ADSORPTION OF CATIONIC DYES FROM SYNTHETIC TEXTILE EFFLUENT BY IRAQI PORCELANITE ROCKS

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ABSTRACT

This study describe the adsorption of two cationic dyes (Methylene blue and Rhodamine 6G) from aqueous solutions on to Iraqi porcelanite rocks as adsorbent .A series of experiments were undertaken in a batch adsorption technique to access the effect of the process variables i.e contact time, initial pH, adsorbent dose and temperature .The equilibrium in the solution was observed within (30 min) which was indicated by UV-visible absorption spectroscopy technique.

The equilibrium data for adsorption were fitted to the Freundlich and Langmuir. The temperature thermodynamic parameters like $\Delta G°$, $\Delta H°$ and $\Delta S°$ have been calculated.

Keywords: Porcelanite rocks, Cationic dyes, Rhodamine 6G, Methylene blue, Adsorption isotherms.

1. INTRODUCTION

Synthetic dyes are used extensively in many industries included dye houses, paper printers and textile dyers. A significant proportion of synthetic dyes are lost annually to waste streams during textile processing, which eventually enters the environment. Textile dyes have synthetic origin and complex aromatic molecular structures that make them difficult to biodegrade when discharged in the ecosystem. Some of dyes are carcinogenic and mutagenic. Colour/dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen and also damage the aesthetic nature of the environment (Raghuvanshi *et al.*, 2004). As such dyeing wastes need to be treated before discharge into the environment (Robinson *et al.*, 2002). There are several

methods for dye removals such as adsorption, oxidation-ozonation, coagulation, coagulation-flocculation and biological methods (Juang *et al.*, 1997; Waranusantigul *et al.*, 2003; Erin and Afsin, 2008; Turabik, 2008).

Adsorption is one of the best conventional waste water treatment methods compared to other treatment methods such as coagulation, flocculation (Panswed and Wongchaisuwan, 1986), reverse osmosis, ozonation (Muthukumar and Selvakumar, 2004), electrochemical techniques (Alinasafi *et al.*, 2005) and fungal decolorisation.

Activated carbon is the most popular and widely used adsorbent because of high adsorption efficiency for the organic compound. But the commercially available activated carbon is very expensive and has problems of regeneration. Hence, production of low cost and effective adsorbents is still a field of interest and research is continuing in this area. On the other hand the Iraqi porcelanite rocks represent one of the most and great adsorbents, because it is containing high percentage of Silicon reached to 50% (Jameel *et al.*, 2010). However, our search through the literature reveals that limit works have been done on the adsorption of dyes by using Iraqi Porcelanite rocks as adsorbents.

In the present paper , the possibility of utilization of the porcelanite rocks as an adsorbent for removal of Methylene blue(MB) and Rhodamine 6G (R6G) dyes from an aqueous medium has been studied. The equilibrium study are investigated to observe the effects of various process parameters such as PH, contact time, temperature and the sorbent dosage on the adsorption process. Equilibrium data are attempted by various adsorption isotherms including Langmuir and Freundlich isotherms in order to select an appropriate isotherm model.

2. EXPERIMENTS

2.1. Materiales

Porcelanite rocks in Iraq are from an industrial bed of (0.5 to 1.3m) thickness in the sefra, and Trafawi site of the Jeed formation in Al-Rutba region, western of Iraq . The adsorption capacity of porcelanite is due to the large surface area within the composition of critobalite and tridymite (Jassim and Jeremy, 2001; Uday, 2009) . Some of the chemical and physical analysis for the porcelanite is shown in Table (1).

Table-1. Chemical and physical analysis for the porcelanite samples of Traifawi Site.

| Chemical composition	SiO$_3$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	P$_2$O$_5$	CaO	MgO	Na$_2$O	K$_2$O	L.O.I
%	83.57	0.62	4.45	0.01	1.82	1.64	0.5	0.16	0.22	5.9
Specific gravity (SG)	Range for 5 Sample			Average			Recommendation			
Porosity	1.5-1.61			1.554			OK			
								0.52		

The crushed and milled samples of porcelanite was washed several times with deionised water then dried to constant weight at (110 C) by using drying oven. Each sample was sieved and the fraction of 75 µm and below was collected for adsorption experiments .Basic dyes, MB and R6G, were

used. All the chemicals were of high purity, commercially available AR grade. The properties of the selected dyes are given in Table (2) and their structures are shown in Fig.1.

