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ADSORPTIVE REMOVAL OF DYE FROM INDUSTRIAL EFFLUENTS USING NATURAL IRAQI PALYGORSKITE CLAY AS LOW-COST ADSORBENT

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ABSTRACT

Palygorskite clay has been investigated as low cost and ecofriendly adsorbent for the removal Basic Red 2(BR-2) from aqueous solution. Batch adsorption studies are carried out by observing effect of amount of adsorbent dose, contact time, pH, initial concentration of (BR-2) and particle size of adsorbent on the adsorption capacity of the adsorbent were studied. Adsorption data fits the Langmuir and Freundlich adsorption isotherms. The calculated value of the Langmuir parameter for adsorption capacity of the dye over the adsorbent is 200mg/g adsorbent. This study shows that natural clay is successfully used to remove the Safranin-O dye from aqueous solutions as alternative to activated carbon.

Keywords: Palygorskite clay, Basic Red 2 removal, Adsorption, Equilibrium isotherms.

1. INTRODUCTION

Textile industries' wastewater causes major hazards to the environment due to the presence of large number of contaminants like acids, bases, dissolved solids and colors and other toxic materials.

Most of commercially used dyes are resistant to biodegradation, thus upsetting the biological treatment process within the treatment plant. Unless and otherwise properly treated , these dyes can significantly affect photosynthetic activity in aquatic life due to reduce light penetration and may also be toxic to certain forms of aquatic life due to the presence of metals and chlorides in them.

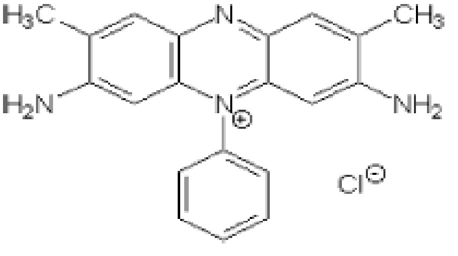
Different treatment methods have been used for treatment , including filtration , flocculation , chemical precipitation , ion exchange , membrane separation , and adsorption (Tarley and Arruda, 2003). The adsorption process provides an attractive alternative treatment, especially if the adsorbent is low cost and readily available. Activated carbon is the most widely used adsorbent, but it is expensive . Therefore , new materials with low – cost, easily available , are used for the dye removal , such as modified clays (Bouberka *et al.*, 2005), natural Iraqi clay (Taha *et al.*, 2009). The aim of this study was to investigate the ability of natural Iraqi palygorskite clay as adsorbent for removal of cationic dyes from wastewaters.

2. MATERIALS AND METHODS

2.1. Adsorbate

The dye used in this study is Safranin-O, which is a basic red dye stuff (Basic Red 2 (BR-2)) IUPAC name as 3,7-Diamino -2,8-dimethyl -5- Phenyl Phenazinium Chloride is a cationic dye which structure is described in Figure (1) .

Fig-1. Structure of Basic Red 2



The physical and chemical properties of the Basic Red 2 dye can be shown by Table (1)

Table-1. Physical and chemical properties of Basic Red 2 dye

Parameter	**Value**
Molecular weight(FW)	350.85 g/mol
Molecular formula	$C_{20}H_{19}N_4Cl$
C.I. Name	50240
Absorption maxima	520 nm
Nature	(cationic dye)Basic red
Solubility	Water+Alcohol

1g of dye dissolved in a liter of distilled water to get the concentration of dye of 1000mg/l. Other solution with approparite concentration can be obtained by diluting method.

