
AMINATION OF GLYCIDYL METHACRYLATE-G-JUTE COPOLYMER AND IT'S UTILIZATION IN THE REMOVAL OF Cu⁺⁺ IONS

A. ABOU-OKEIL¹, M. A. YOUSEF², M. FIKRY¹ AND E. A. EI-ALFY¹

1 Textile Research Division, National Research Center, Dokki, Cairo, Egypt

2 Faculty of Science, Helwan University

* aokei12004@yahoo.com

Abstract

Glycidyl methacrylate-g-jute copolymer of an epoxy content of 0.529 mole/100g was aminated with any of cyclohexyl amine (CRA), hexyl amine(HA) or N-ethyl butyl amine (NEBA) at different factors, including amine concentration (0.08-8 mole/l), LR(1: 10-1:40), time (15-120 min.) and temperature(30-90°C). The extent of amination depends on the type of amine and it follows the order: CHA > NEBA > HA. At optimum conditions, viz. amine concentration of 5 mole/l, LR (1:20) for 15 min. at 90°C, 3 aminated jute fibers(AJF) were prepared, viz. CRAJF, HAJF and NEBAJF with % N of 5.92, 5.27 and 5.39% respectively. AJFs were used in the removal of Cu²⁺ ions from aqueous solution at different pRs (2-8), CU²⁺ ion concentration (50-500 mg/l), AJF concentration (1-10 g/l), and time (15-180 min.). The extent of Cu²⁺ ion removal depends on AJF type and follows the order: NEBAJF > CHAJF > HAJF. Optimal removal conditions at room temperature (30°C) were pR 5, Cu²⁺ ion concentration 200 mg/l, adsorbent concentration 2g/l and time of 180 min. The removal of Cu²⁺ ions by the three different AJFs follows Langmuir and Freundlich isotherms.

Introduction

Jute is a natural fiber widely grown in India, Bangladesh, China and Thailand. Jute has been traditionally used as a packing material, it is also utilized in textile and non textile areas for production of jute fine yarn or blended yam, grades of roper and composite for furniture. Wastes of jute were generated during cultivation, retting and also during the processing of jute fiber in industry.

Presence of toxic metals in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effect on receiving water. Various methods exist for the removal of toxic metals from aqueous solution such as Ion exchange, reverse osmosis, adsorption, complexation and precipitation¹⁻³. The adsorption has still been found economically appealing for the removal of toxic metals from waste water by choosing some adsorbent under optimum operation conditions.

Copper and its compounds are present in surface water. The potential sources of copper are mining wastes, plating bathes, fertilizer industry, paints and pigments⁴⁻⁶. The most widely used method for removing of copper (II) is the precipitation as insoluble hydroxide at alkaline medium⁷⁻¹⁰ or sometimes as sulfide¹¹⁻¹².

Ion exchange can be considered a promising tool for the removal of copper from waste water¹³. The present study is therefore dealing with amination of GMA-g-copolymer with different amines, including N-hexyl amine, cyclohexyl amine and N-ethyl butyl amine, then utilizing the so aminated copolymers in the removal of copper II ions from aqueous solutions.

Experimental

Materials

Jute fiber wastes (JFW) were kindly supplied by El Nassr Company for jute industry Egypt. Glycidyl methacrylate (GMA) (Fluka), sodium bisulphate, ammonium persulphate, acetone, copper acetate, N-hexyl amine, cyclo hexyl amine and N-ethyl butyl amine are of laboratory grade chemicals, Cibapon[®] R, a nonionic detergent, was supplied by Ciba speciality chemicals.

Methods

Scouring of Jute Fiber waste (JFW)

JFW was scoured by treating with 7 g/l NaOH solution and 2 g/l Cibapon R[®] at 85°C using liquor ratio 1 :50 for 60 min; then the sample was washed thoroughly with hot, cold water and then, neutralized with 1 % acetic acid solution and finally dried at ambient conditions.

Preparation of GMA-g-jute copolymer

A known weight of jute fiber was introduced in a stoppard conical flask containing 150 % of GMA monomer (ows), followed by addition of ammonium persulphate/acetone sodium bisulphate adduct¹⁴ at concentration 20 and 40 mmole/l, respectively at liquor ratio (L: R) of 1 :20, a temperature of 20°C and a pH 3 for 120 min. with continuous stirring in a shaking water bath. At the end of the reaction the grafted sample was washed using acetone in soxhlet apparatus to get rid of the homopolymer formed to obtain a grafted jute fibers (GJF) having 0.529 mole/100 g epoxy content.

