Adsorption of Chromium (+3) from Aqueous Solutions using Adsorbent

planting Mauve (*malva parviflora)*

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ABSTRACT

In this research, There is the removal of (Cr^{+3}) ions from aqueous solutions. By adsorption process on malva parviflora, It was attained to the equilibrium (60minute) which investigated by Atomic absorbtion spectrophotometer technique .The results show that the weight had better value (0.2 gm) . The effect of initial pH solution on adsorption had been studied in the range (3-10). The Freundlich and Langmuir equations were applied ,and the parameter of those equations had been calculated . The extent of adsorption was found to decrease as the temperature increased, i.e. exothermic process, and so the thermodynamic functions ΔH, ΔG and ΔS were calculated .

Key words: $Cr(NO_3)_3$,powder malva parviflora, Atomic absorbtion spectroscopy,Adsorption .

INTRODUCTION

The desorption is defined as the percentage of the test substance which is desorbed and related to the quantity of the substance which is previously adsorbed under the test condition[1] .The desorption process is so important to understand the behavior of pesticide in the environment[2] . Desorption is the tendence for accumulation of substance to take place at a surface or at an interface the accummenence of adsorption is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plance and these forces possessing a certain unsaturation[3]. Desorption slower than sorption[1]. Chromium is considered as a priority pollutant among all the heavy metals. Various industrial effluents from pigments, electroplating, dying, canning, textile, leather tanning, paint, and steel industries contain substantial amounts of chromium. In general these industrial effluents contain both Cr(VI) and Cr(III) ions. Excessive buildup of Cr(III) ions can affect the ecological environment [4]. The importance to minimize the amount of Cr(III) ions in industrial effluents and other resources has diverted the interest of scientists towards selective adsorbents Cr(III) adsorption by different materials [5-8]. The commonly used methods for removing metal ion from aqueous waste include precipitation, lime coagula-tion, semisedimentation, electrodialysis, chemical reaction, biological process, ion exchange, filtration, reverse osmosis, solvent extraction, and common adsorption. The latter process being a more useful method for the metal ion[7]. Malva parviflora L. belongs to the family Malvaceae that includes trees, shrubs and herbs. In Lesotho, dried powder or an infusion made from leaves and roots of M. parviflora have been used to clean wounds and sores. A hot poultice made from leaves is also used to treat wounds and swelling and is incorporated into a lotion to treat bruised and broken limbs[9].The leaves of M. parviflora have been used by the Xhosa people of South Africa for drawing swollen, inflamed purulent wounds[10].

MATERIALS AND METHODS

Chemicals

$Cr(NO_3)_3$, powder malva parviflora, (0.1N) HCl and (0.1N) NaOH .

Apparatus

1. Atomic Adsorption Shimadzu 6200 / Japan .
2. Thermostated Shaker Water Bath- JEIO TECH (BS- 11).
3. PH –Meter-Hanna-HI-8417 / England.
4. Vindo Scientific LTD,LDHAM/ England.
5. Electronic Precision Balances / Sartorius / Germany.
6. Remi Centrifuge R8C. Bombay / India .

Preparation of Adsorbent: The malva parviflora was washed several times in distillate water to remove any adhering dirt, then the malva parviflora was dried at 5C ° for 15min in the dry oven. Finally, the dried sample was ground and sieved to obtain a particle size 75µM and stored for further use.

Preparation of Metal Solutions :Stock solutions (1000 mg/L) of Chromium ions were prepared by dissolving an appropriate weight of pure salt $Cr(NO_3)_3$ in the desired volume of distillate water. The stock solution was successively diluted with distillate water to obtain the desired test concentration (10-50and 25 mg/L) of metal ions. Concentration of Chromium ion was measured using Atomic Adsorption Shimadzu type 6200 / Japan.

Contact Time: The experiments were conducted by adding an amount of adsorbent (0.2) g with 25 ml of Cr $(NO_3)_3$ solution of initial concentration (25) mg/L in 100 ml stopper conical flasks, adsorption tests were carried out at different contact time intervals (15 - 90 min). These flasks were placed on a rotating shaker with constant shaking at 160 rpm at 25C^o to maintain the equilibrium condition and the solution were separated by a combination of centrifugation for 30(min) at 3300 rpm than solution was filtered using filter paper and analyzed using Atomic Absorption Shimadzu.