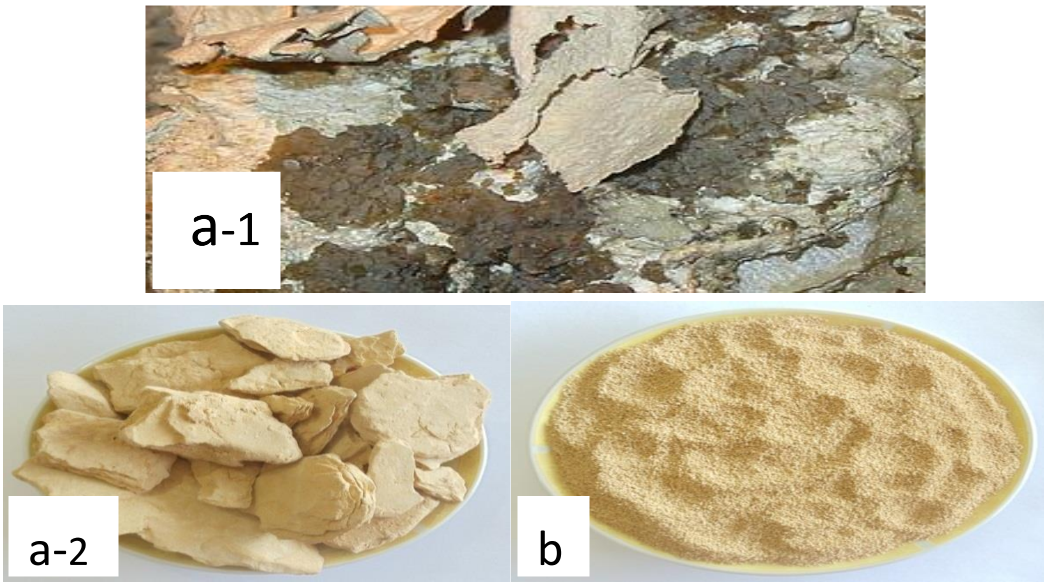
Any concentrations of the dye solutions were determined by measuring the absorbance of the solution at the specified wavelength(λmax.=520 nm. of BR-2 using a double beam UV-Vis spectrophotometer. Final concentration was then determined from the calibration curve already prepared by plot of absorbance versus concentration at maximum wavelength of 520nm. Solution pH was adjusted by adding either HCL or NaOH with concentration of 0.1N.

2.2. The Preparation of Adsorbent

Palygorskite (attapulgite) is a hydrated magnesium aluminum silicate present in nature as a fibrillar clay mineral containing ribbons of 2:1 structure (Bradley, 1940; Galan, 1996). Palygorskite has permanent negative charges on its surface (Li *et al.*, 2004).

Natural Iraqi palygorskite clay was used in this study. It was supplied by the General Establishment for Geological Survey and Mineralogy-Ministry of Industry and Minerals(GEGSM), from Akashat site in the western regions of Iraq. The adsorbent was not subjected to any form of pretreatment, except that the clay was sieved after crushing to obtain particle sizes of (100-1000µm). Figure(2(a1-2, b)) shows the raw and granular clay.

Fig-2. Natural Iraqi palygorskite clay used in this study.
(a-1) The raw palygorskite before preparation
(a-2) The raw palygorskite after preparation
(b)-Granular palygorskite



To remove the adhering impurities and direct at 120C$^{\circ}$ for 24 hours.

The chemical composition of natural Iraqi palygorskite clay are shown in Table(2).

Table-2. The natural Iraqi palygorskite clay composition

SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	SO_3	Loss of ignition	Total
42.2	4.82	9.7	11.7	4	8.5	17.2	98.12

2.3. The Experiments of Adsorption

The adsorption experiments were carried out as a single – stage batch technique in a series conical flask of 250 ml capacity filled with 100 ml of Safranin-O solution .

The conical flasks were shaken at room temperature (27±2C^0) and the shaking speed was 250 rpm .

The adsorption studies were carried out at the following experiments:

Experiment 1. The influence of adsorbent dose: Adsorbent dose of natural clay ranged from 0.05 to 0.3 g / 100 ml , initial dye concentration was 50 mg /l and particle size of adsorbent of 100 µm . The samples were agitated for limited time.

Experiment 2. The influence of shaking time: Shaking time ranged 20 -120 minutes , initial concentration of dye solution was 50 mg/ l , the adsorbent dose used was detected the best value received from previous experiment, adsorbent particle size was 100 µm .

