

Removal of Ni (II) Ion from Aqueous Solution Using Hydrogel Bead and AAS Measurement.

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Abstract

The adsorption removal is one of the techniques used for the treatment of industrial wastewater. In this research the principle of treatment consists on the removal of Ni (II) ion from wastewater. The elimination of this pollutant was done by using commercial hydrogel as adsorbent removal. Batch method removal at different temperature (5 – 25 °C) and different contact time (1 – 48 hr) applied to reach the equilibrium conditions for Ni(II) ion removal. The removal of Ni (II) ion improved by changing the pH, contact time, initial concentration and temperature. The residual (remained) Ni (II) ion was determined by using the Atomic Absorption Spectroscopy (AAS). The highest removal of Ni (II) ion was obtained at equilibrium with 24 hr and pH of 6.3. Maximum removal capacity was found to be 135.6 mg Ni (II) ion per g hydrogel bead. Pseudo – first – order kinetics and Langmuir isotherm were best fits for Ni (II) ion. All thermodynamic parameters were evaluated, ΔH_{ads} was found to be 13.13 KJ/ mole.

Key words: removal, hydrogel, Ni (II) ion, AAS measurements.

إزالة أيون النيكل من المحاليل المائية باستخدام حبيبات الجل المائية وقياسات الامتصاص الذري

د. أحمد مهدي سعيد

جامعة واسط , كلية العلوم , قسم الكيمياء

المخلص

الإزالة بواسطة الامتزاز إحدى التقنيات المستخدمة لمعالجة مخلفات المياه الصناعية. في هذا البحث أساس المعالجة يتضمن إزالة أيون النيكل الثنائي من مخلفات المياه. تقليل هذا التلوث تم باستخدام حبيبات الجل المائية كمادة مازة للإزالة. لقد نفذت التجارب بطريقة الوجبات, وبدرجات حرارية مختلفة تراوحت بين (5 – 25 درجة مئوية) وبزمن تماس تراوح بين (1 – 48 ساعة) لغرض الوصول لحالة التوازن للإزالة. لقد درست الإزالة مع ظروف تتضمن الدالة الحامضية, زمن التماس, التركيز الابتدائي ودرجة الحرارة كعوامل مؤثرة. لقد تم قياس أيون النيكل باستخدام تقنية الامتصاص الذري. أعلى قيمة إزالة لأيون النيكل عند حالة التوازن هي عند زمن 24 ساعة و دالة حامضية تساوي 6.3 . لقد وجد ان السعة القصوى تتلائم بشكل حسن مع قانون الرتبة الأولى الكاذبة وموديل لانكماير. لقد تم حساب المعطيات الترموداينميكية و كانت قيمة الانتالبي للإزالة هي 13.13 كيلو جول لكل مول.

الكلمات المفتاحية : إزالة , حبيبات الجل المائية , أيون النيكل الثنائي , قياسات الامتصاص الذري

Introduction

Wastewater generated from chemical industries contains very harmful pollutants to the environmental. Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide [1]. Another drawback for the presence of heavy metals in wastewater is that they inhibit biological processes during treatment. Furthermore, contamination of groundwater might occur by heavy metals if these wastewaters are allowed to infiltrate into ground water aquifer.

