

## Sorption Study of Methyl Orange on the Iraqi Kaolinite Clay

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### Abstract

The sorption of methyl orange on the kaolinite clay was studied thermodynamically and kinetically, the sorption was of Freundlich type and the multi-layers were formed, and the sorption was a combination of adsorption and absorption, but in some cases the desorption was occurred. The Freundlich constants were calculated to specify the sorption capacity, and sorption intensity. The calculation of thermodynamic parameters revealed that the process was exothermic, ordered, and non-spontaneous at the temperature range(298-328K). Three kinetic models were exploited to calculate the rate constant, diffusion constant, rate of adsorption, and desorption parameter.

Keywords: kaolinite, sorption isotherms, kinetic study, thermodynamic parameters.

### Introduction

In general, there are four main methods of reducing color in textile effluent streams: physical methods such as membrane technology [1], chemical methods such as coagulation, photochemical oxidation processes, biological methods such as anaerobic/aerobic sequential process and physicochemical processes [2]. Among the physicochemical processes, adsorption technology is considered to be one the most effective and proven technology having potential application in both water and wastewater treatment. Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how much those components can be accommodated by a solid adsorbent [3]. Modeling of sorption isotherm data is important for predicting and comparing adsorption performance. A few two-parameter isotherm models are available for modeling adsorption data. Freundlich (Freundlich, 1906) and Langmuir (Langmuir, 1918) models are the most commonly used two-parameter isotherms. The Langmuir has put a mathematical formula, which is expressed as follows:

$$Q_e/Q_{\infty} = (1 + a/K) \cdot C_e \dots \dots \dots (1)$$

Where Q is the amount of adsorbate (mg/g), C<sub>e</sub> is the equilibrium concentration (mg/L), and a, K are constants related to the binding strength respectively or sometimes called Langmuir constants [4].

The Freundlich has put an equation that deals with heterogeneous surfaces [5], at which the multilayer aggregation may occur; the equation could be expressed as follows:

$$Q = K_F C_e^{1/n} \dots \dots \dots (2)$$

Where Q is the adsorbate quantity (mg/g), C<sub>e</sub> is the concentration of adsorbate at equilibrium (mg/L), K<sub>F</sub>, and n are Freundlich constants.

A mono-azo dye methyl orange (p-dimethylamino - azobenzenesulfonicacid), (Meo) supplied by BDH Limited., having molecular formula of C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S and molecular weight of 327.33 g.mol<sup>-1</sup>, was used as sorbate in this study. Methyl orange has been chosen as a simple model of a series of common azo dyes largely used in the industry [6]. Its structure, reported in Fig.(1).

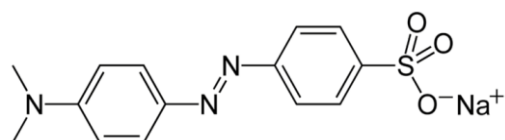


Fig. (1) Structural formula of methyl orange.

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedral[7].

Kaolinite has a low shrink-swell capacity and a low cation exchange capacity (1-15 meq/100g). It is a soft, earthy, usually white mineral (dioctahedral phyllosilicate

clay), produced by the chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors.

Kaolinite clay occurs in abundance in soils that have formed from the chemical weathering of rocks in hot, moist climates for example in tropical rainforest areas. Comparing soils along a gradient towards progressively cooler or drier climates, the proportion of kaolinite decreases, while the proportion of other clay minerals such as illite (in cooler climates) or smectite (in drier climates) increases [8,9].

## Experimental Part

### Chemicals:

Methyl orange was supplied by BDH Limited, and glacial acetic acid supplied by BDH.

Kaolinite clay was taken from the geological survey-Iraq, and collected from Al-Safra, and had the following composition:

**Table (1)**  
**The composition of kaolinite clay.**

Constituent	wt/wt %
SiO <sub>2</sub>	48.57
Al <sub>2</sub> O <sub>3</sub>	35.05
CaO	0.6
MgO	0.77
K <sub>2</sub> O	0.08
Fe <sub>2</sub> O <sub>3</sub>	1.34
TiO <sub>2</sub>	1.19
L.O.I	12
Moisture	0.08
Total	99.68

### Procedure:

A set of methyl orange solutions was prepared of concentration (1,2,4,6,8,10,14 and 20) ppm and calibration curve was made at 475 nm.