Adsorbent Dosage: 25 ml of the metal ion solution of (25 mg/l) was added to various amount of the several adsorbents (0.1-0.5 g) in 100 ml volumetric flasks and agitated for 1hr on a shaker and the solution were separated by a combination of centrifugation for 30(min) at 3300 rpm than solution was filtered using filter paper and analyzed using Atomic Absorption Shimadzu.

Temperature Variation: The batch adsorption process was studied at different temperatures of (25, 35 and 45) C° in order to investigate the effect of temperature on the adsorption process using malva parviflora . This was done by contacting 0.2 g of adsorbents with 25 ml of (10-50) mg/L $Cr(NO_3)_3$ solution for 1hr with agitation speed of 160 rpm by using shaker incubator. The results were used to investigate the thermodynamics of the adsorption process.

pH Variation : It was reported that the suitable pH range for the adsorption of $Cr(NO_3)_3$ was (3,7 and 10). This experiment was conducted at 25 C° to study the effect of initial solution pH on the adsorption of $Cr(NO_3)_3$ by contacting 0.2 g of the adsorbent malva parviflora with 25 ml of 25 mg/L$Cr(NO_3)_3$ solution in a volumetric flasks. The pH of each solution was (5) adjusted to the desired value with adding 0.1N $HNO_3$for one volumetric flask, 0.1N NaOH for other volumetric flask. The volumetric flasks inner in a shaker for 1h and the solution were separated by a combination of centrifugation for 30(min) at 3300 rpm,solution was filtrated using filter paper and the $Cr(NO_3)_3$ concentration in the solution was analyzed by means of Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Effect of Contact Time

The data obtained from the adsorption of $Cr(NO_3)_3$ on the malva parviflora at various concentrations (10-50)ppm showed that contact time of 60 min . The effect of contact time on the percentage removal of $Cr(NO_3)_3$ at optimum conditions of the other factors is the presented in Figs. 1. These figures show that the removal of $Cr(NO_3)_3$ increases with increasing mixing contact time attains equilibrium in 60 min. After this period the removal curves are single smooth and continuous, suggesting the formation of monolayer of adsorbate on the surface of the adsorbent. These results indicated that the sorption process can be considered very fast because of the large amount of $Cr(NO_3)_3$ attached to the sorbent of adsorption. The higher sorption rate at initial period can be attributed to the increase of number of vacant site on the adsorbent available at the initial stage[11] . Table (1) and figure (1) show the variation of Qe with the contact time for 25 ppm of $Cr(NO_3)_3$ solution at 298K to be in attachment 0.2 gm of malva parviflora.

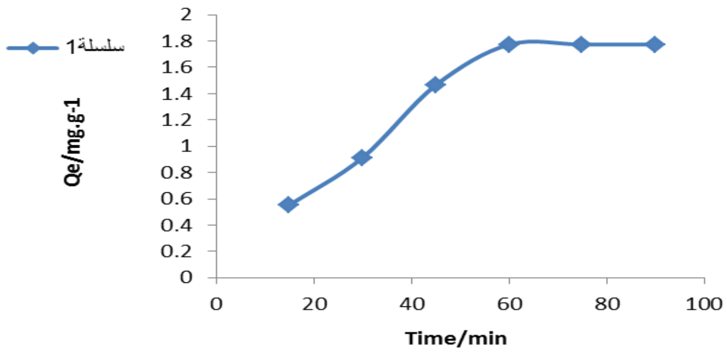


Fig.(1)The variation of Qe with the equilibrium time for 25 ppm of $Cr(NO_3)_3$ solution at 298K.

Table (1) The values of Qe and Ce at different time for 25 ppm of $Cr(NO_3)_3$ solution at 298K.

Time/min.	C_e/mg.L^{-1}	Q_e/mg.g^{-1}
15	20.58	0.5525
30	17.69	0.91375
45	13.28	1.465
60	10.81	1.7737
75	10.81	1.7737
90	10.81	1.7737

Effect of Adsorbent Dosage

The maximum removal is obtained at the adsorbent dose of 0.2 g where a further increase in the quantity of the adsorbent up to 0.2 g has no more effect to the adsorption rate. Therefore,0. 2g of the adsorbent is sufficient to adsorb the maximum ions and that the percent removal by malva parviflora[12].

