

Adsorption Ability and Kinetic of (Congo Red, Methyl Green) Dyes on Iraqi Siliceous Rocks

Israa Mohammed Tawfeeq, Ammar Jasim Mohammed

Chemistry Department, College of Education of Pure Science-University of Baghdad / Iraq.

Abstract

In this study used Iraqi Siliceous Rock powder (SRP) as a suitable surface to study removing of dyes, which are they [Cong red dye (CR) and Methyl green dye (MG)]. Adsorption isotherms and the factors which influence the adsorption process such as temperature and salt effect were studies. Adsorption isotherms of (CR) were found to be comparable to Temkin equation according to Giles classification. Adsorption isotherms of (MG) were found to be comparable to Freundlich equation according to Giles classification. The adsorption process on surface was studies at various temperatures. The results indicate that the adsorption of (CR) on surface decreased with increasing temperature (Exothermic process), while the adsorption of (MG) on surface increased with increasing temperature (Endothermic process). According to above results of thermodynamic functions (ΔG , ΔS , ΔH) were calculated. The salt effect of adsorption of (CR, MG) dyes at (293 K) were studied .The adsorption quantity for (MG) increasing with increasing the salt solution, while the adsorption quantity for (CR) dye decreasing with increasing the salt solution. The Kinetics of adsorption process of (CR, MG) dyes on surface were studied. The results were treated according to (Lagergren equation). The Kinetics experimental data properly correlated with First-order kinetic model.

Keywords: Siliceous Rock, Adsorption, Congo red Dye, Methyl Green Dye.

Introduction

Water pollution is one of the biggest problems of pollution because of the large role of water in our daily lives. Water pollution takes many forms such as poisoning with detergents, pesticides or with industrial waste of virous kinds [1]. Dyes are among organic substance contaminated to water resources because of their widespread use in various industries [2]. Congo Red (CR) a poisonous dye that causes cancer [3], Methyl Green (MG) not generally usable in medical fields [4]. Many problems went after the problem of pollution in previous years to think of finding appropriate methods to remove these pollutants, the most important

techniques are adsorption on a rocky or clay surface and also some chemical methods such as silica gel and ozone [5]. In this research, removal of the dyes (CR, MG) by adsorption on Iraqi Siliceous Rock powder (SRP).

Materials and Methods

Materials

Siliceous Rocks

Siliceous Rocks were providing by (The State Company of Mining and Geological Survey). The rocks were got from Ukashat west of Iraq. The chemical composition of the rocks by the company showed in Table (1).

Table.1: Rocks Analyses

Compound	Wt%
SiO ₂	66.01
Al ₂ O ₃	2.12
Fe ₂ O ₃	0.62
TiO ₂	0.05
P ₂ O ₅	0.93
CaO	8.44
MgO	6.47
Na ₂ O	0.62
K ₂ O	0.13
Loss on Ignition	14.11
Total	99.5

Siliceous Rocks have a yellowish white color, Low density and a large surface area.



Fig.1: Siliceous Rocks powder (SRP)

The rocks powder was washed by huge amounts of deionized water to remove the soluble materials. It was dried for 6 hours at 60 °C [5]. Then the surface was smashed into small parts. The size of particle was 75 µm, and it was used for the surface in work.

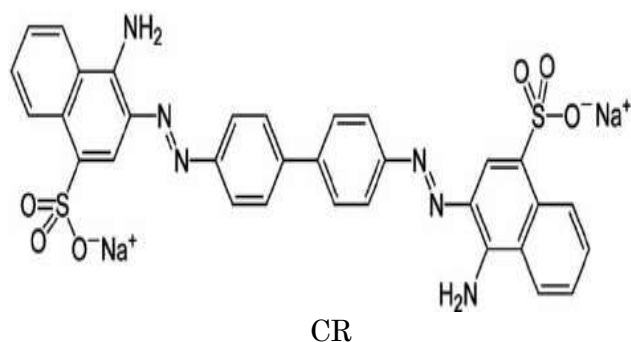


Fig. 2: Structures of CR and MG. [6, 7]

Method

- **Technique:** (UV) Technique was used to determine the adsorption as function of concentration. The wavelength of absorption for Congo Red, Methyl Green were (498, 618) nm respectively.
- **Contact time:** to determine required time for equilibrium between adsorbent and adsorbate mixed certain concentration with (0.05 gm) (0.01 gm) of (SRP) and they were put into water bath shaker at 20 °C, to determine the change in concentration with time passing samples were taken from solution in different sequenced time.
- **Adsorption isotherms:** to determine the adsorption isotherms for (CR, MG) dyes solutions, Putting (0.05 gm) (0.01 gm) of surface in six round flask and add (50 ml) of dyes (CR, MG) solution then placed these flasks in water bath at (20 °C) for (CR=30

