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Natural Iraqi palygorskite clay as low cost adsorbent for the treatment of dye containing industrial wastewater

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Abstract: In this study, natural Iraqi low- cost locally available clay (palygorskite) was studied for its potential use as an adsorbent for removal Congo red from aqueous solutions. Batch type experiments were conducted to study the effect of contact time, initial pH of the dye solution, initial dye concentration, adsorbent dosage, and particle size of adsorbent on adsorption capacity of Congo red. The adsorption occurred very fast initially and attains equilibrium within 60 min. When the effect of pH of solution dye on the yield adsorption has been carried in a range of 2-10, the adsorption obtained was nearly the same with very slightly effect of pH and it was reported that above 49.07 mg/g of Cong red by palygorskite clay occurred in the pH range 2 to 10. It was observed that the removal of Congo red increase with increasing initial dye concentration and adsorbent dose, but, adsorption capacity decrease with increasing adsorbent dose. The adsorption capacity increase with decreasing particle size of adsorbent. The equilibrium adsorption data were interpreted using Langmuir and Freundlich isotherm models. The obtained results revealed that the equilibrium data closely followed both models, but the Langmuir isotherm fitted the data better. The maximum adsorption capacity was found to be 99 mg/g at ambient temperature. Results indicate that Iraqi palygorskite clay could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for the removal of colour and dyes.

Key words: Natural clay, low cost adsorbent, treatment, dye, industrial wastewater

1 Introduction

Water contamination resulted from dyeing and finishing in textile industry is a major concern. Discharging large amount of dyes in water resources accompanied with organics, bleaches, and salts can effect the physical and chemical properties of fresh-water. In addition to their unwanted colors, some of these dyes may degrade to produce carcinogens and toxic products. Consequently, their treatment do not depend on biological degradation alone[1].

The conventional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a conventional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste[2].

Thus, adsorption has been proven to be more efficient, offering advantages over conventional processes[3].

The most widely used adsorbent is an activated carbon because of its high surface area due to the presence of micro and meso porus. But, is very expensive. Furthermore, regeneration using solution produced small additional effluent while regeneration by refractory technique results in a 10-15% loss of adsorbents and its uptake capacity[4].

This had lead to make many investigations to study the economic feasibility of using inexpensive alternative materials, easily available with highly effective.

A number of workers have used different low cost alternative materials for dye removal such as red mud[5], gram husk[6], china clay[7], coconut husk[8], activated clay[9], clay, bagasse pith, and maizecob[10].

This study was aimed to investigate the adsorption capacity of locally available low-cost adsorbent Iraqi palygor-

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skite clay for removal of Congo red dye from wastewaters, because it is easily, abundantly available and naturally occurring in wide sites of western regions of Iraq with very large quantities.

The effects of contact time, pH, initial dye concentration, adsorbent dose, and particle size of adsorbent have been studied and obtained results are discussed. The equilibrium of adsorption was modeled using the Langmuir and Freundlich isotherm models.

2 Material and Methods

2.1 Materials

Congo red dye (Direct red 28) is an anionic direct disazo, CI = 22120; chemical formula: ([$C_{10}H_5(NH_2)(SO_3Na)N$: NC_6H_4]2); molecular weight 696.66 g/mol. and $\lambda_{max.}$ = 498 nm.

The structure of the dye molecule is shown in Fig. 1.

The dye is a benzedene based dye, known to metabolize to benzedene, aknown human carcinogen. Exposure to the dye has been known to cause an allergic reaction (and possibly anaphylactic shock)[11]. The stock dye solution was prepared by dissolving 1g of Congo red in 1000 ml distilled water to obtain 1000 mg/l dye used for preparing different initial dye concentrations. The initial pH values of the solutions throughout the experiment adjusted with 0.1 M HCL or NaOH using pH meter.

2.2 Adsorbent preparation

Palygorskite (attapulgite) is a hydrated magnesium aluminum silicate present in nature as a fibrillar clay mineral containing ribbons of 2:1 structure[12, 13]. Palygorskite has permanent negative charges on its surface[14].

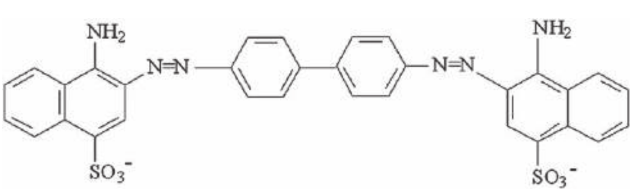

Fig. 1 Structure of Congo red dye.

