

**Adsorption of Co (Ii) Ion from its Aqueous Solution Using Hydrogel
Beads as Adsorbent**

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as Adsorbent**

Amir Fadhil Dawood Al-Niimi¹, Ahmed Mahdi Saeed² and Sara T. Abed³

^{1,2,3}Department of Chemistry- College of Science- Diyala University

¹Dr.amer960@sciences.uodiyala.edu.iq

²dr.ahmedalanbakey@yahoo.com

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Abstract

In this study one of the super absorbent hydrogel beads was used for adsorb Co(II) ion from aqueous solution. The adsorption capacity of the adsorbent is presented and the time required to reach a maximum capacity of bead (112.5 mg/g) from Co (II) ion 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, Freundlich, Dubinin and Temkin. The Langmuir isotherm model gave the highest R^2 value of 0.9998. 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 R^2 value of 0.992.

Key words: adsorption, Co(II) ion, hydrogel beads.

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امتزاز ايون الكوبلت الثنائي من محلوله المائي باستخدام حبيبات الجل المائية كمادة مازة

عامر فاضل داود النعيمي¹، احمد مهدي سعيد² و سارة ثامر عبد³

^{1,2,3}ا قسم الكيمياء - كلية العلوم - جامعة ديالى

الخلاصة

في هذه الدراسة استخدمت حبيبات الجل المائية لامتزاز ايون الكوبلت الثنائي من محلوله المائي عند زمن الاتزان 24 ساعة. تم دراسة تأثير الزمن ، درجة الحرارة ، التركيز الابتدائي و الداله (112.5 mg/g) اذ كانت اقصى سعة امتزاز (الحامضية على عمليه الامتزاز . طبقت نماذج ايزوثيرمات الامتزاز لانكماير ، فريندلس ، دوينين وتمكن وتبين ان الامتزاز يتوافق مع نموذج لانكماير اذ كانت قيمة معامل الارتباط (0.999) ، تم حساب قيم الدوال الترموديناميكية وتم تطبيق معادلات المرتبة الاولى الكاذبة والمرتبة الثانية الكاذبة وتبين ان الامتزاز يسلك سلوك المرتبة الاولى الكاذبة اذ كانت قيمة معامل الارتباط 0.992

الكلمات المفتاحية : الامتزاز ، ايون الكوبلت الثنائي ، حبيبات الجل المائية

Introduction

The elimination of heavy metals from waters and waste waters is important to protect public health metal removal [1]. The adsorption of heavy metal ions on different adsorbent have been studied extensively in order to find a specific adsorbent for each ion to be used in the treatment of wastewater in the environment [2] . Cobalt, one of the common toxic metals affecting the environment, is present in the waste water of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic. High levels of cobalt may affect several health troubles such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects. The standard level of cobalt in drinking water is 2 g l^{-1} , but values up to 107 g l^{-1} have been reported. One of the adsorbent which is widely used for the removal of cobalt and other heavy metals is activated carbon .The application of this adsorbent is limited on the commercial considerations, due to the relative high cost associated with it separation. [3].The commonly used procedures for removing metal ions from effluents include filtration,

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chemical precipitation, ion exchange [4], chemical coagulation, flocculation, ion exchange, reverse osmosis, membrane technologies and solvent extraction [5,6]. These processes may be ineffective or expensive, especially when the heavy metal ions are present in high concentrations. In this study the batch mode studies, the dynamic behavior of the adsorption was investigated on the effect of initial metal ion concentration, temperature, adsorbent dosage and pH. The thermodynamic parameters were also evaluated from the adsorption measurements. The Langmuir, Freundlich and Temkin adsorption isotherms, adsorption Kinetics were calculated from experimental data. [7,8].

Experimental

Apparatus:

Atomic absorption spectrophotometer (AAS) type (AURORA, A1200 – Canada) was used to determine Co(II) 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 metal ion adsorption in this study. All other chemicals used throughout this study were of analytical reagent grade and were purchased from Aldrich Chemical Company (Germany). A 1000 ppm aqueous solution of Co(II) ion were prepared from hydrated metals chloride salt. More dilute solutions of metal ions were prepared from stock solution by simple dilution with distilled water.

