Determination of adsorbed Mn (II) and Cr (III) ions using hydrogel beads and AAS measurements

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Abstract

In this work the hydrogel (Poly acrylic acid) beads used for adsorb Mn (II) and Cr (III) from aqueous solutions. The adsorption capacity of the adsorbents is presented, the time required to reach a maximum capacity of bead (130.62, 123.13) mg/g for Mn (II) and Cr (III) ions respectively was about 24 hr. The initial concentration, temperature, time and pH effect on adsorption process were studied. The experimental data have been analyzed using the Langmuir and Freundlich. The Langmuir isotherm model gave the highest R^2 value of (0.9999 and 0.9992) for Mn (II) and Cr (III) ions respectively. The thermodynamic parameters were studied and calculated. First-order and second- order kinetic models were used and it is shown that the experimental data was in reliable compliance with the first- order model with an R^2 value of (0.984 and 0.993) for Mn (II) and Cr (III) ions respectively. The process is very efficient, especially for the removal of pollutants in aqueous solutions and more than 95% of study cations were removed by this adsorbent. The concentration of metal ion in the solutions was measured using AAS. The method was linear with an R^2 of (0.9992 and 0.9989) for Mn and Cr respectively.

Key words: Mn (II) and Cr (III) ions, Hydrogel beads, AAS, adsorbed, Determination.

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تقديرايونات المنغنيز (II) والكروم (III) الممتزة باستخدام حبيبات الجل المائية وقياسات الامتصاص الذري

عامر فاضل داود النعيمي[1] ، احمد مهدي سعيد[2] و سارة ثامر عبد[3]
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الخلاصة

تم في هذه الدراسة استخدام احد انواع حبيبات الجل المائية عالية الامتصاص (متعدد حامض الاكريلك) لامتزاز ايونات المنغنيز الثنائي والكروم الثلاثي من المحاليل المائية. لقد درست سعة الامتزاز؛ وكان الزمن اللازم للوصول للسعة القصوى للحبيبات (130.62, 123.13) ملغ/غم لكل من الكروم والمنغنيز على التوالي هو 24 ساعة. لقد تم دراسة تاثير التركيز الابتدائي؛ درجة الحرارة؛ الزمن والدالة الحامضية على عملية الامتزاز. لقد تم تحليل النتائج بتطبيق نموذجي لانكماير وفريندلج وقد اعطى ايزوثيرم لانكماير اعلى قيمة لعامل الترابط R^2 وهي (0.9992 , 0.9999) لكل من الكروم والمنغنيز على التوالي. تم دراسة العوامل الثرموداينميكية لعملية الامتزاز؛ كما تم تطبيق معادلتي الدرجة الاولى والثانية للدراسات الحركية وبينت النتائج ان عملية الامتزاز تتوافق مع نموذج الدرجة الاولى بقيمة R^2 هي (0.993 , 0.984) لكل من الكروم والمنغنيز على التوالي. ان العملية ذات كفاءة عالية في ازالة الملوثات من المحاليل المائية وان اكثر من 95% من الايونات المدروسة تمت ازالتها باستخدام المادة المازة. تركيز الايونات في المحلول تم قياسه باستخدام طريقة الامتصاص الذري؛ وان الطريقة خطية وقيمة R^2 هي (0.9989 , 0.9992) لكل من الكروم والمنغنيز على التوالي.

الكلمات المفتاحية: المنغنيز (II) والكروم (III)؛ حبيبات الجل المائية؛ الامتصاص الذري؛ تقدير؛ الممتزة.

Introduction

The water is an essential matter of human and other living organism. Water may be polluted from the effluent of several industries such as chemical industry, electroplating industrial, dye industrial and battery industrial. The heavy metal ions were found to be one of the main pollutants in water [1]. The toxic metals can cause accumulative poisoning cancer and brain damage when found above the tolerance levels [2]. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese and iron are commonly detected in both natural and industrial effluents. Manganese is a heavy metal commonly found in soil, sediment and especially in ground water. Not only it has an effect on appearance and taste of the water, it also causes health problems on neurological and muscle function in humans [3]. The most common treatment techniques of manganese contaminated water are oxidation/filtration and adsorbing onto ion exchange resin [4]. Chromium contamination of soil and water is a major environmental problem. The toxicity of chromium varies greatly among a wide variety of chromium compounds, its oxidation state and its solubility in water. Chromium (III) is considered to be an essential dietary element to the human and mammals [5].

Effective removal of heavy metal ions from aqueous solution is important in the protection of environmental quality and public health [6]. The commonly used procedures for removing metal ions from effluents include chemical precipitation [7], ion exchange [8], membrane separation [9], electrocoagulation [10], nanoparticles [11], dialysis/electrodialysis [12], and adsorption/filtration [13]. Adsorption is an efficient and cost – effective method of heavy metals removal from water and wastewater [14]. Many materials have been used as adsorbents including chitosan [15], clay [16], zeolite [17], sawdust [18], bark [19], lignin [20], and other [21]. However, low adsorption capacity and rate for heavy metal ions are the main problems for these low-cost adsorbents [22]. Recently hydrogel bead was used as adsorbent for the removal of heavy metal ion [23].

In this study, the performance of hydrogel beads as low cost adsorbers for Mn (II) and Cr (III) adsorption from aqueous solution at high level concentration was investigated. In batched experiments, the influence of pH solution, contact time, temperature and initial concentration of solution were studied. The maximum capacity of the adsorbent, kinetic parameters and thermodynamic parameters using different types of isotherms was calculated from experimental data.

