Eng. & Tech. Journal ,Vol.28, No.2, 2010

The Use of Local Sawdust as an Adsorbent for the Removal of Copper Ion from Wastewater Using Fixed Bed Adsorption

Nagham A.Ageena*

Received on: 31/3/2009
Accepted on: 6/8/2009

Abstract

The aim of the present work is to study the removal of copper ion presents in industrial waste water using the local sawdust.

Adsorption column was utilized in the removal process at constant temperature. The effect of the concentration of copper ion in the range (100-500) mg/L was studied. Increasing the inlet ion concentration increases the slope of the break-through curve. The effect of bed height in the range of (10-30) cm on copper ion adsorption from wastewater was studied. The increase in bed height increases the break point values. The effect of flow rate in the range (0.5-1.5) cm^3/sec on copper ion adsorption also was studied. Increasing the flow rate decreases the break-through time. The best operating conditions in this work for copper ion adsorption are 100 mg/L of feed, 30 cm bed height and 0.5 cm^3/sec feed flow rate. It was found that the equilibrium relation agrees with Langmuir & Freundlich equations. Finally accumulation adsorption of copper ion at different operating conditions was calculated.

Keywords: Adsorption, Sawdust, Copper Ion, Wastewater

أستخدام نشارة الخشب المحلية كمادة ممتزة لازالة أيون النحاس من المياة المصرفة بأستخدام الامتزاز بالحشوة الثابتة

الخلاصة

يهدف البحث الى دراسة ازالة ايون النحاس من مياه المخلفات الصناعية بأستخدام مادة نشارة الخشب المحلية. تم استخدام عمود الامتزاز في عملية الازالة تحت درجة حرارة ثابته. تم دراسة تأثير التغيير بتركيز ايون النحاس الداخل في حدود (100-500) ملغم/لتر. وجد ان زياده تركيز الايون الداخل يزيد من ميل منحني الــ Break- through.

تمت دراسة تأثير ارتفاع الحشوة في حدود (10-30)سم على عملية الفصل فوجد انه عند زياده ارتفاع الحشوة تزداد قيمة الــBreak point. ايضاً تمت دراسة تأثير معدل الجريان في حدود (1.5-0.5) سم^3/ثانية على عملية الفصل فوجد انه عند زياده معدل الجريان سوف يتناقص الزمن اللازم للتشبع وتزداد قيمة الــ Break point.كما وجد ان علاقة التوازن تخضع لقوانين الامتزاز الخاصة بمعادلتي لانكمير Langmuir وفريندلش Freundlich. وان افضــــــل ظـــــــروف تشغيل هــــــــــــــــــــــــــي 100 ملغم/لتر تركيز ايون النحاس الداخل، 30 سم ارتفاع الحشوة و 0.5 سم^3/ثانية كمعدل للجريان. تم حساب الامتصاص التراكمي للنحاس في مختلف ظروف التجربة.

Introduction

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures.

Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals.

---

* Chemical Engineering Department, University of Technology/Baghdad

https://doi.org/10.30684/etj.28.2.1
2412-0758/University of Technology-Iraq, Baghdad, Iraq

Industrial wastewater containing Lead, Copper, Cadmium and

Chromium, for example, can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. In drinking water heavy metals can be toxic to consumer and thus affects the health. On the health side, exposure to such chemicals can damage the central nervous system, respiratory system, kidney and blood system if they enter human body. Therefore, removing these toxic heavy metals or decreasing their concentration to the permitted level before discharging becomes a challenging issue (1).

