Zinc(II) ion removal from aqueous solution using commercial hydrogel beads and AAS measurements

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ABSTRACT

In the present study, removal of Zn(II) ion from aqueous solution using commercial hydrogel bead was reported. Batch removal experiments shown the removal of Zn(II) ion by hydrogel bead was fast and occurred at pH ≈ 6.3. Atomic absorption spectrometry (AAS) measurements showed that the maximum capacity (capacity at equilibrium) observed was 132.5 mg of Zinc ion per gram hydrogel bead and was reachedafter 24 hours. Thermodynamic and kinetic parameters for removal of Zinc ion was calculated and tested with isotherm models (Langmuir and Freundlich), and kinetic models (pseudo first order and second order). The parameters study includes contact time, initial concentration, pH and temperature. The removal process was found to be fittedwell with Langmuir model and pseudo first order with R^2 = 1 and 0.993, respectively. The removal enthalpy value was found to be 14.87 KJ/ mol.

Key words: Zinc(II) ion, Hydrogel beads, AAS measurements, Langmuir model.

1. INTRODUCTION

The human exposure to metals is common due to their wide use in industry and environmental persistence. The significant environmental pollutants are heavy metals, due to their toxicity. In general, heavy metals are collective term which applies to the group of metals with atomic density greater than 4 g/ cm^3, or 5 time or more, greater than water [1]. Heavy metals include lead, cadmium, nickel, cobalt, iron, zinc, chromium, arsenic, silver and the platinum group elements. Water is an essential mater to human and other living organism, may be polluted from the effluent of several industries such as chemical industrial, electroplating industrial, dye industrial and battery industrial [2]. The heavy metal ions were found to be one of the main pollutants in water, which can cause accumulative poisoning cancer and brain damage when found above the tolerance levels [3]. By far, the removal of metal ions from aqueous solution, either for pollution or for raw recovery, is being an important challenge [4]. Effective removal of heavy metal ions from aqueous solution is important in the protection of environmental quality and public health [5]. Many processes were used for treatment such as adsorption [6], ion exchange [7] and others. The adsorption method is the most used because of its flexibility in operation and design [8]. Recently, the use of low – cost and environmentally friendly adsorbents process such as clay [9], sawdust [10], lignin [11] and activated fruit [12]to removed metal ions from aqueous solution is an effective and economical. Last two decades, different hydrogelbeads were used as adsorbent for metal ion removal from aqueous solution[13]. The present study focused on the use of hydrogel for the removal of zinc ion, which is an essential element for the living beings when it is micro levels, if it is exceeds the permissible limit it causes a serious threat like vomiting, fever, cough, fatigue, dehydration anemia and even causes damage to lungs etc…[14]. The World Health Organization stated a legal limit of zinc in drinking water is 5 mg/L.

2.EXPERIMENTAL

2.1.Apparatus

Atomic absorption spectrophotometer (AAS) type (Perkin Elmer, Shelton, ct 06484 USA) was used to determine Zn(II) ion 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.

2.2.Chemicals and solution

Commercial hydrogel beads (3.80 mm diameter and 0.0400 g weight) were used for Zinc 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 Zn(II) ion was prepared from Zinc chloride salt. More dilute solutions of metal ion were prepared from stock solution by simple dilution with distilled water.

3.REMOVAL STUDIES

3.1.Effect of contact time on metal ion removal

Removal experiments for Zinc ion were carried out using batch equilibrium processes. One hydrogel bead (w = 0.0400 g, d = 3.80 mm) was immersed in 25 ml of Zn (II) ion solution of 400 ppm at different contact time of 1,4,8,12,24 and 48 hrs. The removal experiments were conduct at constant pH and temperature (6.3 and 25 $^{o}C \mp 2$). The residual 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 bellow [15]:

$$Q = (C_o - C_e)\, V / m \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where Q is the capacity of removal at 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 metal ion (ppm), V is the volume of metal ion solution(L), and m is the weight of hydrogel bead used (g). In the present study, m value equal to 0.0400 g, the removal metal ion concentration was calculated by subtract the remained concentration from initial concentration. The results obtained are illustrated in(Table 1 and Figure 2). The results indicate that the removal process take place via two steps. In the first step, 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 ion. The big advantage of this sorbent is the large removal capacity (i.e. one hydrogel bead with 40 mg weight remove 132.5 mg/g of zinc ion from aqueous solution.