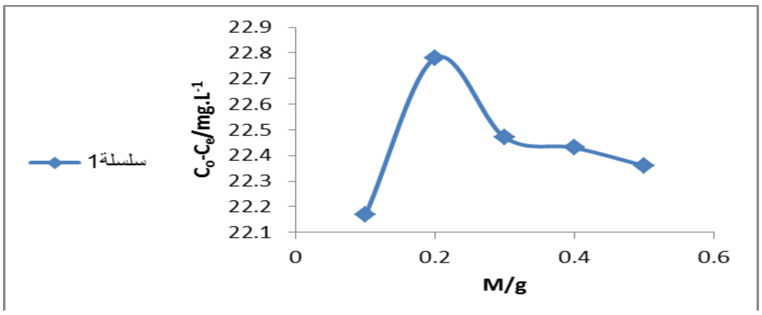


Fig (2)The effect of plant dose on the adsorption process for 25ppm $Cr(NO_3)_3$ solution on malva parviflora at 298 K.

Table (2) and figure (2) shows the variation of C_o-C_e with the amount of adsorbent (malva parviflora).

C_o-C_e/mg.L^{-1}	m/g
22.17	0.1
22.78	0.2
22.47	0.3
22.43	0.4
22.36	0.5

Effect of pH Value

The effect of pH value on the percentage removal of Cr $(NO_3)_3$ at optimum values of the others factor is shown in Figs. 3. From these figures it can be shown that the percentage removal of Cr $(NO_3)_3$ decrease with increasing the pH value from 3 to 10. Better adsorption capacity observed at low pH values at pH =3 may be attributed to the large number of H+ ions present at these pH values, which in turn neutralize the negatively charged hydroxyl group (−OH) on adsorbed surface thereby reducing the hindrance to the diffusion of dichromate ions. At higher pH(10) values, the reduction in adsorption may be possible due to abundance of OH− ions causing increased hindrance to diffusion of dichromate ions[11].

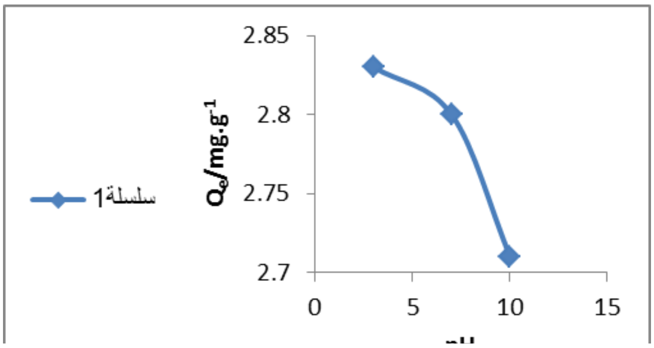


Fig. (3)The quantity of adsorption at different pH value using malva parviflora at 298K for 25ppm $Cr(NO_3)_3$ solution .

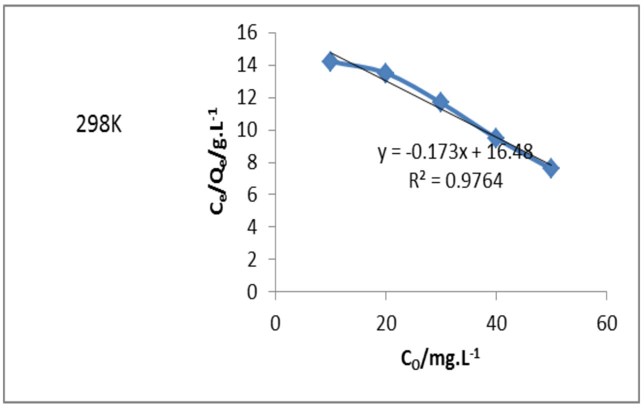
Table (3) The quantity of adsorption at different pH value ,using malva parviflora at 298K for 25ppm $Cr(NO_3)_3$ solution .