Preparation of calibration graph and linearity study:

For determining the linearity, a series of solutions have different metal ion concentrations 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 Co ion by Atomic absorption spectroscopy (AAS). The method is linear with an R^2

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of (0.999) for Co (II) . 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 (0.9991), which indicating that there is a strong correlation between the variation of concentration and response.

Table.1: Summary of linear regression for the variation of absorbance with metal ion concentration using first degree equation of known form $y = b [X] + a$.

Type of metal ion	Linear ranges ppm	Straight line equation Abs. = b [X] + a	Correlation coefficient (r)	Percentage linearity (r ² %)	Calculated (t) values $t_{cal.} = \frac{r/\sqrt{n-2}}{\sqrt{1-r^2}}$
Co (II) ion	1 - 20	$y = 0.0936 [Co] + 0.00498$	0.9995	99.91	$66.63 \gg 2.75$

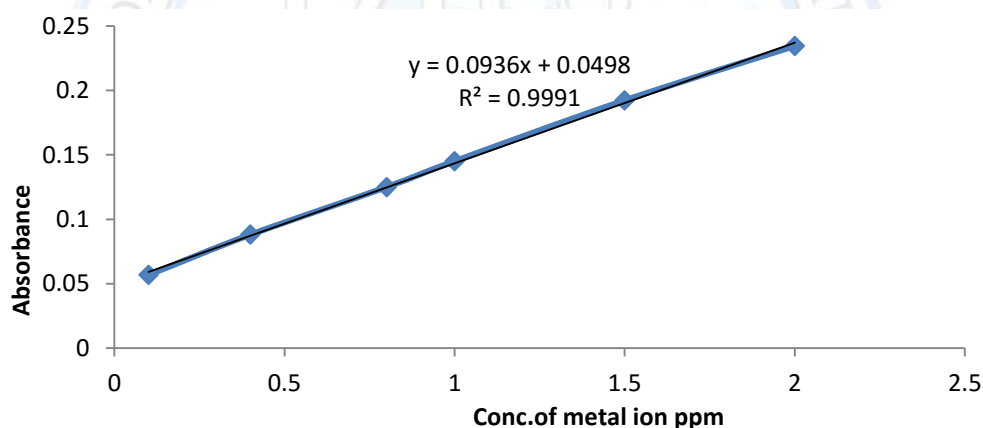


Fig1. Calibration graph of Co using AAS

Results and Discussions

Adsorption Studies:

Effect of contact time:

Adsorption experiments for Co ion were carried out using batch equilibrium processes. One hydrogel bead ($w = 0.0400$ g, $d = 3.60$ mm) was immersed in 25 ml of Co(II) ions solutions of 300 ppm at different contact time of 1 – 48 hrs. The adsorption experiments were conducted at constant pH and temperature (6.5 and 25 °C). The residual metal ion concentration after the

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adsorption process was determined by AAS and the Co (II) capacity at each time value were calculated according to the equation below [9]:

$$Q = (C_o - C_e) V / m \dots\dots\dots (1)$$

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 (at t or at equilibrium) concentrations of Co ion (ppm), V is the volume of metal ion 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 Figure 2). 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 (112.5) mg/g of Co (II) from aqueous solution.

Table 2: Summery of the results obtained from the contact time study.

Time hr.	Remained ion ppm	Adsorption ion ppm	Capacity Q mg/g
1	280	20	12.5
2	265	35	21.88
4	231.2	68.8	43.01
6	198.9	101.1	63.2
8	169	131	81.88
12	145	155	96.88
24	120	180	112.5
48	120	180	112.5

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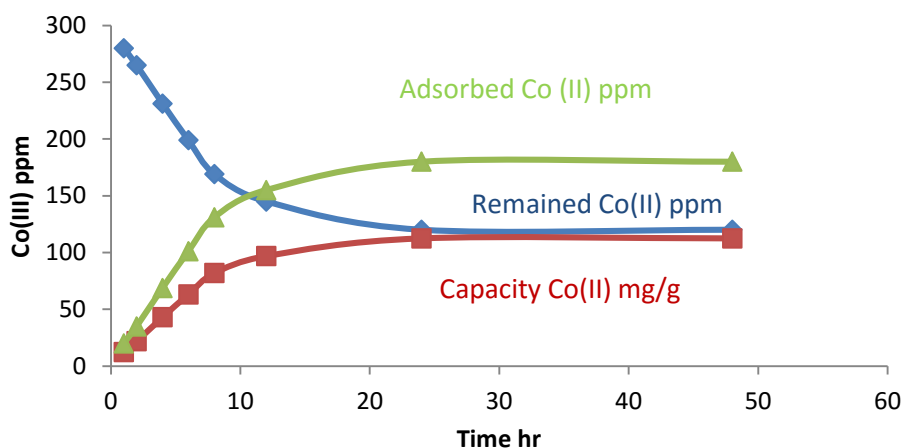