Table-2. Details of selected dyes.

Dyes	Mol. Formula	Mol. Weight g.mol^{-1}	Wave length λ max nm	C.I. No.
Methylene blue	$C_{16}H_{18}N_3SCl$	319.85	609	52015
Rhodamine 6G	$C_{28}H_{31}N_2O_3Cl$	479.02	524	45160

Fig-1. Molecular structures of basic dyes.

(MB)

(R6G)
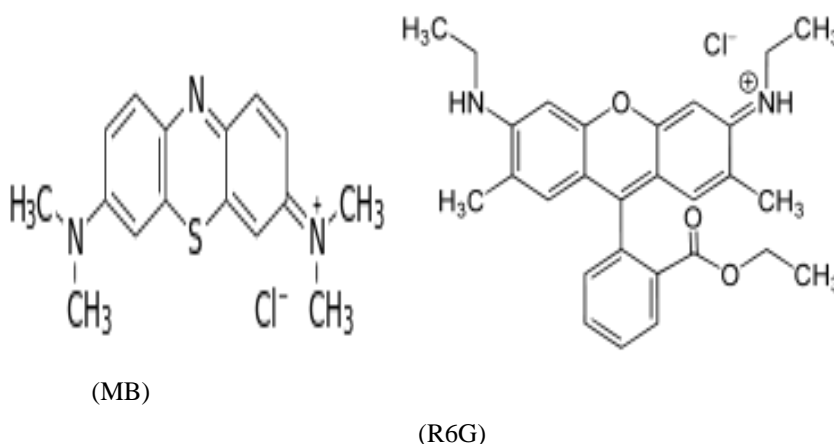
2.2. Batch Adsorption Experiments

The adsorption experiments were carried out by agitating (0.03 mg) adsorbent with (25 ml) of dye solutions (10)mg/L at (150) rpm on an thermo stated shaker water bath. Centrifuge (universal make) at 5000 rpm for (30) min and unabsorbed supernatant liquid was analysed for the residual dye concentration using Shimadzu UV-Vis 1700 digital double beam at a wavelength corresponding to the λmax of each dye. The effect of pH was studied by the adjusting of pH(7) of the adsorptive solution using dilute HCl and NaOH solutions. The effect of temperature was studied using five different temperatures (298 – 333 K).

All experiments were carried out in duplicate and the mean values are reported.

The effect of each parameter (contact time, PH value ,temperature and adsorbent dosage) were evaluated in an experiment by varying the parameter, while keeping the other parameters as constant.The amount of dye on porcelanite adsorbent was calculated using the following equation (Van Der Marcel and Beutelspacher, 1976):

$$Qe = \frac{(C0 - Ce)V}{m} \dots (1)$$

Where Q_e(mg/g) is the amount of dye adsorbed at equilibrium (adsorbent capacity)

C_0 and C_e are (mg/L) the concentrations of dye at initial and equilibrium respectively

V and m is the volume of the solution (L) and the adsorbent mass (g) respectively.

3.   RESULTS AND DISCUSSION

3.1. Characterization Studies

The XRD spectrum Fig.2.indicates existence of certain amount of Quartz (silicon dioxide) and Opal: which are known as irregular interferents between two phases, kretoplyte and traidamayte-alpha; and also some other (kaolin and samktite) which can be found together with fine size silica.