Experimental

Apparatus

Atomic absorption spectrophotometer (AAS) type (AURORA, A1200 – Canada) was used to determine Mn (II) and Cr (III) ions concentration. A metrohm E. 63222 pH meter (Switzerland), fitted with metrohm combined glass electrode was calibrated according to conventional methods and used to adjust the pH of the solution in all experiments. Sartorius BL 210 S (Germany), max. 210 g, D 0.1 mg, was used for hydrogel beads and chemicals weighing. A Vernier caliper with 0.01 mm measuring accuracy was used for measurement of the diameter of the hydrogel beads.

Chemicals and solution

Commercial hydrogel beads (3.60 mm diameter and 0.0400 g weight) were used for metals ions adsorption in this study. All chemicals were of analytical reagent grade from Aldrich Chemical Company (Germany). A1000 ppm aqueous solution of Mn (II) and Cr (III) ions were prepared from hydrated metals chloride salts.

Calibration graph and linearity study

For determining the linearity, a series of solutions have different metals ions concentrations (1, 2, 3, 4, 5, 6, 8, 10, 12, 15 and 20 ppm) were prepared by simple dilution of stock solutions. The absorbance of these solutions was measured. The calibration graph was obtained by plotting absorbance versus known concentrations in ppm. Figure 1, illustrate the calibration graph Mn and Cr by Atomic absorption spectroscopy (AAS). The method is linear with an R^2 of (0.9992 and 0.9989) for Mn (II) and Cr (III) respectively. Linearity was determined by the regression analysis. The obtained results were tabulated in Table (1)which shows that the value of t_{cal} is larger than t_{tab} value, and R^2 values are (0.9992 and 0.9989), which indicating that there is a strong correlation between the variation of concentration and response.

Table.1: Data of Calibration curves for the variation of absorbance with metals ions concentration

Type of metal ion	Linear ranges ppm	Straight line equation Abs. = b [X] + a	Correlation coefficient (r)	Percentage linearity (r^2%)	Calculated (t) values $t_{cal.} = \frac{/r/\sqrt{n-2}}{\sqrt{1-r^2}}$
Mn (II) ion	1 - 20	y = 0.011 [Mn] + 0.002	0.9996	99.92	105.96>>2.26
Cr (III) ion	1 - 20	y = 0.0145 [Cr] + 0.0241	0.9994	99.89	90.31>>2.26

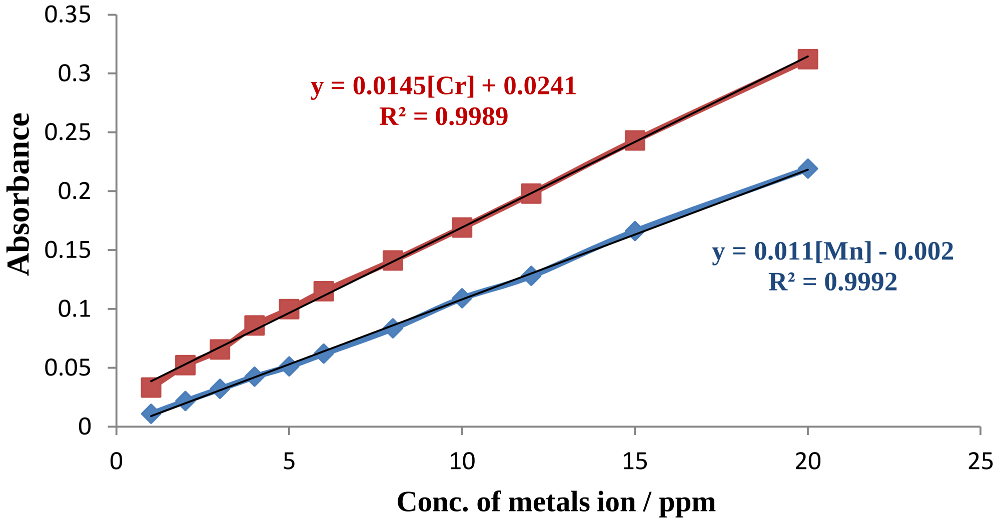

Fig:1: Calibration graph of (Mn and Cr) ions using AAS

Results and Discussions

Adsorption Studies

Effect of contact time

Adsorption experiments for metals ions were carried out using batch equilibrium processes. One hydrogel bead (w = 0.0400 g, d = 3.60 mm) was immersed in 25 ml of Mn (II) and Cr (III) ions solutions of 300 ppm at different contact time of 1 – 48 hr. The adsorption experiments were conducted at constant pH and temperature (6.5 and 25 °C). The residual metals ions concentration after the adsorption process was determined by AAS and the metals ions capacities at each time value were calculated according to the equation below [24]:

Q = (Co – Ce) V / m ……………………….. (1)

Where Q is the capacity of adsorption at a time (t) or at equilibrium (mg/g), C_o and C_e are the initial and remained (concentration at t or at equilibrium) concentrations of metals ions (ppm), V is the volume of metals ions solutions (L), and m is the weight of hydrogel bead used (g). In the present study, m value equal to 0.0400 g, the adsorbed metal ion concentration was calculated by subtract the remained concentration from initial concentration. The results obtained are illustrated in (Table 2 and Figures 2, 3). The results indicate that the adsorption process take place via two steps. In the first step, the adsorption of metal ion increases rapidly due to the availability of a large number of active sites on sorbent surface. In the second step, the adsorption process became less efficient due to the complete occupation of the surface with the metal ion. The big advantage of this sorbent is the large adsorption capacity (i.e. one hydrogel bead with 40 mg weight adsorbed (130.62 or 123.13) mg/g of Mn (II) and Cr (III) ions respectively from aqueous solution.