### Sorption experiments

The sorption experiments were accomplished by using water bath shaker at 298 K and for a contact time 50 minutes with

using 0.5g kaolinite clay which has been activated by washing it with glacial acetic acid and dried at 338 K.

The following formula used to calculate the concentration of sorbate after sorption experiments [10]:

$$Q_e = V_{sol} (C_o - C_e)/m \dots\dots\dots(3)$$

Where  $Q_e$ ,  $V_{sol}$ ,  $C_o$ ,  $C_e$ , and  $m$  are quantity of sorbate in  $mg.g^{-1}$ , volume of solution in L, initial concentration of sorbate in  $mg.L^{-1}$ , concentration of sorbate at equilibrium in  $mg.L^{-1}$ , and weight of sorbent in g respectively.

### Determination of contact time

A 0.5g of kaolinite clay (activated) was put in round flasks and 50 ml of 4,6,8 ppm of methyl orange were poured into the round flasks and all flasks were closed by parafilm and shaken for 10,20,30,40,50,60,70, 80, 90, and 100 minutes. It founded that the steady state occurred at 50 minutes and this contact time fixed for all sorption experiments.

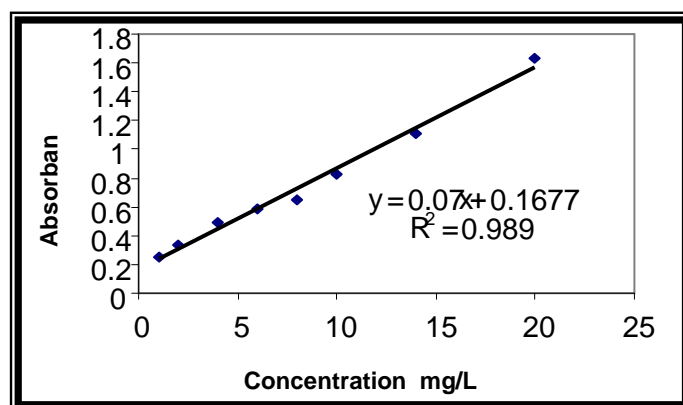
### Determination of sorption isotherms

A 0.5 g of kaolinite was added into three flasks containing 50 ml of 4,6, and 8 ppm methyl orange solutions and shaken for specific periods of time and at 298 K, thereafter, the solutions were filtered and absorbance of each solution was measured at 475 nm by using UV-Visible spectrophotometer.

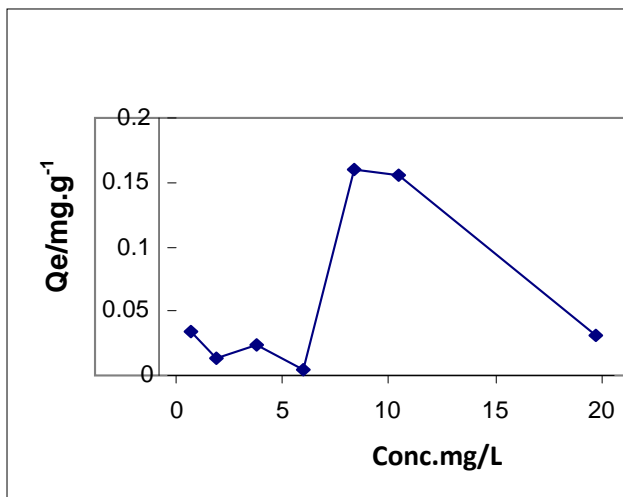
## Results and Discussion

### Calibration Curve

The calibration curve was made for a set of methyl orange solutions and as shown below in Fig.(2):