Experiment 3. The influence of initial pH: pH varied from 4 to 11 with initial concentration of dye solution of 50 mg/ l , particle size of adsorbent of 100 µm . The experiment operates at optimum agitating time and adsorbent dosage which obtained from previous experiments

Experiment 4. The influence of initial dye concentration: These experiments were done by changing the initial dye concentration in the range of (10 – 100 mg /l) with added constant mass of adsorbent , the best value received from previous experiment with size of particle of 100 µm and shaking until equilibrium .

Experiment 5. The influence of adsorbent's particle size: These experiments were done by changing the particle size of adsorbent in the range of (100 - 1000 µm) with initial dye concentration of 50 mg/ l at optimum parameters resulted from previous experiments .

Experiment 6. Equilibrium isotherms for Basic Red-2 over natural palygorskite clay:

Adsorption isotherms at Equilibrium for natural clay were found at shaking rate of 250-rpm at room temperature and different concentrations of adsorbent ranged (10 – 100 mg /l) were added to each flask . (0.08 g/ 100 ml) of adsorbent was pleased in asset of 250 ml flasks . The contents were agitate . Small amount was withdrawing and centrifuged . The supernatant was analyzed for residual dye contents .

At the end of each experiment, small amount was withdrawing and centrifuged , the residual of BR-2 concentration was determined by using UV / Visible spectrophotometer .

The amount of BR-2 adsorbed at equilibrium is found based on the followed equation (Ho *et al.*, 1996):

$$qe = \frac{(C_o - C_e)V}{m} \qquad \text{.. (1)}$$

Where q_e(mg/g) is the amount of BR-2 adsorbed in adsorbent at equilibrium, C_o and C_e(mg/g) are the initial and equilibrium concentration of BR-2 solutions respectively, m(g) is the amount of adsorbent, V(L) is the volume of dye solution.

The percentage removal efficiency of BR-2 can be obtained from the relation:

$$\text{Removal efficiency (\%)} = \frac{Co - Ce}{Co} * 100 \qquad \text{.................................... (2)}$$

Where C_o and C_e are the concentration of BR-2 solution before and after adsorption treatment respectively.

3. RESULTS AND DISCUSSION

3.1. The Influence of Adsorbent Dose

The influence of adsorbent dose on the adsorption percentage of dye is conducted over a range of adsorbent doses of 0.05 to 0.3 gm / 100 ml and the results are presented in Figure (3a).

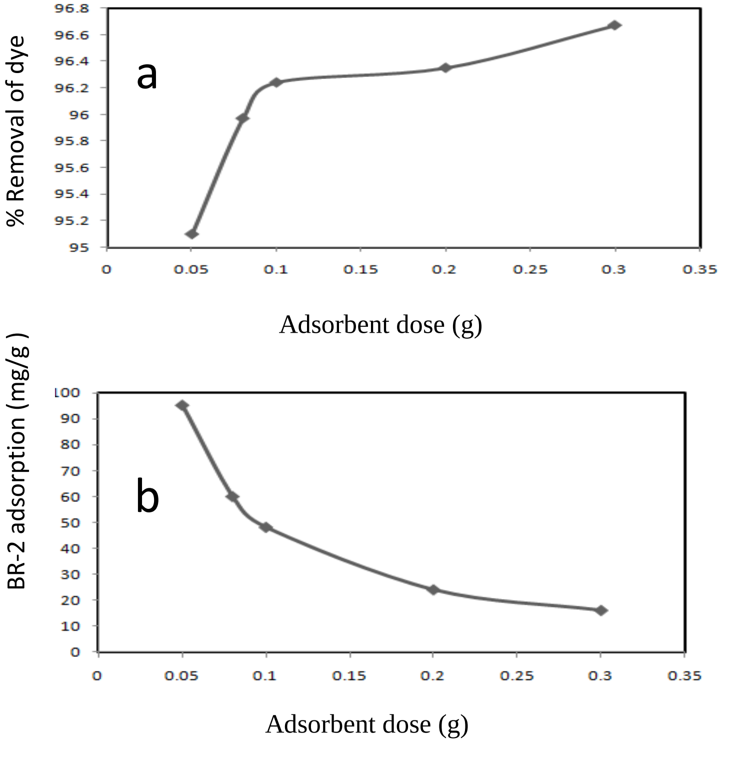
The percentage of dye adsorbed increases from 95.10 to 96.67%. Increase in adsorption with the sorbent dose can be due to increased surface area for sorption of the dye molecule on the surface .and the availability of more adsorption sites. Similar facts were reported by (Mohan *et al.*, 2001; Taha *et al.*, 2009).