Table 2: Results of the effect of contact time.

Time hr	Remained ion ppm		Adsorbed ion ppm		Capacity Q mg/g	
	Mn (II)	Cr (III)	Mn (II)	Cr (III)	Mn (II)	Cr (III)
1	278	279	22	21	13.75	13.13
4	228	231	72	69	45.00	43.13
8	160	167	140	133	87.50	83.13
12	138	142	162	158	101.25	98.75
24	91	103	209	197	130.62	123.13
48	91	103	209	197	130.62	123.13

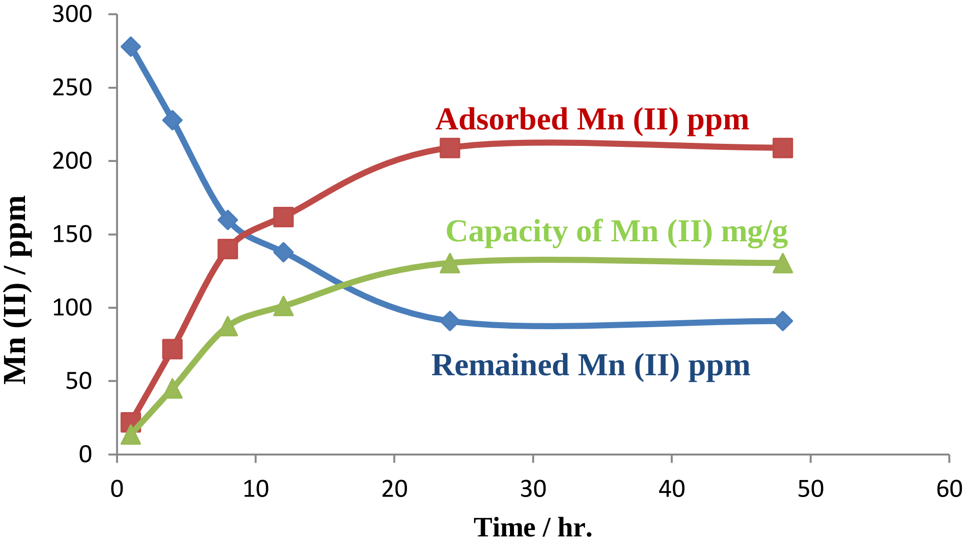

Fig:2: Relationship betweem time Vs. Mn (II) quantity.

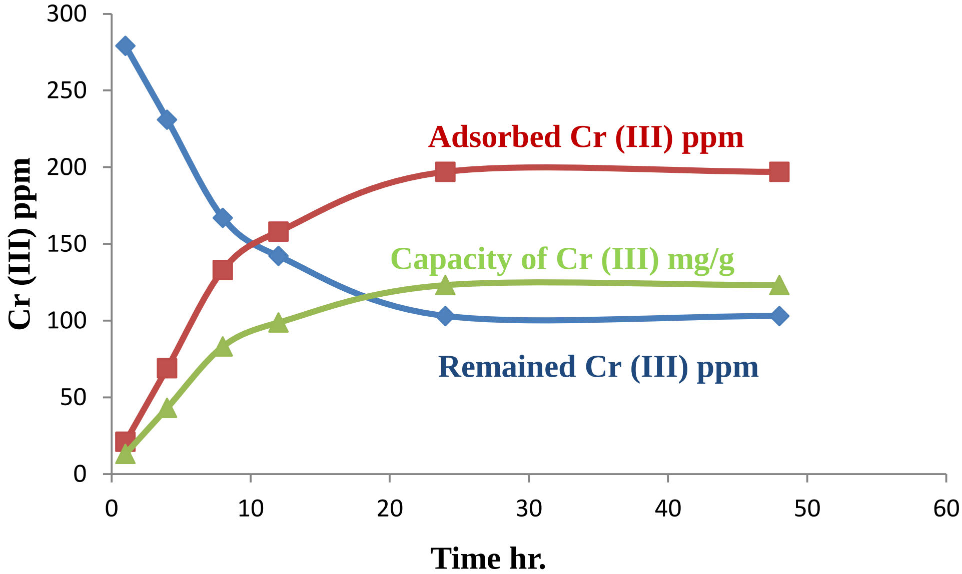

Fig:3: Relationship between time Vs. Cr (III) quantity.

Effect of initial concentration

Batch equilibrium experiments were estimated by varying the metal ion concentration. A 25 ml solution of (50 – 350 ppm) metals ions concentration was used at pH = 6.5. The solutions were left at room temperature for 24 hours . The results obtained (Table 3 and Figure 4) reveals, that the adsorbed metals ions quantity was increased as the initial concentration of metal ion was increased until reach the maximum capacity of the hydrogel beads. At low concentration the hydrogel bead does not reach the maximum capacity, and remained concentration is very low, while at high concentration the hydrogel bead reach its maximum capacity, so that the remained concentration is high. The adsorption percentage calculated as below:

$$\% \text{ adsorption} = \frac{\text{initial conc.} - \text{remained conc.}}{\text{initial conc.}} \text{ x } 100 \text{ .... } 2$$

Table 3: Results obseried of the initial concentration effect.