Amination

GJF was aminated using aqueous solutions of any of cyclohexyl amine (CRA), hexyl amine (RA) or N- ethyl butyl amine (NEBA) as follows. 19 of GIF was introduced into a 100 ml glass stoppard bottle containing different amine concentrations (0.08-8 mole/l), at different LR (1: 10⁻¹ :40) and temperatures (30-90°C). Amination was conducted in a thermostated shaking water bath. At the end of the amination, the content of the bottle was filtered on a sintered glass funnel (G 1) and washed thoroughly with hot and cold water then dried at ambient conditions before analysis.

Utilization of aminated fibers in Cu⁺⁺ removal

Cu⁺⁺ ions were removed from aqueous solution by different aminated jute fibers (AJF) in a thermostated shaking water bath as follows. AJF was introduced into a 100 ml glass stoppard bottle containing different concentrations of Cu⁺⁺ ion solution (50-500 mg/l) at different pHs (2-8), adsorbent concentration (1-10 g/l) and time (15-180 min.), and a fixed temperature of 30°C, followed by filtration and determining the Cu H ions content in the filtrate.

Analysis and test methods

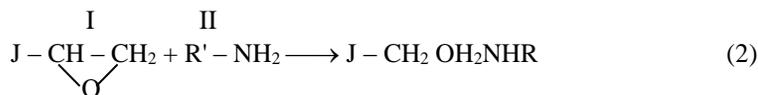
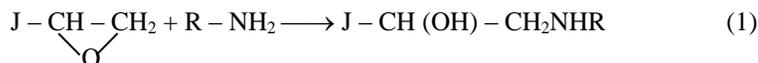
Epoxy content was determined as described elsewhere 15 Nitrogen content was evaluated by Kjldahl method. CuH ions were assessed as given in reference 16.

Results and Discussion

Preparation of aminated lute fibers (AJF)

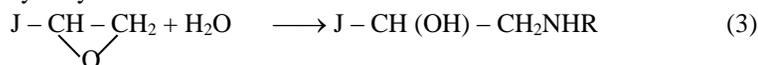
Under the conditions studied, the oxirange rings of GJF can undergo two types of reactions as follows:

a- amination



III

b- Hydrolysis



Where III and III represent GJF, either "CRA or HA" and NEBA respectively. Different factors affecting amination reaction, such as amine concentration, LR, time and temperature were studied. Given below are results obtained with proper discussion.

Amine concentration

Fig. (1) Shows the effect of amine concentration on the extent of amination, expressed as the nitrogen content. Increasing amine concentration in the range 0.08 - 1 mole/l has a pronounced effect on increasing the extent of amination. Further increase in concentration beyond 1 mole/l up to 8 mole/l is accompanied by an approximate leveling off of the extent of amination, regardless the amine used. The order of increasing N content is as follows:

Cyclo hexyl amine > N-ethyl butyl amine > N- Hexyl amine

These results indicate that increasing the amine concentration has an influencing effect on the degree of amination which may be attributed to the increase of the amine molecules in vicinity of GJF¹⁷.

Liquor Ratio

Fig. (2) Shows the effect of liquor ratio on the nitrogen content. It is obvious that increasing liquor ratio leads to a decrease in N content. It is very clear from Fig. (2) that the effect of liquor ratio is almost the same for the three types of amines used. The effect of liquor ratio on (N %) has the same order of the amine concentration¹⁷⁻¹⁸.

Cyclo hexyl amine > N-ethyl butyl amine > N- Hexyl amine

Amination time

We can conclude from Fig. (3) That increasing the amination time plays an important role with respect to the nitrogen content (degree of amination). The results obtained show that increasing the amination time leads to decreasing of the nitrogen content still we have the same order:

Cyclo hexyl amine > N-ethyl butyl amine > N- Hexyl amine

By increasing the amination time from 15 to 90 min. the N content decreases, this may be attributed to the deamination that could be happened with prolonging the time¹⁹.

Amination temperature

Fig. (4) Shows the effect of amination temperature on the nitrogen content. The treatment was done using 8 mole/l amine and 1 :20 L: R, at different temperatures for 15 min. The results of Fig. (4) show that increasing the amination temperature has a valuable effect on the nitrogen content. As the temperature increases the nitrogen content increases regardless to the type of amine used. Elevating the temperature may lead to increasing the possibility of opening the epoxy group that result in increasing N content¹⁷⁻¹⁸.

Utilization of AJF in Cu⁺⁺ ion removal fro aqueous solutions

Three aminated fibers were prepared by reacting GJF with any of the three amines (5 mole/l) at a LR of 1:20 for 15 min. at 90°C. These were termed as CHAJF, NEBAJF and HAJF and their nitrogen contents were 5.92,5.27, and 5.39% respectively.