The adsorption capacity has a decrease with increasing adsorbent dosage. The adsorption capacity dropped from 95.10to 16.11 mg / g by increasing adsorbent dosage from 0.05 to 0.3 gm / 100 ml .(Figure 3-b) Moreover, the removal almost became constant at the doses of more than 0.08 gm / 100 ml , and it is be considered the best dosage of adsorbent. This is basically due to sites remaining unsaturated during the adsorption process.

Fig.-3. Adsorption BR-2 by natural clay as a function of adsorbent dose at initial concentration of 50 mg/l and100µm particle size

(a) Percentage removal

(b) Amount of dye adsorbed(mg/g).

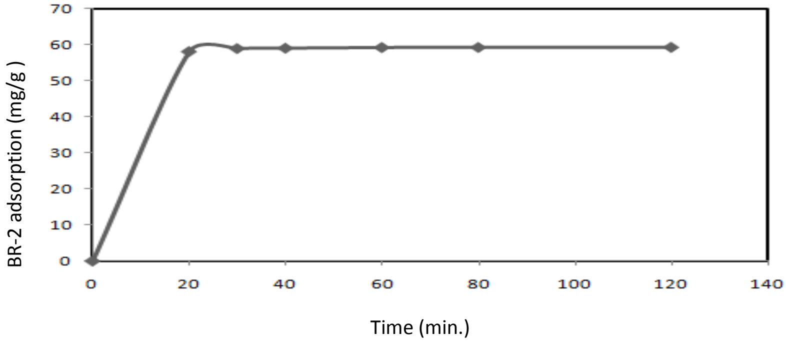


3.2. The Influence of Contact Time

The results can be shown by Figure (4). It can be noticed that the sorption is very fast and equilibrium between the aqueous solution and clay is established in less than 60 min. The time of 30 min. can be considered the saturation time.

The smooth, single and continuous of curve leading to saturation, suggesting the possible monolayer coverage of dye on the surface of the clay. Similar fact was observed by (Tabrez *et al.*, 2009; Taha *et al.*, 2009).

Fig-4. Influence of shaking time on adsorption capacity of BR-2 onto natural clay (initial concentration of 50 mg/l, 100µm particle size and 0.08g adsorbent dose)



3.3. The Influence of Initial pH

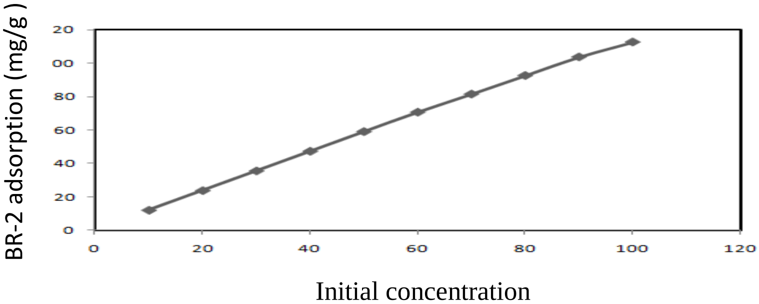
There was no significant change in the percentage removal of dye over the pH range of (4 -11) and the removal efficiency was about 96%. This indicates there is such a strong interaction between the BR-2 and clay that neither H^+ nor OH^- ions could influence the adsorption capacity , and the adsorption does not involve an ion – exchange mechanism.