2-Dyes

(CR) and (MG) were supplied by (BDH), NaCl supplied by (Fluka), and deionized water had been used.

min, MG=90 min). After the equilibrium time, the mixture was separated using centrifuge for (15 min) and at (85 rpm). After the separation the adsorption of solution was measured by UV spectrophotometer.

The adsorption amount was calculated according to the following equation [8]:

$$Q_e = \frac{V_{sol}(C_0 - C_e)}{m}$$

Q_e = the quantity of adsorbate (mg/g).

V = volume of solution (L).

C_0 = initial concentration (mg/L).

C_e = equilibrium concentration (mg/L).

m = mass of the surfaces (g).

To follow the adsorption of dyes on (SRP) surface when the temperature changed the

pervious steps were repeated at different temperatures.

Results & Discussion

Effect of Contact Time

For increasing the adsorption as function of time, the results show the contact time for (CR, MG) dyes at (30min, 90 min) respectively.

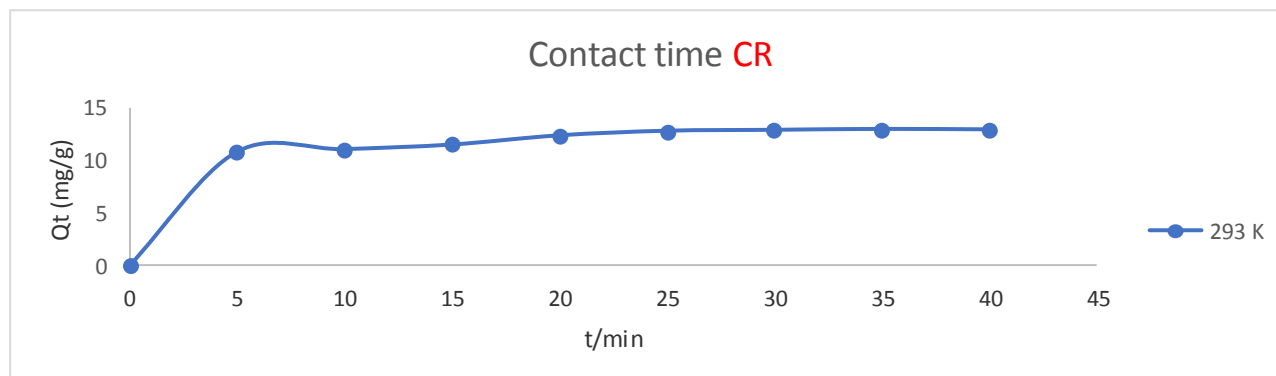


Fig.3: Effect of contact time on CR adsorption on SRP (temperature=20C^o, concertation=60 ppm, rotations per minute=85 rpm, equilibrium time=30 min



Fig.4: Effect of contact time on MG adsorption on SRP (temperature=20C^o, concertation=18 ppm, rotations per minute=85 rpm, equilibrium time=90 min

Adsorption Isotherms

The adsorbed quantities (Q_e) were calculated for each equilibrium concentration. The adsorption isotherm is shown in Figure (5):

