# Removal of Cu (ll) From Aqueous Solution Using Polyacrylic Acid Hydrogel Beads as Adsorbent

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## Abstract

In this article, the adsorption of Cu(ll) ion from aqueous solution into polyacrylic acid (PAA) hydrogel bead has been investigated using a batch method of different temperature (10-30 °C) and different contact time (1-48 hr) to reach the equilibrium of adsorption. Initial concentration and adsorption capacity of the adsorbents is presented, the time required to reach a maximum capacity of bead was about 24hr. The temperature effect on adsorption was studied and the experimental data have been analyzed using the Langmuir and freundlich isotherm models. The adEsorption capacity at equilibrium was found to be 142.68 mg/g; more than 95% of studied cation was removed by the adsorbent. The process is very efficient especially at low concentration of pollutants in aqueous solutions.

**Key word:** Economical, Removal, Polyacrylic acid, Hydrogel

# إزالة ايون النحاس الثنائي من محاليله المائية باستخدام حبيبات الجل المائية لمتعدد حامض الاكريلك كمادة مازه

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## الخلاصة

في هذا البحث تم دراسة استخدام حبيبات الجل المائية لمتعدد حامض الاكريلك لإزالة وسحب ايون النحاس الثنائي من المحاليل المائية, باستخدام طريقة الدفعات بدرجات حرارية مختلفة تتراوح بين (10 – 30 °م) وبزمن تماس يتراوح بين( 1– 48) ساعة لضمان الوصول إلى حالة التوازن . تم دراسة تأثير التركيز الابتدائي و سعة الامتزاز, وبينت النتائج إن الزمن اللازم للوصول إلى أقصى كمية سحب للحبيبات هو 24 ساعة. تم دراسة تأثير درجة الحرارة على عملية سحب ايون النحاس الثنائي , وقد طبقت معادلتي لانكمور وفراندلج لتحليل النتائج المستحصلة. بلغت سعة الامتزاز عند التوازن 142.68 ملغم/غم ونسبة سحب أكثر من 95%. أثبتت الطريقة كفاءة عالية لإزالة ايون النحاس الثنائي من المحاليل المائية وبالأخص التراكيز القليلة.

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## Introduction

The removal of metal ions from aqueous solution, either for pollution control or for raw recovery, is an important industrial challenge. Highly toxic metal ions such as mercury, cadmium, lead, chromium and copper needed to be removed from industrial wastes, because they cause a threat to environment and to all living systems [1]. Copper has received special attention, since it can be detrimental if a given concentration is exceeded [2]. The toxic effect of copper has been recognized in that it can cause gastrointestinal distress (short- term exposure) and liver or kidney damage (long- term exposure) [3]. Substantial effort has been invested in the development of more effective techniques for removing copper ion from aqueous streams at acceptable concentration levels(1.3mg.L$^{-1}$). These include precipitation [4], ion exchange [5], mesoporous materials [6 - 8], adsorption [9], and solvent extraction[10]. However, most techniques present limitation, ranging from low copper removal efficiency and cost feasibility. Adsorption is a conventional but important separation process and has been used widely in the chemical, biological, analytical and environmental fields [11, 12]. In most cases, the adsorbent have large internal porosities to ensure linked three-dimensional network structure of hydrophilic homopolymers or copolymers [13 - 15]. Due to the super hydrophilicity characteristic, they can swell quickly in the aqueous solution, which is beneficial for shortening time to reach the adsorption equilibrium [16]. Polymeric hydrogel have different functional group such as amine, hydroxyl, carboxylic acid. These group attached into the polymeric networks can be tailored easily for a specific application. Owing to higher adsorption rate and adsorption capacity. Polymer hydrogel can provide many advantages, fast responsive and high capacity adsorbent in an adsorption process [17, 18]. They possess a high ability to control the diffusion of many metal ions from solution [19] and they can bind chemical species such as Cu(ll) via functional group forming strong interaction with this species [20, 21]. The present study focused on the use of the polyacrylic acid PAA with carboxylic acid functional group for removal of Cu(ll) from aqueous solution.