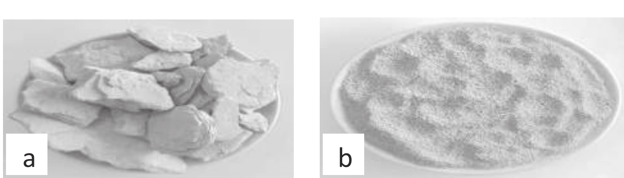

Fig. 2 Natural Iraqi palygorskite clay used in this study. (a)-The raw palygorskite. (b)-Granular palygorskite.

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 (100-1000 μm). Fig. 2 (a), (b) shows the raw and granular clay.

To remove the adhering impurities and direct at 120℃ for 24 hours.

The chemical composition of natural Iraqi palygorskite clay are shown in Table 1.

2.3 Adsorption Studies

Batch adsorption experiments were carried out at room temperature.

All adsorption experiments were conducted using 250 ml flasks with dye solution volume of 100 ml and the mixture of solution and adsorbent was agitated in 250 rpm. After shaking, the flasks for predetermined time intervals, samples were filtered and analyzed. All the adsorption experiments were conducted in duplicate and average values used in data analysis. Replicate experiments showed a maximum deviation of 2.5% in dye uptake measurements.

● Adsorption parameters studied

The following adsorption experiments were carried out to study the adsorption parameters:

The effect of contact time: contact time ranged from 20-140 minutes, initial dye concentration was 50 mg/l, adsorbent dose 0.1 g/100 ml, and particle size of adsorbent was 100 μm.

The effect of initial pH: pH ranged from 2 to 10. The initial dye concentration was 50 mg/l, adsorbent dose was 0.1 g/100 ml and particle size of adsorbent was 100 μm. This experiment operates at optimum contact time which result from previous experiment.

The effect of initial dye concentration: initial dye concentration rangrd from 10 to 100 mg/l, adsorbent dose was 0.1 g/100 ml; particle size of adsorbent was 100 μm at optimum contact time and initial pH from previous experiments.

The effect of adsorbent dosage: adsorbent dosage ranged from 0.05 to 0.3 g/100 ml at optimum contact time, initial dye pH and solution dye concentration from previous experiments.

The effect of particle size: particle size of adsorbent

Table 1 The chemical composition of natural Iraqi palygorskite clay used in this study, (GEGSM).

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

ranged from 100 to 1000 μm with initial dye concentration of 50 mg/l at optimum parameters obtained from previous experiments.

Adsorption isotherms studies for Congo red dye onto palygorskite

Adsorption isotherms were performed in a series of flasks (250 ml) where solutions of Congo red (100 ml) with different initial dye concentrations (10-100 mg/l) were placed in these flasks. Equal mass of 0.1 g of clay with particle size of 100 μm was added to Congo red solutions and shaking at room temperature. Then, the mixture was agitated for predetermined period of time at a constant speed (250 rpm).

Analysis: The concentration of residual dye was measured using UV/VIS spectrophotometer (UV/VIS-1650 PC SHIMATZU) at λ_{max}. corresponding to the maximum absorption for the dye solution (λ_{max} = 498 nm) by withdrawing samples at fixed time intervals, filtered and the supernatant was analyzed for residual Congo red.

Dye uptake: The amount of dye adsorption at equilibrium, q_e (mg/g), was calculated using the following equation[15]:

$$q_e = (C_o - C_e) V m^{-1} \quad (1)$$

where, C_o, C_e = The initial and equilibrium dye concentration in liquid phase (mg/l) respectively.

V = The volume of dye solution used (L)

m = The mass of adsorbent used (g)

The percentage of dye removal (p) was calculated using the relationship below:

$$P\% = \frac{(C_o - C_e)}{C_o} * 100 \quad (2)$$

3 Results and Discussion

3.1 Effect of contact time

The effect of contact time on the adsorption of Congo red dye onto clay can be shown by Fig. 3. It can be noticed, that the amount of dye adsorbed (mg/g) was rapid in the initial stages of the contact period (20-140 min.) and become slow near the equilibrium. In between these two stages of the uptake, the rate of adsorption was found to be nearly constant after equilibrium time (60 min.) with higher value of uptake.

This result is expected because a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to occupy due to repulsive forces between the solute molecules of the solid and bulk phases[16].