Fig 2.Relationship between time Vs.Co(II) quantity

Effect of initial concentration:

Adsorption equilibrium and isotherm studies were estimated by varying the metal ion concentration. A 25 ml solution of (50 – 350 ppm) metal ion concentration was used at pH = 6.5. The solutions were left at room temperature for 24 hours and the remained metal ion concentration was determined using AAS measurements. The results obtained (Table 3 and Figure3) reveals, that the adsorbed metal ion 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:

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

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Table 3: The results obtained from the initial concentration effect study.

Initial Conc.ppm	Remained ion ppm Co(II)	Adsorbed ion ppm Co(II)	Adsorption %	Capacity Q mg/g Co(II)
50	0.5	49.5	99	30.9
100	5	95	95	59.4
150	10	140	93.33	90.62
200	18	182	91	113.75
250	54	196	78.6	122.5
300	103	197	65.6	123.13
350	153	197	56.28	123.13

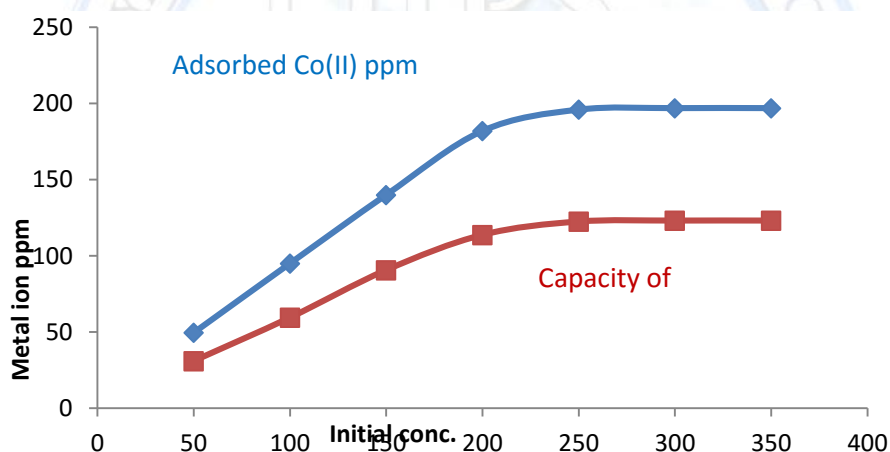


Fig 3. Relationship between initial conc. Vs metal ion quantity

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 pH range of (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 metal ion was (5 - 7.5) for Co ion. At low pH values, protons were available to protonate all sites on the hydrogel bead

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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 [10] and to avoid the precipitation of metal ion as hydroxide. Figure 4; show the relationship between pH with remained metal ion concentration adsorption percentage and capacity.

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

pH value		1	3	5	6.5	7.5
Metal ion						
Remained ppm	Co (II)	45	34	25	15	15
% adsorption	Co (II)	55	66	75	85	85
Capacity mg/g	Co (II)	34.37	41.3	46.9	53.13	53.13