## Experimental

### Materials

All reagents used in this study were of analytical reagent grade and were used as received. Commercial polyacrylic acid (PAA) and $CuSO_4$.5H2O was purchased from Riedal-Dehaen. Working solution of 1000 mg.L$^{-1}$ Cu(ll) ions was prepared as a stock, and then different solutions were prepared from this stock solution, by simple dilution with distilled water.

### Instrumentation

Flow injection analysis system with (homemade) spectrophotometer was used for the determination of the remained metal ion in solution according to the method suggested by Al-Awady [22].

### FTIR Spectroscopy

A shimadzu FTIR spectrometer model (Pretige 21) with KBr pellets was used. Figure 1 shows the FTIR of loaded with metal ion, and non loaded sorbent spectrum.

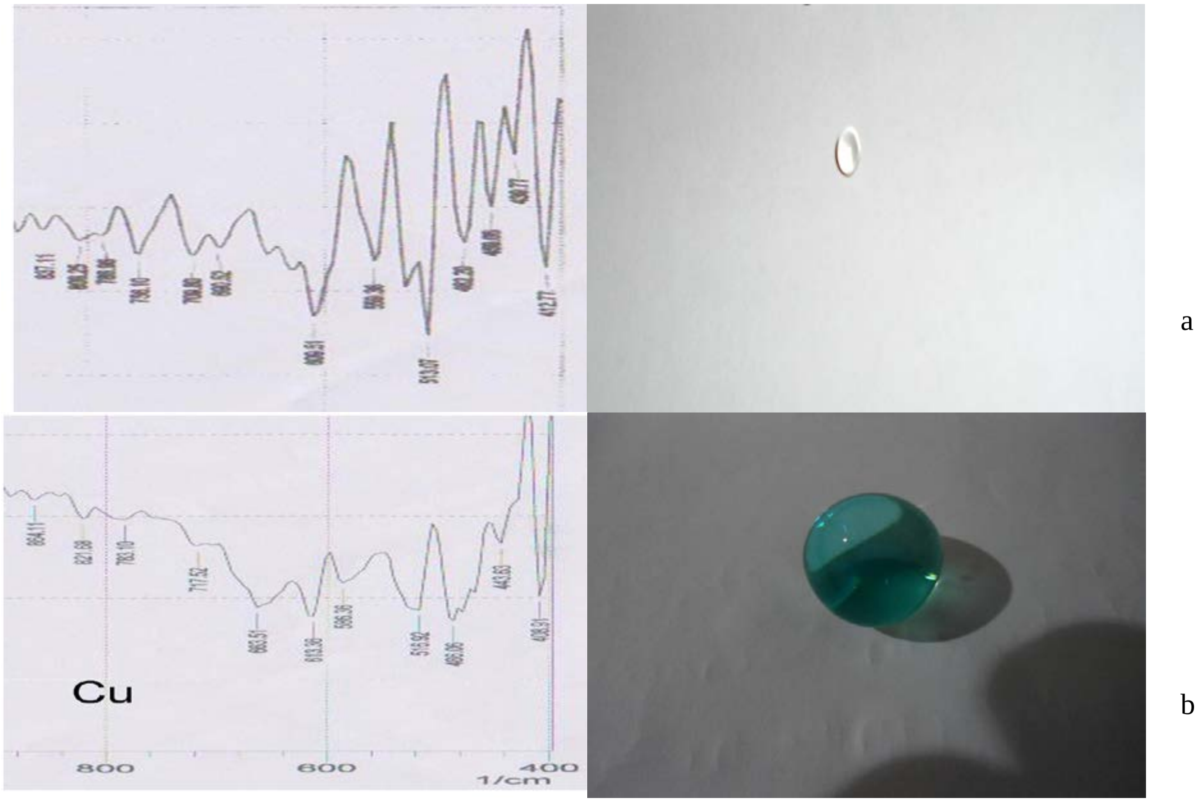

**Figure 1-** The profile and size of gel bead before (a) and after (b) entrapment of Cu(ll) ion, with IR spectra of loaded and original gel bead at 400-800 nm

