Study of The Ability and Kinetics of Adsorption in Aqueous Solution of Cationic Dyes (Malachite Green , Methylene Blue) on Iraqi Siliceous Rocks Powder

Ammar Jasim Mohammed**

Huda Yassien Khuder*

Hameed Khalid Ali*

***chemistry Department- College of Education for Pure Sciences-University of Anbar /Iraq**

**** chemistry Department- College of Education Ibn Al - Haytham Pure Sciences- University of Baghdad/Iraq**

chemhuda2@gmail.com

Abstract

This study involves removing of cationic dyes ,were which [Malachite green dye (MG)and Methylene blue dye (MB)] by using Iraqi Siliceous Rocks Powder (SRP). Adsorption isotherms were studied and the factors which influence it ,such as temperature ,acidic effect and salt effect . Adsorption isotherms of (MG) were found to be comparable to Temkin equation. adsorption isotherms of (MB) were found to be comparable to Freundlich equation. The adsorption process on this surface was studied at different temperatures . the results showed that the adsorption of (MG) on surface increased with increasing temperature (Endothermic process),while adsorption of (MB) on surface decreased with increasing temperature (Exothermic process) . According to the above results the thermodynamic functions (ΔH, ΔG, ΔS) were calculated. The adsorption quantity increasing for (MG,MB) with increasing the acidity solution .The Kinetics of the adsorption of (MG,MB) on surface was studied .The results were treated a according (Lagergreen equation). The Kinetic experimental data properly correlated with First – order kinetic model.

Key word :- Adsorption- Siliceous Rocks- Cationic dyes- Malachite Green Dye- Methylene blue Dye.

Introduction

The dyes are widely used , but they are polluting and harmful , (MG) dye causing cancerous diseases which affects the lung Respiratory system[1] .the presence of (MB) dye in the water is harmful to health [2] .so many studies have been conducted on how to removal this dyes from water in different ways[3,4,5,6,7,8,9,10] . Adsorption on surface pored was one way other methods were used، such as :. (silica[11],Zeolite[12]).

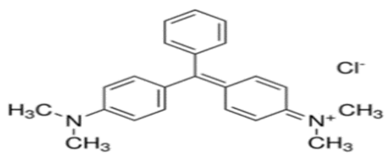
In this research the dyes (MG,MB) removal from aqueous solution by Adsorption on Iraqi Siliceous Rocks powder(SRP).they are white color porous and high surface area, low density.

Fig.1: Siliceous Rocks powder(SRP)

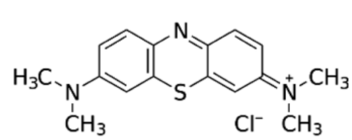
Experimental

Materials

MG,MB ,HCl، were supplied by (BDH).and deionized water had been used . (Figuer.2) shows the structures of (MG and MB).



MG



MB

Fig. 2: Structures of MG and MB[13,14]

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

Constituent	**%wt**
SiO_2	66.01
Al_2O_3	2.12
Fe_2O_3	0.63
TiO_2	0.05
P_2O_5	0.93
CaO	8.44
MgO	6.47
Na_2O	0.62
K_2O	0.13
Loss on ignition	14.61

Table 1: Result of Rocks Analyses

The rocks powder it was washed excessive amounts of deionized water to remove the soluble materials . it was dried for (6 hours) at 60C^o [15] .The surface was then cracked into small parts . The particle size of (75µm) was used for the surface in this work.

Method

1- Technique: UV technique was used to determine the absorption as function for concentration. the wavelengths of absorption were (615, 665) nm for Malachite green , Methylene blue respectively.

2- Contact time : to determine required time for equilibrium between adsorbent and adsorbate, some certain concentration were mixed with (0.02gm) of SRP and they were put into water bath shaker under 20C^o, samples were taken from the solution in different sequenced times to determine the change in the concentration with time passing.

3- Adsorption isotherms: to determine the absorption isotherms for dyes solutions, (0.02gm)of the surface six round flask was weighed and then added to each (50ml) flask of dyes (MG,MB) with certain concentration. These flasks were placed in a water bath at (20 C^o)

for(MG=60min,MB=50min). After the separation of the mixture ,adsorption was absorbed by UV spectrophotometer .

The adsorption quantities were calculated by used following equation [16] :

$$Q_e = \frac{(C_\circ - C_e)V}{m}$$

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

V= volume of solution (L).

$C_\circ$= initial concentration (mg/L).