Figure 3 reveals that the curve are smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dye on the adsorbent[17, 18].

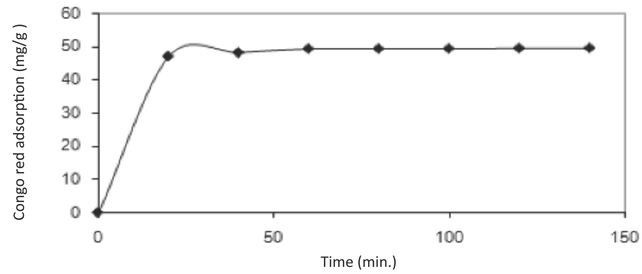

Fig. 3 Effect of contact time for adsorption of Congo red onto natural Iraqi palygorskite at initial dye concentration of 50 mg/l, adsorbent dose of 0.1 g, and particle size of 100 μm.

3.2 Effect of pH

pH is one of the most important parameters, that affects the adsorption of dye onto adsorbent particles. The adsorption capacity influencing the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process[19].

The rate of H^+ concentration was examined from samples at different pH covering a range of 2-10 (Fig. 4a, b).

During batch experiments, as the pH of the system increases, the number of negatively charged sites on adsorbent increases and the number of positively charged sites

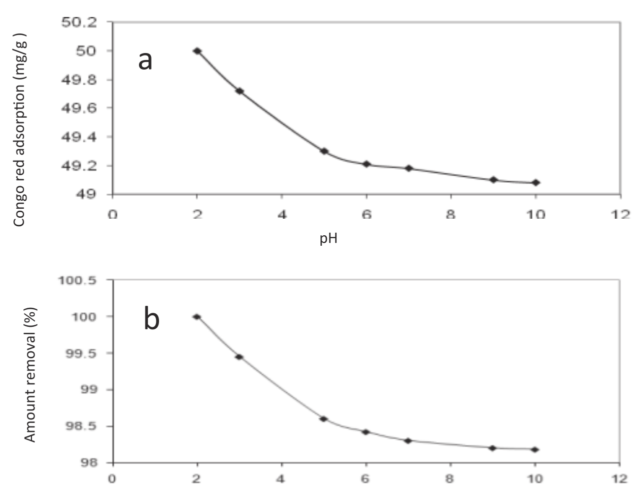

Fig. 4 Adsorption of Congo red by palygorskite as a function of solution pH at initial concentration of 50 mg/l and adsorbent dosage of 0.1 g with 100 μm particle size. (a) Amount of dye adsorbed (mg/g). (b) Percentage uptake.

decreases. The adsorption capacity and removal nearly constant over a wide range of pH2 to pH10 is suggestive of chemisorptions as more favored mechanism over electrostatic mechanism of adsorption[20].

Similar result was observed for the adsorption of Congo red dye by waste banana pith[21].

3.3 Effect of initial dye concentration

From Fig. 5, it can be seen that the amount of dye adsorbed (mg/g) increased with increased initial dye concentration. The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phase[22, 23]. Hence a higher initial concentration of dye will enhance the adsorption process. The actual amount of dye adsorbed per unit mass of palygorskite increased from 9.89 to 90.25 mg/g.

A similar trend was also observed for methylene blue adsorption onto parthenium hysterophorus[24] and methylene blue onto bamboo-based activated carbon[18, 25].

3.4 Effect of adsorbent dosage

Figure 6a shows the percentage removal versus adsorbent dose. It was found that the removal efficiency of dye increased with increasing adsorbent dose from 0.05-0.3 g. That is, in the case of Congo red the removal efficiency increased from 97% at 0.05 g/100 ml to 100% at 0.1 g/100 ml. The removal efficiency almost become constant at the doses of more than 0.1 g/100 ml. It was apparent that the number of available adsorption sites increases by increasing the adsorbent dose and that results in the increase of removal efficiency. Another reason may be due to the aggregation/agglomeration of adsorbent particles at higher concentration. Such aggregation would lead to decrease in total surface area of palygorskite particles available to Congo red adsorption and an increase in diffusional path length[26].

Similar fact was reported by Mumin et al.[27], Hameed et al.[25] and Taha et al.[18]. However, the amount of Congo red adsorbed per unit weight of adsorbent decrease with increase in adsorbent dose Fig. 6b. The adsorption capacity dropped from 99.67 to 16.67 mg/g by increasing the adsorbent dosage from 0.05 to 0.3g/100 ml. The drop in adsorption capacity is basically due to sites remaining unsaturated during the adsorption process. Similar result was observed by Hsu et al.[9], Malarvizhi and Sulochana[28], and, Patil and Shrivastava[29].