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

Time hr.	Remained Zn(II)ion ppm	Removal Zn(II)ion ppm	% removal	Capacity Q mg/g
1	385.0	15.0	3.7	9.4
4	330.0	70.0	17.5	43.8
8	275.0	125.0	31.3	78.1
12	235.0	165.0	41.3	103.1
24	188.0	212.0	53.0	132.5
48	188.0	212.0	53.0	132.5

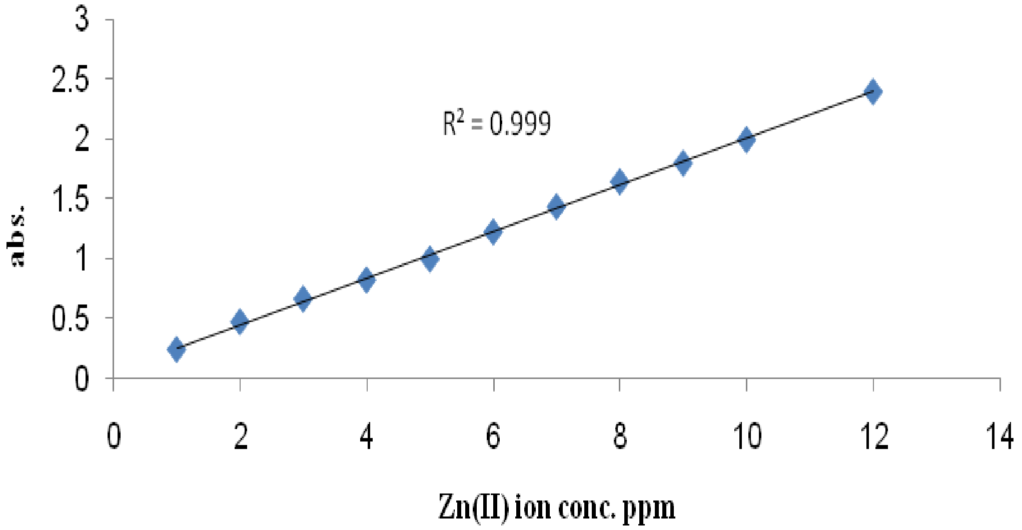


Fig (1): Calibration graph for Zn(II) ion using AAS

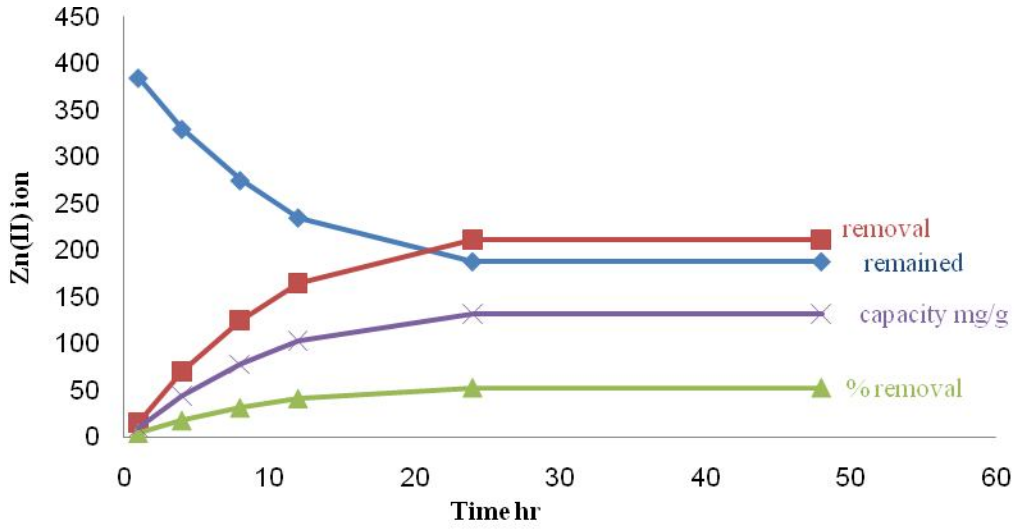


Fig (2): Effect of time variation on removal of Zn ion

3.2.Effect of initial concentration of metal ion

Removal equilibrium and isotherm studies were estimated by varying the metal ion concentration. A 25 ml solution of 100, 200, 300 and 400 ppm metal ion concentration was used at pH = 6.3. 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 2, Figure 3 and Figure 4)reveals, that the removal percentage was higher at low concentration rather than high concentration. At low concentration the sorbent does not reach the maximum capacity, and remainedconcentration is very low, while, at high concentration the sorbent reach the maximum capacity and the remained concentration is high. The removal percentage calculated as bellow:

$$\%\ removal = \frac{initialconc. - remained\ conc.}{initialconc.}\ x\ 100\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

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	61.9
200	4.0	196.0	98.0	122.5
300	89.0	211.0	70.3	131.9
400	188.0	212.0	53.0	132.5