C_e= equilibrium concentration(mg/L).

m= mass of the surfaces(g).

The previous step were repeated at different temperatures to follow the adsorption of the dyes on the surface when the temperatures changed .

Results and discussion

1- Effect of contact time

for the increase of adsorption as a function of time , the result show the contact time for (MG,MB) dyes at (60min,50min) respectively.

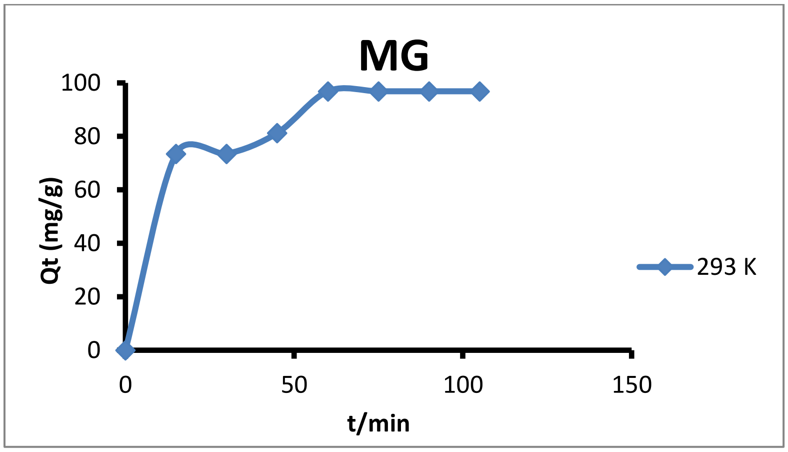


Fig. 3: Effect of contact time on MG adsorption on SRP (Temperature = 20°C, rotations per minute=85rpm, Concentration of dye= 70 ppm, equilibrium time =(60min).

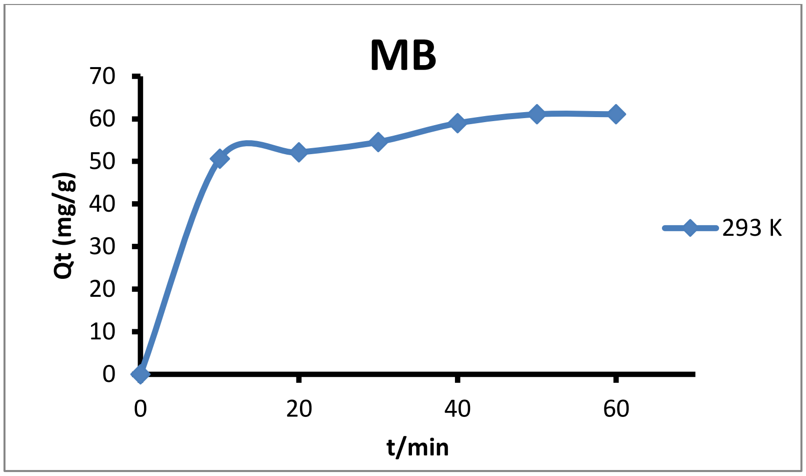
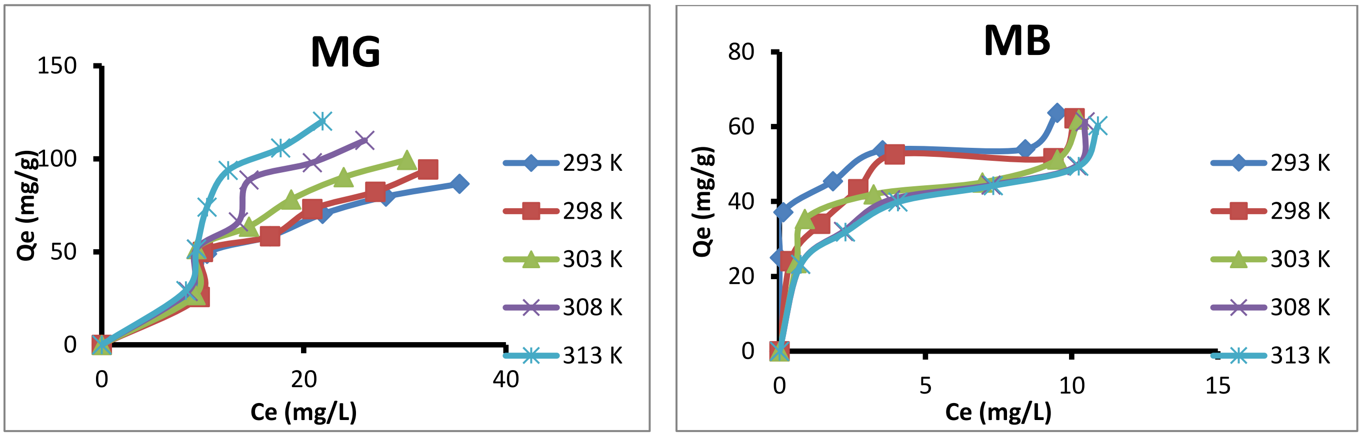