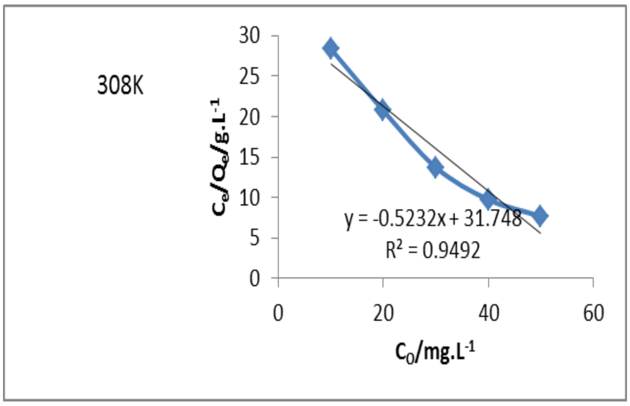
PH	Q_e/mg.g^{-1}	C_e/mg.L^{-1}
3	2.83	2.36
7	2.80	2.59
10	2.71	3.30

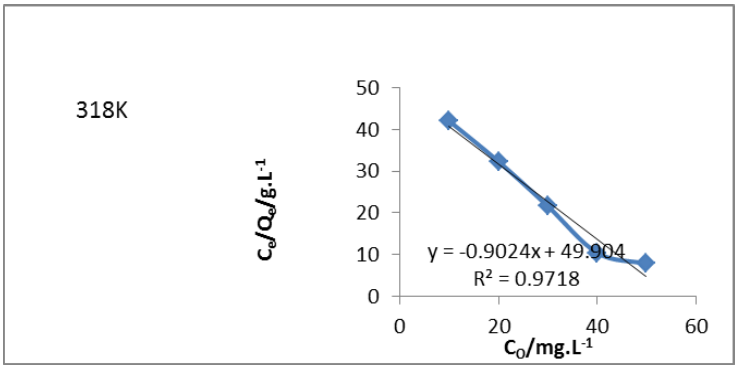
Table (4) and Figure (4) show the Langmiur data and Linear relationship between C_e/Q_e and C_e of series $Cr(NO_3)_3$ solution at (298,308 and 318)K.

Table (4) The value of C_o,C_e and C_e/Q_e for the adsorption of series $Cr(NO_3)_3$ solution at(298,308 and 318)K.

298K			308K			318K		
C_O/ mg.L^{-1}	C_e/ mg.L^{-1}	C_e/Q_e /g.L^{-1}	C_O/ mg.L^{-1}	C_e/ mg.L^{-1}	C_e/Q_e/ g.L^{-1}	C_O/ mg.L^{-1}	C_e/ mg.L^{-1}	C_e/Q_e/ g.L^{-1}
10	6.4	14.22	10	7.8	28.3	10	8.4	42
20	12.56	13.5	20	14.43	20.73	20	16.03	32.32
30	17.80	11.67	30	18.96	13.73	30	21.9	21.6
40	21.69	9.48	40	21.98	9.75	40	22.64	10.43
50	24.33	7.58	50	24.52	7.69	50	24.71	7.82







Fig(4)The plot of C_e/Q_e against C_O for the adsorption of series $Cr(NO_3)_3$ solution at different temperatures.

Freandlich isotherm are the most frequently employed models to describe the equilibrium characteristics of adsorption isotherm .The linear from of the Freandlich equation is as follows[3]:

Log Q= Log K_f+1/n Log C_e-------------------(1)

The Freandlich isotherm constants K_f and 1/n can be calculated from the plot between Log Q and Log C_e fig.(5). K_f(mg/g), 1/n(L/g) and n are the Freandlich constants. Table (5) and Figure (5) are shown the Freandlich data which are indicators of adsorption capacity and adsorption intensity ,respectively .

Table (5)The values of C_O, C_e, Q_e, Log Q,and Log C_e for the adsorption of $Cr(NO_3)_3$ solution at different temperatures.

298K					308K				
C_O/ $mg.L^{-1}$	C_e/ $mg.L^{-1}$	Q_e/ $mg.g^{-1}$	Log C_e	Log Q	C_O/ $mg.L^{-1}$	C_e/ $mg.L^{-1}$	Q_e/ $mg.g^{-1}$	Log C_e	Log Q
10	6.4	0.45	0.806	-0.346	10	7.8	0.275	0.892	-0.560
20	12.56	0.93	1.098	-0.0315	20	14.43	0.696	1.159	-0.157
30	17.8	1.525	1.250	0.183	30	18.96	1.380	1.278	0.139
40	21.69	2.288	1.33	0.359	40	21.98	2.253	1.342	0.352
50	24.33	3.208	1.38	0.506	50	24.52	3.186	1.389	0.503