The three AJF were utilized in the removal of Cu⁺⁺ ions from aqueous solutions. Removal mechanism was best illustrated elsewhere in some reference²⁰.

Factors affecting the removal, such as pH, adsorbent concentration and time were studied. Langmuir and Freundlich adsorption isotherms of the process of removal were studied. Given below are the results with suitable discussions.

pH

It is clear from fig (5) that the removal of AJF for Cu²⁺ is dependent on the pH of the aqueous solution. Where the removal remarkably decreases with the decrease in pH of the solution, this is in accordance with a previous study²¹. For example the percentage of removal of Cu²⁺ on AJF was 13% at pH 2 while it became 31.6% at pH 5 (original pH of Cu²⁺ solution) for NEBAJF and CHAJF. It is obvious that at low pH value W ions compete with metals for the adsorption sites in the system, thereby partially replace the latter, so the Cu²⁺ released completely under extreme acidic solution²¹. The trend appears the same irrespective to the type of the aminated substrate used²²⁻²³.

Adsomtion concentration

Fig (7) shows the effect of adsorption concentration on the % removal of Cu²⁺. The study was conducted at 200 mg/l initial Cu²⁺ concentration at pH 5 at 30°C for 3 hrs. It is obvious that increasing adsorption concentration is accompanied by

increasing of % Cu²⁺ removal, that is hold true for the 3 aminated substrates. This may be attributed to the increase in the adsorption sites at high adsorbent concentration²⁴. The % removal of Cu²⁺ increased from 5 to about 49%, from 4 to 42% and from 6.4 to 41.87% by increasing the adsorption concentration for NEBAJF, CHAJF and HAHF respectively.

Time

Figs 8, 9, and 10 show the effect of time on the removal of Cu²⁺ by CHAJF, HAIF and NEBAIF respectively. Removal was conducted at three initial Cu²⁺ concentrations of 100, 200 and 400 mg/l. Obviously, increasing the time is accompanied with increasing the extent of removal, irrespective of the aminated substrate or Cu²⁺ ion concentration used. Moreover, the higher the initial Cu²⁺ ion concentration the higher is the removal by a substrate at a given time.

Langmuir Isotherm

Langmuir model assumes that the adsorption of Cu²⁺ occurs at homogeneous surface, by applying Langmuir isotherm on the adsorption of Cu²⁺ on AIF.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \cdot b}$$

Where

- C_e = equilibrium concentration mg/l
- q_e = amount of Cu²⁺ adsorbed per gram (mg/g) at equilibrium.
- Q_{max} = adsorption capacity mg/g
- b = constant l/mg.
- KL = Q_{max} · b

The linear plot of C_e/ q_e versus C_e (Fig. 11-13) shows that the adsorption of Cu²⁺ onto AJF obeys Langmuir isotherm model.

[R₂ = 98.12, 99.4 and 99.79] for N-ethyl butyl amine, Cyclohexyl amine and N-Hexyl amine respectively. The values of b, K_L, Q_{max} and R₂ are listed in table (1).

The important parameter in Langmuir isotherm is the dimensionless constant separation factor RL which can be calculated from the following equation²⁶. The RL values are listed in table (3). It is obvious that all RL values are less than 1 and more than zero which leads to say that adsorption of Cu²⁺ onto AGJF obeys Langmuir Isotherm system.

$$R_L = (1/1 + b C_o)$$

Freundlich Isotherm

Freundlich isotherm is an indication of surface heterogeneity of the adsorbent, it assumes that the sites on the surface of adsorbent are no similar and each has different adsorption energy.

$$\text{Log } q_e = \text{log } K_F + 1/n \text{ Log } C_e$$

Where:

q_e = mg/g at equilibrium

C_e = mg/l at equilibrium

K_F = dimensionless parameter for favorability.

The linear plot of $\text{log } q_e$ versus $\text{Log } C_e$ (Fig. 14-16) is an indication of obeying the adsorption of Cu^{2+} onto AGJF to Freundlich model for all the amine used.

Freundlich parameters R_2 , $1/n$, K_F are listed in table (5). The values of $1/n$ are <1 for all amines used indicating the favorability of Freundlich isotherm.

It is obvious that Langmuir isotherm is an indication for homogeneity while Freundlich isotherm hints toward heterogeneity of adsorbent. It is concluded that the surface of AGJF is considered as small heterogeneous adsorption sites which are very similar to each other with respect to the adsorption.