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According to the Food and Agriculture Organization (FAO (1985), Heavy metals such as, Nickel is considered hazardous if its concentration exceed the permissible limits in the water and for plantation. The concentration of nickel should not exceed 0.015 mg / g for Ni (II) ion in drinking water according to FAO and 0.02 mg/L according to US-EPA report [2]. Nickel occurs in two oxidation states in nature namely Ni^0 and Ni^{2+} . Divalent nickel is toxic to most organisms and carcinogenic agent in animals for concentrations higher than 0.05 mg/L. It is frequently encountered in raw wastewater effluent from industries, such as non-ferrous metal, mineral processing, electroplating, porcelain enameling, copper sulfate manufacturing, and battery and accumulator manufacturing [3]. Higher concentrations of nickel cause cancer of lungs nose and bone relate. Acute poisoning of divalent nickel causes headache, dizziness, sickness and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [4]. There are a few methods for removal of heavy metals, such as ion exchange [5], reverse osmosis [6], chemical precipitation [7], electro coagulation [8],.. etc., Conventional treatment technologies for the removal of these toxic heavy metals are not economical and furthermore generated a huge quantity of toxic chemical sludge [19]. Various methods have been used for removal of divalent nickel from industrial wastewater, including: filtration, chemical precipitation, reduction process, electrode position and membrane systems or even ion exchange process [10, 11]. Chemical precipitation and reduction process need other separation techniques for the treatment and disposal of high quantities of waste metal residual sludge produced. These techniques also require a lot of treatment chemicals. The application of membrane systems for the wastewater treatment has major problems such as membrane scaling, fouling and blocking, while the disadvantage of the ion exchange process is the high cost of the resin. In the other hand the electrode position method requires more intensive energy than other methods [12, 13]. Adsorption is one of alternative methods for effective purification and separation techniques which used in the water and industrial wastewater treatment [14]. The ineffective-adsorption of heavy metals such as cadmium, nickel and copper ions from industrial wastewater present challenging problems for industry and environment. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water and wastewater, but the high cost of activated carbon inhibits its large scale use as adsorbent [15]. To solve these problems, in recent years, investigations have been carried out for the effective removal of large quantities of divalent nickel from wastewater using low cost adsorbents hydrogel beads. It can be economically used for the removal of heavy metals in wastewater. In this paper, the possibility of using hydrogel beads to remove divalent nickel from aqueous solution investigated using batch adsorption studies. The effect of various factors such as contact time, pH, initial divalent nickel concentrations and temperature on the removal efficiency of hydrogel beads was also studied. Adsorption isotherm and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiencies of hydrogel beads.

Experimental

Apparatus:

Atomic absorption spectrophotometer (AAS) type (Perkin Elmer, Shelton, ct 06484 USA) was used to determine Ni (II) ion concentration. An Ametrohm E. 63222 pH meter (Switzerland), fitted with an Ametrohm combined glass electrode was calibrated according to conventional methods and used to adjust the pH of the solution in all experiments.

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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 (3.90 mm diameter and 0.0442 g weight) were used for nickel ion removal 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 Ni (II) ion was prepared from nickel chloride salt. More dilute solutions of metal ion were prepared from stock solution by simple dilution with distilled water.

Removal studies:

Effect of contact time on metal ion removal:

Removal experiments for Ni (II) ion were carried out using batch equilibrium processes. One hydrogel bead with 0.0442 g weight and 3.90 mm diameter was immersed in 25 ml of Ni (II) ion solution of 400 ppm at different contact time 1,4,8,12,24 and 48 hours. The removal experiments were conducted at constant pH and temperature (6.3 and 25 °C ± 2). The residual (remained) metal ion concentration after removal process was determined by AAS and the metal ion capacities at each time value were calculated according to the equation below (16):

$$Q = (C_0 - C_e) V / m \dots\dots\dots 1$$

Where Q is the capacity of removal at time t or at equilibrium (mg/g). C₀ and C_e are the initial and residual concentration (concentration at t or at equilibrium) of metal ion (ppm) respectively. V the volume of metal ion solution (L) and m is the weight of hydrogel bead used (g), in this study the m value equal 0.0442 g, the removal metal ion concentration was calculated by substrate the residual(remained) concentration from initial concentration. The results obtained are illustrated in(Table 1 and Figures 1, 2 and) which were showing the calibration graph and image of hydrogel before and after absorb nickel ion. Fig 3 shown the relation between time versus residual, removal, capacity of hydrogel and % removal of Ni (II) ion. The results indicate that the removal process takes place via two steps. In the first steps, the removal of metal ion increases rapidly due to the availability of a large number of active sites on sorbent surface. In the second step, the removal process became less efficient due to the complete occupation of the surface with the metal ions. The big advantage of this sorbent is the large removal capacity (i.e. one hydrogel bead with 44.2 mg weight can remove 135.6 mg/g of nickel ion from aqueous solution.

Table 1: Summery of the results obtained from the contact time study.

Time hr.	Remained Ni(II) ion (ppm)	Removal Ni(II) ion (ppm)	%Ni(II) removal	Capacity Q mg/g
1	378	22	3.5	13.75
4	320	80	20	50
8	263	137	34.3	85.6
12	220	180	45	112.5
24	183	217	54.3	135.6
48	183	217	54.3	135.6