Initial Conc. ppm	Remained ion ppm		Adsorbed ion ppm		Capacity Q mg/g		% adsorption	
	Mn (II)	Cr (III)	Mn (II)	Cr (III)	Mn (II)	Cr (III)	Mn (II)	Cr (III)
50	0.5	0.5	49.5	49.5	30.94	30.9	99	99
100	1.2	5	98.8	95	61.75	59.4	98.8	95
150	2.4	10	147.6	140	92.25	90.62	98.4	93.33
200	12	18	188	182	117.5	113.73	94	91
250	48	54	202	196	126.25	122.5	80.8	78.6
300	91	103	209	197	130.62	123.13	69.97	65.5
350	141	153	209	197	130.62	123.13	59.71	56.28

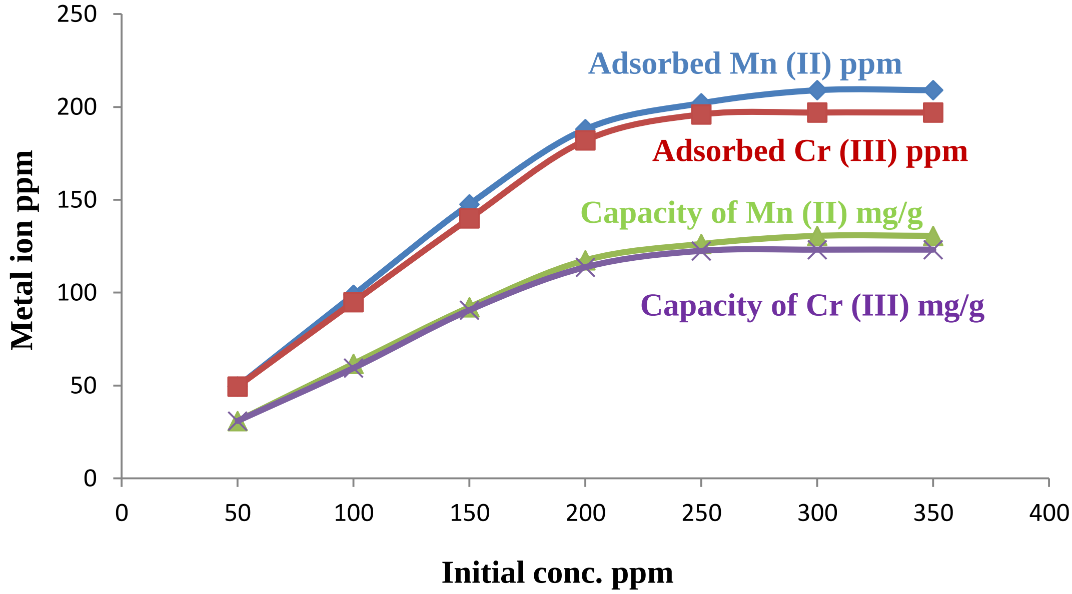

Fig:4: Relationship between initial conc. Vs. metal ion quantity.

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Effect of pH

To conduct this experiment, 25 ml volumetric flasks each of which contains 25 ml of 100 ppm metal ion solution and one hydrogel bead was used. The pH of solution was adjusted at range (1–7.5) and left at room temperature for 10 hr. The capacity and adsorption percentage were calculated from equation 1 and 2, respectively. The results obtained were tabulated in Table 4, which indicate that the optimized pH for the adsorption of metals ions was (5 - 7.5) for Mn (II) and Cr (III) ions. At low pH values, protons were available to protonate all sites on the hydrogel bead surface, therefore, the attraction to cationic ions decrease. The pH value which was chosen for this study at 6.5 (near the pH of deionized water) due to the high degree of deprotonation of the sites in the hydrogel bead surface is occurring at high value of pH [25] and to avoid the precipitation of metal ions as hydroxide. Figure 5 and 6; show the relationship between pH with remaining metal ion concentration adsorption percentage and capacity.

Table 4: Summary of results obtained from the pH effect study.

pH value / Metals ions		1	3	5	6.5	7.5
Remained ppm	Mn (II)	68.9	42.6	22	20	20
	Cr (III)	37	30	21	20	20
% adsorption	Mn (II)	31.1	57.4	78	80	80
	Cr (III)	63	70	79	80	80
Capacity mg/g	Mn (II)	19.43	35.87	48.75	50	50
	Cr (III)	39.4	43.8	49.4	50	50

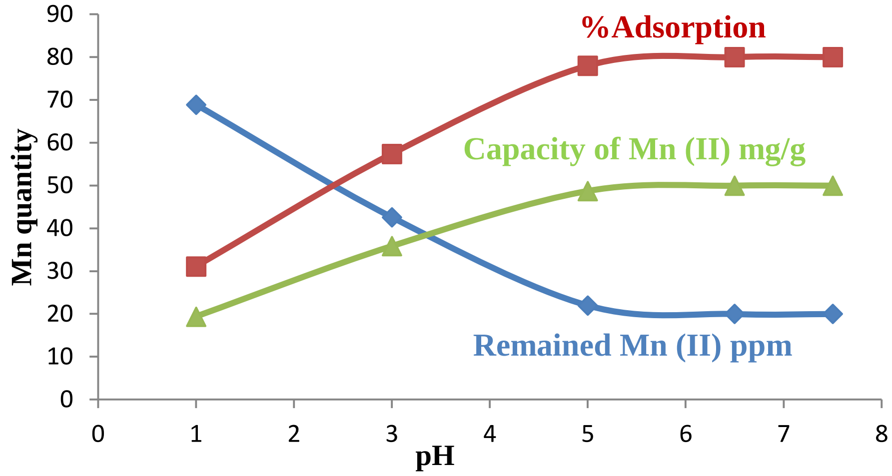

Fig:5: Relationship between pH Vs. Mn (II) quantity.