## Adsorption and analysis

Adsorption experiments were carried out by immersed one hydrogel with 0.0382 g weight in 25 ml of Cu (ll) solution of different concentration of 100, 200,300 and 400 mg.L$^{-1}$, and with different time (1-48hr) to reach the adsorption equilibrium. Cu(ll) left in the solution was determined by (FIA). The adsorption capacity of the hydrogel bead for Cu(II)was calculated through the following equation[23]:

$$Q = (C_o - C_e)\ V / m \quad \text{……….}(1)$$

Were Q is the amount of Cu (ll) adsorbed at time t or equilibrium (mg/g), $C_o$, $C_e$ are the initial and final concentration of Cu (ll) (mg.L$^{-1}$), V is the volume of Cu(ll) solution used ( L ), and m is the weight of the hydrogel bead used (g). All assay were carried out in triplicate and the average was used in the analysis. For the adsorption kinetic studies a series of solution containing 100, 200,300 and 400 mg.L$^{-1}$ of Cu (ll) were allowed to contact with 0.0382 g hydrogel with different time (1-48hr). The sample was then analyzed for the residual Cu (ll) concentration.

## Results and discussion

All the results obtained are tabulated in tables(1-9)

## Adsorption Kinetic For Cu (ll)

The effect of contact time on the adsorption capacities of the hydrogel with different Cu (ll) concentration were studies as shown in table.1 and figure 2.

**Table 1**-The results of time variation effect on the Cu(ll) ion adsorption.

| Time hr | Concentration of Cu(ll) ion $mg.L^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 100 $mg.L^{-1}$ | | 200 $mg.L^{-1}$ | | 300 $mg.L^{-1}$ | | 400 $mg.L^{-1}$ | |
| | $C_t$ $mg.L^{-1}$ | $Q_t$ mg/g | $C_t$ $mg.L^{-1}$ | $Q_t$ mg/g | $C_t$ $mg.L^{-1}$ | $Q_t$ mg/g | $C_t$ $mg.L^{-1}$ | $Q_t$ mg/g |
| 1 | 88.3 | 7.6 | 170.0 | 19.6 | 251.5 | 31.7 | 339.7 | 39.4 |
| 2 | 78.0 | 14.3 | 158.1 | 27.3 | 228.6 | 46.7 | 301.2 | 64.6 |
| 4 | 49.0 | 33.0 | 90.3 | 72.4 | 144.0 | 102.0 | 232.0 | 109.9 |
| 8 | 15.0 | 55.6 | 27.6 | 102.5 | 109.7 | 124.5 | 200.0 | 130.8 |
| 12 | 5.5 | 61.8 | 17.7 | 119.3 | 96.5 | 133.1 | 190.0 | 137.4 |
| 24 | 3.3 | 63.2 | 13.0 | 122.3 | 88.5 | 138.3 | 181.9 | 142.6 |
| 48 | 3.3 | 63.2 | 13.0 | 122.3 | 88.5 | 138.3 | 181.9 | 142.6 |

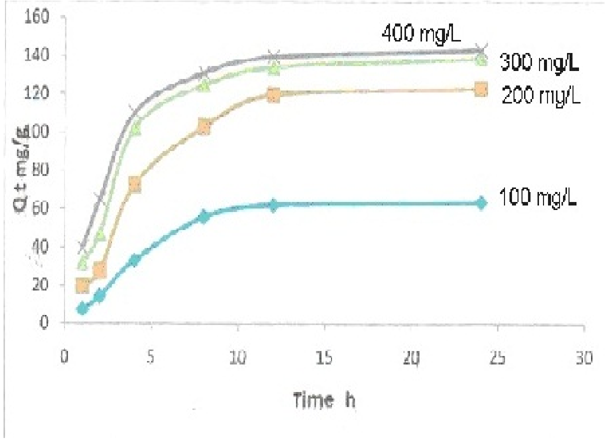

**Figure 2-** C(II) adsorption capacity Qt vs time

The results indicated that the time needed to reach the maximum adsorption was 24 hr. In order to examine the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equation were used to test the experimental data[24,25]:

$$\text{Log}\,(Q_e - Q_t) = \text{Log}\,Q_e - k_1 / 2.303t \quad \ldots\ .. \qquad (2)$$