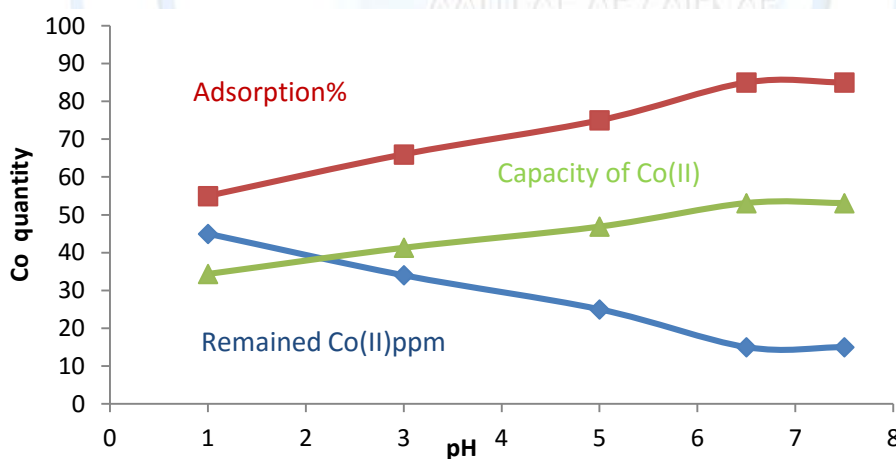


Fig 4. Relationship between pH Vs.Co(II) quantity

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Effect of temperature

The adsorption studies were conducted at four different temperatures (5 – 30 °C). The obtained results (Table 5) reveal that the adsorption of Co (II) ion 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 [11] as shown in Fig.5.

Table 5: summary of the results obtained from temperature study.

Temperature °C		5	10	20	25	30
Metal ion						
% Adsorption	Co (II)	11.30	15.20	17.20	18.00	18.00
Capacity mg/g	Co (II)	70.62	95	107.5	112.5	112.5

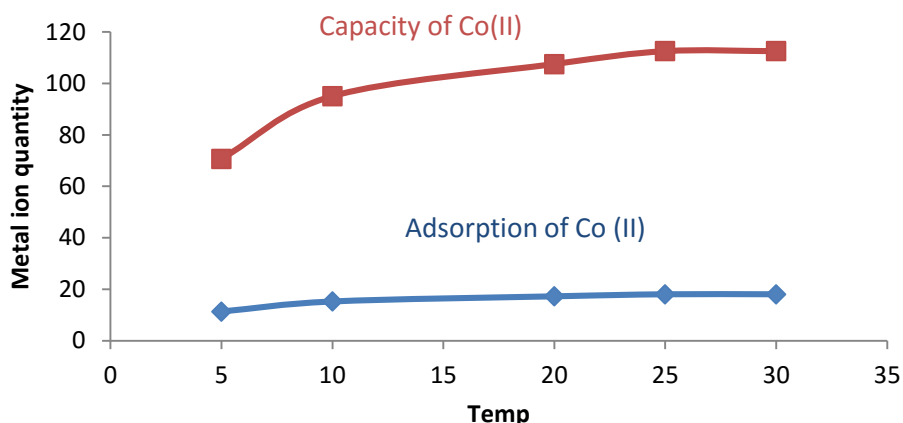


Fig 5. Relationship between temperature Vs.metal quantity

Adsorption kinetic study:

In order to examine the mechanism of the adsorption process the pseudo – first – order and pseudo – second – order equations were used to test the experimental data (12):

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

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

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Where Q_e , Q_t are the amount of metal ion adsorbed (mg/g) at equilibrium and time t respectively. k_1 and k_2 are the 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 (0.9922) for Co(II) ion . Figure 6,7 shown the straight plots of $\log(Q_e - Q_t)$ vs. t and t / Q_t vs. t , respectively.