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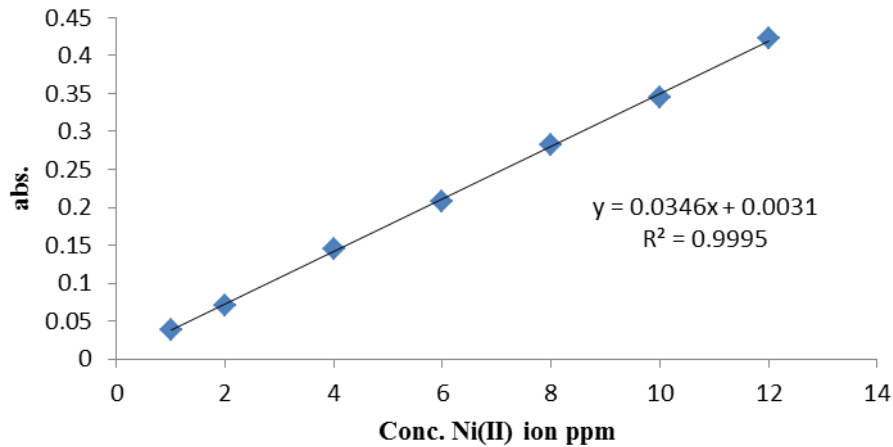


Fig: 1: calibration graph of Ni(II) ion by AAS

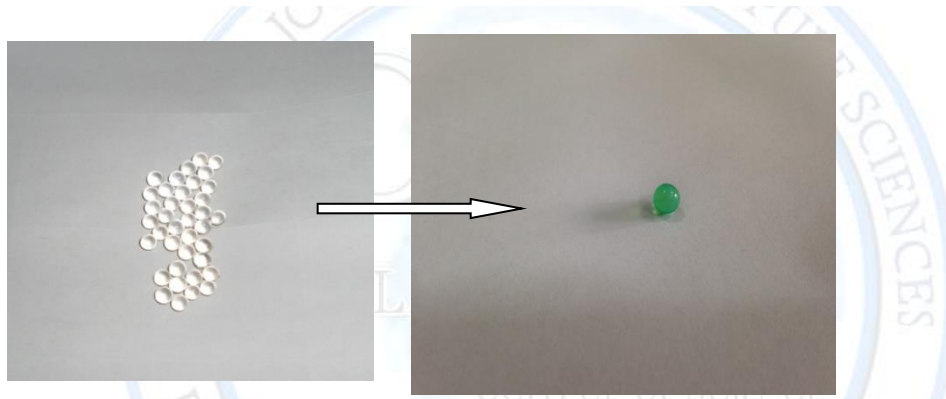


Fig:2: Image of hydrogel bead before and after absorb of Ni(II) ion.

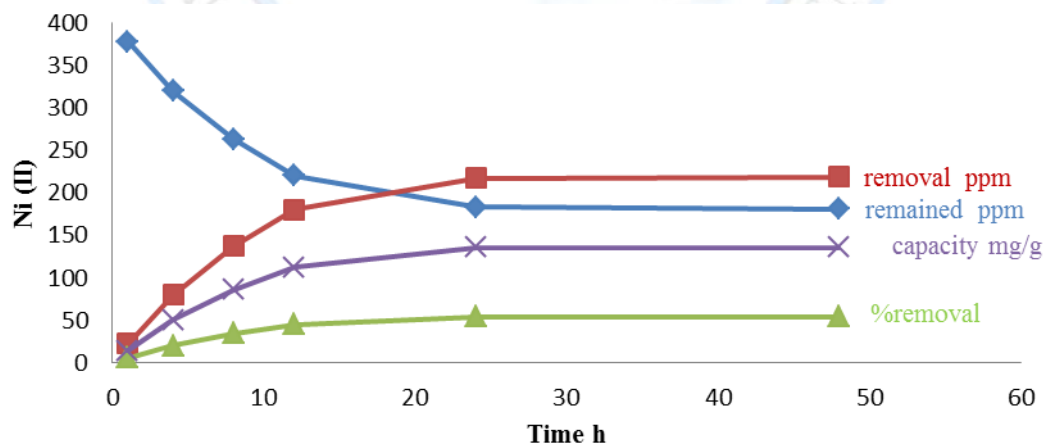


Fig:3: Relationship between time Vs residul, removal, capacity and % removal of Ni (II) ion

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Effect of initial metal ion concentration:

Removal equilibrium and isotherm studies were estimated by varying metal ion concentration. A 25 ml solution of 100, 200, 300 and 400 ppm metal ion concentration was used at pH of 6.3 value. The solutions were left at room temperature for 24 hours and the residual Ni (II) ion concentration was determined using AAS measurements. The results in (Table 2, Figure 4 and Figure 5) are revealed that the removal percentage of Ni (II) ion was higher at low concentration rather than high concentration. At low concentration the sorbent dose not reach the maximum capacity due to its ability to absorb large quantity of Ni (II) ion and the residual concentration is very low, while at high concentration the sorbent reach the maximum capacity and the residual concentration is high. The removal percent calculated as bellow:

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

Table 2: The results obtained from initial concentration effect study.