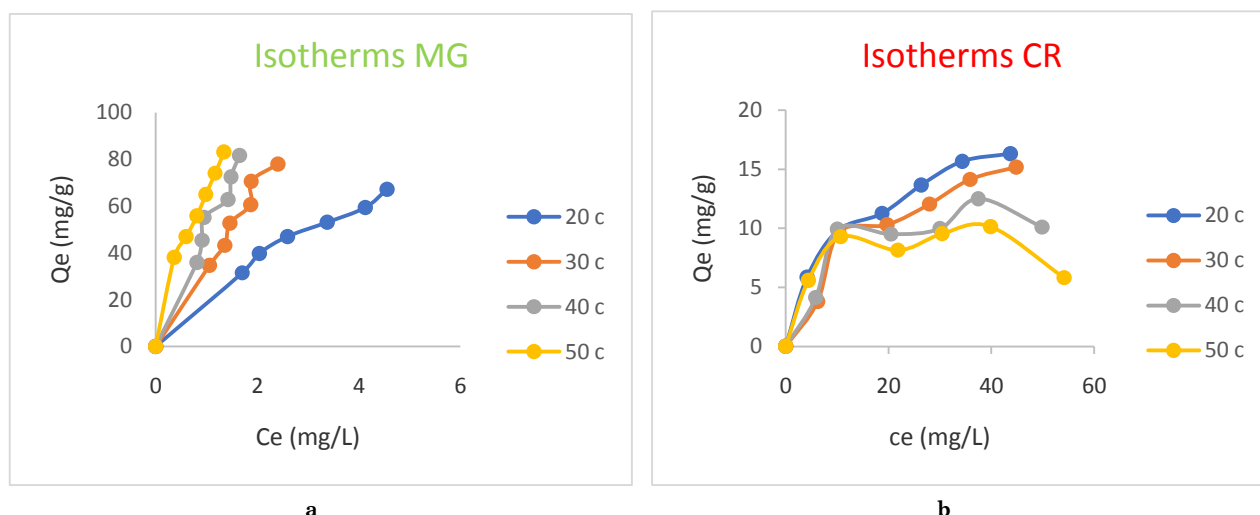


Fig. 5: (a, b) Adsorption isotherms models of (Congo red, Methyl Green) on SRP at different temperature

The general sketch of adsorption isotherms of (CR) on SRP surface according to the classification of Giles pointing out that was

(L₃), where the orientation of the adsorbate particles on the surface is measured horizontally [9]. Depend Temkin equation:

$$Q_e = b_T \ln K_T + b_T \ln C_e \qquad \dots \dots \dots \text{Temkin equation}$$

Where b_T, k_T Temkin constant. Q_e Vs $\ln C_e$ was plotted as shown in Figure (6). Temkin constant were calculated for (CR, MG) dyes as shown in Table (2).

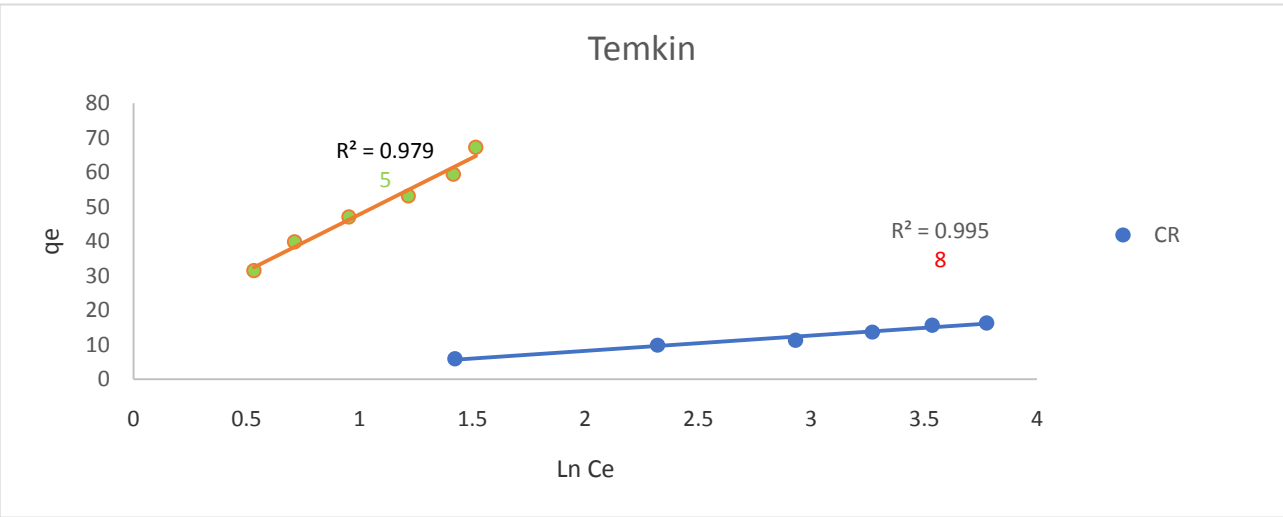


Fig. 6: Liner application of Temkin equation

Table 2: The value of Temkin constant (b_T, k_T) for adsorption of (CR, MG) on SRP

293 K			
Dyes	b_T	k_T	R^2
CR	6.4909	4.1885	0.9958
MG	32.884	1.5729	0.9795

While the adsorption isotherms of (MG) dye on the surface through the general sketch show that was (S_3) according to Giles classification, where the isotherm is taken in the S-shape form and the orientation of the particles that are adsorbate on the surface is either diagonal or vertical [9]. Depend Freundlich equation:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad \dots \dots \dots \text{Freundlich equation}$$

Where k, n = Freundlich constant. $\ln Q_e$ Vs $\ln C_e$ was plotted as shown in Figure (7), and Freundlich constant were calculated for (CR, MG) dyes as shown in Table (3).