**Fig-2.**XRD spectrum of Iraqi porcelanite rocks.
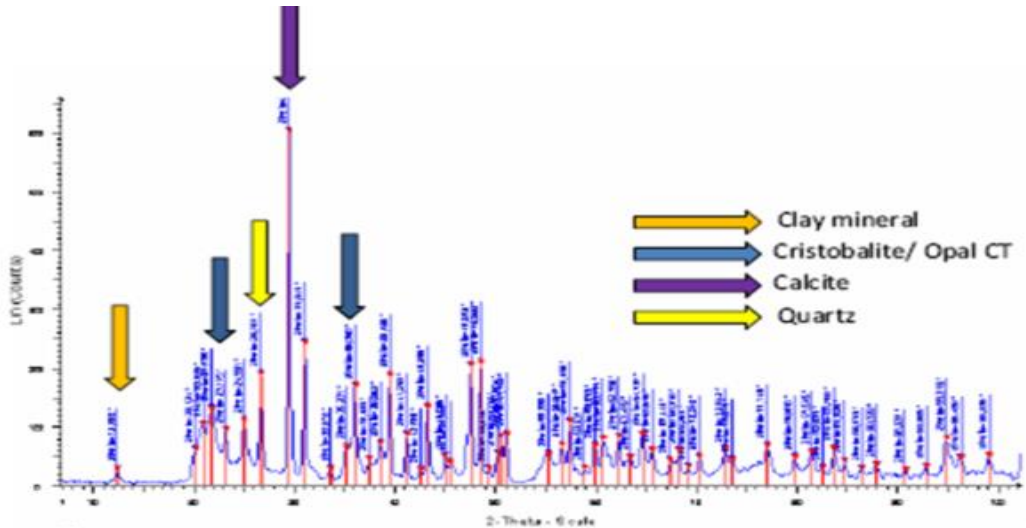
The surface morphology of Iraqi porcelanite rocks was visualized via scanning electron microscope (SEM) at 10000 magnification .Examination of SEM micrographs of the Iraqi porcelaniterocks showing clearly the porous nature of the sample surface Fig.3.

Fig-3. SEM photograph of Iraqi porcelanite rocks.
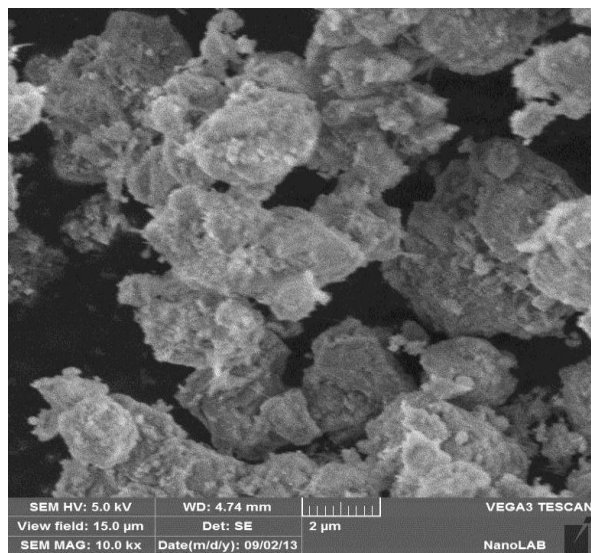
The FT-IR spectra Fig.4. Shows existence of the terminal silanol-OH and to the brighe Si-OH-Si .The band at (1600 cm^{-1}) could be attributed to the deformation of water molecules $\beta(H_2O)$. The band at (1100 cm^{-1}) that appear as strong band can be assigned to the symmetric ($^\gamma$Si-O-Si) or asymmetric ($^\gamma$Si-O-Si) stretching viberations. The bands at (796 cm^{-1}) are characteristic of Quartz and those at (455 cm^{-1}) can be attributed to β(Si-O-Si) or β(Si-O-Si) bending vibrations (Pie-Ling *et al.*, 2009).