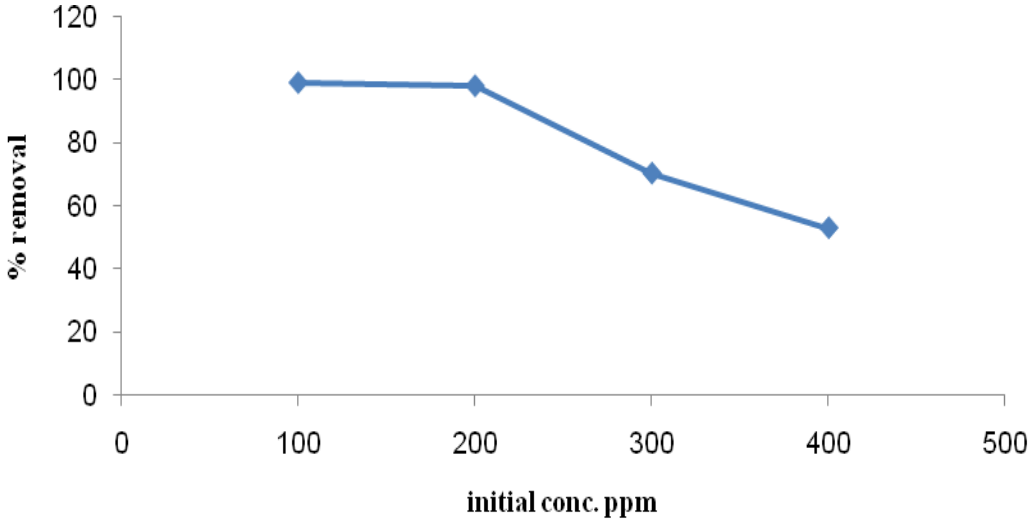


Fig (3): initial conc. vs % removal of Zn(II) ion

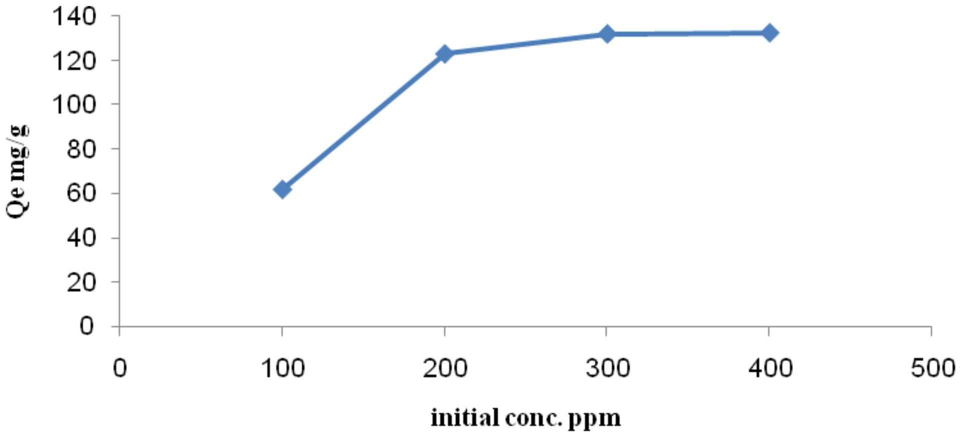


Fig (4): initial conc. vs. capacity

3.3. Effect of pH

Effect of pH on the removal of Zn(II)ion by hydrogel bead was studied to gain further insight into the removal process. To conduct this experiment, 25 ml volumetric flasks each of which contains 25 ml of 400 ppm metal ion solution and one hydrogel bead was used. The solution was adjusted at pH range of (1–7) and left for 24 hours at room temperature. The remained metal ion concentration was determined using AAS and the capacity and removal percentage were calculated from equation 1 and 2, respectively. The results obtained were tabulated in Table 3, which indicate that the optimized pH for the removal of Zn (II) ion was in the range 6-7. At low pH values, protons were available to protonate all sites on the sorbent surface, therefore, the attraction to cationic Zn(II) ion decrease. While near the basic condition the cation will begin to precipitate from the solution