The methods of removing heavy metals from wastewater are numerous and varied. Precipitation is probably the most common of all methods of removing metals from aqueous solution. It is quite simple and is based on the fact that some metal salts are insoluble in water. The ion- exchange method of water treatment uses ions on a matrix to exchange with metal ions in the water. Biological processes are probably the newest technology used to treat water contaminated with heavy metals. Biological methods represent an area in which a great deal of innovation is taking place all the time. Reverse osmosis uses a membrane and high pressure to filter out the metal ions. Adsorption phenomenon has been found economical for the removal of toxic metals from wastewater by choosing some adsorbent under optimum operation conditions (2). The most widely used adsorbent for the removal of impurities from water is activated carbon. In recent years, many low cost adsorbents including agricultural and waste by product have also been tested in batch and fixed bed sorption system by a number of researchers(3). Several adsorbents have been used for the removal of heavy metals from wastewater by adsorption of copper. It has been reported that some aquatic plants, waste tea leaves and sawdust have an efficient role. Since copper is a common pollutant introduced into natural water from a variety of industrial wastewater including those from electroplating and metal finishing industries (2), It is recognized to be one of the heavy metals most wide spread heavy metal contaminants in the environment. For this reason copper content of industrial wastewater must be decreased to the limits given in the international regulations (4). Many researchers have worked in this field. Al-Zboon observed that activated carbon shows a very high preference for copper. The equilibrium isotherm for adsorption of Cu was obtained in batch experiments. The experimental data was fitted to the Langmuir and Freundlich (1). Erdem studied the adsorption behavior of natural Zeolites (Clinoptiloite) with respect to Co^{+2}, Cu^{+2}, Zn^{+2} and Mn^{+2}. The selectivity sequence can be given as $Co^{+2} > Cu^{+2} > Zn^{+2} > Mn^{+2}$. These results show that natural zeolites hold great potential to remove cation of heavy metals species from industrial wastewater (5). Muhammed showed that slow sand filters are effective in the removal of heavy metals. The maximum adsorption capacity of sand is highest for Pb followed by Cu, Cr and Cd. Adsorption of Pb, Cu, Cr and Cd on to sand satisfied the Langmuir and Freundlich isotherms (6). Douglas steadied the efficiency of removing copper ions from copper chloride solution using soybean hulls. The results have demonstrated that soybean hulls show the greatest potential as copper ion adsorbents. The copper ion removal efficiency using soybean hulls is 97.68% (7). Esmaeili found the ability of an activated carbon prepared from the algae Gracilaria removes copper ions from aqueous solution. The study shows the benefit of using activated carbon from marine red alage as a low cost adsorbent for the removal of Cu^{+2} from aqueous solution of wastewater (4).

Adsorption Phenomenon

Adsorption is the interaction between a fluid (adsorbate) and a solid surface (adsorbent) and it occurs on the surface of a solid because of the attractive force of the atoms or molecules with the surface of the solid (8). There are two types of adsorption: physisorption and chemisorption (9, 10).In order to investigate the adsorption isotherm, two equilibrium models, Langmuir and Freundlich, were analyzed (4).The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$Qe = \frac{X_m.K.C_e}{1 + K.C_e}$$

where:

Q_e: the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per gm of adsorbent).

Ce: the concentration of adsorbate in solution (mg/ l).

X_m: the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per gm of adsorbent).

K: the Langmuir constant related to energy of adsorption (L of adsorbent per mg of adsorbate).

The above equation can be rearranged to the flowing linear from:

$$\frac{C_e}{Q_e} = \frac{1}{X_m.K} + \frac{C_e}{X_m}$$

The linear form can be used for linearization of experimental data by plotting $\frac{C_e}{Q_e}$ against C_e. The Langmuir constants X_m and K can be evaluated from the slope and intercept of linear equation (6, 4).

The Frendlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$Q_e = K_f.C_e^{\frac{1}{n}}$$

where;

Q_e: the adsorption density (mg of adsorbate per gm of adsorbent).

C_e: the concentration of adsorbate in solution (mg/ l).

K_f and n : the empirical constants dependent on several environmental factors and n is greater than one.

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e$$

A plot of $\log C_e$ against $\log Q_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and intercept (6, 5). The purpose of this research was to study the effect of sawdust, that is obtained as industrial by product from local furniture shops, in removing Cu(II) ions from $CuS0_4$-$5H_2O$ solution

Experimental

Materials

Local sawdust was used as an adsorbent directly without any treatment for the removal of copper(II) from synthetisized aqueous solutions. The synthetic solution was prepared from $CuSO_4$-$5H_2O$ from (BDH Limited pool England), purity 98.5% with distilled water at different concentrations (100, 200, 300, 400, 500) mg/l respectively Freshly prepared solutions were used in the experiments.

Equipment

A schematic representation of the experimental equipment is shown in Fig. (1). A glass column with a height (50 cm) and diameter (5 cm) was used. The sawdust bed was confined in the column by fine stainless steel screen at the bottom and a glass cylindrical packing at the top of the bed to ensure a uniform distribution of influent through the bed. The influent solution was introduced to the column through a perforated stainless steel plate, fixed at the top of the column.