Initial conc. ppm	Remained conc. ppm	Removal conc. ppm	% removal	Capacity mg/g
100	1.1	98.9	98.9	61.88
200	3	197	98.8	123.1
300	85	215	71.7	134.4
400	183	217	54.3	135.6

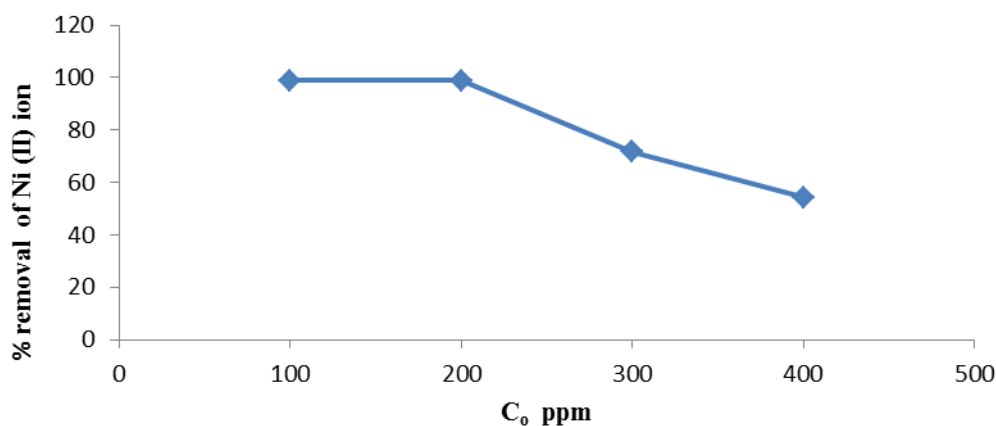


Fig: 4: Initial concentration of Ni (II) ion Vs %Ni (II) ion removal

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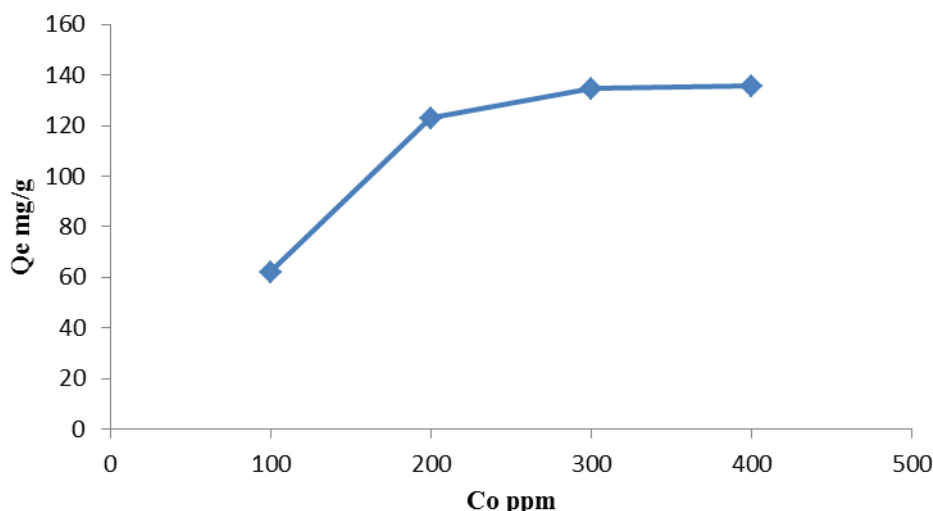


Fig:5: Initial concentration of Ni (II) ion Vs capacity Q

Effect of pH:

The effect of pH on the removal of Ni (II) ion by hydrogel bead was studied to gain further insight in to the removal process. 25 ml volumetric flasks were used, each one contain 25 ml of 400 ppm metal ion solution and one hydrogel bead. The pH of solution was adjusted at a range of (1 – 7) and left for 24 hours at room temperature. The residual Ni (II) ion concentration was determined using AAS and the capacity and removal percentage were calculated from equation 1 and 2 respectively. The results are tabulated in Table 3, which indicated that the optimal pH for the removal of Ni (II) ion is ranged between 6 and 7. At lower pH values, protons were available to protonate all sites on the sorbent surface, there for the attraction of cationic Ni (II) ion to the sorbent surface decrease, while near the basic condition the cation will begin to precipitate from the solution and the removal percent decrease. The pH value was chosen for this study is 6.3 (the pH of distilled water) due to the high degree of deprotonation of the sites in the sorbent surface occurs at high value of pH (17). Figure 6 shows the relationship between pH with removal percentage of Ni (II) ion and capacity.