Conclusion

The extent of amination of GMA-g-jute copolymer (0.529 mole epoxy/100 g) depends on the kind of amine used and follows the order: $\text{CHA} > \text{NEBA} > \text{HA}$. The optimal amination conditions were, amine concentration of 5 mole/l, LR (1:20) for 15 min. at 90°C . The extent of removal of Cu^{2+} ions from aqueous solution depends on the type of

AJF used and follows the order: $\text{NEBAJF} > \text{CHAJF} > \text{HAJF}$. Optimal Cu^{2+} ion removal by any of AJFs are pH 5, Cu^{2+} ion concentration 200 mg/l, adsorbent concentration 2g/l and time of 180 min. at 30°C . The removal of Cu^{2+} ions obeys Langmuir and Freundlich isotherm models.

Table (1): Langmuir constants

AJF	R	Q_{\max}	K_L	b
NEBAJF	98.29	48.3	0.5792	0.0119
CHAJF	99.4	53.48	0.4926	0.0092
HAJF	99.79	25.44	0.8300	0.0326

Table (2)

R_L Value	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Reversible

Table (3): R_L values for the adsorption of Cu^{2+} by AJFs

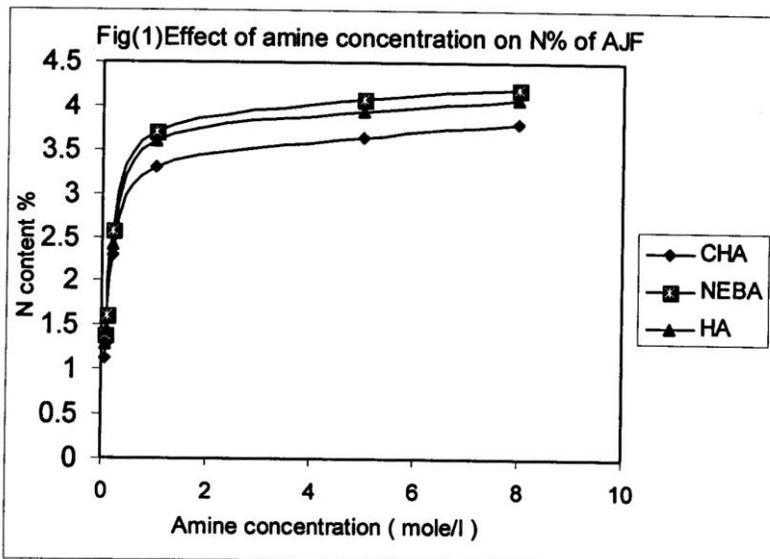
C_o	R_L		
	N-Ethyl Butyl amine	Cyclo hexyl amine	N- hexyl amine
50	0.6270	0.6849	0.3802
100	0.4566	0.5208	0.2347
200	0.2959	0.3521	0.1330
300	0.2188	0.2660	0.0928
400	0.1736	0.2137	0.0712
500	0.1439	0.1786	0.0578
600	0.1229	0.1534	0.0486
700	0.1072	0.1344	0.0420
800	0.0951	0.1196	0.0369

Table (4)

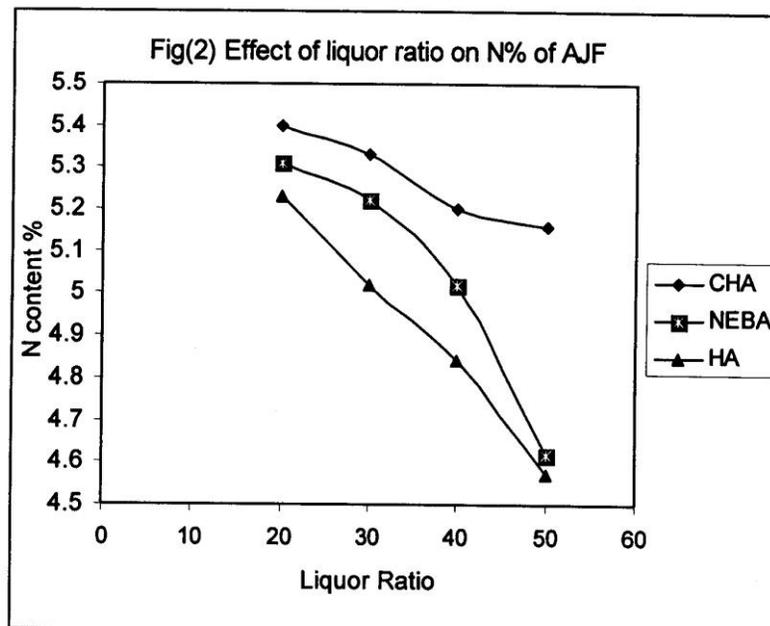
$1/n$ Value	Type of Isotherm
$1/n = 1$	Linear
$1/n < 1$	Normal Langmuir
$1/n > 1$	Cooperative isotherm