A cylindrical glass container was used with the volume of ($0.1*10^6$ cm^3) as a storage for the wastewater and feeder to the column. (Q.V.F.) glass calibrated rotameter to measure the influent flow rate, ranged between (0-60 l/hr).The wastewater was pumped by means of a (EHEIM Type 1034) of (60 watt) from the feed container to the top of the bed. Part of solution was circulated to the feed container to achieve constant through-put (Q.V.F.) valves were used to control the desired flow rate through the column. All pipes and fittings were made of glass.The determination of copper ion concentration using atomic absorption spectrophotometer model SP 9-01 supplied from Buck, England. For pH measurements, the universal pocket meter Multi Line P4, which consists of a pH combined electrode with temperature probe Sen Tix 41 was used.

Procedure

Experiments were carried out at various initial concentrations (C_o), bed heights and flow rates. All experimental conditions are summarized in Table (1).

The experimental procedure for the system experiments is as follow:

The sawdust was placed in the adsorption column for the desired bed height. The solute solution with the desired concentration was prepared in the feed container, using distilled water. The prepared solution was circulated via the pump to achieve homogeneous solution. The prepared solution was pumped to the adsorption column through the calibrated rotameter at desired flow rate. Water samples were taken at intervals of (900 sec).

Results and Discussion

Effect of Initial Cu (II) Concentration

Five experiments were carried out at different copper(II) ion concentrations of (100, 200, 300, 400, 500) mg/l . The break-through curves for the above experiments are plotted in Fig. (2). From this figure, it can be clearly seen the slope of the break-through curves increases as the initial ion concentration increase especially at initial period time, although these curves have the same (S-shape). After a period of time sawdust bed became exhausted that the adsorption zone has progressed through the full depth of the bed and reached its bottom, the break through began and the break through curves rise sharply. So the break point decreases as the initial concentration increases. For high initial metal ion concentration, steeper break through curves are found because the equilibrium is attained faster for higher initial metal ion concentration, which would be anticipated with the basic increase in the driving force for mass transfer with increase in initial Cu(II) concentration. The time required to reach saturation decreases with increasing the inlet solute concentration. This may be explained by the fact that since the rate of adsorption is controlled by the concentration gradient, it takes a longer time to reach equilibrium for the case of low value of initial solute concentration. Similar findings have been obtained by (Danny 3), (Ahmed 11) and (Al-Najar 12).

To show the adsorption rate at different Cu (II) concentrations the solute adsorbed versus time is plotted in Fig.(3). From this figure the indication is obtained that both the mass transfer rate and total quantity of solute removed from solution at any period of time increase with increasing influent concentration which would be anticipated on the basis of increased driving force transfer with increased concentration of solute in solution, this is in agreement with results obtained by (Abdul- Hameed 13).

Langmuir and Freundlich Isotherms

The plot (C_{eq}/q_{eq}) versus C_{eq} shows a straight line, Fig.(4). This means that the equilibrium data correlate well with Langmuir's equation. The value of (X_m) and the Langmuir constant (K) are calculated from the slope and the intercept of the straight line. These values are tabulated in Table (2).

The plot of log (C_{eq}) against log (q_{eq}) shows a straight line, Fig.(5). This means that the equilibrium data for the adsorption correlate well with Freundlich's equation. The Freundlich's equation constants (1/n) and (K_f) are calculated from the slop and the intercept of the straight line. These values are listed in Table (2).It can be seen that the correlation factor R^2 is close to the unity for both models, indicating a good representation of the experimental results by using linear Langmuir or Freundlich isotherms.

Effect of Bed Height

Three experiments were carried out at different bed heights, (10, 20, 30) cm. The break-through curves for the above experiments are plotted as shown in Fig.(6). From this figure it is observed that the shorter bed heights are generally responsible for earlier break points, this is because a short bed height would exhaust the bed more rapidly. Moreover, the time provided for the contact of the adsorbate with the adsorbent is reduced at a short bed height, furthermore; increasing the bed height will give a sufficient contact time for these molecules to be adsorbed on the sawdust surface. The break points for the long bed height have high value and the time provided for the contact of the adsorbate with adsorbent is longer at a long bed height noting that increasing the bed height will be a accompanied by an increase in the bed cost. These results are in agreement with those obtained by (Abdul-Hameed 13) and (Ahmed 11).