318K				
C_O/ $mg.L^{-1}$	C_e/ $mg.L^{-1}$	Q_e/ $mg.g^{-1}$	Log C_e	Log Q
10	8.4	0.2	0.924	-0.698
20	16.03	0.496	1.205	-0.305
30	21.9	1.0125	1.340	0.00539
40	22.64	2.17	1.355	0.336
50	24.71	3.161	1.393	0.499

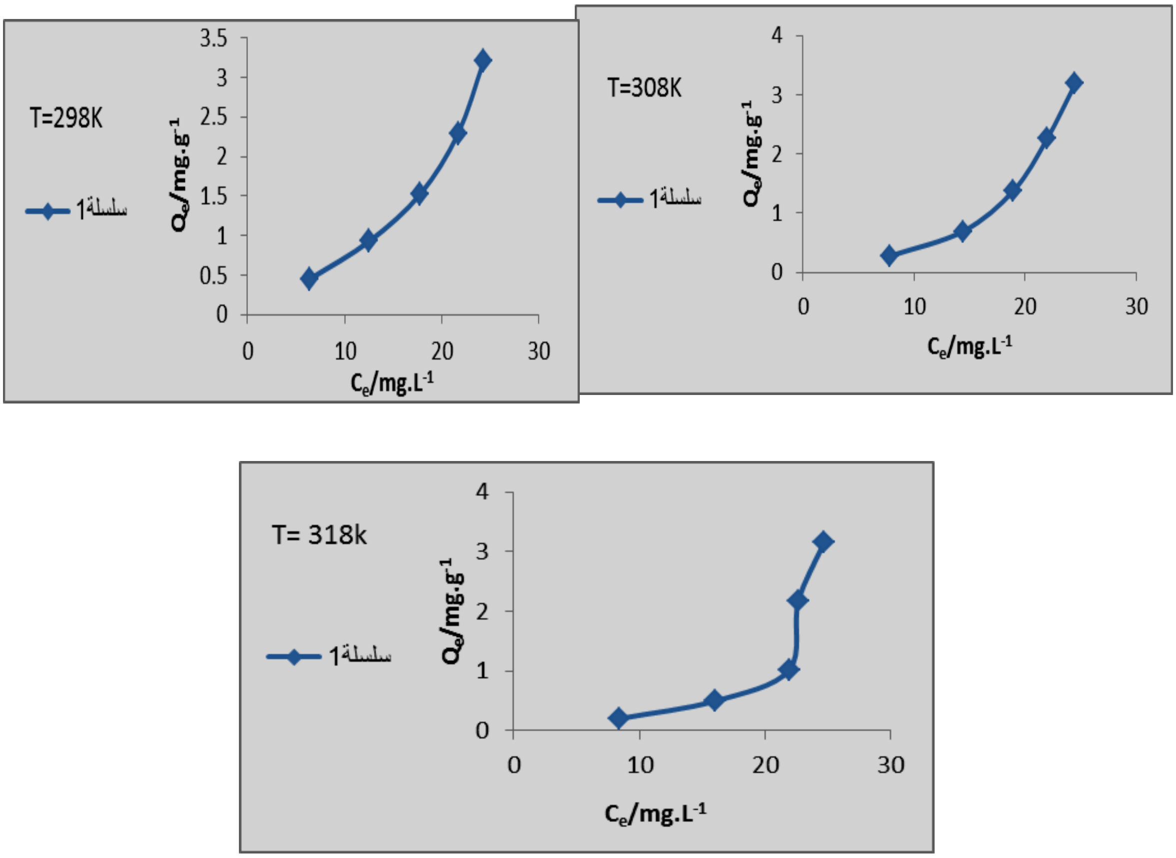


Fig.(5) The plot of Q_e against C_e for the adsorption a series $Cr(NO_3)_3$ solution at different temperatures .