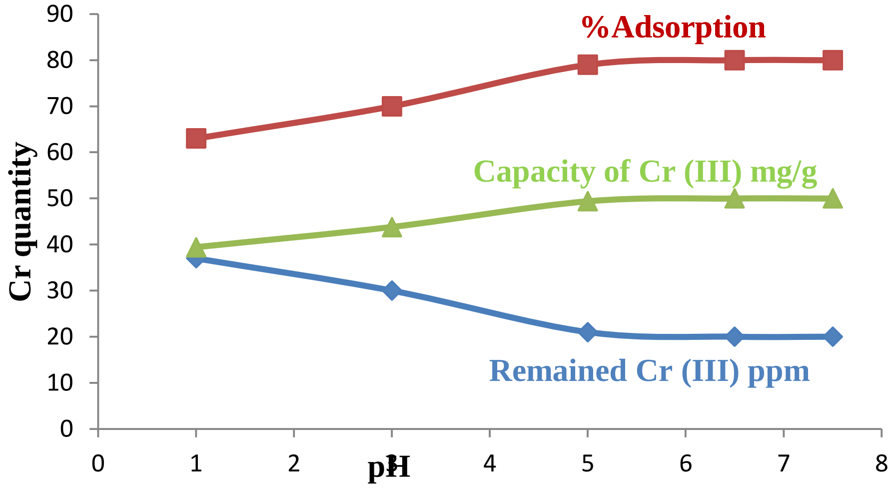

Fig:6: Relationship between pH Vs. Cr (III) quantity.

Effect of temperature

The adsorption studies were conducted at four different temperatures (5 – 30 ºC) ,the initial concentration(50-250 mg/l). The obtained results (Table 5) reveal that the adsorption of Mn (II) and Cr (III) ions increases as temperature increases; this may be due to the increase in ion mobility, which may also cause a swelling effect within the internal structure of hydrogel leading to more penetrate of metal ion [26] as shown in Fig. 7.

Table 5: The effect of temperature on adsorption process

Temperature °C / Metal ion		5	10	20	25	30
% Adsorption	Mn (II)	37.15	47.2	54.3	59.70	59.70
	Cr (III)	34.86	44.0	52.0	56.29	56.29
Capacity mg/g	Mn (II)	81.25	103.25	118.75	130.62	130.62
	Cr (III)	76.25	96.25	113.7	123.13	123.13

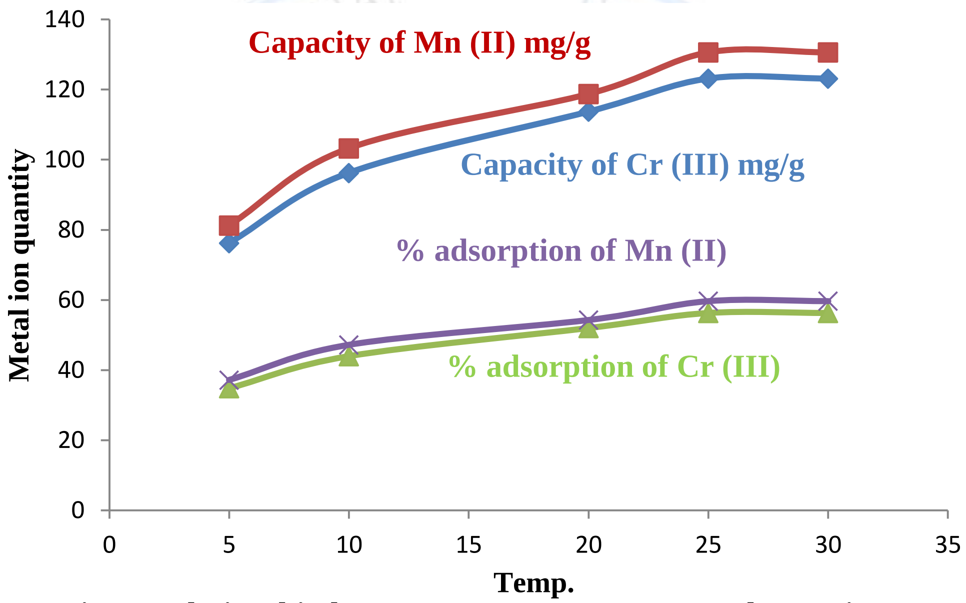

Fig:7: Relationship between temperature Vs. metal quantity

Adsorption kinetic study

The Lagergren pseudo – first – order and pseudo – second – order equations were used to test the experimental data by application equations (3 and 4) [27]:

$$\text{Log}\,(Q_e - Q_t) = \text{Log}\,Q_e - k_1 / 2.303\, t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3$$

$$t / Q_t = 1/ k_2 Q_e^2 + t / Q_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4$$

Where Q_e, Q_t are the amount of metals ions adsorbed (mg/g) at equilibrium and at any time t respectively. $k_1$and k_2 are the adsorption rate constant of pseudo – first – order (hr $^{-1}$) and pseudo – second – order (g/mg. hr). The results obtain are summarized in Table 6, which indicate that the adsorption process follow a pseudo – first – order with a correlation coefficient R^2 value of

(0.9882 and 0.993) for Mn (II) and Cr (III) ions respectively. Figure 8 and 9, shown the straight plots of Log ($Q_e - Q_t$) vs. t which gives the slpoe = $-k_1/ 2.303$ and intercept =log Qe and the k_2 and Qe are found from the intercept and slope of t/Q_t versus t,linear plot such that Qe = 1/slpoe and k_2 = slope ^{2} / intercept respectively.