Table 3: Summary of results obtained from pH effect study.

pH value	1	2	3	4	5	6	7
Residual Ni (II) ion ppm	380.0	350.0	295.0	225.0	195.0	185.0	192.0
% Ni(II) ion removal	5.0	12.5	26.3	43.8	51.3	53.7	52.0
Capacity mg/g	12.5	31.3	65.6	109.4	128.1	134.4	130.0

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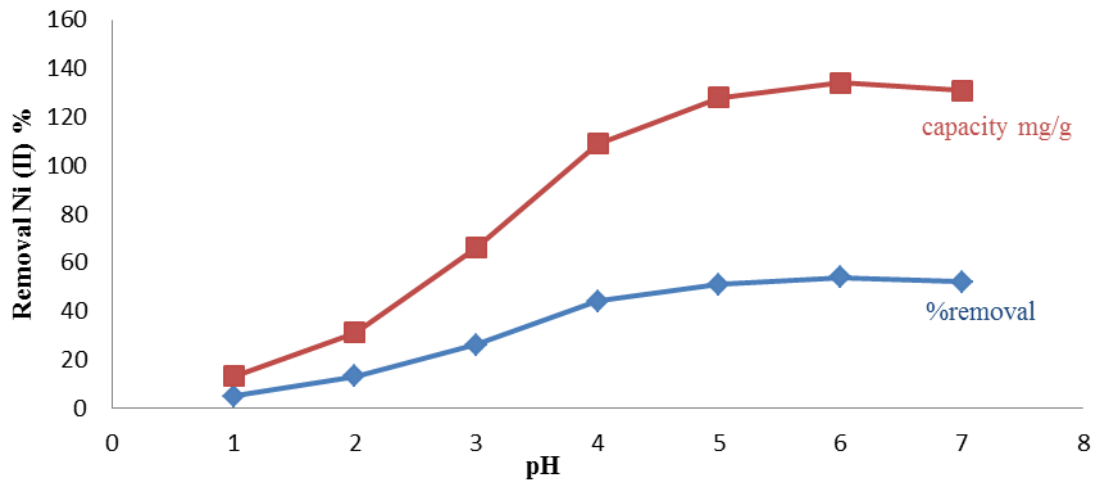


Fig: 6:relationship between pH with Qe and %removal of Ni(II) ion

Effect of temperature:

The removal studies were conducted at four different temperatures (5, 10, 20 and 25). The obtained results which are tabulated in (Table 4) reveals that, at the range of studied temperatures, the removal of Ni(II) ion increases as temperature increase. This could be due to the increase of mobility, in the Ni (II) ion, which may also led to more penetrate of Ni (II) ion (18) as shown in Fig. 7.

Table 4: summary of the results obtained from temperature study:

Temperature °C	5	10	20	25
%Ni (II) removal	32.5	37.5	52.5	54.3
Capacity mg/g	81.0	93.7	131.3	135.6

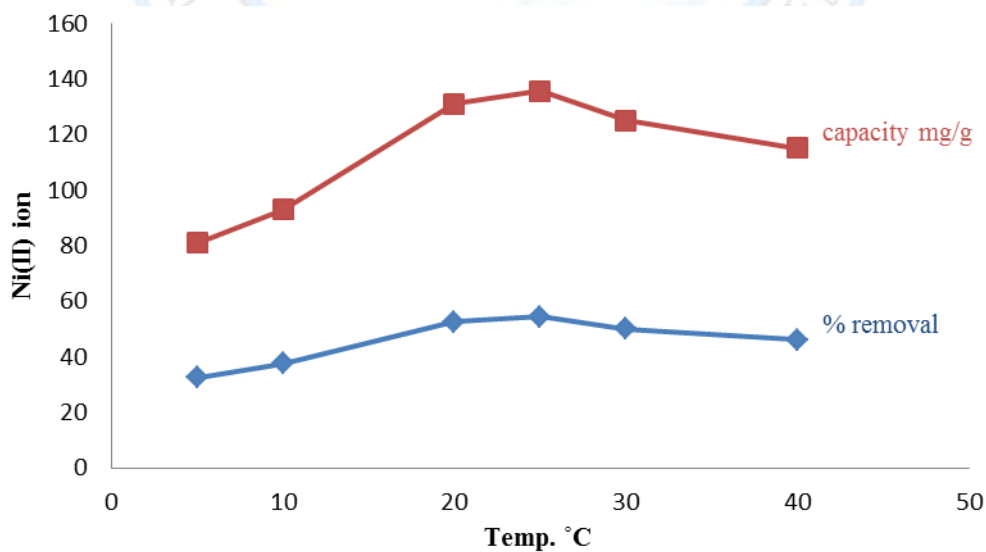


Fig:7: relationship between Temp. Vs Qe and %Ni(II) ion removal

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Removal kinetic for Ni (II):