To find the adsorption rate at different bed heights, the amount of Cu(II) ion adsorbed versus time is plotted in, Fig.(7). From this figure, the adsorption rate decreases as the bed height increases, since increasing bed height will provide an extra surface for the adsorption process to be carried out. These results are in agreement with those obtained by (Zablouk 14).

Effect of Flow Rate

Four experiments were carried out at different flow rates (0.5, 1, 1.5) in cm^3/sec. The break-through curves for the above experiments are plotted. Fig.(8). This figure shows that as the flow rate increases the time of break through point decreases. This is because the residence time of solute in the bed decreases as the flow rate increases and therefore there is not enough time for adsorption equilibrium to be reached which results in low bed utilization and the adsorbate solution leaves the column before equilibrium. These results are in agreement with those obtained by (Zablouk 14), (Danny 3) and (Al- Najar 12).

To show the effect of flow rate on the adsorption rate, the adsorption rate versus time is plotted in Fig. (9). From Fig. (9) it can be seen that the adsorption rate of higher flow rate is much faster than that for the lower one. This is due to the high flow rates which will make a good disturbance for the laminar sub-layer just over the sawdust particles. Hence, that will reduce the film thickness to the mass transfer and in turn make the adsorption process faster. But it will not give enough period of time for wastewater molecules to accumulate on the surface of the sawdust. Also, it can be observed from Fig.(9) that the lower the flow rate the longer the linear portion on of the curve, indicating that film diffusion remains rate limiting for longer periods. This observation may be explained by considering that film diffusion is continuing until the external surface area becomes essentially saturated with copper (II) ion (pollutant). These results are in agreement with that obtained by (Zablouk 14).

Conclusions

1. The results show that local sawdust could be used as an effective adsorbent for the removal of copper ion from aqueous solution. The results show that this material has a high retention capacity.
2. The break-through time obtained from break-through curves increase with decrease in the inlet copper ion concentration and feed flow rate, also it increases with increasing bed height.
3. The adsorption rate increases with increasing influent concentration and feed flow rate, and also increases with decreasing bed height.
4. The equilibrium isotherms, for the system, copper sawdust, is of a favorable type and was found to agree with both the Langmuir and Freundlich equations in the range of concentration studied. The equations constants are calculated.

References

[1] Al-Zboon, M., Kandah, M. and Shawabkeh, R., "Removal of Copper by New Activated Carbon", proceeding of the Jordan International Chemical Engineering Conference, P77, Sep.,2005.

[2] Larous S1, Meniai A-H1 and Lehocine M1, "The Use of Sawdust as Adsorbent of Trace Toxic Metals from Wastewater: Adsorption of Copper", Proceeding of the Jordan International Chemical Engineering Conference, P155, Sep-2005.

[3] Danny, K., Porter, J. and Mckay, G., "Film Pore Diffusion Model for the Fixed-Bed Sorption of Copper and Cadmium Ions onto Bone Chare", Wat. Res., vol.35, No.16, 2001.

[4] Esmaeili, A., Ghasemi, S. and Rustaiyan, A., "Evaluation of The Activate carbon Prepared From The Algae Gracilaria for The Biosorption of Cu(II) from aqueous Solution ", African Journal of Biotechnology Vol.7(12), June 2008.

[5] Erdem, E., Karapinar, N. and Donat, R., "The Removal of Heavy Metal Cations by Natural Zeolites", Journal of Colloid and Interface Science 280, (309-314), 2004.

[6] Muhammad, N., Parr, J. and Smith, M., "Adsorption of Heavy Metals

in Slow Sand Filters," 24th WEDC, Conference Islamabad, 1998.

[7] Douglas, S., Pongamphai, S. and Lerdthrailuck, S., "Adsorption of Copper (II) Ion from Aqueous Solution Using Soybean Hulls",proceedings of the 2nd Joint International Conference on SEE, Nov., 2006.

[8] Thurner, F. and Stietz, M., International Chemical Engineering, Vol.30, No1, P.36, 1990.

[9] Cheremisinoff, P.N. and Ellerbush, F., Carbon Adsorption Handbook, by ann Arbor Science Publishers, Inc. P.1, 1978.