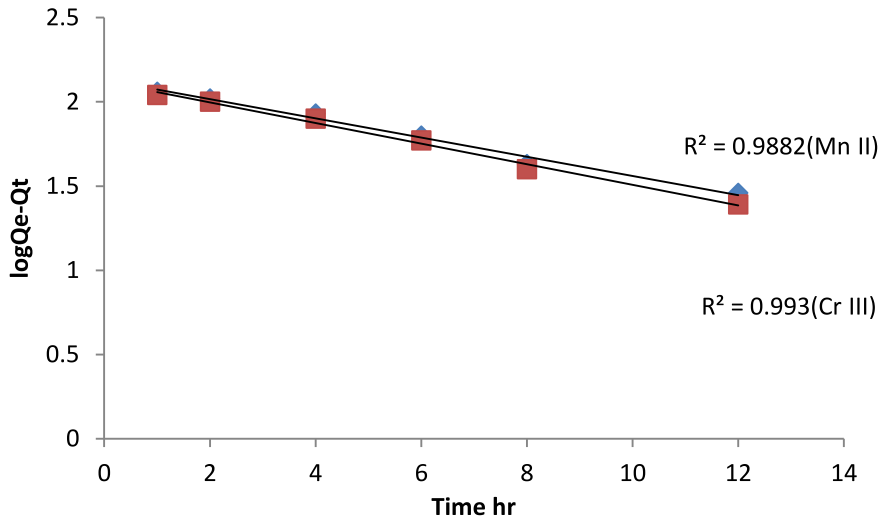

Fig: 8 Plots of pseudo -first – order

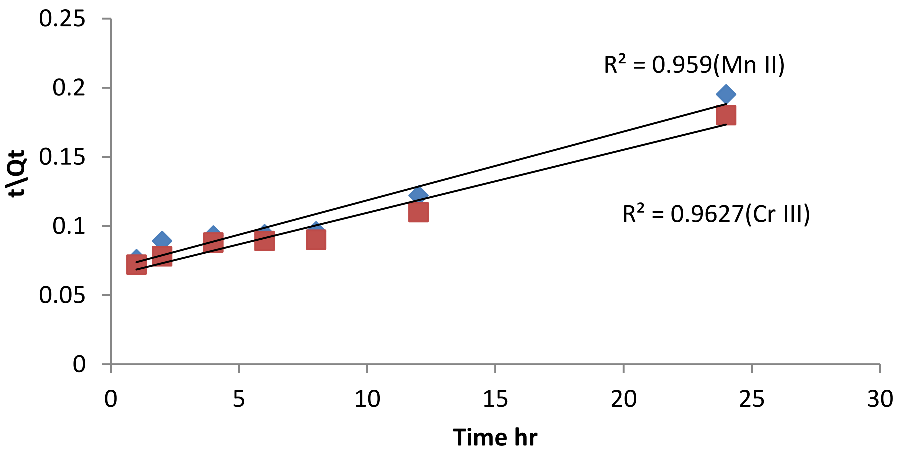

Fig: 9 Plots of pseudo - second - order

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Table 6: Estimated adsorption kinetic parameters for metals ions.

Model	pseudo – first – order				pseudo – second – order		
parameters / Metal ion	Q_{exp}	k_1	Q_{cal}	R^2	Q_{cal}	k_2	R^2
Mn (II)	130.6	0.115	137.08	0.9882	333.33	0.00012	0.9672
Cr (III)	123.11	0.140	131.52	0.993	200.0	0.00036	0.959

Adsorption isotherms

Adsorption of metals ions using hydrogel bead was determined as a function of equilibrium remained metals ions concentration C_e ,Two adsorption isotherms were used Langmuir and Freundlich and plotted as shown in Figures 10, 11, 12 and 13.. The Langmuir and Freundlich equations are given in the following equations[28]:

Langmuir: $C_e / Q_e = 1/K_L\, Q_{max} + C_e/ Q_{max}$ **………………. 5**

Freundlich : $\text{Log } Q_e = \text{Log } K_F + 1/ n \text{ Log } C_e$ **…………… 6**

Where Q_{max}, Q_e are the maximum ion uptake per unit mass of hydrogel bead (mg/g)related to adsorption capacity and capacity at equilibrium (mg/g) respectively, C_e is the equilibrium concentration (ppm), K_L and K_F are Langmuir and Freundlich constant and n is Freundlich exponents.Therfore, Langmuir parameters calculeated from the slope and intercepts of the linear plots of C_e/Q_e versus. C_e gives a stragth line of slope1/ Q_{max},and intercept$1/K_L\, Q_{max}$ while the Freundlich parameters can be calculated from the slope and intercepts of the linear plots of Log Q_e vs. Log C_e. It was found from this study that the adsorption of the two metal ions was followed Langmuir's isotherm. The value of n is larger than 1, which represents a favorable removal condition. All evaluated parameters are present in Table 7.