and the removal percentage decrease. The pH value which was chosen for this study at 6.3 (the pH of distilled water) due to the high degree of deprotonation of the sites in the sorbent surface is occurs at high value of pH [16]. Figure 5 shows the relationship between pH with removal percentage and capacity.

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

pH value	1	2	3	4	5	6	7
Remainedppm	390.0	355.0	300.0	230.0	200.0	190.0	200.0
% removal	2.5	11.3	25.0	42.5	50.0	52.5	50.0
Capacitymg/g	6.3	28.1	62.5	106.3	125.0	131.3	125.0

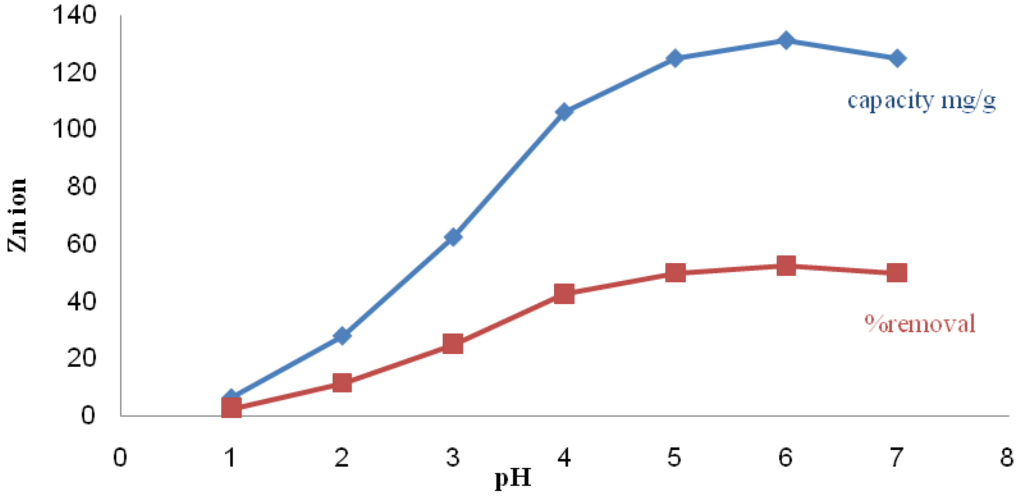


Fig (5): relationship between pH vs %removal and capacity of Zn(II) ion

3.4. Effect of temperature

The removal studies were conductedat four different temperatures (5, 10, 20 and 25). The obtained results (Table 4) reveals that the removal of Zn(II) ion increases as temperature increases, this may be due to the increase in ion mobility, which may also causes a swelling effect within internal structure of hydrogel leading to more penetrate of metal ion [17] as shown in Fig. 6.