Table (5): Freundlich constants

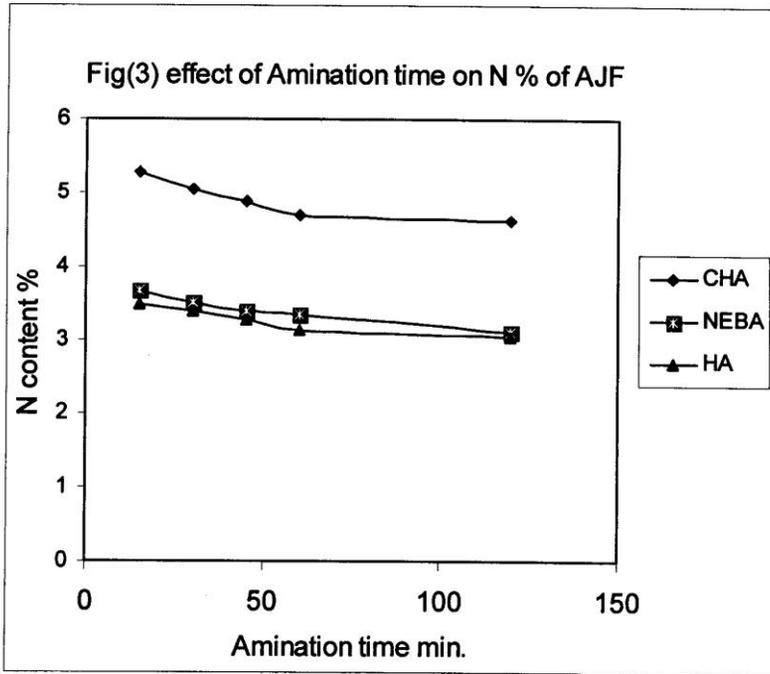
AJF	R	$1/n$	K_f
NEBAJF	98.12	0.5386	2.0137
CHAJF	98.81	0.5594	1.7800
HAFJ	97.70	0.2389	5.6990



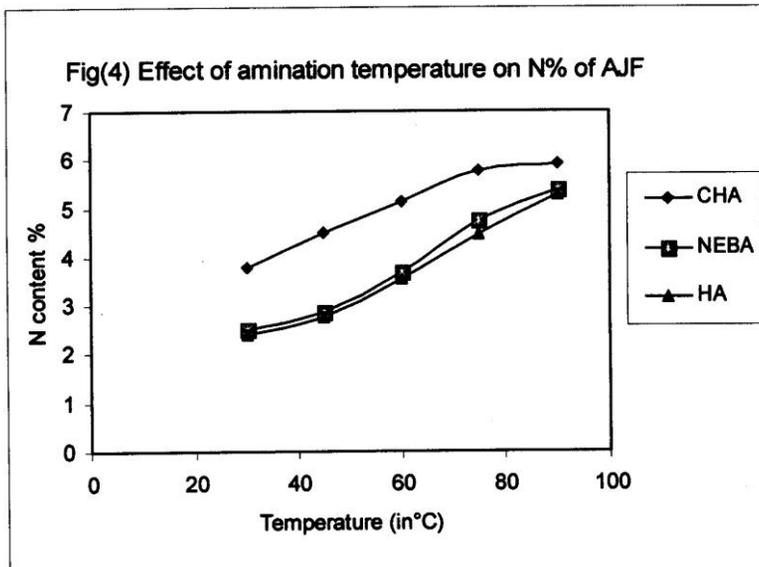
Time 60 min.. Temp.45 °C and L.R = 1:20



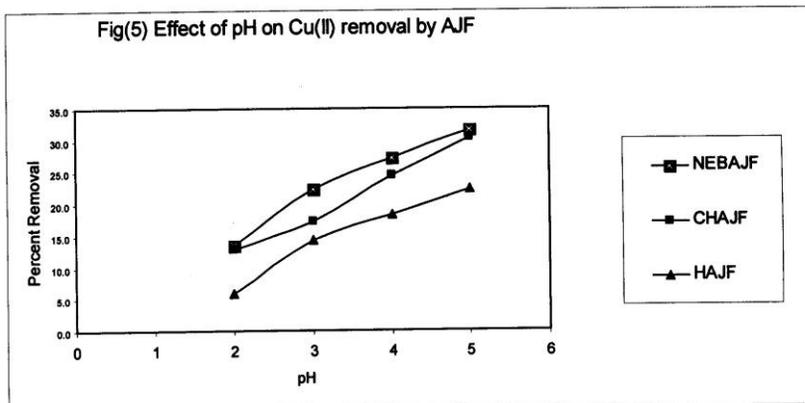
Time 60 min., Temp.45 °C and Amine Concentration = 5 mol/l