Fig-4.FTIR Spectrum of Iraqi porcelanite rocks.
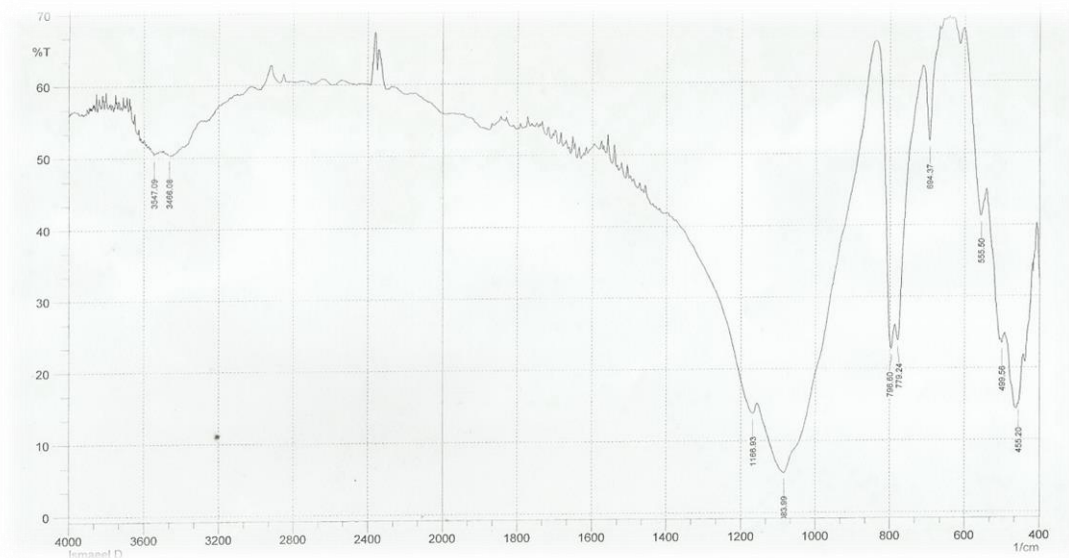
3.2. Effect of pH

The pH is the important factor which controls the adsorption process especially for cationic dyes . The effect of pH of the dye solution on the removal of MB and R6G with Porcelanite were determined at fixed concentration 10 mg/L of dyes over a pH range of (1.0 to 12) as shown in Fig.5. The maximum adsorption of the dyes was observed above pH 4.0. There was no significant variation in adsorption capacity with range in pH above 4.0. Hence, the rest of parameters were optimized at the original pH (7) for the two dyes . Lower adsorption of dyes at low pH is probably due to the presence of H$^+$ ions competing with the cationic groups on the dye for adsorption sites. As surface charge density decrease with an increase in the solution pH, the electrostatic repulsion between the positively charged MB and R6G and the surface of Porcelanite is lowered, this may result in an increase in the rate of adsorption.
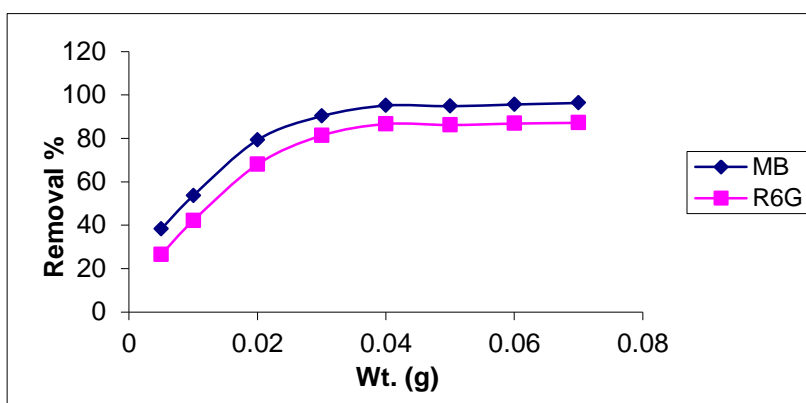
Fig-5. Effect of pH on the adsorption of: (a) MB (b)R6G by Iraqi Porcelanite rocks.Temperature(298K), agitation speed (5000 rpm) , contact Time(20 min) and initial dye concentration(10 mg/L).
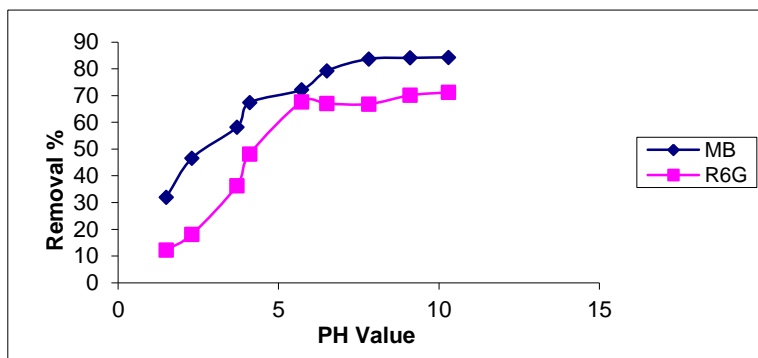
3.3. Effect of Adsorbent Dose

