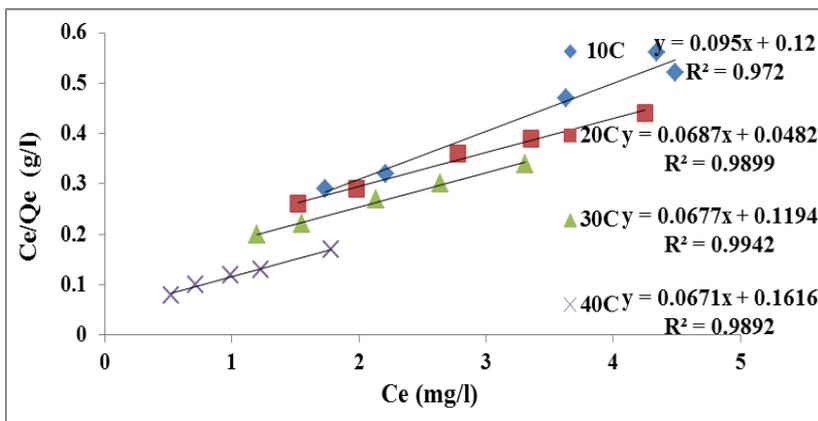

Fig. (11): Linear form of Langmuir isotherm of MB dye on porcellanite at different temperatures.
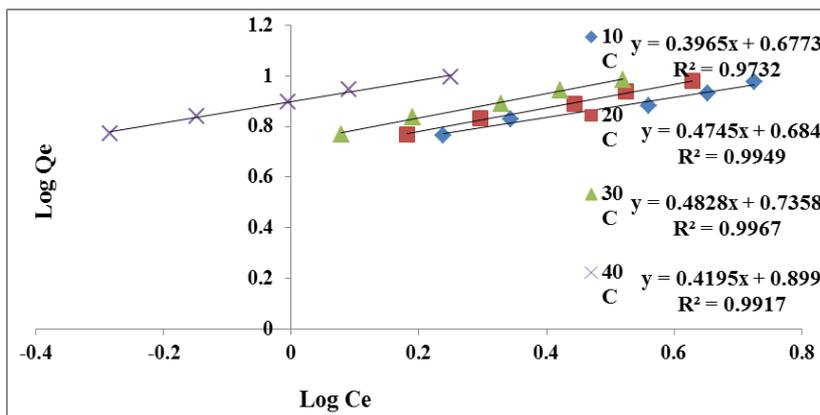

Fig. (12): Linear form of Freundlich isotherm of MB dye on porcellanite at different temperatures.

Thermodynamic Study

The adsorption of methylen blue onto porcellanite was investigated as a function of temperature The effect of temperature was studied for temperatures ranging from 10°C to 40°C using different initial concentration, and the thermodynamic parameters free energy change (ΔG), enthalpy change ΔH and enthalpy change ΔS, which are important in determining the feasibility, spontaneity and the nature of adsorbate-adsorbent interactions, can be obtained by using the following mathematical relations:

$$Ink = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \ldots\ldots\ldots 5$$

K = Csolid / Cliquid……… 6

$$\Delta G = - RT \ln K \ \text{……. ……. 7}$$

Where ΔG is the Gibbs energy change (KJ.mol-1), K is the equilibrium constant, Csolid is the solid phase concentration at equilibrium (mg/l), **Cliquid** is the liquid phase concentration at equilibrium (mg/l), T is the temperature in Kelvin and R is the gas constant (0.008314 KJ. mol^{-1}. K^{-1}).

The ΔG obtained have negative sign that indicates the adsorption process was spontaneous and from slope and intercept of van't Hoff plot Fig. (13), ΔH and ΔS are calculated. The thermodynamic results summarized in Table (2) which shows positive value of enthalpy indicates endothermic adsorption reaction and positive value of entropy indicate increase in randomness.

Table (2): Thermodynamic function for adsorption of studied dye.