[10] Alberty, R.A., Physical Chemistry 6th ed., John Wiley & Sons; P.287, 1983.

[11] Ahmed, K.W., "Removal of Multi Pollutants from Wastewater by Adsorption Method", Ph.D. thesis, University of Baghdad, Baghdad, 2006.

[12] Al- Najar, J., A., A., "Removal of Heavy Metals by Adsorption Using Activated Carbon and Kaolinite", Ph.D. thesis, University of Technology, Baghdad, Iraq, 2009.

[13] Abdul- Hameed, H.M., "Reduction of Organic Concentration in Wastewater by Adsorption onto Activated Carbon", M.Sc. thesis, University of Baghdad, Baghdad, Iraq, 1996.

[14] Zablouk, M.A. and Kalaf, I., "The Removal of Benzen and Toluene Binary Mixture by Adsorption in a Fixed Bed", Al- Muhandis , vol.133, No.1, Mar., 1998

Table (1) Experimental Conditions

Adsorbent	Local sawdust
Bed height, cm	10, 20, 30
Weight of bed, gm	15, 30, 45
Flow rate, cm^3/sec	0.5, 1, 1.5
Copper ion concentration,mg/l	100, 200, 300, 400, 500
pH	5.5
Temperature, C^o	34

Table (2) Langmuir and Freundlich's equation constants

Models	X_m (mg/gm)	K (L/mg)	K_f (mg/gm)	1/n (L/gm)	R^2
Langmuir	**22.72**	**0.0057**	/	/	**0.9841**
Freundlich	/	/	**0.893**	**0.4837**	**0.9367**

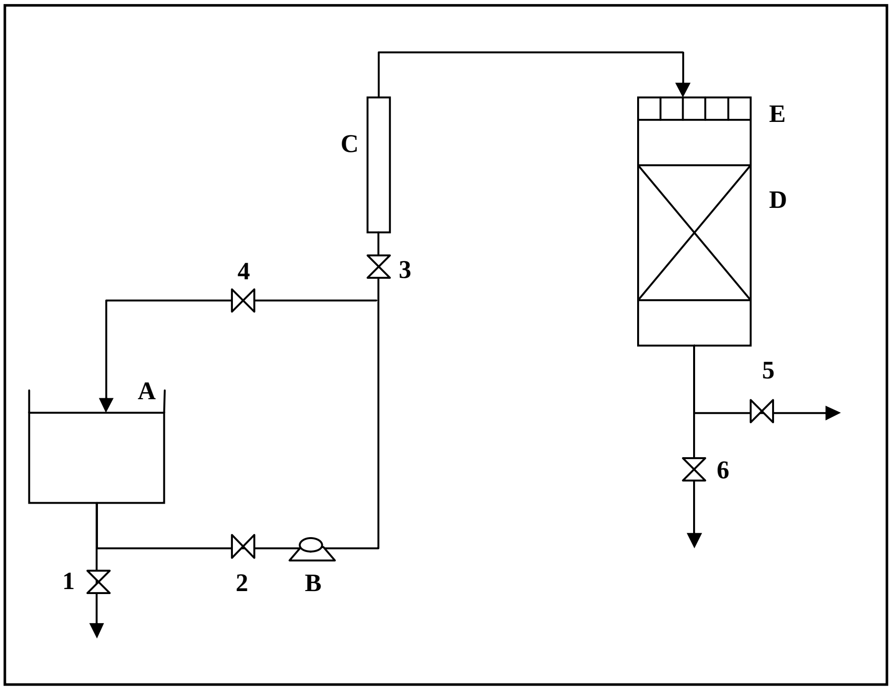

Figure (1) Schematic Representation of Experimental Apparatus

A: cylindrical feed tank
B: pump.
C: rotameter.
D: packed bed.
E: perforated plate.
1: drain valve.
2: pumps valve.
3: flow adjustment valve.
4: recycle adjustment valve.
5: drain valve.
6: sampling valve.