Effect of adsorbent dose on removal of dye was studied by varying the dose of adsorbent (0.005 – 0.07gm) in the test solution while keeping the initial dye concentration (10mg/L   ) ,temperature(298 K) at pH (7) . Experiments were carried out at contact time equal (20 min). As shown in Fig.6, the percent of adsorption increased with increasing adsorbents doses .The increase in the percent removal of dyes with the increase in adsorbent dosage is due to the availability of larger surfaces area with more active functional groups (Santhi *et al.*, 2009). This phenomenon can be also explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption (Jain *et al.*, 2003).

Fig-6. Effect of adsorbent dosage on the percentage removal of: (a)MB (b)R6G by Iraqi Porcelanite rocks .Temperature(298 K),initial dye concentration(10 mg/L), pH(7), contact time (20 min) and agitation speed (5000 rpm).


3.4. Effect of Contact Time

The influence of the contact time on the adsorption capacity of two dyes by Iraqi Porcelanite rocks was conducted through batch experiments to achieve the equilibrium as shown in Fig.7. The

mechanism of colour removal can be described in migration of the dye molecule from the solution to the adsorbents particle and diffusion through the surface. The results showed that the equilibrium time was reached within 30 min.

Fig-7. Effect of contact time on adsorption of:(a) MB (b)R6G by Iraqi Porcelanite rocks.Temperature(298 K), pH(7),agitation speed (5000 rpm) initial dye concentration(10 mg/L) and adsorbent dosage(0.03 g).
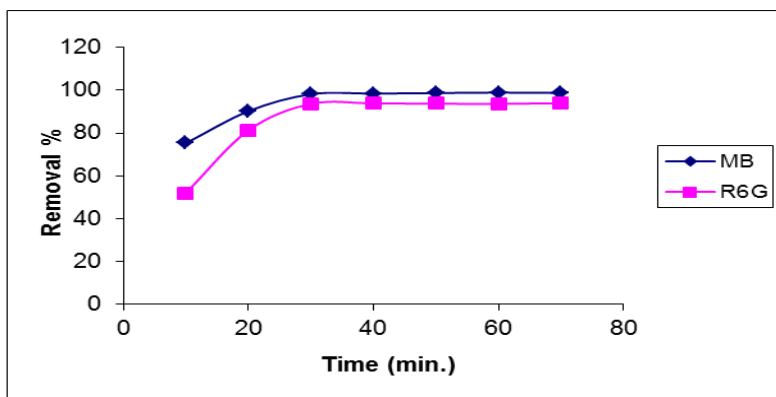

3.4. Effect of Temperature

The removal of MB and R6G dyes using Iraqi Porcelanite rocks has been studied at 298 to 333 K. Determine the adsorption isotherms and thermodynamic parameters, which is presented in Fig.8. Thermodynamic parameters, i.e. free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy($\Delta S°$) changes were also calculated using eqs. (2-4) (Atkins, 2006) and are given in Table (3).

$$\Delta G = -RTlnK \text{ .... (2)}$$

$$\log Xm = \left(-\frac{\Delta H}{2.303RT}\right) + con. \text{ .... (3)}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \text{ .... (4)}$$

Fig-8. Temperature dependence of the adsorption of (a) MB and (b) R6G on the Iraqi Porcelanite rocks surface.