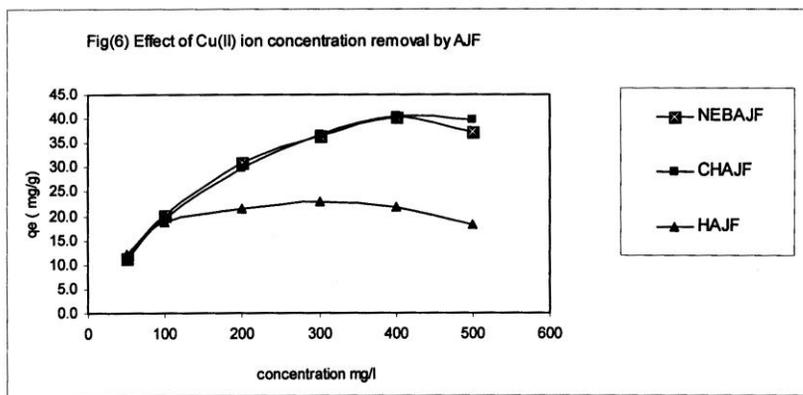
L.R= 1:20, Temp.45 °C ,and Amine Concentration = 5 mol/l



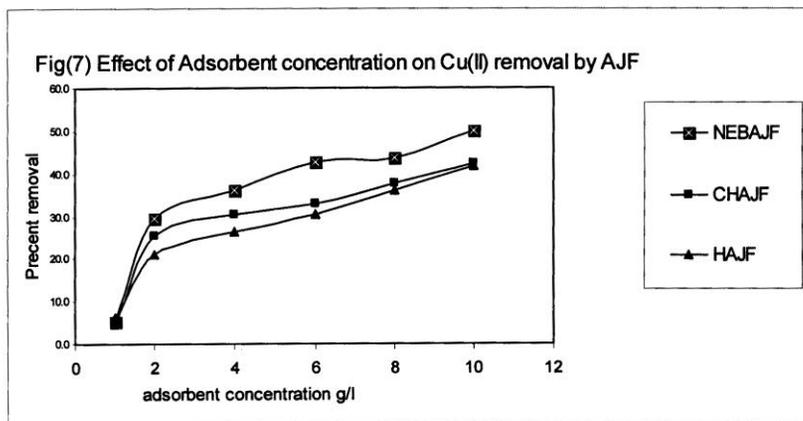
L.R= 1:20, Time 15 min. and amine Concentration = 8 mol/l



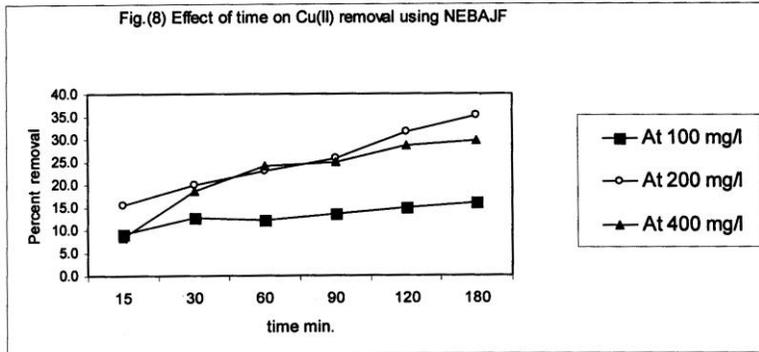
Adsorbent 2g/l , Temp.=30°C , Time= 2 Hrs. and [Cu(II)] =200mg/l



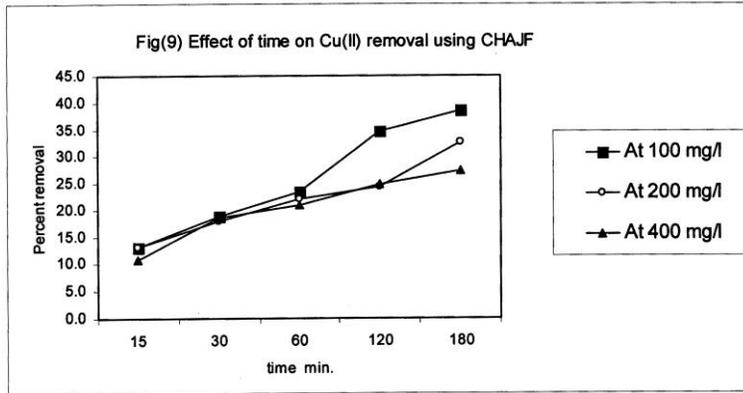
Adsorbent 2g/l , Temp.=30°C , Time= 3 Hrs. and pH=5