3.4. The Influence of Initial Dye Concentration

By Figure (5), It has been observed that the adsorption of BR-2 increases with increasing concentration. With increasing concentration of the dye from 10 to 100 mg/l the adsorption capacity increases from 12 to 112.51 mg /g because important driving force can be obtained by increasing in dye concentration to overcome all mass transfer resistance of the dye between the aqueous and solid phases (Ho *et al.*, 2005).

A similar results were cited by (Lata *et al.*, 2007; Taha *et al.*, 2009)

Fig.-5. Influence of initial concentration on adsorption capacity of BR-2 onto natural clay (100µm particle size and 0.08g adsorbent dose)

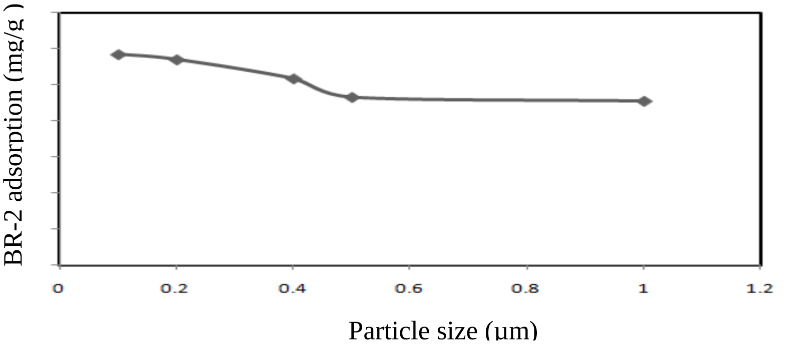


3.5. The Influence of Adsorbents Particle Size

Influence of adsorbent's particle size is shown in Figure (6). The adsorption capacity increased with decreasing particle size (about 58.5 mg /g) . Maximum uptake of dye could be achieved at the smaller particle size (100µm)

This can be attributed to adsorption being limited to the external surface area of the adsorbent, as small particles have a larger external surface area. Similar facts were cited by (Quek *et al.*, 1998; Ponnusami *et al.*, 2009).

Fig-6. Influence of particle size on adsorption capacity of BR-2 onto natural clay at initial dye concentration of 50 mg/l and adsorbent dose of 0.08g



3.6. Adsorption Isotherm

The adsorption isotherm of Basic Red 2 was studied at different initial dye concentration and the data were modeled into the of Langmuir and Freundlich.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

The Langmuir model depend on the assumption of that uniform energies of adsorption onto the surface and no transmigration of adsobate in the plane of the surface.

The Langmuir model represented the following equation (Langmuir, 1918):

$$qe = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad \text{..} (3)$$

Where q_e is the quantity of dye adsorbed per unit mass of adsorbent (mg/g); $q_m$andK_a are empirical constants, and C_e is the equilibrium concentration of adsorbate in dye solution after adsorption; q_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of adsorbate per g of adsorbent).

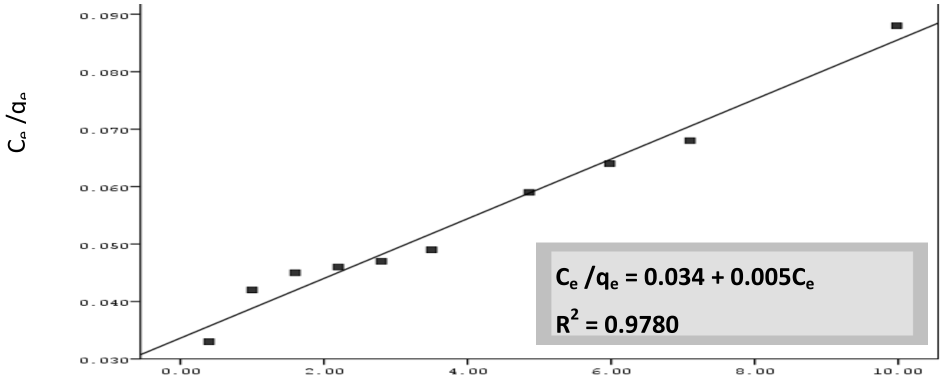
Langmuir adsorption parameters are determined by transforming the Langmmir model to linear form (Eq. 4) by plot C_e/q_e versus C_e, entire the concentration range as shown in Figure (7).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \qquad \text{..} (4)$$

The values of Langmmir constants shown in Table (3).