Fig. 4: Effect of contact time on MB adsorption on SRP (Temperature = 20°C, rotations per minute=85rpm, Concentration of dye= 35 ppm, equilibrium time =(50min).

2- Adsorption isotherms

The adsorbed quantity (Qe) for each equilibrium Concentration was calculated . Qe Vs Ce plotted to show the general scheme of adsorption isotherms as show in figures (5) .



a b

Fig. 5: (a,b) Adsorption isotherms of Malachite green ,Methylene dyes on SRP at different temperature.

The general scheme of adsorption isotherm of (MG) on SRP surface pointing out that was of (S_3) class according to Giles classification where the orientation of the adsorbate particles on the surface is bevel vertical [17]. Depend Temkin equation :.

$Qe = b_T Lnk_T + b_T LnCe$ ……. … . … *Temkin equation*

Where b_T ,k_T = Temkin constant

Qe Vs LnCe was plotted as shown in figure(6) .Temkin constant were calculate for MG,MB dyes as shown in Table(2).

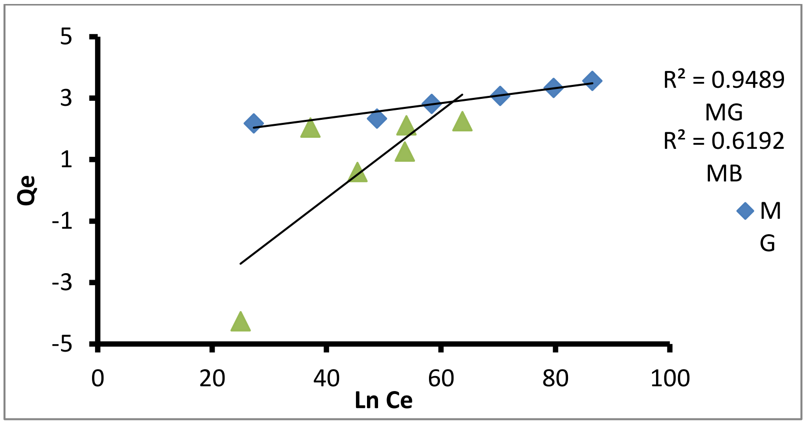


Fig. 6: Linear application of Temkin equation

293K			
Dyes	b_T	Lnk_T	R^2
MG	0.0244	56.319	0.9489
MB	0.142	41.783	0.6192

Table 2 : The value of Temkin constant (b_T,k_T) for adsorption of (MG,MB) dyes on SPR

While (MB) dye through the general scheme of adsorption isotherm show that was of (L_3) class according to Giles classification where the orientation of the adsorbate particles on the surface is straight [17]. Depend Freundlich equation .

$$lnQ_e = lnk_f + \frac{1}{n} lnC_e \qquad \dots\dots\dots\dots\dots\dots \mathit{Freundlich\ equation}$$

where KF, n= Freundlich constant

LnQe Vs LnCe was plotted as shown in figure(7) .Freundlich constant were calculate for (MG,MB) dyes as shown in Table(3).

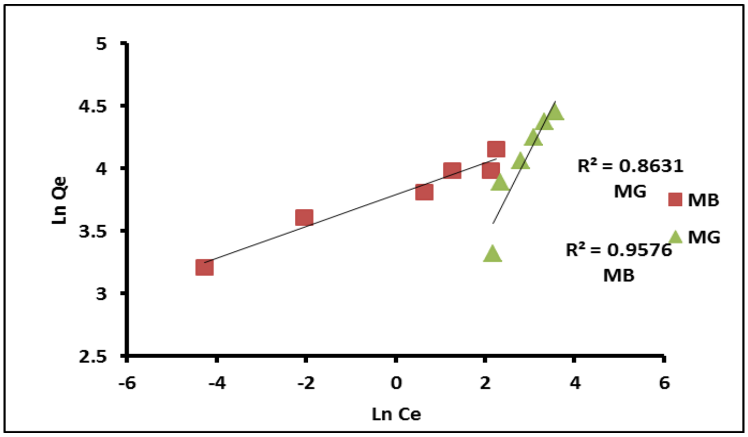


Fig. 7: Linear application of Freundlich equation

293K			
dyes	k_f	n	R^2
MG	7.5503	1.4168	0.8631
MB	44.283	7.8678	0.9576

Table 3: The value of Freundlich constant (k_f,n) for adsorption of (MG,MB) dyes on SPR