(a)   (b)
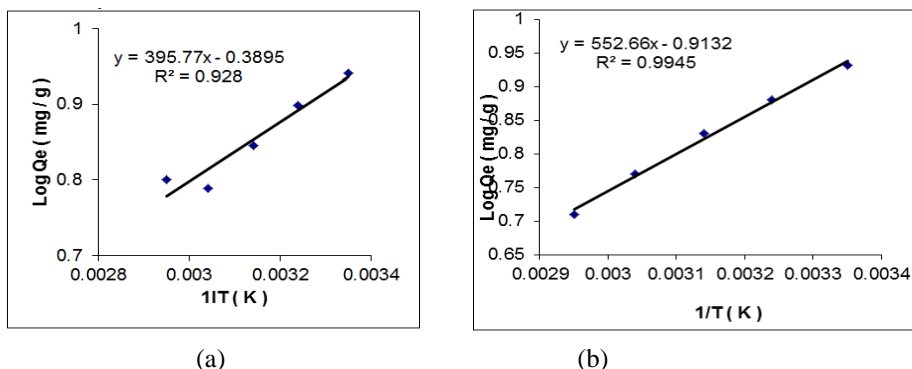
Table-3. Thermodynamic function ΔG°, ΔS° and ΔH° of MB and R6G on the adsorbent surface Iraqi Porcelanite rocks at 298 K.

Adsorbate	ΔG° kJ/mol	ΔS° kJ/mol	ΔH° kJ/mol
Mb	-6.52	-3.54	-7.57
R6G	-5.73	-16.25	-10.58

The ΔG° values obtained in this study for the two dyes are < -10 Kj/mol, which indicates that physical adsorption was the predominant mechanism in the sorption process (Raghuvanshi *et al.*, 2002).The change in enthalpy (ΔH°) was found to be negative (Table.3). The negative values confirm the exothermic nature of adsorption .

3.5. Adsorption Isotherms

The experiment equilibrium adsorption data were analyzed using Langmuir and Freundlich adsorption isotherm models (Freundilch, 1906; Langmuir, 1918):

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a}..............(5)$$

Here C_e (mg.L^{-1}) is the equilibrium concentration of dye,Q_e is the amount of dye adsorbed at equilibrium (mg.g^{-1}). a and b are Langmuir constants related to the adsorption capacity and energy of adsorption respectively (Khatteri and Singh, 2000).

The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms (Fig.9). The values of a and b were determined from slope and intercept of the plot (Table.4). the essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, RL that is given as follow:

$$RL = \frac{1}{1+bC_o}.........(6)$$

Where C_o is the initial dye concentration in solution (mg.L^{-1}) and b is the Langmuir constant (L.mg^{-1}). The value of RL indicates the type of the isotherm to be either favourable (0 < RL < 1), unfavourable (RL > 1), linear (RL = 1) or irreversible (RL = 0) (Ren Jian-min *et al.*, 2010). The value of RL was found to be (0.328 – 0.452) ,that's mean the adsorption process is favourable .

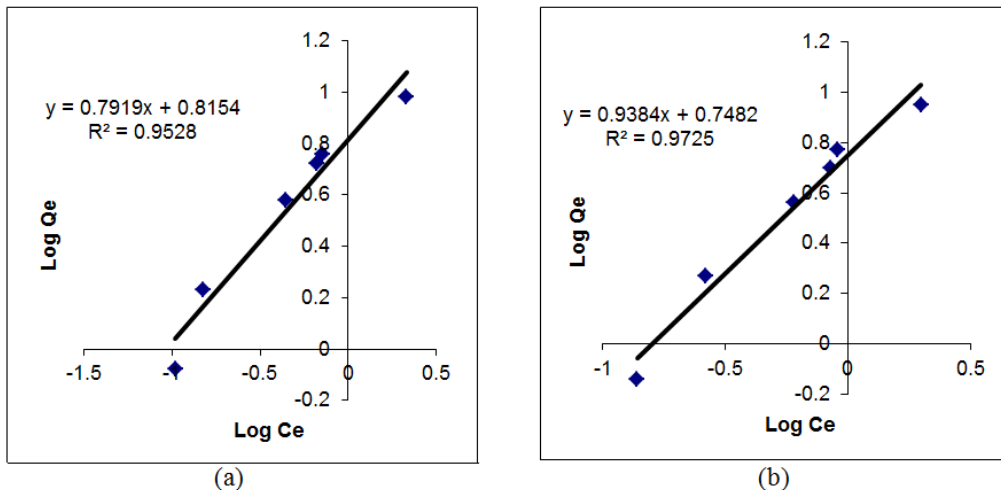**Fig-9.**Langmuir adsorption isotherms for adsorption of (a) MB (b) R6G on adsorbent Iraqi porcelanite rocks.