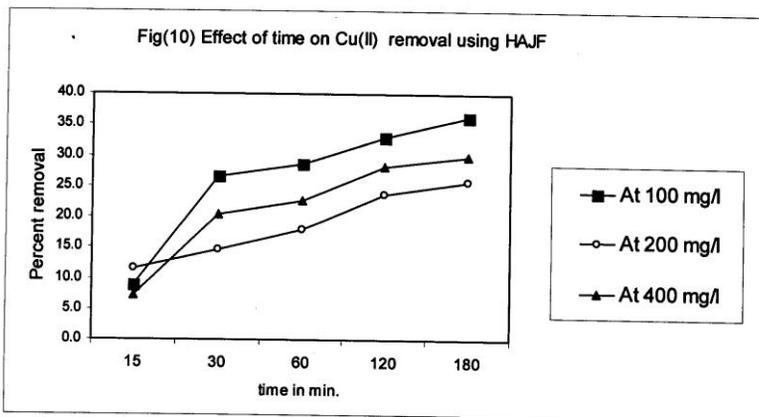
Temp.=30°C , Time= 3 Hrs. pH=5 and [Cu(II)] =200mg/l and



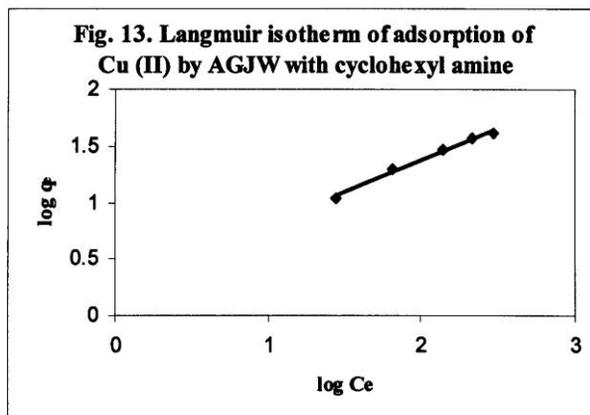
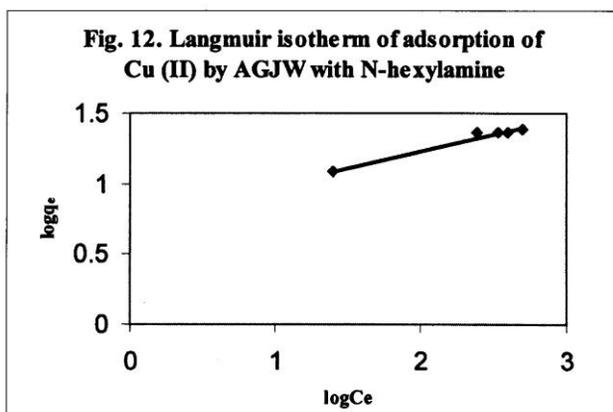
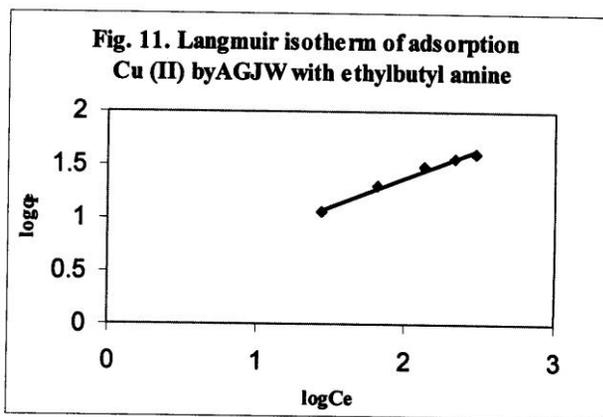
adsorbent concentration 2g/l and Temp.=30°C .