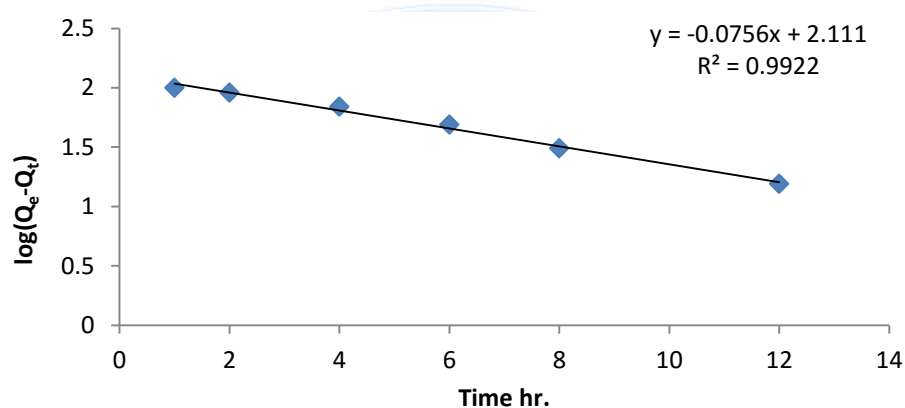


Fig 6. Plot of pseudo-first-order

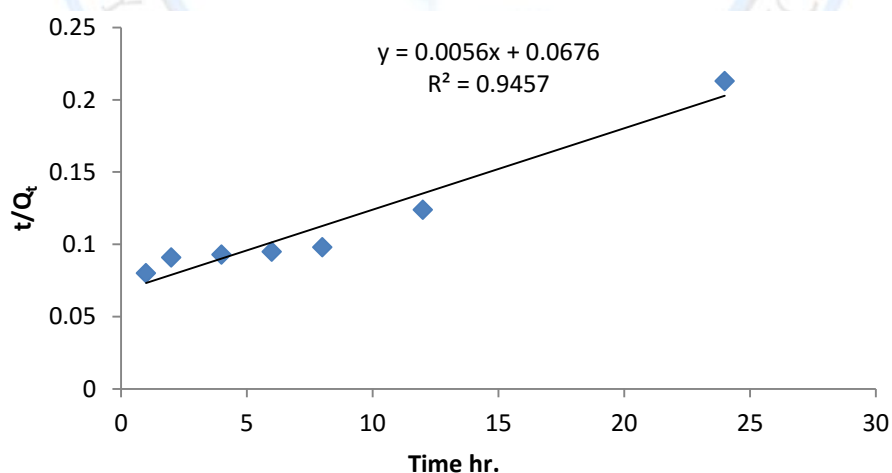


Fig 7. Plot of pseudo-second-order

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Table 6: Estimated adsorption kinetic parameters for metals ions.

Model	pseudo – first – order				pseudo – second – order		
	Q _{exp}	k ₁	Q _{cal}	R ²	Q _{cal}	k ₂	R ²
parameters							
Metal ion							
Co(II)	112.5	0.174	129.12	0.9922	178.57	0.00046	0.9457

Adsorption isotherm study:

To identify the mechanism of the adsorption process, the adsorption of Co ion using hydrogel bead was determined as a function of equilibrium remained (residual) metal ion concentration C_e and the corresponding adsorption isotherms were plotted as shown in Figures 8 ,9,10 and 11. The data can then be correlated with a suitable isotherm Langmuir, Freundlich, Temkin and Dubinin. The Langmuir ,Freundlich ,Temkin and Dubinin equations are given in the following (13):

Langmuir equation: $C_e / Q_e = 1 / K_L Q_{max} + C_e / Q_{max}$ 5

Freundlich equation: $Log Q_e = Log K_F + 1/ n Log C_e$ 6

Temkin equation: $Q_e = B lnK_T + B lnC_e$ 7

Dubinin equation: $lnQ_e - \beta \epsilon^2 = q_{max}$ 8

Where Q_{max}, Q_e are the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), and capacity at equilibrium (mg/g) respectively, C_e is the equilibrium concentration (ppm), K_L, K_F, B and K_T are Langmuir ,Freundlich and Temkin constant and n is Freundlich exponents. Langmuir ,Freundlich, Temkin and Dubinin parameters can be evaluated from the slopes and intercepts of the linear plots of C_e/Q_e vs. C_e , Log Q_e vs. Log C_e , Q_e vs ln C_e and ln C_e vs ε² respectively . 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 and 8.

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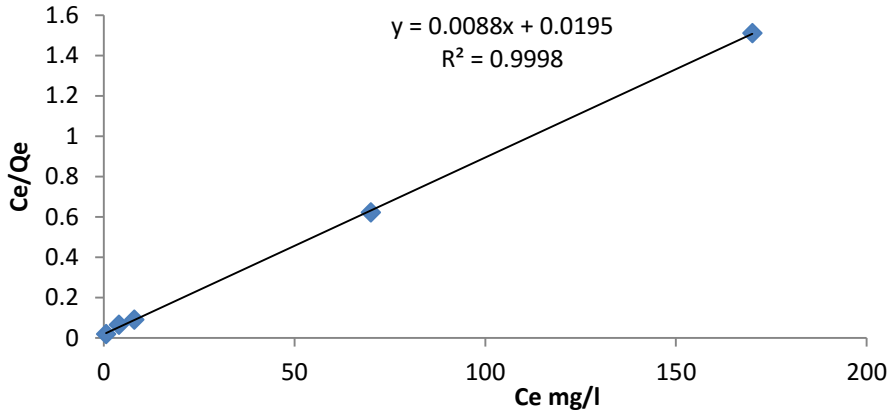