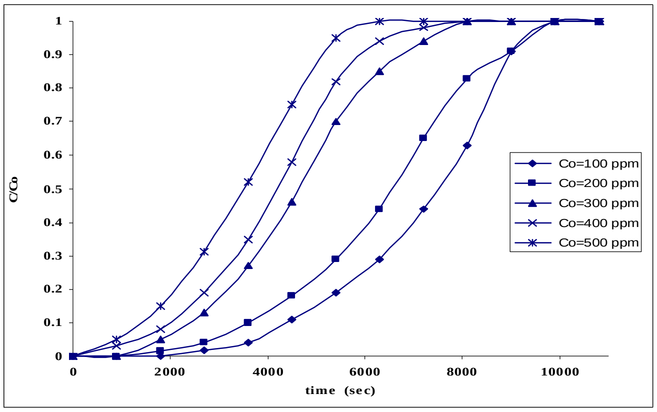

Figure (2) Breakthrough Curve for Isothermal Adsorption of Cu+2 at Different Initial Concentrations (Q=0.5cm3/sec, pH=5.5, T=34 Co, bed height= 30 cm, weight of bed=45 gm)

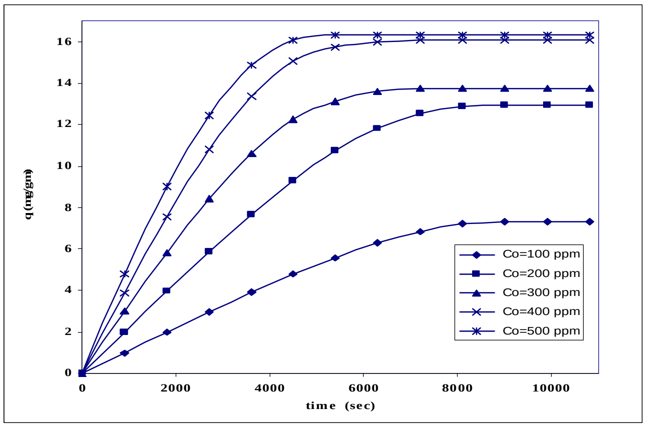

Figure (3) Cumulative Adsorption at Different Initial Concentrations

(Q=0.5cm3/sec, pH=5.5, T=34 Co, bed height= 30 cm, weight of bed=45

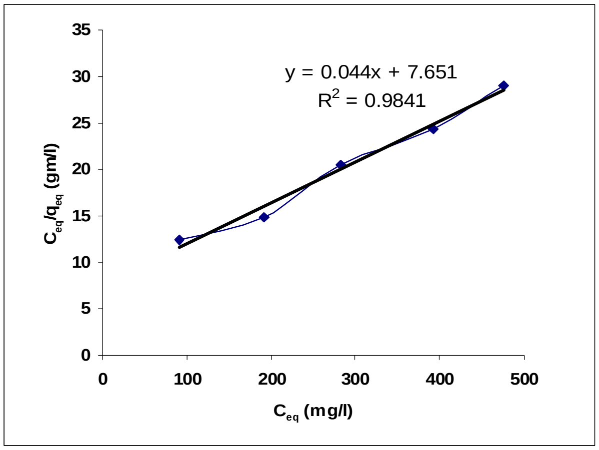

Figure (4) Plot of (Ceq/qeq) vs (Ceq) for determination of Langmuir Constant

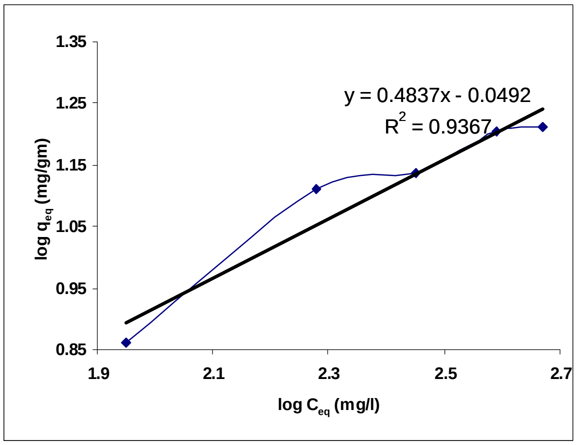

Figure (5) Plot of (log qeq) vs (log Ceq) for determination of Frenudlich Constant