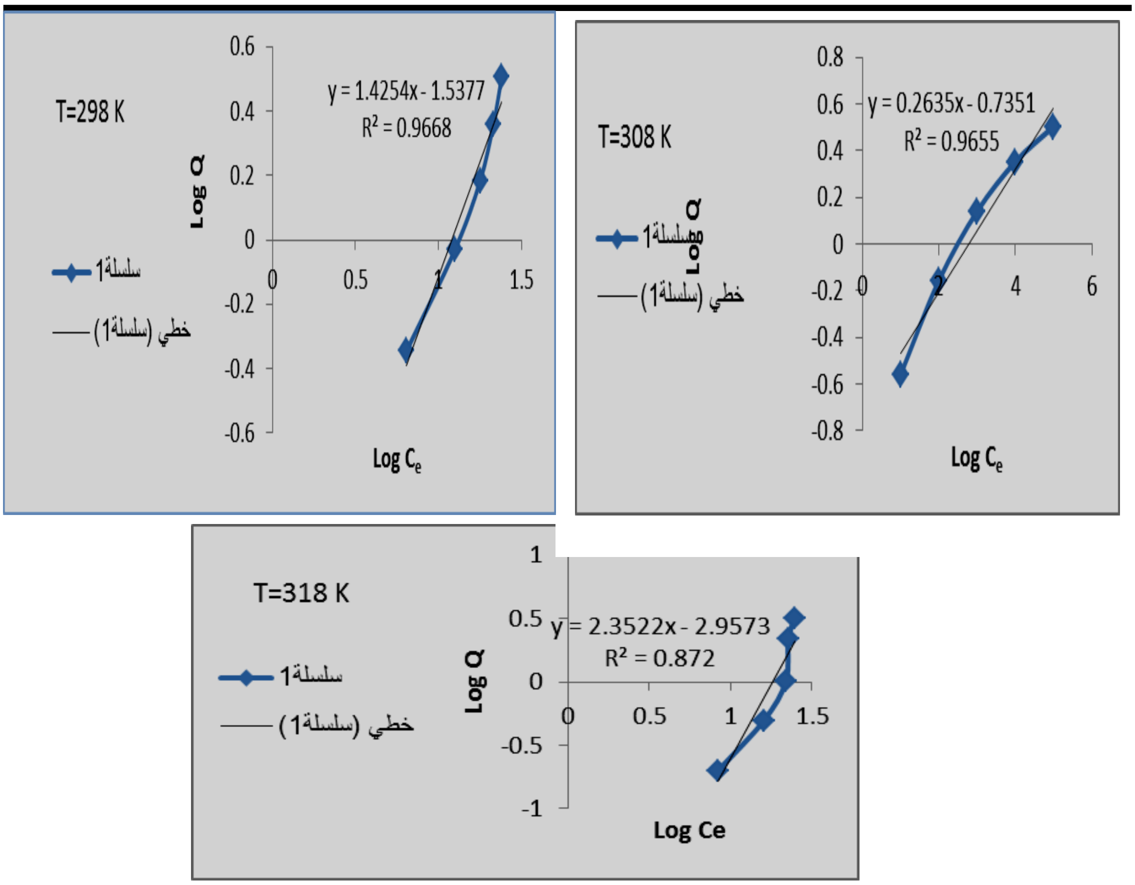


Fig.(6) Freundlich linear relationship between Log Q and Log C_e for a series $Cr(NO_3)_3$ solution at different temperatures .

Table(6) shows the Freundlich constants at different temperatures.

T(K)	Log K_f	K_f mg/g/(mg/L)n	1/n	n	R^2
298	1.537 -	0.02904	1.425	0.7017	0.966
308	0.735 -	0.1840	0.263	3.8022	0.965
318	2.957 -	0.001104	2.352	0.4251	0.872

Effect of Temperature and Thermodynamic parameters:

The thermodynamic functions , ΔH, ΔG.and ΔS were calulated using the following formulas [13].

ΔG = -RT LnK---------------(2)

LnK = - ΔH/RT+constant ----------(3)

ΔG = H- T ΔS-------------(4)

In the equation (2) ,where ΔG is the change in the value of free energy ($KJ.mol^{-1}$), R was the gas constant [8.318]$J.mol^{-1}.deg^{-1}$),K is the thermodynamic equilibrium counstant of adsorption process.Where K is the maximum adsorption quantity for series $Cr(NO_3)_3$ solution at different temperatures and could be obtained from the plot of C_e/Q_e against C_O Fig.(7) . The equation (3) was used to calulate the Δ H ,by plotting ln K vs. 1/T ,table (7)and Figure (7) showed a linear relationship and the slope represents to ΔH/R ,where R is the gas constant ($8.318 J.mol^{-1}.K^{-1}$), and Δ H were calculated.