	Co mg/l	Equilibrium constant K Temperature °C				-ΔG KJ.mol -1 Temperature °C				-ΔH KJ.mol^{-1}	ΔS Jmol^{-1}K^{-1}
		10	20	30	40	10	20	30	40		
MB dye	60	**33.68**	**38.47**	**48.58**	**114.3**	**7.701**	**9.031**	**10.36**	**11.69**	**29.938**	**0.133**
	70	**30.67**	**34.35**	44.16	97.59	**7.731**	**8.971**	**10.21**	**11.45**	**27.361**	**0.124**
	80	**21.03**	**27.77**	**36.55**	**79.80**	**6.620**	**7.960**	**9.300**	**10.64**	**31.302**	**0.134**
	90	**19.04**	**25.86**	**33.09**	**72.17**	**6.637**	**7.88**3	**9.213**	**10.54**	**31.086**	**0.133**
	100	**17.79**	**22.52**	**29.21**	**55.17**	**6.365**	**7.535**	**8.705**	**9.875**	**26.746**	**0.117**

The plots of **lnK** versus **1/T** were found to be liner with a correlation coefficient (R^2 =0.911 –0.927) (Figure - 13**).**
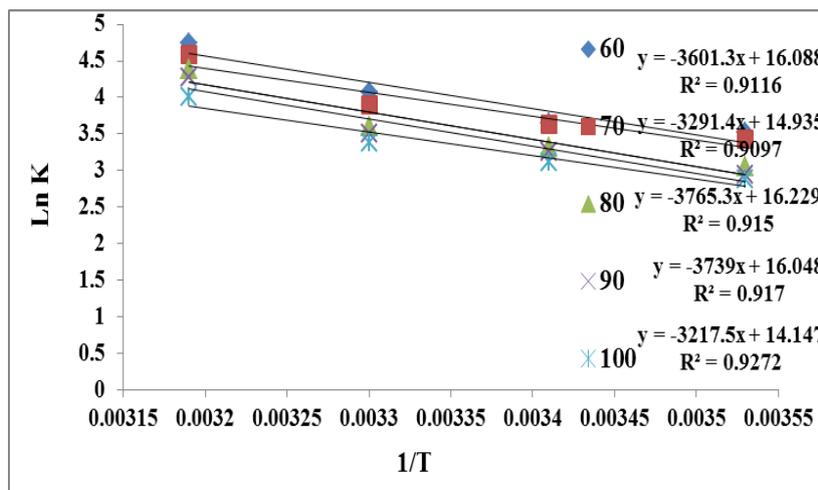

Fig. (13): Plot of van't Hoff relationship between lnK and 1/T.

Kinetics of adsorption

Kinetics adsorption data of MB dye on porcellanite was analyzed using two kinetic models: pseudo-first-order and pseudo-second order. The pseudo-first-order kinetic model is shown by the following equation.[22]

$$\ln (Q_e - Q_t) = \ln Q_e - k_1 t \quad \ldots\ldots..8$$

Where Q_e and Q_t the adsorption capacity at equilibrium and time t respectively and (k_1) (min^{-1}) is the rate constant of the first-order adsorption and t is the contact time (min).

The application of the pseudo-first-order (Lagergren) rate equation (8), the plot of versus (*t*) gave liner relationships, from which the calculated value **k1** are determined from the slope and intercept respectively. The results obtained are given in table (3) and show in figure (14).

The pseudo-second order equation written as follows,

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \ldots\ldots9$$

Where (K_2) (g mg-1 min -1) is the rate constant of the second order adsorption.