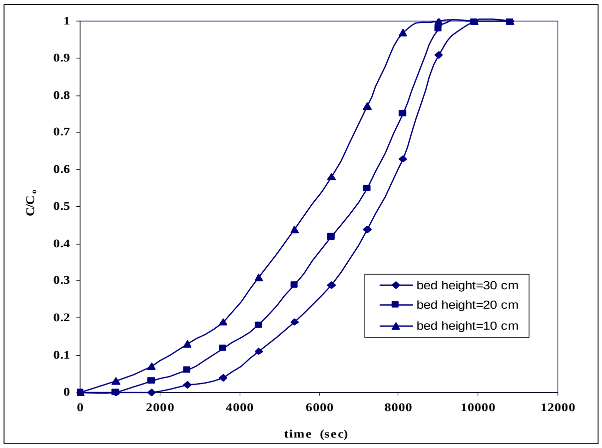

Figure (6) Breakthrough Curve for Isothermal Adsorption of Cu^{+2} at Different Bed Depths (Co=100 ppm, Q=0.5cm^3/sec, pH=5.5, T=34 C^o)

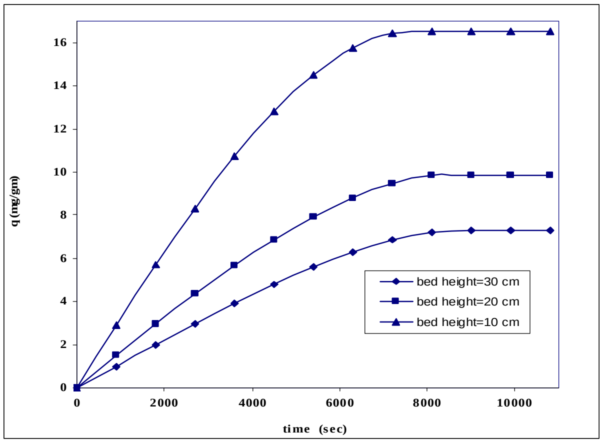

Figure (7) Cumulative Adsorption at Different Bed Depths (Co=100 ppm, Q=0.5cm^3/sec, pH=5.5, T=34 C^o)

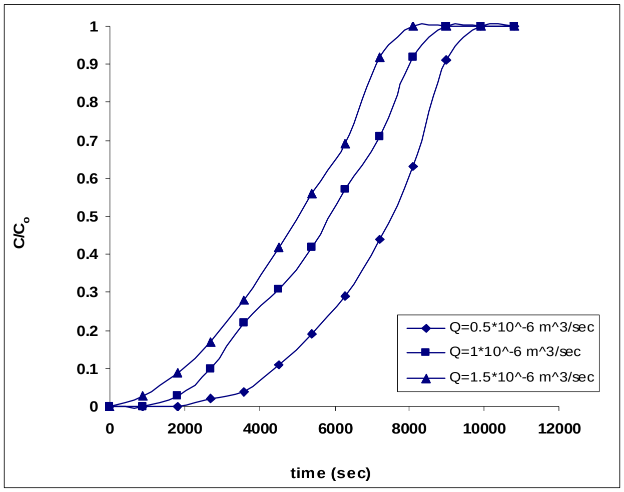

Figure (8) Breakthrough Curve for Isothermal Adsorption of Cu^{+2} at Different Flow Rates (C_o=100 ppm, pH=5.5, T=34 C^o, bed height= 30 cm, weight of bed=45 gm)

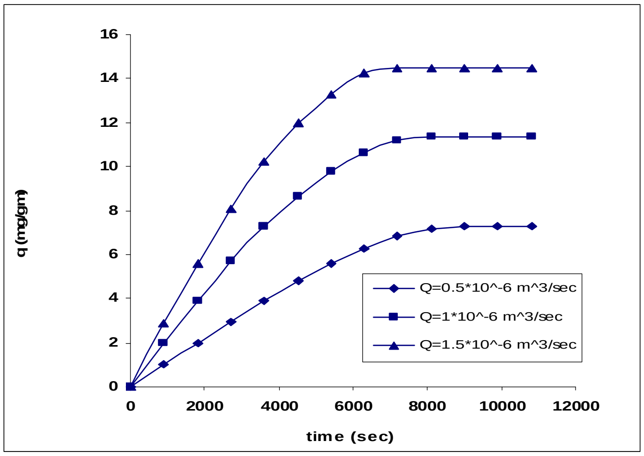

Figure (9) Cumulative Adsorption at Different Flow Rates (C/Co=100 ppm, pH=5.5, T=34 C^o, bed height= 30 cm, weight of bed=45 gm)