Fig 8. Langmuir plot for Co(II) ion

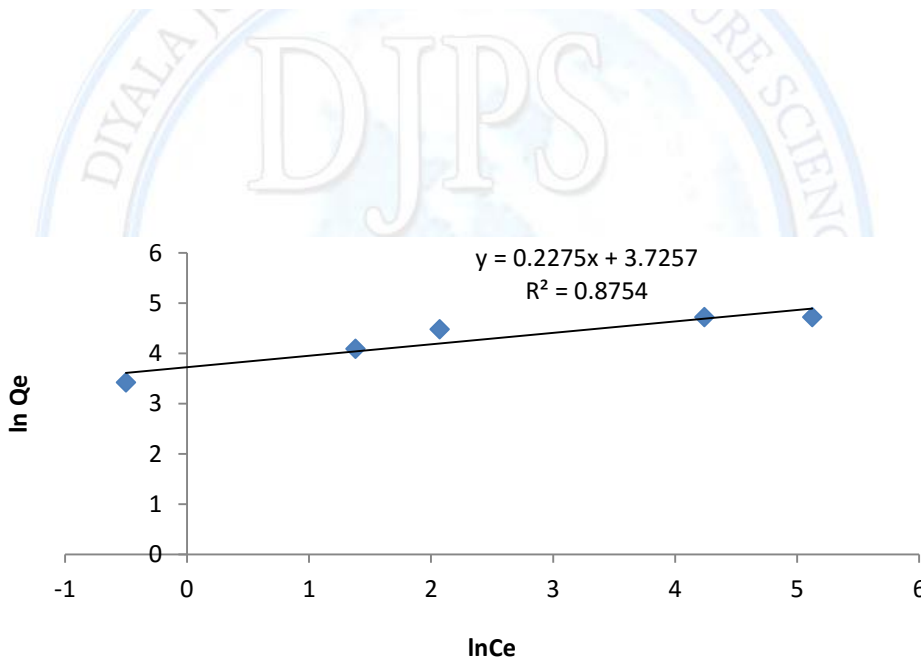


Fig 9. Freundlich plot for Co(II) ion

Table 7: Estimated adsorption isotherm parameters.

Model parameters	Langmuir parameters			Freundlich parameters		
	Q _{max}	K _L	R ²	K _F	n	R ²
Metal ion						
Co(II)	133.63	0.383	0.9998	41.50	4.39	0.8754

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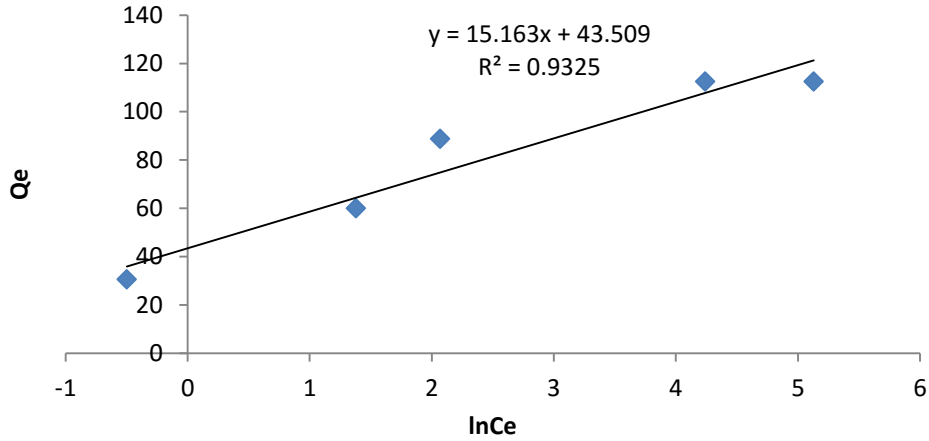