The maximum adsorption capacity (q_m) was 200 mg / g dye per gram of natural palygorskite for BR-2 .

Fig.-7. Langmuir adsorption isotherm of BR-2 onto natural clay



C_e(mg /L)

R_L is the dimensionless constant separation factor which is express the essential characteristic of Langmuir isotherm , and it is defined by (Weber and Chakravorti, 1974) as follow :

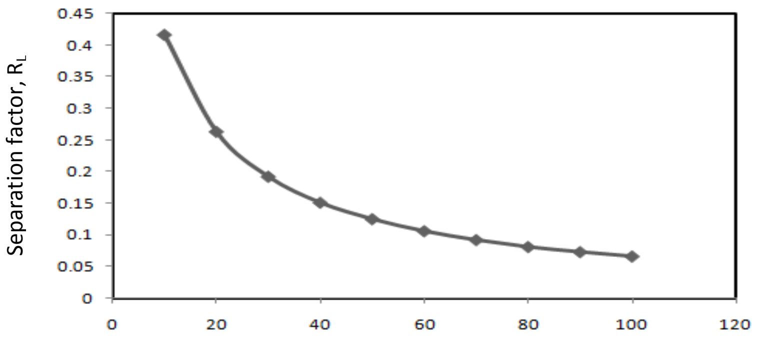
$$R_L = \frac{1}{1 + K_L C_o} \quad \text{...} (5)$$

Where C_0 is the initial concentration (mg / g) and K_L is the Langmuir constant .

The value of R_L indicates of shape of the isotherm to be either favorable ($0< R_L <1$) , $R_L> 1$ for unfavorable , R_L=1 for linear and R_L>0 for irreversible

In this investigation , the values of R_L were found to be less than 1 and greater than 0 indicating the favorable adsorption of BR-2 dye on clay (Figure 8).

Fig.-8. Separation factor, R_L for the adsorption of BR-2 onto natural clay



Initial concentration (mg/l)

The Freundlich model is (Freundlich, 1906)

$q_e= K_F C_e^{1/n}$ ....(6)

An empirical relationship exists between the adsorption of solute to the surface of the adsorbent. This model could be effectively utilized to study the heterogeneity and surface energies .

The linear form of this model takes the form:

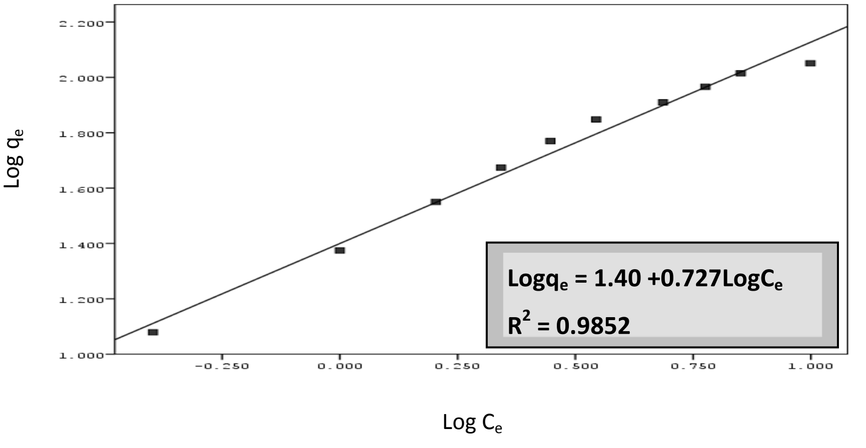
$\log q_e = \log K_F + \frac{1}{n} \log C_e$ ……………………………………………………..........(7)

Where K_F and 1/n are coefficients; q_e = weight adsorbed per unit weight of adsorbent(mg/g) ;C_e = is equilibrium concentration of dye (mg/l) .

The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process.