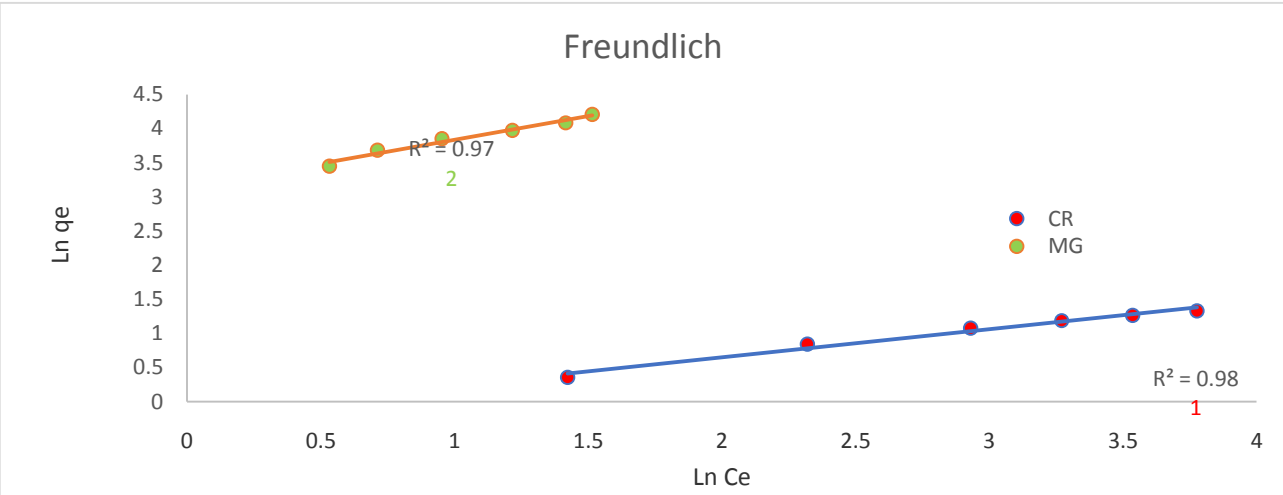


Fig. 7: Liner application for Freundlich equation

Table 3: The value of Freundlich constant (k_F, n) for adsorption of (CR, MG) dyes on SRP

293 K			
Dyes	k_F	n	R^2
CR	1.1929	2.4289	0.9816
MG	23.0946	1.4386	0.9729

The results shows that the adsorption quantity degraded for (CR) dye on surface when the temperature increased (Exothermic).While adsorption for (MG) dye on surface increased when the temperature increased (Endothermic), because the arrival of the surface to saturation and closure of pores on the surface.

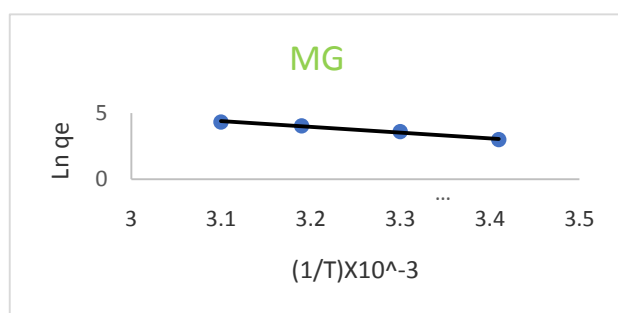
The Vant Hoff-Arrhenius equation was used to calculate the values of (ΔH).

$$\ln X_m = \frac{-\Delta H}{RT} + \text{Constant}$$

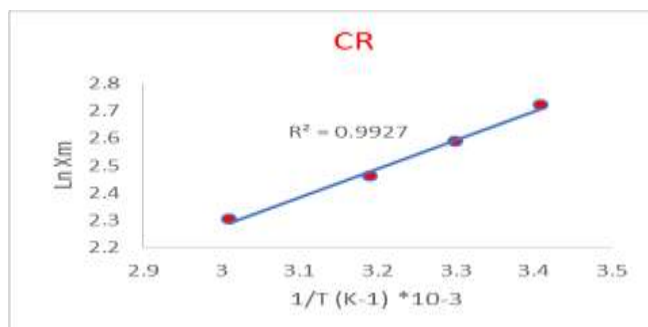
Where X_m = Maximum adsorbed quantity.