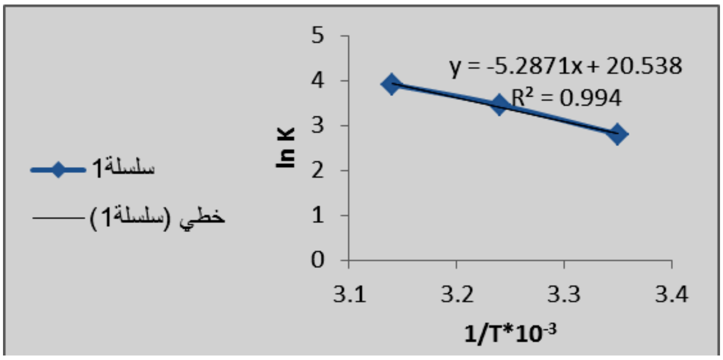


Fig.(7)The plot of ln K vs.the reciprocal of temperature .

Table (7) The value of the reciprocal of temperature and ln K

T(K)	$1/T*10^{-3}$	K	ln K
298	3.35	16.48	2.8021
308	3.24	31.74	3.4575
318	3.14	49.90	3.9100

Table (8)show the thermodynamic function of the adsorptin process .

T(K)	ΔG ($kJ.mol^{-1}$)	$\Delta S*10^{-2}$ ($J.mol^{-1}.K$)	$\Delta H*10^{-2}$ ($kJ.mol^{-1}$)
298	-6.9424	-2.3149	-4.3956
308	-8.8536	-2.860	
318	-10.337	-3.236	

From the Table (8) .It is clear the ΔH has the negative value , which indicator the ideal this may be due to endothermic reaction and the maximum value of physics-sorption process. All value of ΔG were negative so the adsorption Cr^{+3} on malva parviflora was considered spontaneous process ,also ΔS was had the negative value this indicates that the adsorbed molecules are arranged on the surface as a results of its association with malva parviflora.

Kinetic analyses:

The Kinetic of the adsorption process was studied by introducing three model, also the rate constant was calculated .

1.Lagergren Model

The kinetic study of metal ion adsorption is important to give insight into the adsorption rate, provide information on the contact time required for considerable adsorption to take place and also the factors affecting or controlling the adsorption rate. In order to investigate the mechanism of $Cr(NO_3)_3$ solution adsorption by malva parviflora and potential rate controlling steps one of the most commonly used kinetic model, psedo-fist orderwas employed to evaluate the adsorption of $Cr(NO_3)_3$ solution . the equation for the pseudo-first order kinetic model can be represented by eq.5

$\ln q_e - q_t = \ln q_e - k_{ads}\ t$-------------------(5)

Where qt is the adsorption capacity at time t (mg/g), k1 is the first order reaction rate constant (L/min) [14]. qt and qe values are given in table table (9). The liner relationship was obtained via plotting $\ln q_e - q_t$ vs. t/min. as show in figure (8).

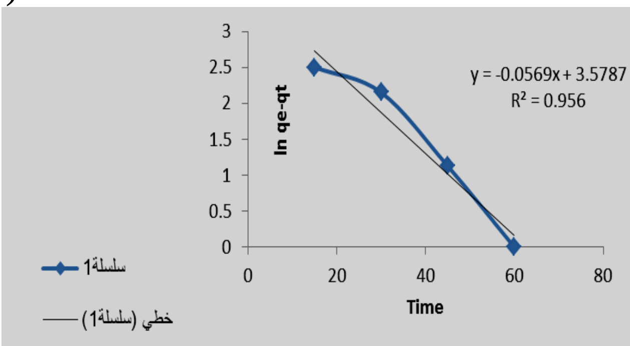


Fig.(8)The Lagergren model for $Cr(NO_3)_3$ solution at 298K.

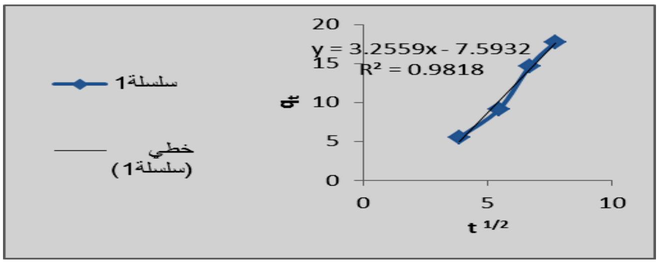
Table (9) the values qt ,qe-qt and qe of 25 ppm $Cr(NO_3)_3$ solution at 298K.