A plot of Log q_e versus Log C_e gives a straight live as shown in Figure (9) , with slope and intercept of which correspond to 1/n and Log K_F , respectively .

Fig-9. Freundlich adsorption isotherm of BR-2 onto natural clay



The value of 1/n is smaller than 1 points out the normal adsorption.
If n=1, then the partition between the two phases are independent of the concentration. On the other hand, 1/n being greater than 1 indicates cooperative adsorption (Mohan and Karthikeyan, 1997).

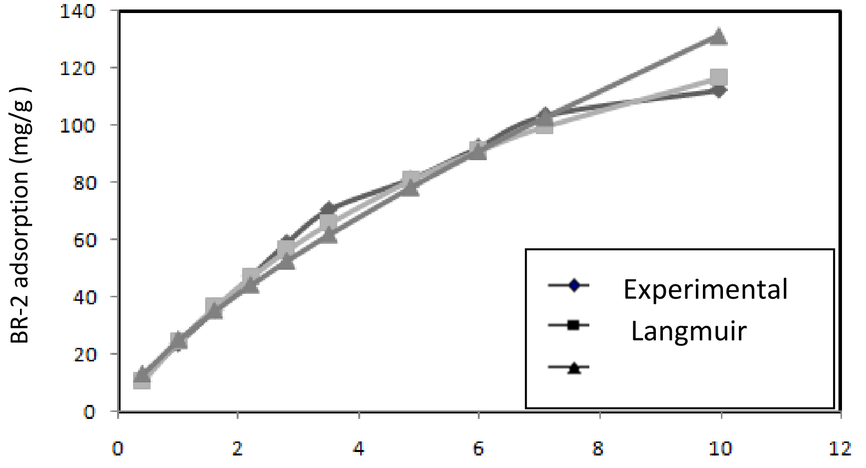
T Table (3) shows the values of Freundlich constants .

Table-3. Isotherm parameters for adsorption of BR-2 onto natural Iraqi palygorskite

Langmuir (95% Confidence level)		**Freundlich (95% Confidence level)**	
q_m (mg g^{-1})	200	K_F(mg g^{-1})(l mg^{-1})$^{1/n}$	25.11
K_a (l mg^{-1})	0.14	1/n	0.72
R	0.9889	R	0.9925
R^2	0.9780	R^2	0.9852
Standard error of the estimate(S.E.)	0.0025	Standard error of the estimate(S.E.)	0.040
R_L	(0.066 - 0.416)		
Equation	q_e= 28C_e/1+0.14 C_e	Equation	q_e= 25.11 $C_e^{0.72}$

The deviation between experimental data and data obtained by two models of adsorption capacity can be explained by Figure (10). It can be noticed that the adsorption pattern for BR-2 onto natural clay obeyed both Langmuir and Freundlish isotherms exhibiting heterogeneous surface conditions and monolayer adsorption (Lee *et al.*, 1999).

Fig-10. Comparison of experimental and calculated data by Langmuir and Freundlich equilibrium isotherms for the system BR2-natural Iraqipalygorskite



BR-2 equilibrium concentration C_e(mg/L)

4. CONCLUSIONS

On the basis of the results obtained, it can be concluded that natural Iraqi palygorskite act as potential adsorbent for the removal of Basic Red 2 form industrial wastewater.

Adsorption is highly dependent on the adsorbent dose, shaking time, dye concentration and particle size of adsorbent.

The adsorption capacity increased with increased of shaking time and achieves equilibrium at 30 minutes. There was no significant effect in percentage removal of dye over the entire pH range studied.

The removal of BR-2 increases with increase of adsorbent dosage used. The adsorption capacity decreases with increase of adsorbent dosage, but, increases with increases of initial dye concentration.

The monolayer adsorption capacity obtained from Langmuir isotherm was 200 mg /g.

Adsorption process fits both the Langmuir and Freundlich adsorption isotherms.

Natural clay is a cheap and easily available material in large quantity in Iraq that thus can act as a better replacement for activated carbon. Being a naturally occurring material, the use of clay as adsorbent would also solve its disposal problem.

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