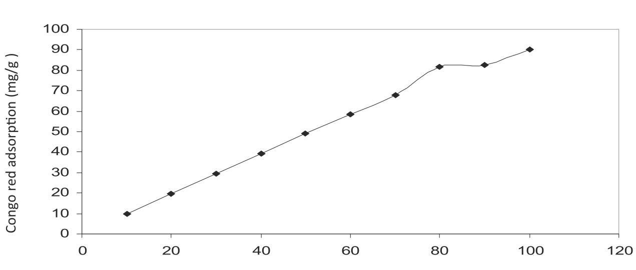

Fig. 5 Effect of initial concentration on adsorption capacity of Congo red onto palygorskite (100 μm particle size and 0.1 g adsorbent dose).

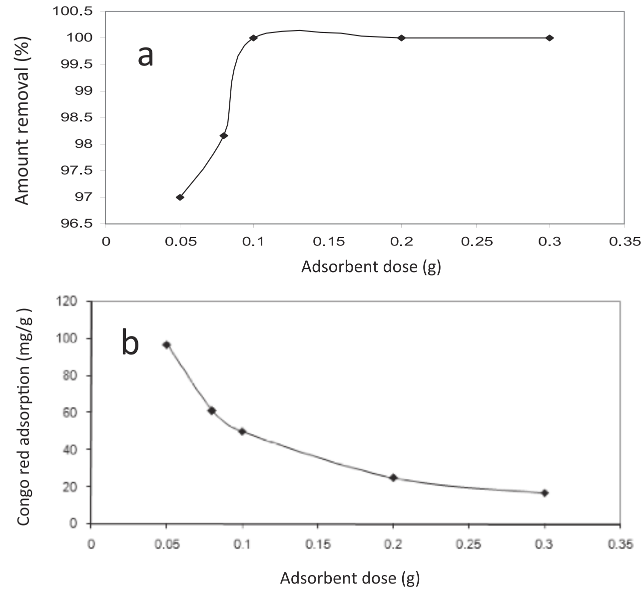

Fig. 6 Adsorption of Congo red by palygorskite as a function of adsorbent dosage at initial concentration of 50 mg/l and 100 μm particle size. (a) Percentage uptake. (b) Amount of dye adsorbed(mg/g).

3.5 Effect of particle size of adsorbent

The relationship between the amounts of dye adsorbed at range of 100-1000 μm palygorskite particle sizes is shown in Fig. 7, which shows that the particle size of palygorskite has a strong effect on the adsorptive processes when the diameter reduction of particles achieves the μm scale.

It can be seen that the adsorption capacity increases with decreasing particle size of the adsorbent. This indicates that the smaller the palygorskite particle size for a given mass of palygorskite, the more surface area is available and as a consequence the greater the number of binding sites available[30−32]. Adsorption capacity at 1000 μm is lower than at other sizes between 100-500 μm. Then higher adsorption capacity obtained at smaller particle size (100 μm) and it is equal to 48.36 mg/g. Therefore, 100 μm is considered as optimum particle size.

3.6 Modeling of adsorption isotherm data

Adsorption isotherms were investigated to evaluate the applicability of the adsorption process for the removal of dyes from industrial wastewater. The interactions between the adsorbates and adsorbents have been described by

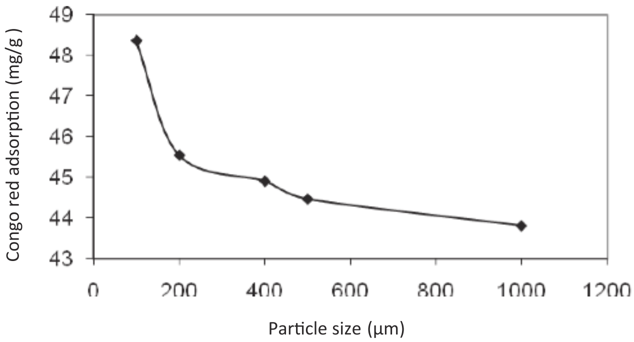

Fig. 7 Effect of particle size on adsorption capacity of Congo red onto palygorskite at initial dye concentration of 50 mg/l and adsorbent dose of 0.1 g.