(a)   (b)
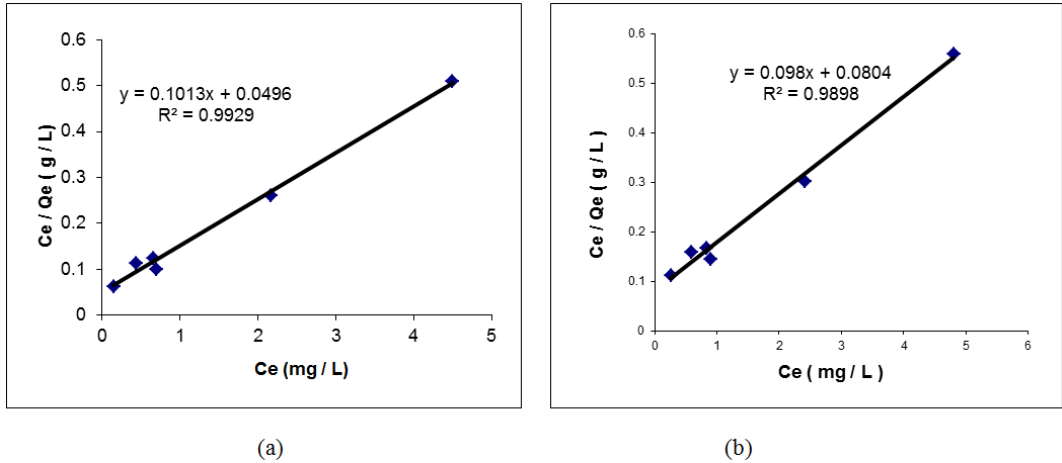
Freundlich adsorption isotherm model used to explain the adsorption phenomenon is represented by the following equation:

$$logQe = logKf + \frac{1}{n}logCe........(7)$$

Here K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of $logQ_e$ versus $loqC_e$ shows that the adsorption of MB and R6G follows the Freundilch isotherm (Fig.10). The values of K_f and n were calculated from the intercept and slope of the plot. The magnitude of the exponent (n) gives an indication of the favourability and K_f the capacity of the adsorbent/adsorbate. The value of the constant 1/n in Freundlich model being smaller than 1, implies that the adsorption process of the dyes on the surface is favourable (Khenif *et al.*, 2007).

Fig-10. Freundlich adsorption isotherms for adsorption of (a) MB (b) R6G on adsorbent Iraqi porcelanite rocks.

(a)   (b)

Table-4. Langmuir and Freundlich parameters of adsorption isotherms at 298 K.

adsorbate	Langmuir isotherm				Freundlich isotherm		
	A	b	Correlation coefficient R^2	R_L	K_f	N	Correlation coefficient R^2
MB	9.87	2.04	0.9929	0.328	6.53	1.26	0.9528
R6G	10.20	1.21	0.9898	0.452	5.60	1.06	0.9725

4. CONCLUSION

The main object of the present work was to explore the possibility of using Iraqi porcelanite rocks as adsorbents for the removal of MB and R6G dyes from aqueous solution .The Iraqi porcelanite rocks , were purified ,sampled and characterized by XRD,FTIR spectroscopy and SEM .The surface of the porcelanite particles was porous ,heterogeneous, non-specific and non-uniform in nature .Different operational parameters observed during the process of investigations reveal that the PH, temperature , contact time and adsorbent dose govern the overall process of adsorption .The exhaustive capacities determination are 8.75 and 8.50 $mg.g^{-1}$of adsorbent for MB and R6G dyes respectively . The equilibrium adsorption is achieved at 30 min .Furthermore, the equilibrium data of adsorption are in good agreement with the Langmuir. The adsorption of MB and R6G dyes on Iraqi porcelanite rocks were exothermic and spontaneous process.

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