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \qquad (3)$$

**Table 2**-The results of $\text{Log}(Q_e - Q_t)$ values **.**

| Time hr | Concentration of Cu(ll) ion $mg.L^{-1}$ | | | |
|---|---|---|---|---|
| | 100 $mg.L^{-1}$ | 200 $mg.L^{-1}$ | 300 $mg.L^{-1}$ | 400 $mg.L^{-1}$ |
| 1 | 1.75 | 2.01 | 2.03 | 2.01 |
| 2 | 1.69 | 1.98 | 1.96 | 1.89 |
| 4 | 1.48 | 1.69 | 1.56 | 1.51 |
| 8 | 0.88 | 1.29 | 1.14 | 1.07 |
| 12 | 0.15 | 0.49 | 0.71 | 0.72 |

**Table 3**-The results of $t/Q_t$ values.

| Time hr | Concentration of Cu(ll) ion $mg.L^{-1}$ | | | |
|---|---|---|---|---|
| | 100 $mg.L^{-1}$ | 200 $mg.L^{-1}$ | 300 $mg.L^{-1}$ | 400 $mg.L^{-1}$ |
| 1 | 0.13 | 0.05 | 0.032 | 0.025 |
| 2 | 0.14 | 0.07 | 0.043 | 0.031 |
| 8 | 0.144 | 0.078 | 0.064 | 0.061 |
| 12 | 0.194 | 0.101 | 0.090 | 0.087 |
| 24 | 0.38 | 0.196 | 0.173 | 0.168 |

Where $Q_e$, $Q_t$ are the amount of Cu (ll) adsorbed into hydrogel (mg/g) at equilibrium and at time t, respectively, $k_1$ and $k_2$ are the rate constants of pseudo-first-order ($hr^{-1}$ ) and pseudo-second-order (g/mg hr ) adsorption. The straight line plots of log ($Q_e$-$Q_t$) against t, and $t/Q_t$ against t (table.2,and 3) were used to determine the rate constant $k_1$ and $k_2$ and correlation coefficient R values (figures 3and 4)These parameters were calculated and summarized in table 4, which was shown that the process follow a pseudo-first-order in concentration ranged between 100-400 $mg.L^{-1}$.

**Table 4**-Estimated adsorption kinetic parameters for Cu(ll) adsorption**.**

| Initial Cu(II) $mg.L^{-1}$ | Pseudo – first –order | | | | Pseudo – second – order | | |
|---|---|---|---|---|---|---|---|
| | Qe Exp mg/g | $Qe_{cal}$ mg/g | $k_1$ ($h^{-1}$) | $R^2$ | $Qe_{cal}$ mg/g | $k_2$ ($g/mg/hr^{-1}$) | $R^2$ |
| 100 | 63.25 | 96.36 | 0.34 | 0.9865 | 97.46 | 0.0012 | 0.9063 |
| 200 | 122.37 | 169.04 | 0.31 | 0.9742 | 165.5 | 0.0089 | 0.9488 |
| 300 | 138.35 | 137.09 | 0.28 | 0.9889 | 163.7 | 0.0017 | 0.9805 |
| 400 | 142.68 | 119.95 | 0.27 | 0.9808 | 159.6 | 0.0027 | 0.9946 |