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

Temperature °C	5.0	10.0	20.0	25.0
% removal	28.8	35.0	51.0	53.0
Capacity mg/g	72.0	88.0	128.0	132.5

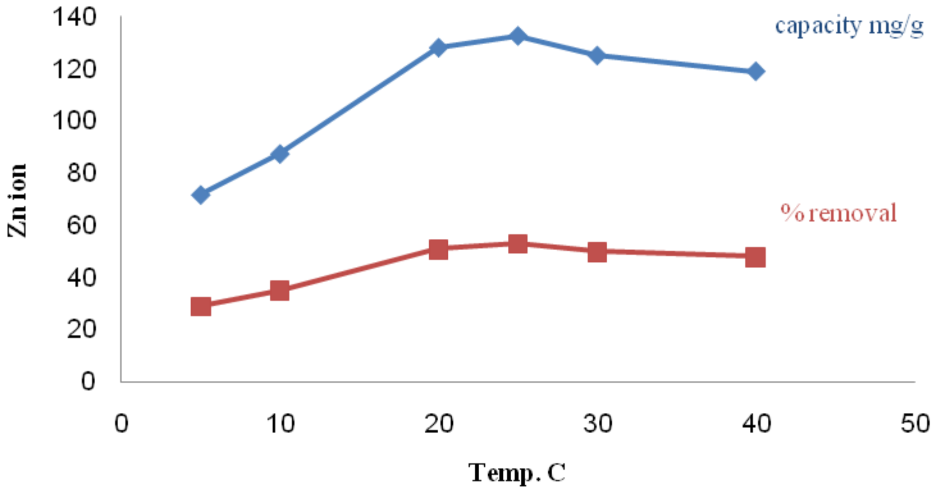


Fig (6): relationship between Temp. vs Qe and % removal

3.5. Removal kinetic for Zn (II)

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

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

$$t/Q_t = 1/k_2Q_e^2 + t/Q_e \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Where Q_e, Q_t are the amount of Zn(II) ion removal (mg/g) at equilibrium and time t, respectively. k_1(hr $^{-1}$) and k_2(g/mg. hr), are the rate constant of pseudo–first–order and pseudo–second–orderrespectively. The results obtain are summarized in Table 5, which indicate that the removal process follow a pseudo – first – order with correlation coefficient R^2 = 0.993. Figure 7 and 8, shows 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 Zn (II) ion.

Zn (II)ion ppm	pseudo – first – order				pseudo – second – order		
	Q_{exp}	k_1	Q_{cal}	R^2	Q_{cal}	k_2	R^2
400	132.5	0.1289	145.55	0.993	333.3	0.00011	0.853

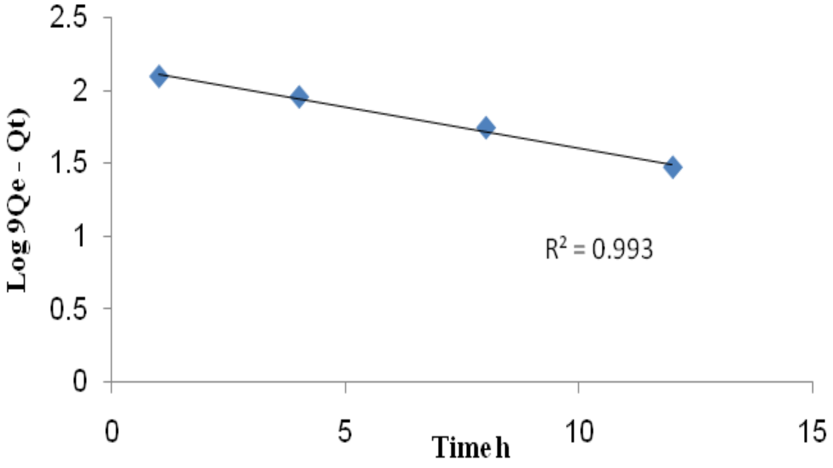


Fig (7): Pseudo - first- order kinetic plot .