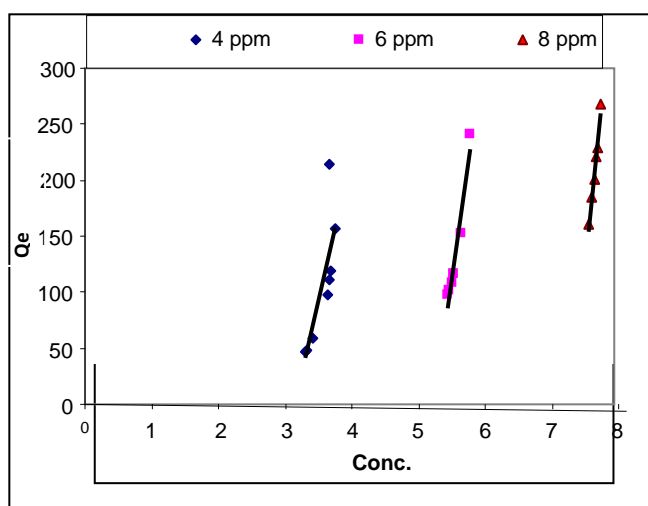


**Sorption isotherms**



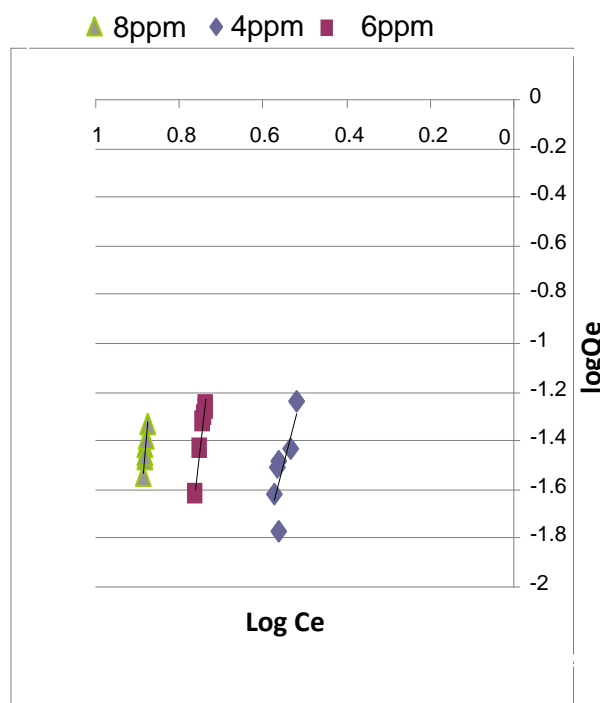
**Fig. (3) The sorption Isotherm of concentration range (1-20ppm) at 298K.**

Fig.(3) showed that the sorption isotherm was non-linear, since it may be considered like S-shape, thereafter the sorption may occur as a multilayer form, and the molecules of methyl orange will aggregate on the surface of kaolinite to form multilayers.



**Fig. (4) The Langmiur isotherms of 4,6,and 8ppm solutions at 298K.**

Fig.(4) showed that the Langmiur isotherms of sorption process were not in match with standard isotherms, (i.e.) linearity of isotherms were not good enough to judge that the sorption occurred as a monolayer.



**Fig. (5) The Freundlich isotherm at 298K.**

Fig. (5) showed that the Freundlich isotherms were in better linearity than Langmiur isotherms, so the sorption process occurred in a multilayer aggregation.

The Freundlich parameters were calculated from the plot via applying equation 2, and as listed below:

**Table (3)  
The Freundlich parameters.**

Concentration/mg.L <sup>-1</sup>	K <sub>F</sub>	n
4	4.6x10 <sup>-7</sup>	0.5
6	1.8x10 <sup>-15</sup>	0.164
8	3.6x10 <sup>-20</sup>	0.063

K<sub>F</sub> is a constant related to the extent of sorption, and n is a constant related to the intensity of sorption or the degree of dependence of sorption on concentration [11], so at 4 ppm the sorption intensity is maximum, whilst, the sorption capacity is low but still greater than the values at 6 or 8 ppm.

**Kinetic Study**

Three kinetic models were employed in this study to calculate the rate of adsorption and the rate-limiting step of the process and the energy of activation as well.

**Lagergren Model [12]**

The rate constant **ksorp** was determined from the following pseudo-1st order rate expression, which could be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_{sorp} t \dots\dots\dots(4)$$

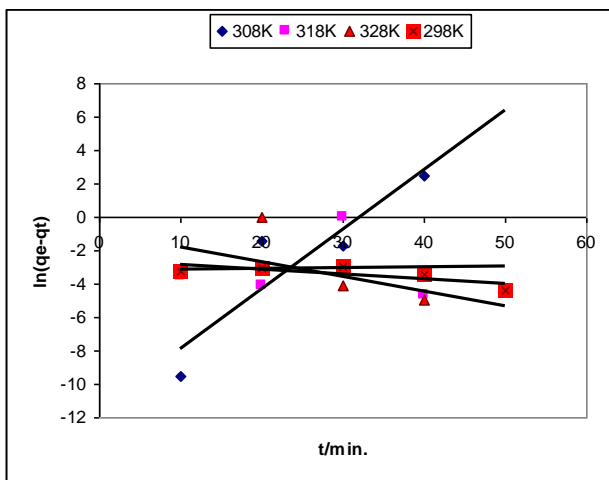
Where  $q_t$  and  $q_e$  (mg/g) are the amount sorbed at time  $t$  (min.) and at equilibrium successively, and **ksorp** ( $\text{min}^{-1}$ ) is the rate constant.