The adsorption quantity decreases at (MB)dye when increasing temperature (Exothermic process),because the arrival of the surface to saturation and closure of pores on the surfaces . while adsorption is increased in (MG) dye when temperature increasing (Endothermic) .

The value of (ΔH) calculated by using Vant Hoff- Arrhenius equation :

$$Ln\ Xm = \frac{-\Delta H}{RT} + Constant$$

Where Xm : Maximum adsorbed quantity .

R : gas constant .

T: temperature .

LnXm Vs Inverted temperature (1/T) was plotted as show in (figure 8) and (Table 4) .

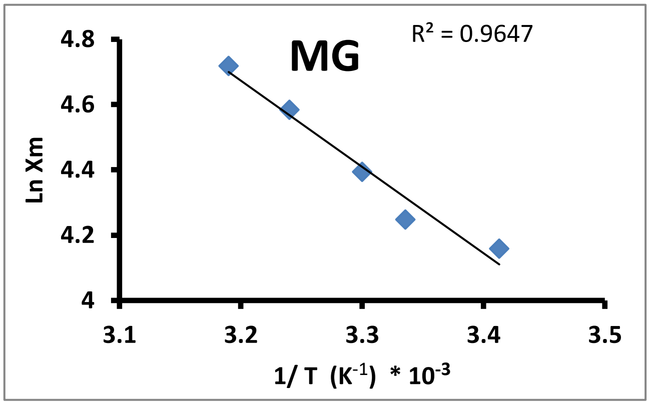
The value of (ΔG,ΔS) were calculated as shown in Table (5), depending on following equations:

$$\Delta G = -\frac{nRTLnQe}{Ce}$$

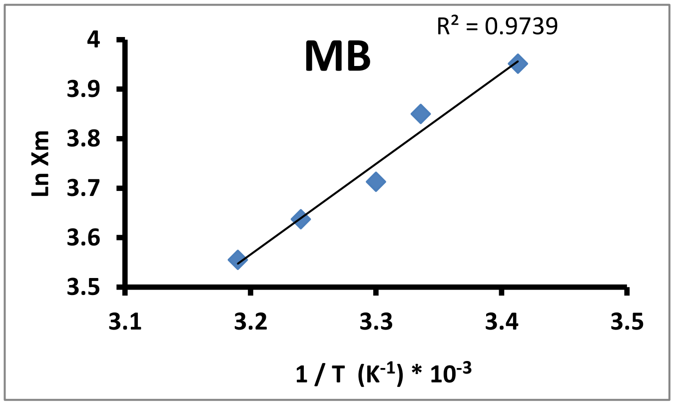
$$\Delta G = \Delta H - T\Delta S$$

T(K)	MG		MB	
	Xm (mg/g) When C_e=20 (mg/L)	Ln Xm	Xm (mg / g) When C_e= 3 (mg/L)	Ln Xm
293	64	4.158	52	3.951
298	70	4.248	47	3.850
303	81	4.394	41	3.713
308	98	4.584	38	3.637
313	112	4.718	35	3.555

Table 4: The value of LnXm , T for (MG,MB) dyes on SPR



a



b

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

Dyes	Δ H $(J\backslash mole)$	Δ G $(J\backslash mole)$	Δ S $(J\backslash mole.K)$
MG	21970	-2833.4	-84.65
MB	-15230	6949.01	28.26

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

The positive value of (ΔH) while (ΔG,ΔS) were negative values for (MG) dye . the adsorbent molecules arranged on the surface [18].

The negative value of (ΔH) , while (ΔG) and(ΔS) they were positive for (MB) dye . prove that the adsorbed molecules were increasing randomly [19].

3- Effect of acidity

The adsorption was studied in different acidity range (0.023 M, 0.093 M) to (MG,MB) dyes as shown in figure (9).