In order to examine the mechanism of the removal process the pseudo – first – order and pseudo – second – order equations were used to test the experimental data(18,19):

Log (Q_e – Q_t) = Log Q_e – k₁/ 2.303 t 3

t/Q_t = 1/k₂Q_e² + t/Q_e 4

where Q_e, Q_t are the amount of Ni (II) ion removal (mg/g) at equilibrium and time t respectively. k₁ and k₂ are the rate constant of pseudo – first – order (hr⁻¹) and pseudo – second – order (g/mg. hr). The results obtain are summarized in Table 5, which indicated that the removal process follow a pseudo – first – order with correlation coefficient R² value 0.987. Figure 8 and 9 shown the straight plots of Log (Q_e – Q_t) vs. t and t/Q_t vs. t, respectively.

Table 5: Estimated removal kinetic parameters for Ni (II) ion.

Ni (II) ion ppm	pseudo – first – order				pseudo – second – order		
	Q _{exp}	k ₁	Q _{cal}	R ²	Q _{cal}	k ₂	R ²
400	135.6	0.1497	150.3	0.987	250	0.0003	0.972

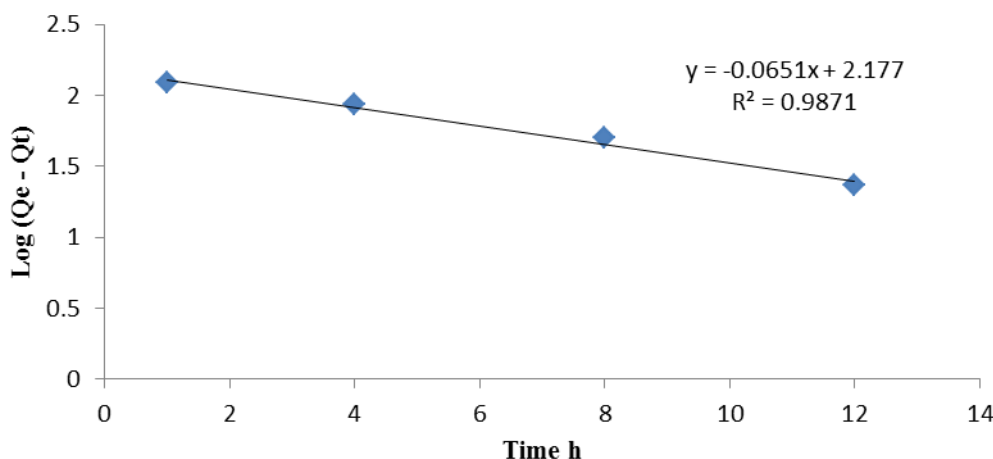


Fig: 8: Pseudo - first - order kinetic plot

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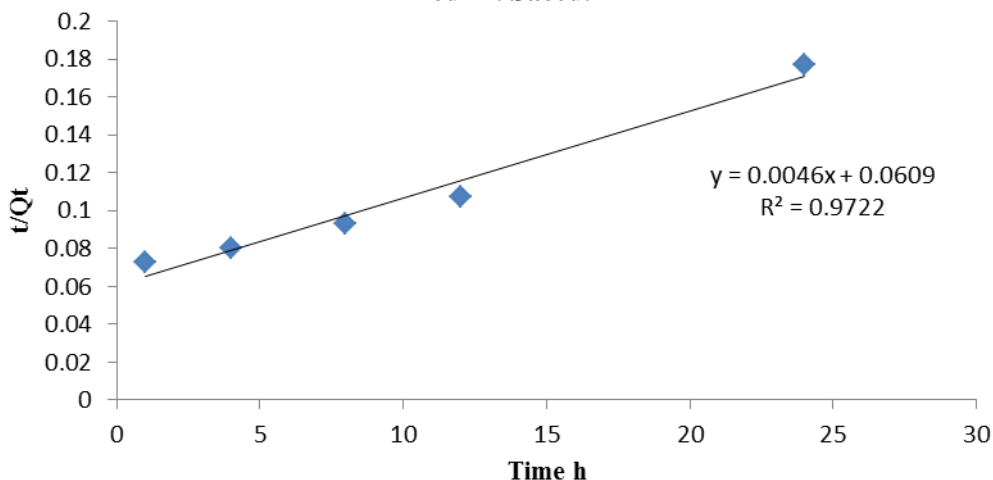