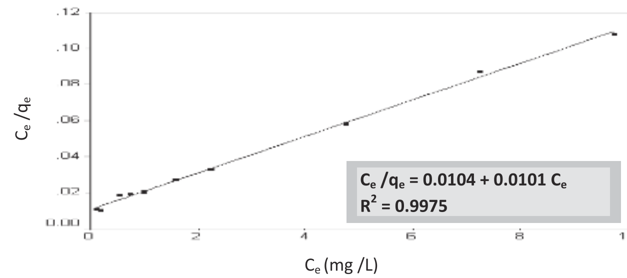

Fig. 8 Linear Langmuir model for adsorption of Congo red onto natural palygorskite.

several models for the adsorption isotherms[33]. The equilibrium adsorption isotherm is very useful to design the adsorption systems. In present study, the equilibrium data were treated by Langmuir and Fruendlich isotherm models.

Langmuir isotherm takes an assumption that the adsorption occurs at specific homogenous sites within the adsorbent; the equation is the following[34]:

$$q_e = \frac{qmKaC_e}{1 + KaC_e} \quad (3)$$

The linearized form of the Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a\, q_m} \quad (4)$$

Where, q_e is the amount of Congo red adsorbed per unit mass of adsorbent (mg/g) and C_e is the concentration of the dye solution at equilibrium (mg/l). q_m and K_a are Langmuir constants related to the maximum adsorption capacity (mg/g) and the adsorption energy between the adsorbate and adsorbent (l/mg). The constants q_m and K_a can be calculated from the plot between C_e/q_e versus C_e (Eq.4) entire the concentration range.

The values of q_m and K_a shown in Table 3 were determined from the slope and intercept of the linear plot (Fig. 8).

The maximum adsorption capacity (q_m) was 99 mg/g dye per gram of palygorskite for Congo red.

Table 2 lists the maximum monolayer adsorption capacity of Cong red dye on various adsorbent.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter called separation factor (R_l) which is defined by following equation[35, 36]:

$$R_L = \frac{1}{1 + K_a\, C_o} \quad (5)$$

Where K_a is the Langmuir constant and C_o is the initial concentration (mg/l). The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The results that the R_L values were in the range of 0-1 as shown in Fig. 9, indicate that the Langmuir isotherm model was favorable for adsorption of Congo red dye onto palygorskite under the conditions used in this study.

The Freundlich isotherm[37] based on adsorption on hetero-

Table 2 Maximum monolayer adsorption capacities (q_m) of Congo red on various adsorbents reported in literature.

Adsorbent	q_m (mg/g)	Reference
Australian kaolines	7.27	Vimonses et al.[40]
Cattail root (aquatic plant)	38.79	Hu et al.[41]
Perlite	55.55	Vijayakumar et al.[42]
Palm kernel coat	79.37	Oladoja et al.[43]
Waste red mud	4.05	Namasivayam and Arasi[44]
Soil	15.03	Camelia et al.[45]
Jute stick	35.7	Panda et al.[46]
Open burnt clay	22.86	Mumin et al.[27]
Bagasse fly ash	11.88	Mall et al.[47]
Coir pith	6.7	Namasivayam and Kavitha[20]
Natural Iraqi palygorskite clay	99	This study

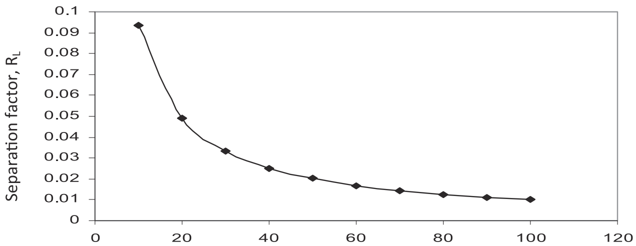

Fig. 9 Separation factor versus initial Congo red concentration onto natural palygorskite.

geneous surface is the earliest known relationship describing the adsorption equilibrium and is given by:

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

The linear form of this model takes the form:

$$\text{Log } q_e = \log K_F + 1/n \log C_e \quad (7)$$

Where K_F and 1/n are the Freundlich constants that are associated with adsorption capacity and adsorption intensity respectively. The values of K_F and 1/n are shown in Table 3.

The other parameters have been defined as in equation (3) and (4).

A plot of log q_e versus log C_e gives a straight line (Fig. 10), with slope and intercept of which correspond to 1/n and log K_F, respectively.