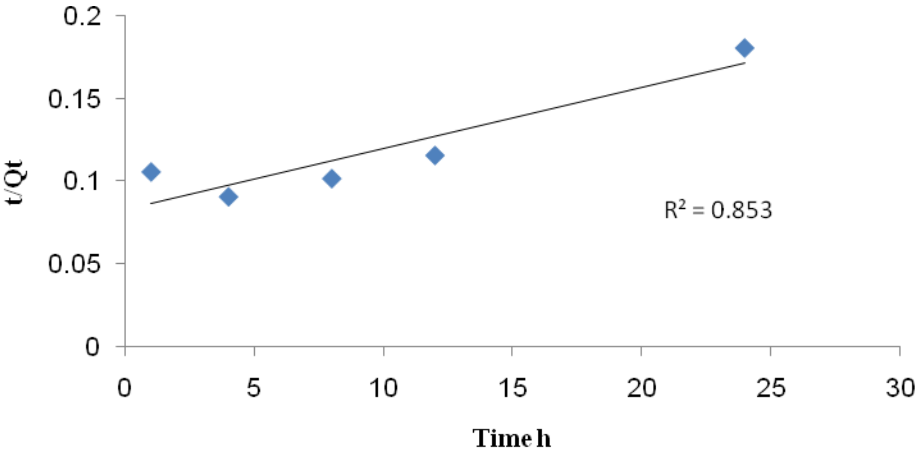


Fig (8): Pseudo - second order plot.

3.6.Removal isotherm for Zn (II) ion

To identify the mechanism of the removal process, the removal of Zn(II) ion using hydrogel bead was determined as a function of equilibriumremained Zn (II) ion concentration C_e and the corresponding removal isotherm was plotted as shown in Figures9 and 10. The data can then be correlated with a suitable isotherm Langmuir and Freundlich equations which 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 ofLog Q_e vs. Log C_e. It was found from this study that the removal of Zn (II) ion obey the 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 and this confirm that a favorable removal of Zn(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	22.08	8.40	0.634

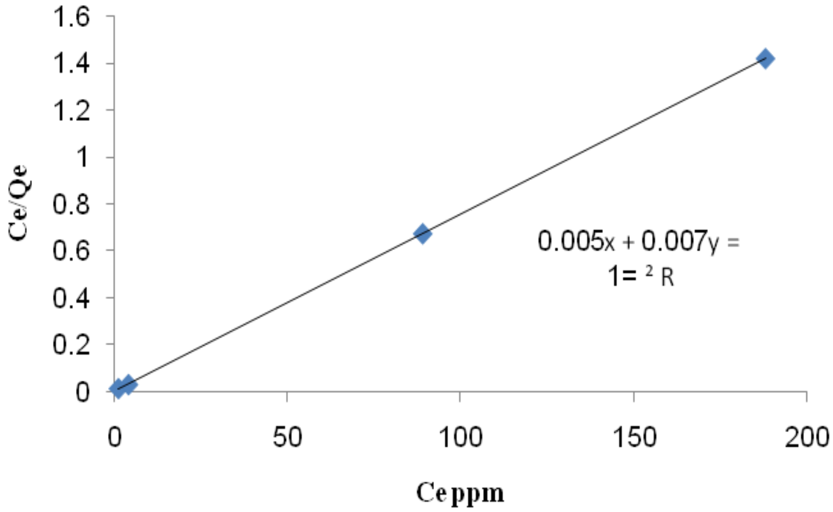
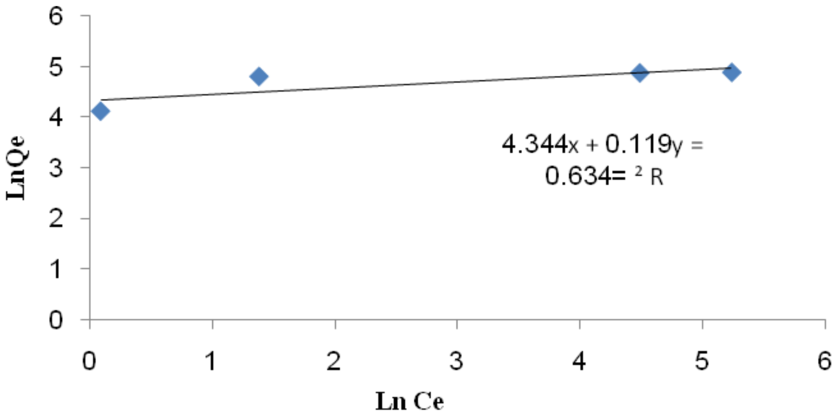