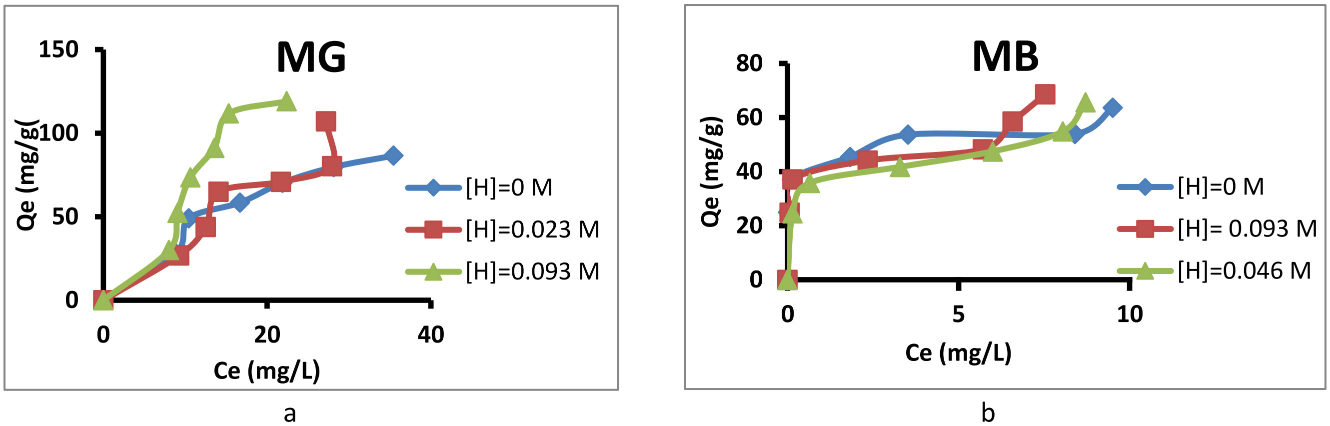


Fig. 9: (a,b) Effect of acidity on Adsorption of (MG,MB) dyes on SRP at T = 298 K

Increasing of adsorption with increase of acidity is refer to that the SRP surface is heterogeneous and contains negative charged group and positive charged group [20]. The negative charge in the dyes will be combined with positive charge on acid as a result , it will give greater liberty to the positive ion in dyes to bind with negative positives on the surface , thus adsorption will increase [21].

4- Adsorption Kinetic

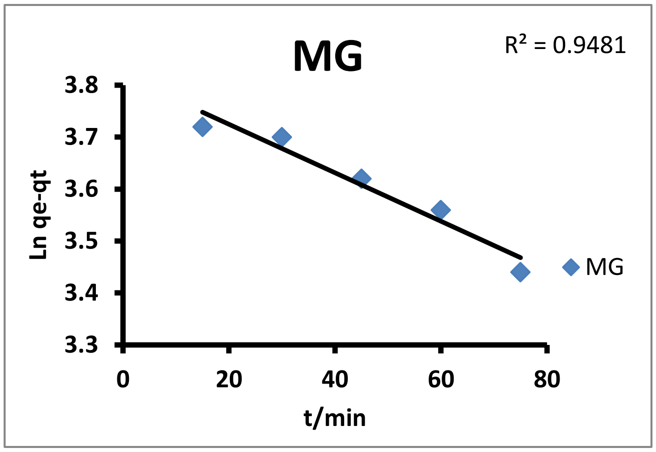
Kinetic studies for dyes (MG,MB), by used (Largergreen equation) :

$ln (q_e - q_t) = lnq_e - k_{ad}$

where qe and qt : are the adsorption capacity at equilibrium and at time (t) respectively (mg/L).

Ked : the rate constant of pseudo firs- order kinetic adsorption (min^{-1}).

The adsorption results that the adsorption kinetics followed pseudo first- order kinetics model , as shown in figure (10), table(6) shown value the rate constant of adsorption.



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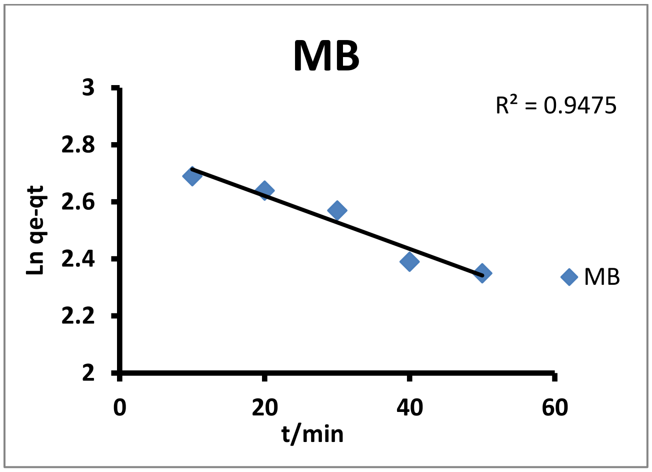