The linear relationship was obtained via plotting  $\ln(q_e - q_t)$  versus  $t$  (min.), and as shown below in Fig.(6).

The energy of activation was calculated via introducing Arrhenius equation:

$$\ln k_{sorp} = \ln A - E_a/RT \dots\dots\dots(5)$$

where  $A$  is Arrhenius parameter, which is a temperature independent factor.  $E_a$  is the activation energy ( $\text{kJ}\cdot\text{mol}^{-1}$ ) and  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ), and  $T$  is the temperature in kelvin. and  $E_a$  was  $4.956 \text{ kJ}\cdot\text{mol}^{-1}$ , the low value of energy of activation means that the sorption process occurred easily.



**Fig.(6) The Lagergren model at (298-328K).**

**Morris-Weber Model [13]**

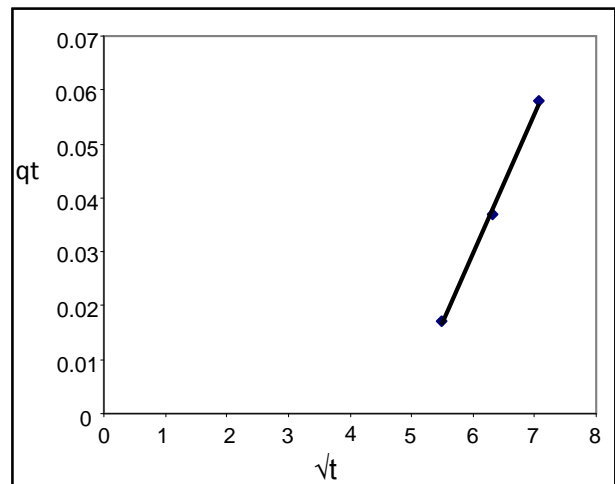
Morris and Weber (Swedish Scientists) introduced this kinetic model in 1963, and by using this kinetic model, the rate limiting step of any physi-sorption process could be easily estimated, and they have presented an equation which could be expressed as follows:

$$q_t = K_d \sqrt{t} \dots\dots\dots(6)$$

Where  $q_t$  is the quantity of the sorbed material at any time (mg/g),  $K_d$  is the diffusion constant, and  $t$  is the time of diffusion (min.).

The plotting of  $q_t$  versus  $\sqrt{t}$  was accomplished and as shown below in Fig. (7).

The value of  $K_d$  was  $2.5 \times 10^{-2}$  which indicated that the rate-limiting



**Fig.(7) Morris-Weber model at 298K.**

Step of sorption process is adsorption at 298K, but the diffusion of methyl orange molecules from the bulk solution was so slow, meanwhile the interaction with the surface of kaolinite clay was good, in other words the accommodation of methyl orange molecules on the surface of kaolinite clay needed a long time in order to be fair enough to adsorb much more molecules from the bulk, and that's why the contact time for sorption was relatively long.

**Elovich Model [14]**

This model is generally expressed as in the following equation

$$q_t = \ln \alpha \beta + \ln t / \beta \dots\dots\dots(7)$$

Where  $\alpha$  is the initial adsorption rate ( $\text{mg}/\text{g}\cdot\text{min}$ ),  $\beta$  is the desorption constant,  $q_t$  is the adsorption quantity at any time, and  $t$  is the time in minutes.