Fig (9): Langmuir plots for Zn(II) ion removal



Fig(10): Ferundlich plots for Zn(II) ion removal

3.7. Thermodynamic studies for Zn(II) ion removal

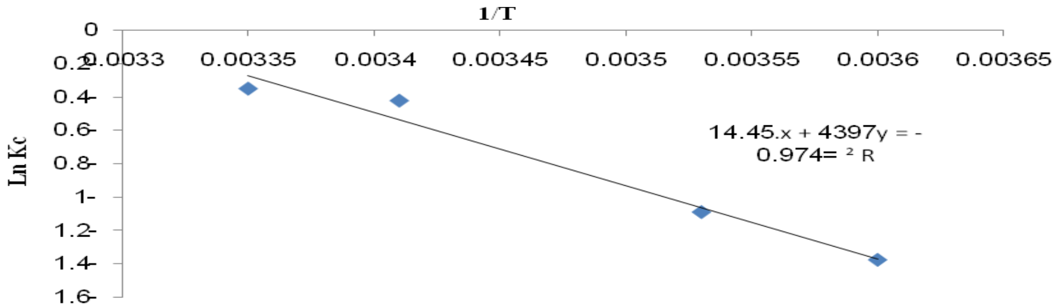
The thermodynamic parameters of the removal of Zn(II) ion on hydrogel bead can be evaluated using the following equations:

$$K_c = Q_e / C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

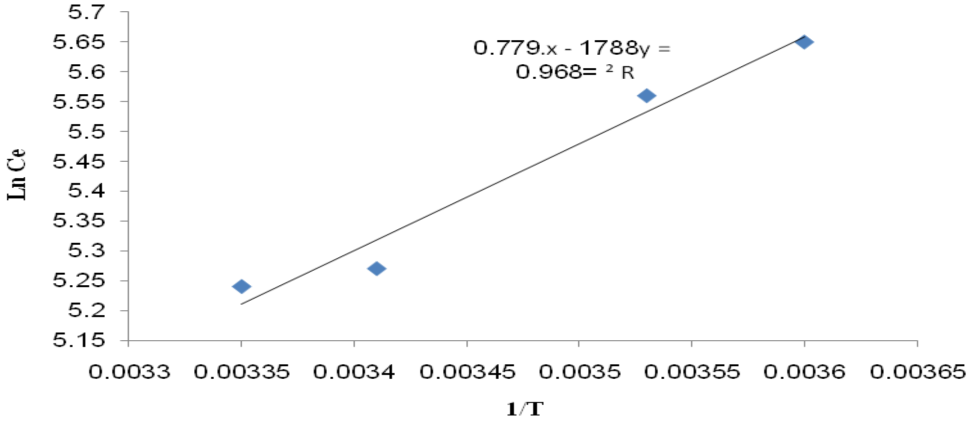
$$\text{Ln } K_c = \Delta S^o / R - \Delta H^o / R \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

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 slops and intercept of the Ln K_c vs. 1/T plotting (Figure 11), the results obtained are tabulated in Table 7, which reveals that the removal process is endothermic with increase of randomness at the solid/ solution interface occur in the internal structureof hydrogel bead.The value of ΔH_{ads} can be estimated from the slop of Ln C_e vs. 1/T as shown in Figure 12.



Fig(11): Ln Kc vs 1/T plot



Fig(12): Ln Ce vs 1/T plot

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

Temperature K	ΔG^o KJ/ mol.	ΔH^o KJ / mol	ΔS^o J/ mol.K	ΔH_{ads} KJ/ mol
278	3.16	36.56	120.14	14.87
283	2.56			
293	1.36			
298	0.76			

4. CONCLOSIONS

In this study a hydrogel bead was used to removal the Zn(II) ion from aqueous solution. The results shown that, the removal of zinc ion was increased with increasing temperature and time. The maximum capacity was 132 mg/g which was reached after 24 hrs. The kinetic equilibrium was found to be fitted with pseudo–firstorder model, and the isotherm agrees well with the Langmuir model during the whole removal process. The removal of zinc ion using hydrogel bead was found to be endothermic process.

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