Table 4: The value of $\ln X_m$, T for (CR, MG) dyes on SRP

T (K)	CR		MG	
	X_m (mg/g) When $C_e=35$ (mg/L)	$\ln X_m$	X_m (mg/g) When $C_e=1.2$ (mg/L)	$\ln X_m$
293	15.2	2.72	20	3.04
303	13.3	2.60	37	3.60
313	11.7	2.46	57	4.06
323	10.0	2.30	76	4.27



a



b

Fig. 8: (a, b) Vant Hoff curves for adsorption of (CR, MG) dyes on surface

Table 5: The values of the thermodynamic functions at (293 K) of (CR, MG) dyes

Dyes	ΔH (J/mole)	ΔG (J/mole)	ΔS (J/mole)
CR	-9165	2057.6	-1971.82
MG	32953	-6934.1	32976.81

The negative values of (ΔH , ΔS) while (ΔS) were positive for (CR) dye. Prove that the adsorbed molecules were increasing randomly [10].

The positive values of (ΔH , ΔS) while (ΔG) were negative for (MG) dye. The adsorbent molecular arranged on surface [11].

= gas constant.

T = Temperature.

$\ln X_m$ Vs ($1/T$) inverted temperature was plotted as shown in Figure (8) (Table 4).

The Value of (ΔG , ΔS) was calculated depending on following equation. The value of (ΔG , ΔS) shown in (Table 5).

$$\Delta G = -nRT \ln \frac{Q_e}{C_e}$$

$$\Delta G = \Delta H - T\Delta S$$

Effect of Salt

The adsorption was studied in different salty range (0.01 M, 0.03 M) to (CR, MG) dyes as shown in Figure (9) .

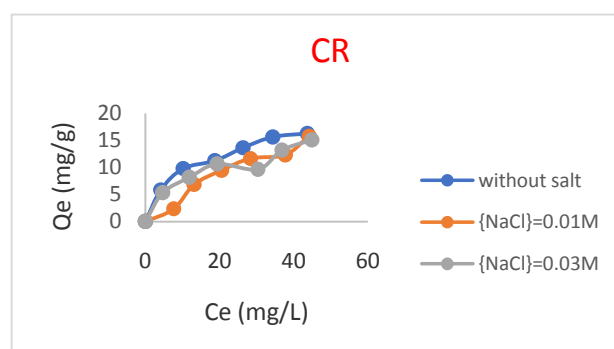
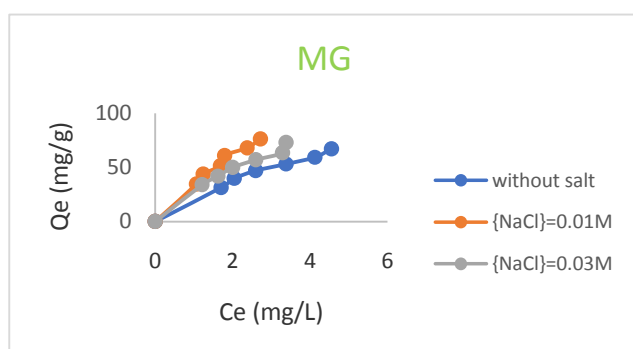


Fig. 9: Effect of salt on adsorption at (293 K) of (CR, MG) dyes on SRP

Increasing or decreasing adsorption with increase or decrease the solubility of the dyes in water solution is due to the fact that the interaction between the solvent and (NaCl) ions is higher or less than (CR, MG) dyes interference. This behavior can be explained by (Ambition) because this process results in the release of the Rock powder and the decompression of the saline solution, which change the geometry of the Rock powder pores, and thus increases or decreases adsorption according to surface change [12].