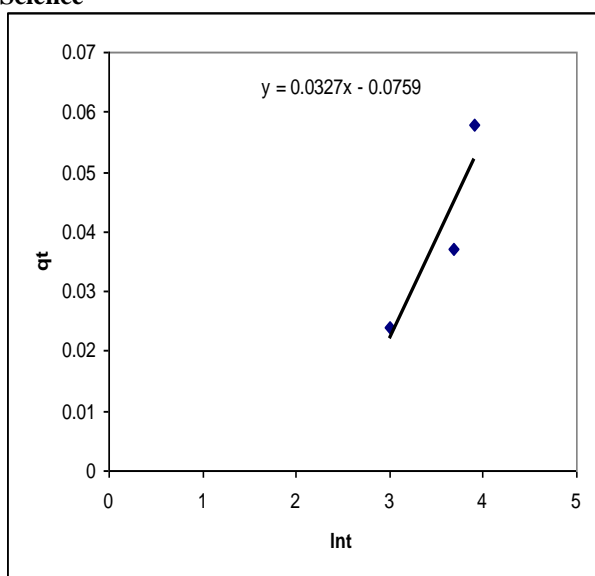


Fig. (8) Elovich Mode.

The  $\alpha$ , and  $\beta$  were calculated, since  $\alpha = 1.0785 \text{ mg.g}^{-1}.\text{min}^{-1}$ , and  $\beta = 30.58$ , the low value of  $\alpha$  means that the adsorption process

was too slow in comparing with desorption constant  $\beta$  which is relatively high, which means that the desorption process at the entire concentration may occur.

### Thermodynamic Parameters

The thermodynamic parameters were calculated using the following formulas [15] and listed in Table (4).

$$b = a \cdot \exp(\Delta H/RT) \dots \dots \dots (8)$$

$$\ln b = \ln a - (\Delta H/R) \cdot 1/T \dots \dots \dots (9)$$

$$\ln a = \Delta S/R \dots \dots \dots (10)$$

$$\Delta G = \Delta H - T\Delta S \dots \dots \dots (11)$$

Where  $b$  is the maximum sorption quantity which could be calculated from the Langmuir isotherms,  $a$  is the pre-exponential factor,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  are enthalpy, entropy, and Gibbs free energy respectively.

Table (4)  
Thermodynamic paramaters.

T/K	$\Delta H/\text{kJ.mol}^{-1}$	$\Delta S/\text{kJ.mol}^{-1}.\text{K}^{-1}$	$\Delta G/\text{kJ.mol}^{-1}$
298	-9.481	-9.49	+2818.5
308	-9.226	-7.63	+2340.8
318	-8.999	-5.97	+1889.4
328	-9.135	-5.52	+1801.4

All the  $\Delta H^s$  were negative, thereafter the sorption processes were exothermic; hence, the adsorption is highly expected at the entire range of temperatures.

All the  $\Delta S^s$  were negative, so the adsorption processes have low entropy; since the low entropy means low disorder and the system is ordered; but when the temperature was raised; the entropy was significantly raised, this could be attributed to the high temperature that increases the kinetic energy and the methyl orange molecules will be in random orientation on the surface of kaolinite clay.

The  $\Delta G^s$  were positive, hence the sorption process was non-spontaneous, but when the temperature was raised the  $\Delta G$  was decreased; hence the sorption process is a combination of two processes, absorption, and desorption at

high temperature, but at low temperature the adsorption and absorption occurred.

### Conclusions

1. The sorption process at 298K is exothermic, less entropy, and less free energy, hence, the process is chemisorption, and is a blend of adsorption and absorption as well, more ordered, and non-spontaneous.
2. The energy of activation is low and the sorption is so fast.
3. The desorption process could be occurred at higher concentrations of methyl orange.
4. The kaolinite is a good sorbent for the methyl orange; and the dye was adequately removed from the solution.

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### الخلاصة

تمت دراسة امتزاز المثيل البرتقالي على طين الكاولين دراسة حركية وثرموديناميكية، ولقد كان الامتزاز من نوع فرويندلش وتكونت عدة طبقات للامتزاز على سطح المادة المازة، وقد كانت العملية عبارة عن خليط بين الامتزاز والامتصاص، ولكن في بعض الحالات حصلت عملية الابتزاز. تم حساب ثوابت فرويندلش لغرض تحديد سعة الامتزاز وشدته على السطح، وايضا تم حساب المعاملات الثرموديناميكية وقد بينت ان عملية الامتزاز كانت باعثة للحرارة، ومنظمة، وغير تلقائية ضمن المدى الحراري (٢٩٨-٣٢٨ كلفن). تم استخدام ثلاث اشكال حركية لغرض حساب ثابت سرعة العملية، وثابت الانتشار، معدل عملية الامتزاز، ومعامل الابتزاز.