A linear plot of against time give the straight line and from the slope and intercept value of K_2 and Q_e can be calculated. The results obtained are given in table (3) and show in figure (15).
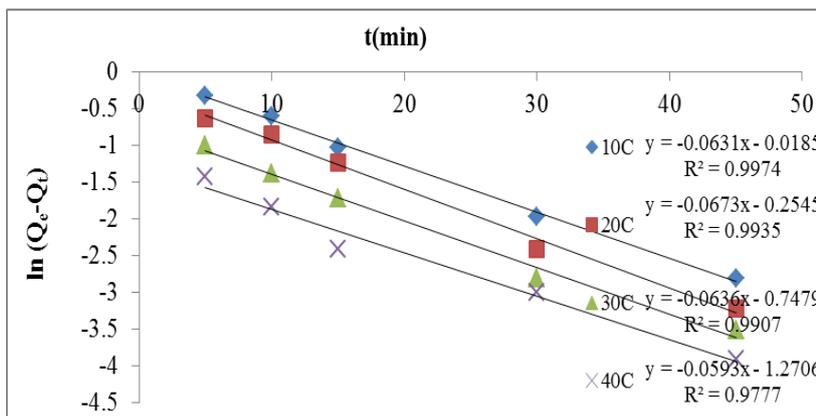

Fig. (14): Linear form of Pseudo-First-Order (Lagergren) Kinetic model of MB dye on Porcellante at different temperatures.
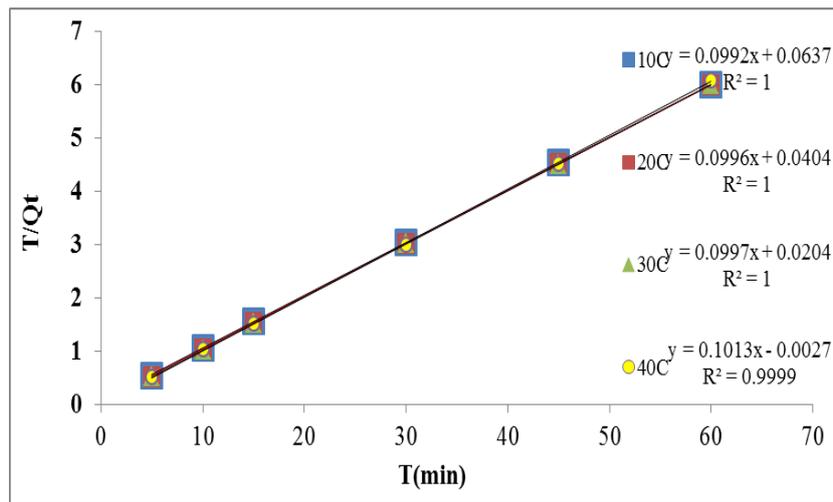
Fig. (15): Linear form of Pseudo-Second-Order Kinetic model of MB dye on porcellante at different temperatures.

Table (3): First order and Second order kinetic rate constant, calculated and experimental Q_e values and R^2.

	Temp. °C	Pseudo-First-Order				Pseudo-Second-Order			
		Q_e exp. mg/g	Q_e Cal. mg/g	K_1 hr-1	R^2	Q_e exp. mg/g	Q_e Cal. mg/g	K_2 hr-1	R^2
MB DYE	**10**	9.97	1.01	0.063	0.997	9.97	10.1	0.155	1
	20	9.98	1.28	0.067	0.993	9.98	10.1	0.245	1
	30	9.99	2.11	0.063	0.990	9.99	10.1	0.450	1
	40	9.99	3.56	0.059	0.977	9.99	9.90	5.101	0.999

CONCLUSION

The results of present investigation show that porcellante has very high adsorption capacity with regard to the removal of methylene blue from its aqueous solution. The experimental equilibrium data obtained were applied to the Langmuir, and Freundlich isotherm equations to test the fitness of these equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of methylene blue obeys Freundlich isotherm, The results suggested that the percentage removal of methylene blue on porcellanite increased with increased pH, The maximum percentage removal of (99.98%) occurred at pH 11. The adsorption capacity of MB decreased with increased ionic strength but increased with increased temperature., Thermodynamic studies shows the adsorption process spontaneous and endothermic, Adsorption kinetic was found to followed the pseudo second order kinetics rate expression.

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