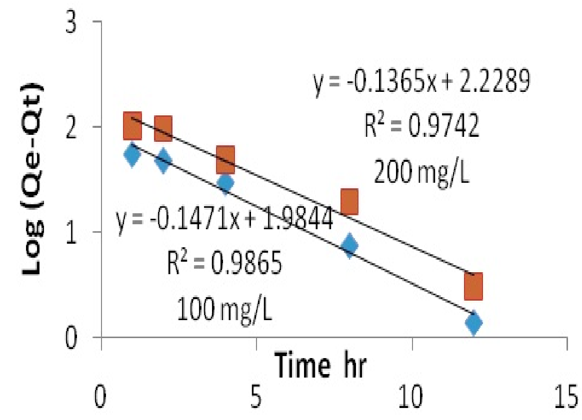

**Figure 3-**The pseudo- first-order relation

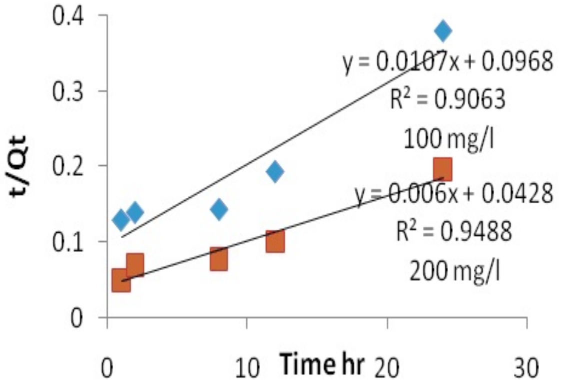

**Figure 4-**The pseudo-second-order relation.

## Adsorption Isotherm for Cu (ll).

Figure 5,and table 5 show the amount of Cu(ll) adsorbed increase with increasing of the initial Cu (ll) concentration, and remains constant after the initial Cu (ll) concentration reach 400 mg.L$^{-1}$. Adsorption properties and equilibrium data commonly known as adsorption isotherm, describe materials. Then it is important to establish the how metal ion pollutants interact with adsorbent most appropriate correlation for equilibrium curve. In this study two typical isotherm were used for fitting the experimental data:

**Table 5-**The results of temperature variation effect on

| **Temp. K** | **Concentration of Cu(ll) ion mg.L$^{-1}$** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **100 mg.L$^{-1}$** | | **200 mg.L$^{-1}$** | | **300 mg.L$^{-1}$** | | **400 mg.L$^{-1}$** | |
| | **$C_t$ mg.L$^{-1}$** | **$Q_t$ mg/g** | **$C_t$ mg.L$^{-1}$** | **$Q_t$ mg/g** | **$C_t$ mg.L$^{-1}$** | **$Q_t$ mg/g** | **$C_t$ mg.L$^{-1}$** | **$Q_t$ mg/g** |
| **283** | **33.2** | **43.7** | **85.5** | **74.23** | **155.2** | **94.4** | **250.1** | **98.10** |
| **293** | **13.7** | **56.4** | **25.3** | **114.3** | **101.3** | **130.0** | **195.2** | **134.0** |
| **298** | **5.00** | **61.6** | **18.2** | **118.9** | **90.30** | **177.2** | **182.5** | **142.3** |
| **303** | **3.36** | **63.2** | **13.0** | **122.3** | **88.59** | **138.3** | **181.9** | **142.6** |

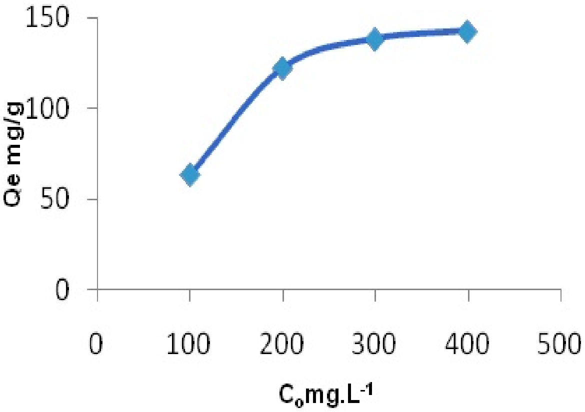

**Figure 5-** Cu (II) adsorption capacity Qe vs initial concentration of Cu (II)

Langmuir equation[26]:

$C_e / Q_e = 1 / Q_{max} K_L + C_e / Q_{max}$ …… …. 4

Freund lich equation[27]:

$\text{Log } Q_e = K_F + 1 / n \ \log C_e$ …… … .. 5

Where $Q_e$ is the amount of Cu (ll) adsorbed at equilibrium (mg/g), $C_e$ is the equilibrium concentration of Cu (ll) solution mg/L, $Q_{max}$ is the maximum capacity of adsorption (mg/g) and $K_L$ is the Langmuir adsorption constant (L/g) and is related to the free energy of adsorption, $K_F$ (ml/g) and n are the freundlich adsorption isotherm constants, being indicative of the adsorption extent and the degree of nonlinearity between solution concentration and adsorption, respectively. The isotherm constant and correlation coefficients R were calculated from the linear Langmuir and freundlich plots by plotting

$C_e/Q_e$ vs $C_e$ and log $Q_e$ vs log $C_e$,(figures .6 and 7.) the results obtained are summarized in table.6.

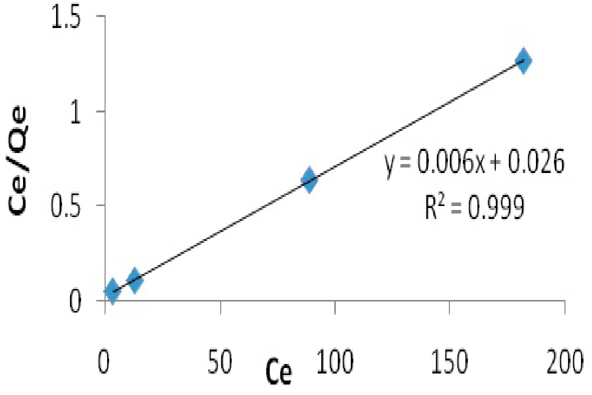

**Figure 6-** Relation ship of Ce\Qe vs Ce in langmuir isotherm.

**Table 6-**Estimated adsorption isotherm parameters for Cu (ll) at different temperature**.**

| Temp. K | Langmuir model | | | Ferundlich model | | |
|---|---|---|---|---|---|---|
| | $Q_{max}$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_f$ (mg/g)(L/mg) | n | $R^2$ |
| 283 | 147.1 | 0.0153 | 0.9949 | 4.26 | 1.51 | 0.9529 |
| 293 | 143.8 | 0.0752 | 0.9948 | 29.38 | 2.51 | 0.6237 |
| 298 | 147.5 | 0.1606 | 0.9999 | 74.10 | 4.42 | 0.7978 |
| 303 | 147.2 | 0.2491 | 0.9999 | 91.45 | 5.38 | 0.7899 |

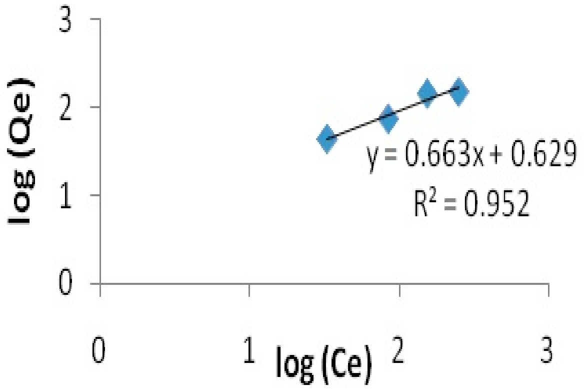

**Figure 7-** Relation ship of log (Qe) and log (Ce) in Freundlich isotherm

Its clear from table 6, that the values of the freundlich exponent, n, were greater than (n>1) which represents a favorable adsorption condition. Examination of the linear isotherm plots suggested that the Langmuir model yielded a much better fitting than freundlich mode. The Langmuir adsorption constant can be evaluated from the slop and intercept of the linear plots of $C_e/Q_e$ vs Ce.

Slop = 1 / $Q_{max}$ intercept = 1 / $Q_{max}$ $K_L$

The freundlich constant and n values can be obtained from the slop and intercept of the linear plots of log $Q_e$ vs log $C_e$.