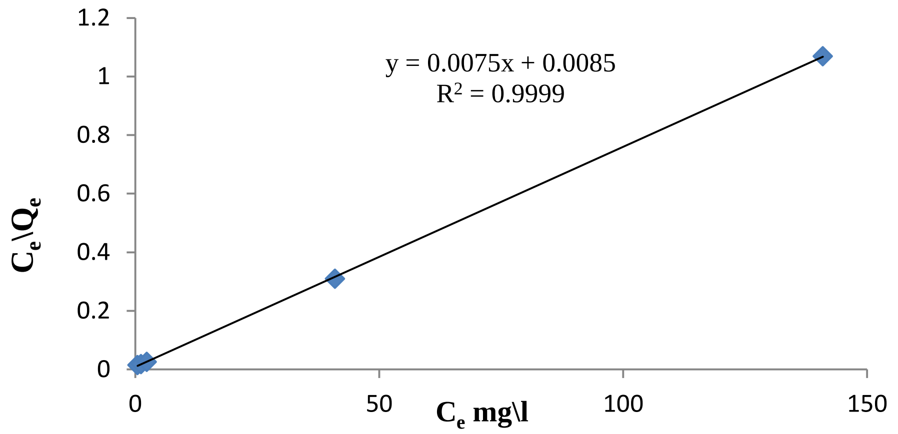

Fig:10: Langmuir plots for Mn (II) ion

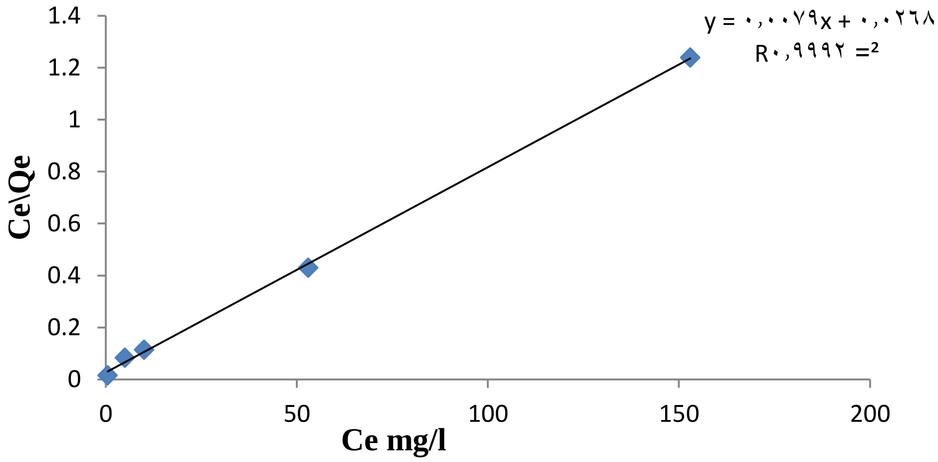

Fig:11: Langmuir plots for Cr (III) ion

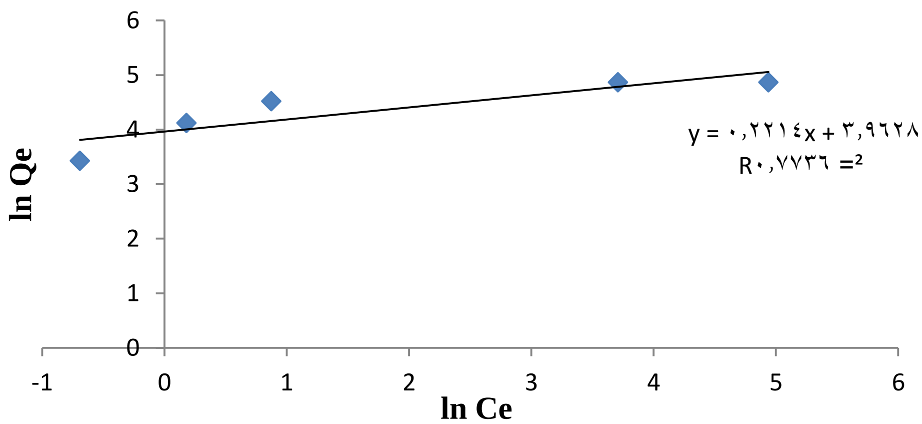

Fig:12: Freundlich plots for Mn (II) ion

Table 7: Estimated adsorption isotherm parameters.

Model / parameters / Metal ion	Langmuir parameters			Freundlich parameters		
	Q_{cal}	K_L	R^2	K_F	n	R^2
Mn (II)	142.85	0.875	0.9999	52.56	4.52	0.7736
Cr (III)	142.80	0.270	0.9992	40.326	3.937	0.935

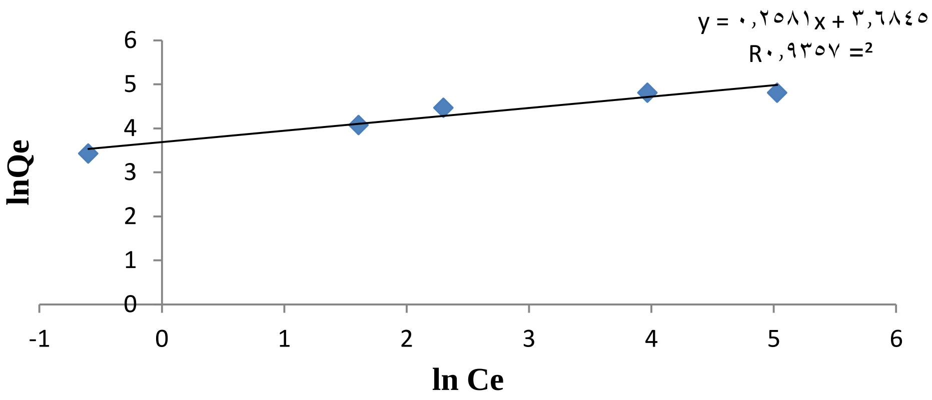

Fig:13: Freundlich plots for Cr (III) ion

Thermodynamic study

The thermodynamic functions (ΔG°,ΔH°,ΔS°) of the removal of metals ions on hydrogel bead calclated using the following relations(7,8and 9):