Time (min.)	q_t	q_e	q_e-q_t	$\ln q_e-q_t$
15	5.525	17.74	12.215	2.5026
30	9.137		8.603	2.1521
45	14.65		3.09	1.128
60	17.74		0	0

2.Morris -Weber model:

The Kinetic model was used to estimate the rate limiting step of any adsorption process ,the equation of this model could be expressed as follows [15] : $qt = K_d\ t^{1/2}$-------------------(6)

Where qt is the quantity of adsorbed material at any tim /mg.g^{-1} ,K_d is the diffusion constant , $t^{1/2}$ is time of diffusion /mint, the plotting of qt against $t^{1/2}$ was accomplished at 298 K . Figure (9) shows the plot of qt against $t^{1/2}$ for 25 ppm $Cr(NO_3)_3$ solution at 298K.



Fig(9)The plot of q_t against $t^{1/2}$ for 25 ppm $Cr(NO_3)_3$ solution at 298K.

3-Reichenberg model

The kinetic model was proposed to discuss the dehavior of many adsortion process in solution and Reichenberg had introduced following formlua[13]:

$F =(1-6/ \pi^2)\ e^{-Bt}$-------------(7)

$Bt =-0.4977 - Ln\ (1-F)$-------------(8)

$F =q_t/q_e$---------------(9)

plotting of time (mint) against Bt revealed a linear relationship with relatively acceptable R^2 values . Figure (10) shows the variation of Bt with time for 25ppm $Cr(NO_3)_3$ solution at 298K. According to this model ,it characterized the rate determining mechanisms which was diffusion process for Cr ions from the bulk solution to the absorbent surface and absorption occurred.

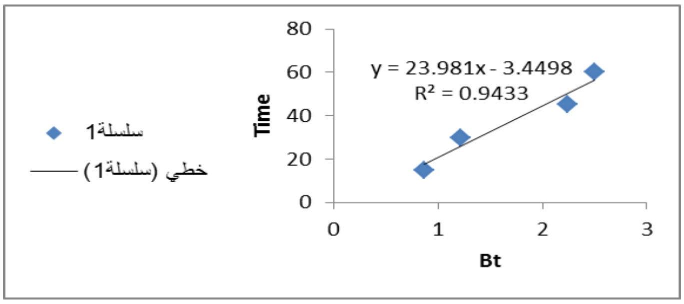


Fig (11)The variation of Bt with time for 25ppm $Cr(NO_3)_3$ solution at 298K.

CONCLUSIONS

The removal of Cr^{+3} from waste water by using powder malva parviflora has been investigatedl under several condition such as at different pH, different dosage and contact time. The optimum pH of Cr^{+3} adsorption was found at pH of 3 for powder malva parviflora . The optimum dosage was 0.2g for malva parviflora . The optimum contact time is 60 min .These results strongly suggest plausible reuse of powder malva parviflora in the treatment of waste water contaminated with heavy metal.

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أمتزاز الكروم الثلاثي من المحاليل المائية بأستخدام مواد مازة ميوفا(النبات الخباز).

رشا عبد جاسم

قسم الكيمياء/ كلية العلوم للبنات/ جامعة بغداد.

الخلاصة:

في هذا البحث تم ازاله Cr^{+3}من المحاليل المائيه بواسطة امتزازه على سطح نبات الخباز تم تحديد زمن الاتزان٦٠دقيقه باستعمال جهاز قياس الامتصاص الذري وبينت النتائج ان افضل وزن للسطح للعمليه الامتزاز ٠,٢ غرام وكذللك اجريت الدراسات في مدى (pH=3,7and 10)و كذلك تم استعمال معادلتي لانكماير ,فرندلش الايزوثيرميتين وكذللك تم حساب كميه الامتزاز ووجد انه كميه الامتزاز تقل مع زياده درجه الحراره وهذا التفاعل يكون باعث للحراره وكذللك تم حساب القيم الثرموديناميك(ΔS, ΔG and ΔH).