Fig 10. Temkin plot Co(II) ion

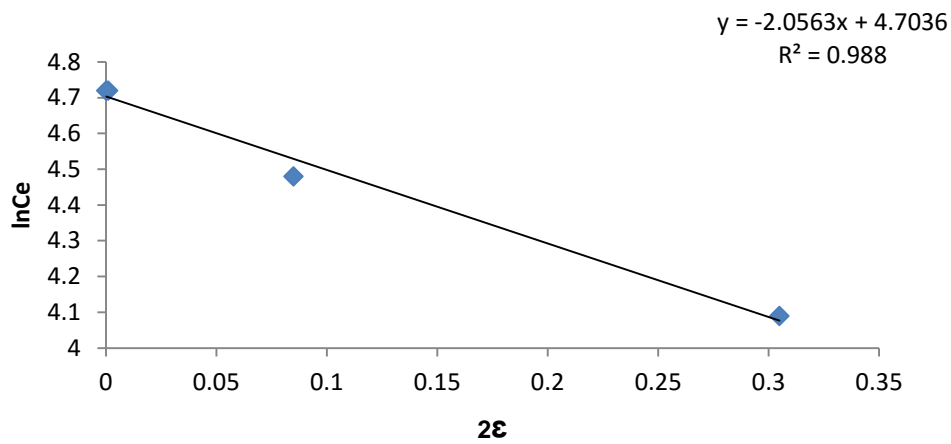


Fig 11. Dubinin plot Co(II) ion

Table8: Estimated adsorption isotherm parameters.

Model parameters	Temkin parameters			Dubinin parameters			
	B	K_T	R^2	β	q_{max}	E	R^2
Metal ion							
Co(II)	15.163	17.626	0.9325	-2.0563	110.34	0.641	0.988

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Thermodynamic studies:

The thermodynamic parameters of the removal of metals ions on hydrogel bead can be evaluated using the following relations:

$$K_c = Q_e / C_e \dots\dots\dots 9$$

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \dots\dots\dots 10$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots\dots\dots 11$$

Where R is the universal gas constant, T is the absolute temperature and K_c (L/g) is the standard thermodynamic equilibrium constant. The thermodynamic parameters can be calculated from the slop and intercept of the Ln K_c vs. 1/ T plotting (Figure12), the results obtained are tabulated in Table 9, which reveals that the removal process is endothermic with increase of randomness at the solid/ solution interface occur in the internal structure.

Table9: Thermodynamic parameters of adsorption process at different temperature.

C ₀	hermodynamic paramete	5 °C	10 °C	20 °C	25 °C
50mg/l	ΔH KJ.mol ⁻¹	+111.55			
	ΔG KJ.mol ⁻¹	0.284	-2.07	-5.72	-7.721
	ΔS J.mol ⁻¹ .k ⁻¹	400.24			

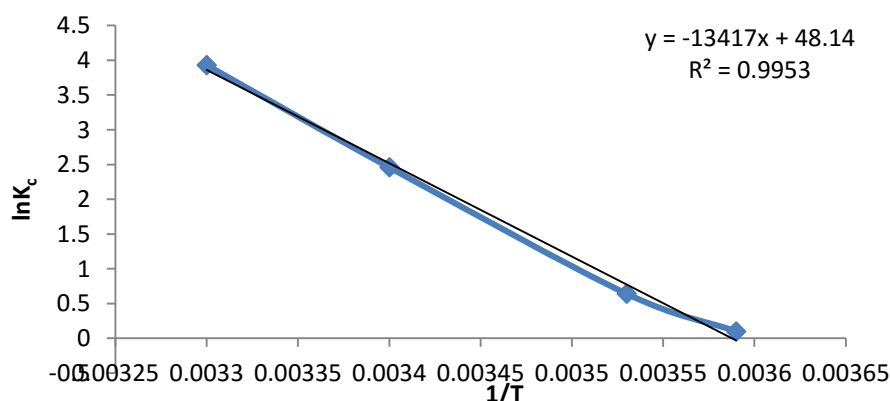


Fig 12. plot of lnKc Vs.1/T for Co(II)

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Conclusions

In this study a hydrogel beads were used to adsorb the Co (II) ion from aqueous solution. The results shown that, the adsorption of metal ion was increased with increasing temperature and time. The maximum capacity are (112.5) mg/g for Co (II) ion , which were reached after 24 hrs. The kinetic equilibrium was found to be fitted with pseudo– first order model, and the isotherm agrees well with the Langmuir model during the whole adsorption process. The adsorption of Co ion using hydrogel bead was found to be endothermic process.

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