$K_c = Q_e / C_e$ ………………………………… 7

$\ln K_c = \Delta S^o / R - \Delta H^o / RT$ ………………… 8

$\Delta G^o = \Delta H^o - T\Delta S^o$ ………………………….. 9

Where K_c (L/g) is the standard thermodynamic equilibrium constant. The thermodynamic parameters can be calculated from the slope and intercept of the Ln K_c vs. 1/T plotting (Figure 14 and 15), the results obtained are tabulated in Table 8, which reveals that the adsorption process is endothermic and increase of randomness at the solid/ solution interface occur in the internal structure.

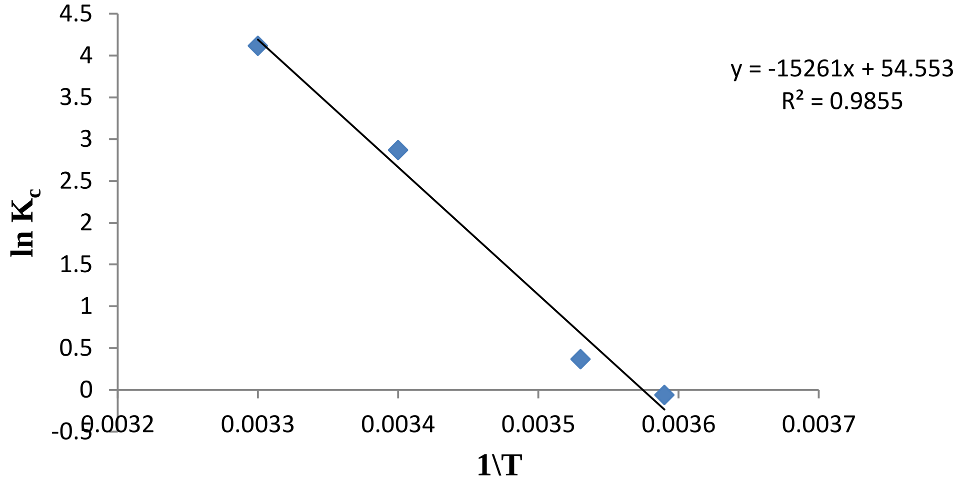

Fig: 14: Plots of lnK $_c$ Vs. 1\T for Mn (II)

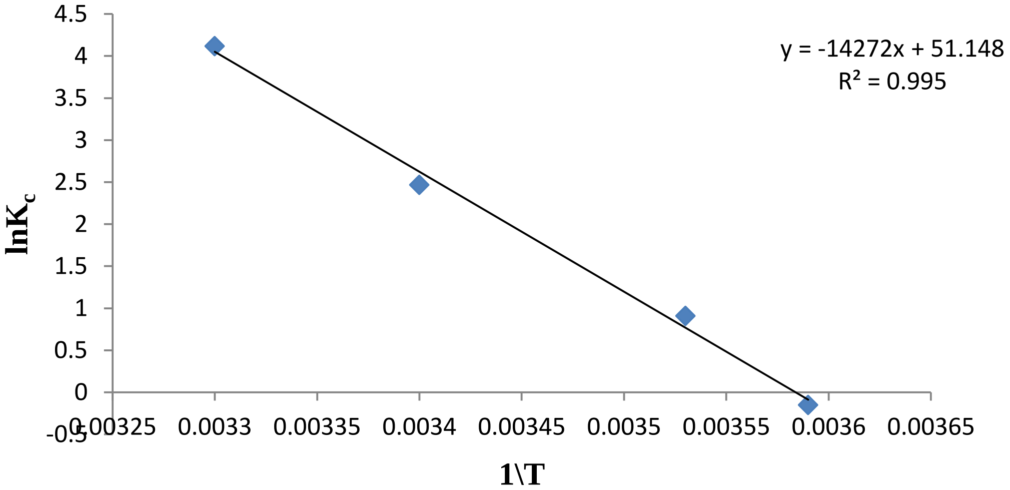

Fig:15: Plots of lnKcVs. 1\T for Cr (III)

Table 8: Thermodynamic parameters for the adsorption of Mn(11) and Cr (111) ions

Temperature (K)	ΔG° (KJ/ mol)		ΔH° (KJ / mol)		ΔS° (J/ mol. K)	
	Mn (II)	Cr (III)	Mn (II)	Cr (III)	Mn (II)	Cr (III)
278	0.822	- 0.45	126.90	118.65	453.52	425.177
283	- 1.446	- 1.675				
293	- 5.981	- 5.926				
298	- 8.248	- 8.053				

Conclusions

In this study a hydrogel beads were used to adsorb the Mn (II) and Cr (III) ions from aqueous solution. The extent of adsorption of metals ions was found increased with increasing temperature,i.e endothermic process,. The maximum capacities are (130.62, 123.13) mg/g for Mn (II) and Cr (III) ions respectively, which were reached after 24 hrs. The kinetic equilibrium was found to be fitted with pseudo– first order kinetic, and the isotherm agrees with the Langmuir equation during the whole adsorption process.

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