Slop = 1 / n intercept = log $K_F$

The thermodynamic parameter can be obtained from Vants hoof equation[28]:

$$\text{Ln Kc} = -\Delta H° / RT + \Delta S° / R \quad ........ \quad (6)$$

Where Kc (L/g) is the standard thermodynamic equilibrium constant defined by $Q_e/C_e$ . ΔH° and ΔS° can be calculated from the slop and intercept of the linear plot of ln Kc vs 1/T, (Figure .8.)

Slop = - ΔH° / R intercept = ΔS° / R

Where R is the universal gas constant (8.314 J/mol.K).The resulting thermodynamic parameters are given in table 7.

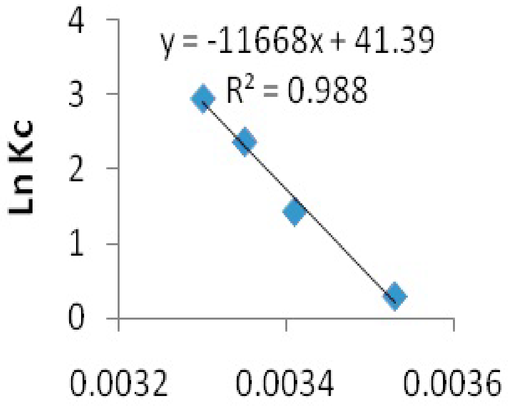

**Figure 8-** LnKc vs 1/T

**Table 7-**Estimated thermodynamic parameters.

| Temp. K | ΔG° kJ/mol. | ΔH° kJ/mol. | ΔS° J/mol.K |
|---|---|---|---|
| 283 | -0.34 | 97.01 | 344 |
| 293 | -3.78 | | |
| 298 | -5.50 | | |
| 303 | -7.22 | | |

The negative values of ΔG° obtained indicated that the Cu (ll) adsorption process is spontaneous, and the positive values of Δ H° and ΔS° indicated that the process is endothermic with increased randomness at the solid/solution interface occur in the internal structure of the adsorbent.

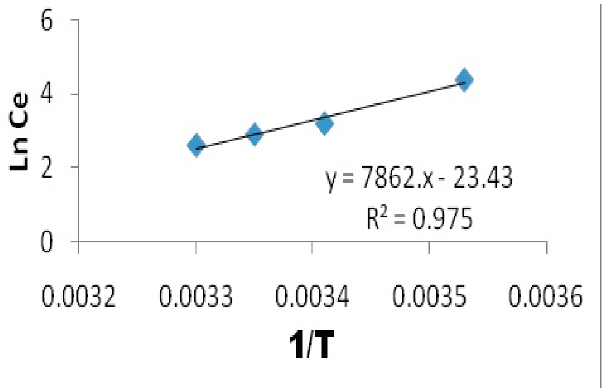

**Figure 9-** Ln (Ce) versus 1/T for Cu (II) adsorption

The values of $\Delta H°_{ads}$ can be calculated from the slop of the plot of ln $C_e$ vs 1/T, (figure 9.) according to: Clapeyron equation[29]:

$\Delta H_{ads}=R[d(LnC_e)/d(1/T)]$……… .(7)

Where $\Delta H°_{ads.}$ is the heat of adsorption (kJ/mol.) .The resulting values are given in table 8.

**Table 8-** Estimated heat of adsorption for Cu(ll) adsorption

| **Initial Cu(ll) ion concentration mg.L$^{-1}$** | **$\Delta H^o_{ads.}$ kJ/mol.** |
|---|---|
| **100** | **85.53** |
| **200** | **65.36** |
| **300** | **19.58** |
| **400** | **12.07** |

## Effect of PH:

The influence of pH on the removal of Cu (ll) by PAA was studied to gain further insight in to the adsorption process. The effect of pH was checked over a pH range (1-6.3) using 100 mg.L$^{-1}$ of Cu (ll). The pH values were adjusted by using (0.5) M HCI. The samples were let for (20hr) contact time with 0.0382 g hydrogel. The results obtained are tabulated in table.9.