Fig:9: Pseudo - second - order kinetic plot

Removal isotherm for Ni (II) ion:

To identify the mechanism of the removal process, the removal of Ni (II) ion using hydrogel bead was determined as a function of equilibrium residual Ni (II) ion concentration C_e and the corresponding removal isotherm was plotted as shown in Figures 10 and 11. The data can then be correlated with a suitable isotherm Langmuir and Freundlich. The Langmuir and Freundlich equations are given in the following (20):

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

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

Where Q_{max} , Q_e are the maximum removal 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 and K_F are Langmuir and Freundlich constant and n is Freundlich exponents. Langmuir parameters can be evaluated from the slop and intercepts of the linear plots of C_e/Q_e vs. C_e while the Freundlich parameters can be calculated from the slop and intercepts of the linear plots of $\text{Log } Q_e$ vs. $\text{Log } C_e$. It was found from this study that the removal of Ni (II) ion 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 6. The R_L value equal to 0.0017 which is in the range of 0 – 1 at 25 °C studied and this confirm that a favorable removal of Ni (II) ion.

Table 6: Estimated removal isotherm parameters.

Langmuir parameters				Freundlich parameters		
Q_{max} mg/g	K_L	R_L	R^2	K_F	n	R^2
142.85	1.40	0.0017	1	23.496	2.22	0.602

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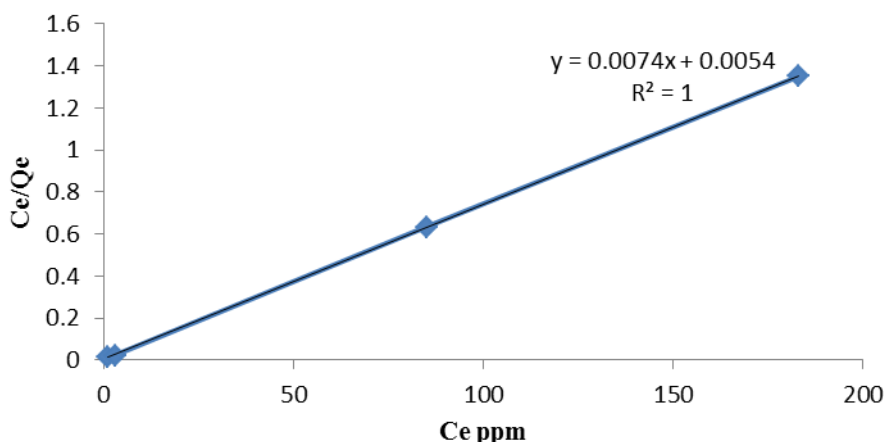


Fig:10:Langmuir plot for Ni (II) ion removal

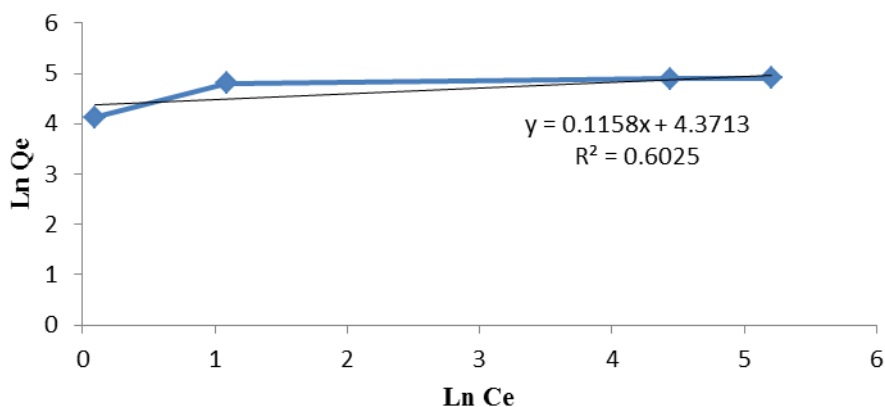


Fig:11:Freundlich plots for Ni ion removal

Thermodynamic studies for Ni (II) ion removal:

The thermodynamic parameters of the removal of Ni (II) ion on hydrogel bead can be evaluated using the following relations:

$K_c = Q_e / C_e$ 7

$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / R$ 8

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ 9

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 slopes and intercept of the $\ln K_c$ vs. $1/T$ plotting(Figure 12), the results obtained are tabulate in Table 7, which reveals that the removal process is endothermic with increase of randomness at the solid/ solution interface occur in the internal structure

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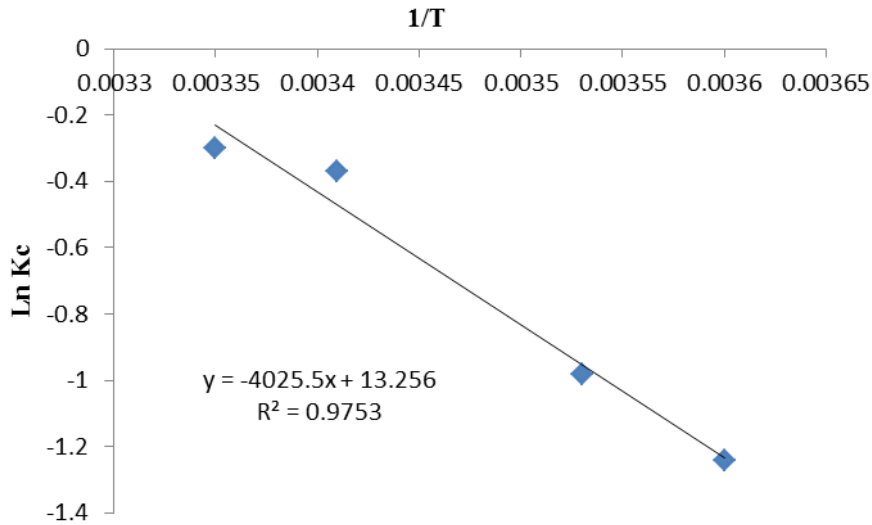


Fig: 12: Ln Kc vs 1/T plot

of hydrogel bead. The value of ΔH_{ads} can be estimated from the slop of $\ln C_e$ vs. $1/T$ as shown in Figure 13.

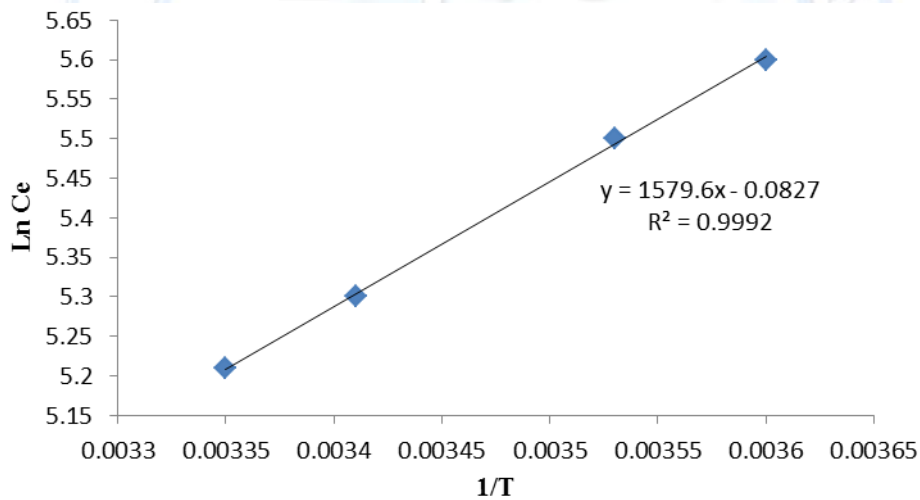


Fig:13: Ln Ce vs 1/T plot

Table 7: Thermodynamic parameters of removal process at different temperature:

Temperature K	G° KJ/ mol.	H° KJ / mol	S° J/ mol. K	H _{ads} KJ/ mol
278	2.83	33.46	110.16	13.31
283	2.28			
293	1.18			
298	0.63			

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Conclusions

In this study a hydrogel bead was used to removal the Ni (II) ion from aqueous solution. The results shown that the removal of nickel ion was increase with increasing the temperature and time. The maximum capacity was achieved at 24 hr. with value of 132.5 mg/g. 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 removal process. The removal of nickel ion using hydrogel bead was found to be endothermic process. The results obtained proved that the use of hydrogel as adsorbent materials for Nickel (II) ion removal is one of the efficiency method in comparison with other results obtained from applied of different other methods, due to its high capacity, low cost and environment friendly.

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