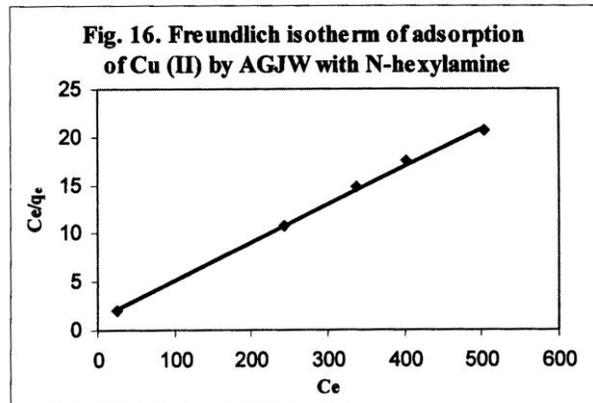
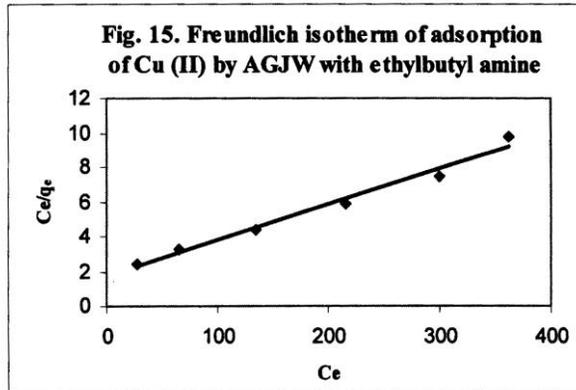
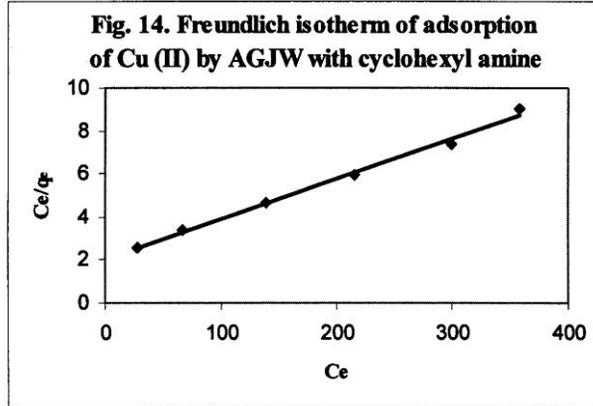


Adsorbent concentration 2g/l , and Temp.=30°C .



Adsorbent concentration 2g/l, and Temp. =30°C.





References

1. B. Volesky, Z.R. Holon, *Biotechnol. Bioeng. prog.* 11 (1995) 235.
2. M. Tsezos, B. Volesky, *Biotechnol. Bioeng.* 24 (1982) 385.
3. R. H.crist, J. R. Martin, J.Chanko, D. R.Crist, *Environ. Sci. technol.* 30(1996) 2456.
4. J. A. Tallmange (1965) First edition in *Chemical Technol. Vol. 2*, Academic press, Inc., New York.
5. G. C. Gupta, F. L. Harison, *pollut. Res.* 1 (1983) 1.
6. J. G. dean, F.L. Borqui and K. H. Labouette, *Environ. Sci. technol.* 6 (1972) 518.
7. R. F. Weiner *Plating*, 54 (1967) 1354.
8. G. L. Culp and R. L. Culp, *New concept in water purification*, van Norstrand reinhold co., New York, (1974).
9. H. Scilling, P. Schilling, K. Fashwasser, M.Milduer, (*VEB.Projektierung wasserwirtschaft Halla*), (1986).
10. Z. Zhon, Y. Xue, *Kuangye Geongcheng*, 7 (4) (1987) 24.
11. H. P. Larsen, J. K. P. Shon and L. W. Ross, *J. Water Pollut. Cont. Fed.* ,45(8) (1973) 1982.
12. E. Mann and A. Denne, *Korresp. Abwasser*, 33 (10) (1986) 942.
13. G. H. Botham and W. R. Bryson, *J. dairy Res.* 20(1953) 154.
14. S.H. Samaha, H.E. Nasr and A. Hebeish, *J. Polym. Research* 12: 343-353 (2005).
15. Hans Jahn and Peter Goetzky, *Introduction to epoxy resins*, John Wiley and sons, N.Y., (1978) 663-664.
16. A. Vogel, *A text book in quantitative inorganic analysis*, Longman (1961).
17. M. H. Abou-Shosha and N. A. Ibrahim, *Makromol. Chem. (Nr.3005)* (1990)1-13.
18. M. I. Khalil, A. Waly, S. Farag, and A. Hebeish, *Starch*, 43 Nr. 9(1991) 349-355.
19. A. S. Aly, Ph. D. thesis, Faculty of science, AI-Azhar University 1994.
20. S. Larous, A.H. Meniani, M.Bencheikh Lehocine, *Desalination* 185 (2005)483-490.
21. H. A. Elliot and C. P. Huang, *Water Res.* 15(1981) 549.
22. S. R. Shukla, Roshan S. Pai, *Bioresource Technol.* 96(2005)1430-1438.

23. K. Anoop Krishnan and T. S. Anirudhan, *Water SA*, 29(2) (2003) 270-278.
24. E. Pehlivan, S.Cetin and B.H.Yanik, *J. Hazardous Materials* Vol.135, 1-3(2006) 193-199.
25. Langmuir, *J. Chem. Soc.*, 40 (1918) 1361.
26. C.K.R Hall, LC. Eagleton, A. Acrivos, *Ind. Eng. Chem. Foundam*, 5 (1966) 212.