Adsorption Kinetic

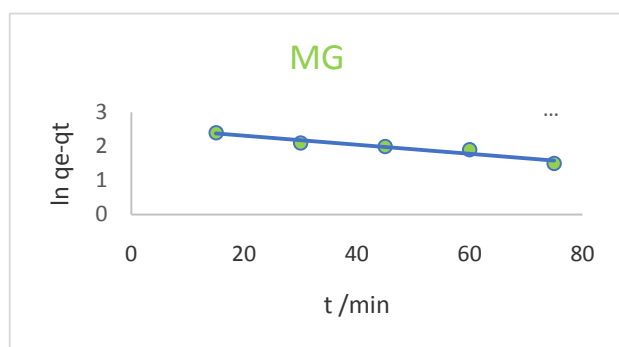
Using (Lagergren equation) the Kinetic studied for (CR, MG) dyes.

$$\ln (q_e - q_t) = \ln q_e - K_{ad}$$

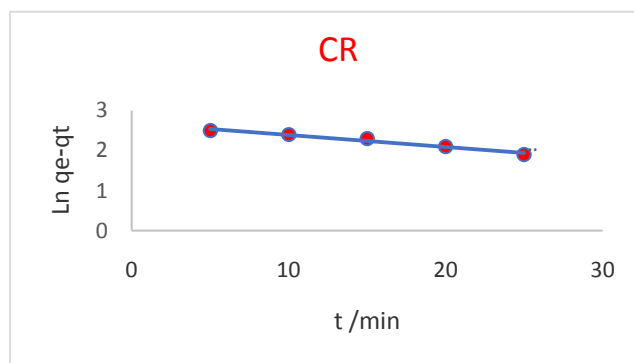
Where q_e & q_T = the adsorption capacity at equilibrium and time (t) (mg/L) respectively.

k_{ad} = the rate constant of pseudo first- order kinetic adsorption (min^{-1}).

The results of the study of the adsorption kinetics model of the first- order by plotting ($\ln q_e - q_T$) against time (t/min) as shown in Figure (10), Table (6) shows value of the rate constant of adsorption.



a



b

Fig. 10: (a, b) the adsorption kinetics of the (CR, MG) dyes on surface

Table.6: Value of the rate constant of adsorption for (CR, MG) dyes on surface

Dyes	$k_{ad} (\text{min}^{-1})$
Congo Red	2.69
Methyl Green	2.58

References

1. PC Vandervier, R Bianchi, WJ Verstraet (2001) "Flutes du monde Chem", Tech. Biotechnal., 17(4): 289-302.
2. PA Meginn J (2002) "State of the Word", Ed1, New York.
3. Yusef Omid Khaniabadi1, Mohammad Javad Mohammadi, Mojtaba Shegerd, Shahram Sadeghi, Sedigheh Saeedi, Hassan Basiri (2017) "Removal of Congo Red Dye from Aqueous Solutions by a low-cost Adsorbent: Activated Carbon prepared from Aloe Vera leaves Shell", Environmental Health Engineering and Management Journal, 4(1): 29-35.
4. Georgiadis IK, Papadopoulos A, Filippidis A, Godelitsas A, Tsirambides A, Vogiatzis D (2013) "Removal of Malachite Green Dye from Aqueous Solutions by Diasporic Greek Raw Bauxite", Bulletin of the Geological Society of Greece, 2: 927-933.
5. Al-Jarjary IA (2005) "Study of the factors affecting the Adsorption of same Azo Dyes complexes and calculations of the thermodynamic functions". M.Sc. Thesis, Mosul University, Iraq.
6. Muhammad Imran Khan, Shahbaz Akhtar, Shagufta Zafar, Aqeela Shaheen, Muhammad Ali Khan, Rafael Luque and Aziz ur Rehman (2015) "Removal of Congo red from Aqueous Solution by Anion Exchange Membrane (EBTAC): Adsorption Kinetics and Thermodynamics", Materials, 8: 4147-4161.
7. Suha Saheb Abd (2018) "Modification and Characterization of Iraq Bauxite Clay and its use as Adsorbent for the Methyl Green Dye from Aqueous Solution", M.SC. Thesis, University of Baghdad, Iraq.

8. Krut HR, Over Book JTG (1964) "Introduction to Physical Chemistry", Hott, Rinehart and Winston, Inc, 91.
9. FJ Hesselink (1977) "On the Theory of Polyelectrolyte Adsorption: The effect on Adsorption Behavior of the Electrostatic Contribution to the Adsorption free Energy", Colloid Interface Sci., 60: 448-664.
10. KK Panday, Guppresad NV Singh (1985) "Water Research ", 19(7):869 -873.
11. EHM Wright, NC Partt (1961)"Current Chemical Papars", J. Chem. Soc. Faraday Trans., 70: 14-61.
12. D Hillel (1980) "Fundamentals of Soil Physics", Academic Press, New York.