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Fig.10: (a,b**)**The adsorption kinetics of the(MG MB) dyes on the surface

Dyes	k_{ad} (min^{-1})
Malachite green	0.0047
Methylene blue	0.0093

Table.6: value the rate constant of adsorption for dyes on the surface

References

1- F. Mwryer, T. Jorgenson, (1983). "Teratoglogical and other effects of malachite green on development of rainbow trout and rabbits", *Trans Am. Fish Soc*., 112, 818-824.

2- S. Wang, Z.H. Zhu , A. Coomes , F. Haghseresht , G.Q. Lu., (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *J. Colloid. Interface. Sci*. 284, 440-446.

3- M.EL Alouani, S. ALehyen, M.ELAchouri, M.Taibi,(2018)." Removal of cationic Dye- Methylene blue from Aqueous Solution by Adsorption on Fly Ash- based Geopolymer" J.Mater.Environ. Sci, (9), 32-46.

4- A.C.Oluchukwa ,O.I.Maxwell ,A.C.Albert,(2018)." Equilibrium Isotherm Studies on The Adsorption of Malachite Green and lead Ion from Aqueous solution Using Locally Activated Ugwaka clay (Black clay)".Archives of current Research International, 12(2):1-11.

5- N.C. Corda and M.S. Kini. (2018)." A Review on Adsorption of Cationic Dyes using Activated Carbon", MATEC Web of conferences, 144,02022.

6- D.Njoya , J. N. Nsami , A. N. Rahman ,R.B. L. Ngouateu, M. Hajjaji, C. Nkoumbou , (2017). "Adsorption of methylene blue from Aqueous solution on to Cordierite based Ceramic", *Journal of Materials and Environmental*,8(5),1803- 1812.

7- Noor A. Abd AL-Hussein , (2017). "Adsorption of methylene blue dye from aqueous solution by using some Plant material", *Journal of Mesopotemia Environmental* , 3(3),74-78

8- Kuntari and D. A. Priwidyanjati ,(2017)."Adsorption of malachite green Dye from Aqueous solution on the Barnboo leaf Ash", Published py the American Institute Physics ,(19), 020011-1-020011-7.

9- S.Abdelkarim , H. Mohammed , B.Nouredine,(2017). "Sorption of Methylene Blue Dye From Aqueous Solution Using an Agricultural Waste", *Imedpud Journals*, 3(1-4).

10- M. Fatihaa, B. Belkacem., (2016)." Adsorption of methylene blue from aqueous solutions using natural clay", *J. Mater. Environ. Sci*. 7 (1) 285-292.

.

11- G.Mchkay, M.S.Otterburn and A.G.Sweency,(1980)." Water Research, 14,pp21-27.

12- Yensh. F.T.Jeng,(1997).J. of Environ. Sci. of Health , 32(8)pp. 2087-2100.

13- The Merck index: "An Encyclopedia of chemicals", Drugs, And Biological, 15th Edition.

14- Momcilovici, Milan Z, Antonije E. ONJIA1, Milovan M. Purenovic2, AleksandraR. Zarubiva2 and Marjans (2012).. Randelovic2(0)*J. Serb. Chem., Soc*. 77 (6) 761–774.

15- R. H. Ali , (2009). " A Study of Adsorption of some Metals Cations from their Aqueous solution on some Iraqi Mineral Surfaces and their Modifications" A Thesis Ph.D , College of Science for Women-University of Baghdad.

16- H.I. Tarkih, (1973). " Liquid- Solid Adsorption Studies : an experimental study and A Mathematical Modulation of Multi stage adsorption Apparatus ", Victoria University of Manchester .

17- F. J. 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.

18- K.K.Panday, Gup.presad N.V. Singh, (1985), ,Water Research .,19(7),pp.869 -873.

19- E.H.M.Wright and N.C. Partt, (1961)."Current chemical Papars", *J. Chem. Soc. Faraday Trans.*, **7**0 , 1461.

20- D.Hillel, (1980). " Fundamentals of Soil Physics " , Academic Press, New York.

21- D.G.Hollander.(1980)." Essentials of Risk Theory" , J. Chem Soc. Faraday Trans. I, 76, 386 .