**Table 9-**The results of pH effect on the Cu(ll) ion adsorption**.**

| **pH value** | **Remained Cu(ll) ion mg.L$^{-1}$** | **Removal Cu(ll) ion mg.L$^{-1}$** | **Q mg/g** |
|---|---|---|---|
| **1** | **60.00** | **40.00** | **26.10** |
| **2** | **53.80** | **47.20** | **30.90** |
| **3** | **40.10** | **59.90** | **39.20** |
| **4** | **32.74** | **67.26** | **44.00** |
| **5** | **20.83** | **79.17** | **51.80** |
| **6.3** | **7.74** | **92.26** | **60.40** |

Figure .10. showed that the optimum pH for the removal of Cu(ll) was at 6.3 .The adsorption process occurs mainly due to static attraction between the metal ion and the carboxyl group in adsorbents . At lower pH values, protons are available to protonate the carboxyl group of PAA. Therefore, the attraction of cationic Cu (ll) ions decrease while near the basic condition the cations will begin to precipitate from the solution and the removal percentage was decrease.

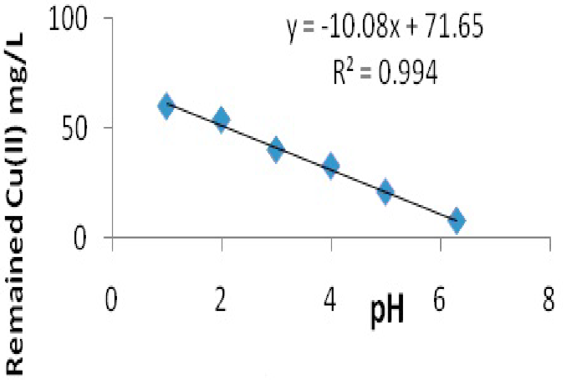

**Figure 10-** Effect of pH on the removal of Cu (II)

## Regeneration of beads

For practical use, the metal ion adsorbed by a polymeric bead must be desorbed easily and the polymer can be reused again after repeated regeneration. Desorption of PAA polymer are investigated with batch experimental technique under competitive condition. The amount of adsorbed and desorbed metal ions was determined. This study was carried out by using different acid solution (HCl, $HNO_3$, $H_2SO_4$, and $CH_3COOH$ ) within the concentration ranged between 0.05 – 0.5 M for the recovery of the adsorbed ions. The results obtained revealed that all acid used gave a high percentage of recovery ranged between 93.7% - 99.2%, figure 11. Using of $HNO_3$ and $H_2SO_4$ acid causes the destructions of the polymer beads, and the beads cannot be reused again. Hydrochloric acid of concentration of 0.5 M was found to be suitable for the desorption of the metal ion from PAA polymer with desorption efficiency of 97% and did not cause destruction of the beads structure and shape and the PAA polymer can be reused again.

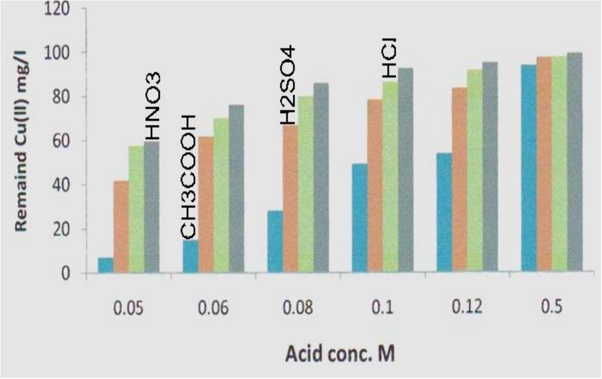

**Figure 11-** Effect of acid type on removal of Cu(II)

## Conclusions

In this study, a hydrogel bead of polyacrylic acid (PAA) was used to adsorbed Cu (ll) from aqueous solution. The results indicate that adsorption of Cu (ll) was increase with increasing of the temperature and time. The maximum capacity was reached at 24 hr with 142.68 mg/g value. The adsorption kinetic data can be described by the pseudo-first-order model, and the adsorption isotherm agrees well with the Langmuir model, during the whole adsorption process.

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