The value of 1/n smaller than 1 points out the favorable adsorption conditions[38, 39].

This is in a great agreement with the findings regarding to R_L value. The value of Freundlich constant indicated easy uptake of Congo red from aqueous solution.

The adsorption pattern for Congo red onto palygorskite clay obeyed both Langmuir and Freundlich models, but taking into consideration the values of (R, R^2, S.E.) listed in Table 3 as a criterion for goodness of fit for the investigated system, and comparing by Fig. 11, it can be seen that Langmuir isotherm model is better in describing the adsorption of Congo red than Freundlich, because, the Langmuir model shows better correlation between the theoretical and experimental data for the whole concentration range.

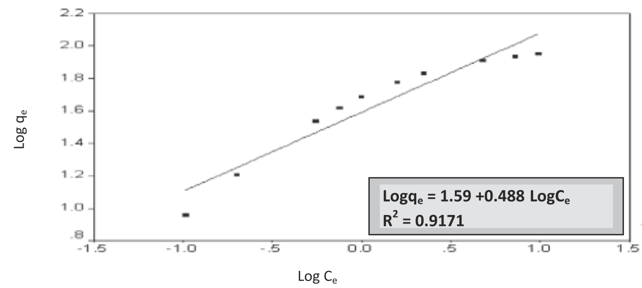

Fig. 10 Linear Freundlich model for adsorption of Congo red onto natural palygorskite.

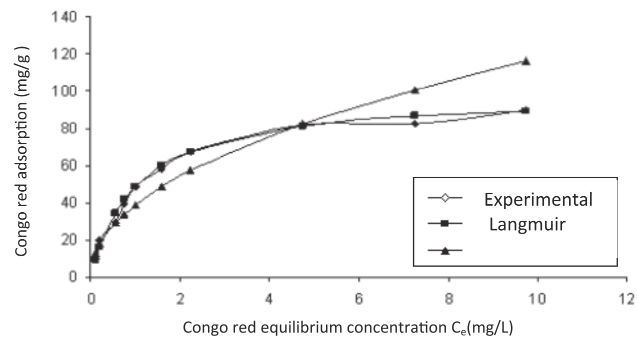

Fig. 11 Comparison of experimental and calculated data by Langmuir and Freundlich equilibrium isotherms for the system Congo red-natural Iraqi palygorskite.

The fitting of Langmuir's model indicated the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. The Ntural Iraqi palygorskite clay adsorbent was capable of adsorbing direct dyes with high affinity and capable indicating its potential as low cost alternative adsorbent.

Table 3 Isotherm parameters for adsorption of Congo red onto natural Iraqi palygorskite.

Langmuir (95% Confidence level)		Freundlich (95% Confidence level)	
q_m (mg/g)	99	K_F (mg/g) $(l/mg)^{1/n}$	39
K_a (l/mg)	0.97	1/n	0.488
R	0.9987	R	0.9576
R^2	0.9975	R^2	0.9171
Standard error of the estimate (S.E.)	0.0018	Standard error of the estimate (S.E.)	0.1008
R_L	(0.0102-0.0934)		
Equation $q_e = 96.03\ C_e/1 + 0.97\ C_e$		Equation $q_e = 39\ C_e^{0.488}$	

4 Conclusions

Certain general conclusions may be deduced from the experimental and theoretical analysis of adsorption studies of Congo red onto natural Iraqi palygorskite:

- The present study shows that the natural Iraqi palygorskite, an abundant low-cost clay, can be successfully used for the removal of Congo red dye from aqueous solutions.
- The amount of dye sorbed was found to vary with contact time, initial pH, initial Congo red concentration, adsorbent dose, and particle size of adsorbent.
- The experimental results were analyzed using 2 adsorption isotherm models- the Langmuir and Freundlich. Based on the correlation coefficients value from the 2 models along with the values of $R_L < 1$, the analytical data showed that the Langmuir isotherm offers the best fit of the data, indicating monolayer adsorption on a homogenous surface.
- The value of the monolayer saturation capacity of Iraqi palygorskite was comparable to the adsorption capacities of some other adsorbents for Congo red dye.
- As the material is cheap, abundantly available and naturally occurring in wide sites of western regions of Iraq with large quantities, no regeneration is necessary. On other hand, the adsorbed organic dye is burned off at 1000-1100 F° and the clay is re-used.

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