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

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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/I, 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 Cu^{2+} ions from aqueous solution at different pRs (2-8), CU2+ ion concentration (50-500 mg/l), AJF concentration (1-10 g/I), and time (15-180 min.). The extent of Cu^{2+} ion removal depends on AJF type and follows the order: NEBAJF > CHAJF > HAJF. Optimal removal conditions at room temperature (30°C) were pR 5, Cu^{2+} ion concentration 200 mg/l, adsorbent concentration 2g/1 and time of 180 min. The removal of Cu^{2+} 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 precipitation[1-3]. 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 pigments[4-6]. The most widely used method for removing of copper (II) is the precipitation as insoluble hydroxide at alkaline medium[7-10] or sometimes as sulfide[11-12].

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 11 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 speciallity 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-iute 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 adduct[14] 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/1), 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/1) 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.
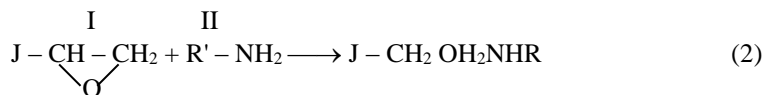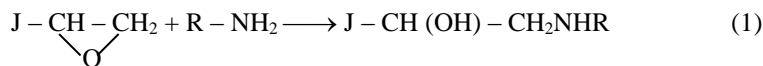
Analysis and test methods

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
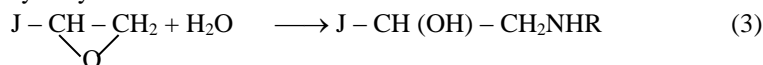
Preparation of aminated lute fibers (AJF)

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

a- amination

$$J - \underset{\underset{O}{\diagdown \diagup}}{CH - CH_2} + R - NH_2 \longrightarrow J - CH\,(OH) - CH_2NHR \qquad (1)$$

$$\qquad\qquad I \qquad\quad II$$

$$J - \underset{\underset{O}{\diagdown \diagup}}{CH - CH_2} + R' - NH_2 \longrightarrow J - CH_2\ OH_2NHR \qquad (2)$$

$$\qquad\qquad\qquad III$$

b- Hydrolysis

$$J - \underset{\underset{O}{\diagdown \diagup}}{CH - CH_2} + H_2O \longrightarrow J - CH\,(OH) - CH_2NHR \qquad (3)$$

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/I has a pronounced effect on increasing the extent of amination. Further increase in concentration beyond I mole/I up to 8 mole/I 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 ofGJF[17].

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 concentration[17-18].

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 time[19].

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 contentI7-18.

Utilization of AJF in Cu^{++} ion removal fro ag,ueous solutions

Three aminated fibers were prepared by reacting GJF with any of the three amines (5 mole/I) 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 reference[20].

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 Cu^{2+} 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 study 21. For example the percentage of removal of Cu^{2+} on AJF was 13% at pH 2 while it became 31.6% at pH 5 (original pH of Cu^{2+} 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 Cu^{2+} released completely under extreme acidic solution[21]. The trend appears the same irrespective to the type of the aminated substrate used[22-23].

Adsomtion concentration

Fig (7) shows the effect of adsorption concentration on the % removal of Cu^{2+}. The study was conducted at 200 mg/l initial Cu^{2+} concentration at pH 5 at 30°C for 3 hrs. It is obvious that increasing adsorption concentration is accompanied by

increasing of % Cu^{2+} removal, that is hold true for the 3 aminated substrates. This may be attributed to the increase in the adsorption sites at high adsorbent concentration[24]. The % removal of Cu^{2+} 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 l0 show the effect of time on the removal of Cu^{2+} by CHAJF, HAlF and NEBAlF respectively. Removal was conducted at thee initial Cu^{2+} 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 Cu^{2+} ion concentration used. Moreover, the higher the initial Cu^{2+} ion concentration the higher is the removal by a sustrate at a given time.

Langmuir Isotherm

Langmuir modefs assumes that the adsorption of Cu^{2+} occurs at homogeneous surface, by applying Langmuir isotherm on the adsorption of Cu^{2+} on AlF.

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

Where

Ce = equilibrium concentration mg/l

qe = amount of Cu^{2+} adsorbed per gram (mg/g) at equilibrium.

Q_{max} = adsorption capacity mg/g

b = constant l/mg.

KL = Qmax. b

The linear plot of C_e/ q_e versus Ce (Fig. 11-13) shows that the adsorption of Cu^{2+} onto AJF obeys Langmuir isotherm model.

[R2 = 98.12, 99.4 and 99.79] for N-ethyl butyl amine, Cyclohexy1 amine and N-Hexyl amine respectively. The values ofb, K_L, Qmax and R_2 are listed in table (1).

The important parameter in Langmuir isotherm is the dimension1ess 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 Cu^{2+} 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.

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

Where:

q_e = mg/g at equilibrium

C_e = mg/l at equilibrium

K_F = dimensionless parameter for favorability.

The linear plot of log q_e versus 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, KF 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: CHA > NEBA > HA. The optimal amination conditions were, amine concentration of 5 mole/I, 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: NEBAJF > CHAJF > HAJF. Optimal Cu^{2+} ion removal by any of AJFs are pH 5, Cu^{2+} ion concentration 200 mg/l , adsorbent concentration 2g/1 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

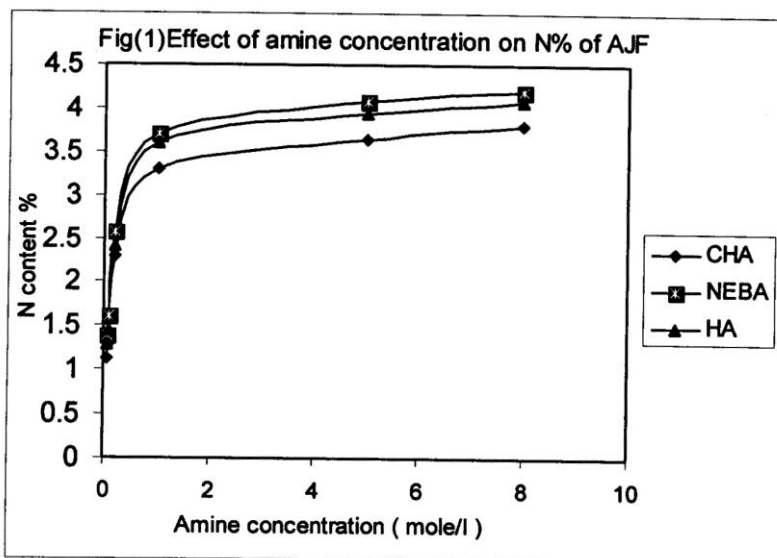Table (3): R_L values for the adsorption of Cu^{2+} by AJFs

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
HAJF	97.70	0.2389	5.6990
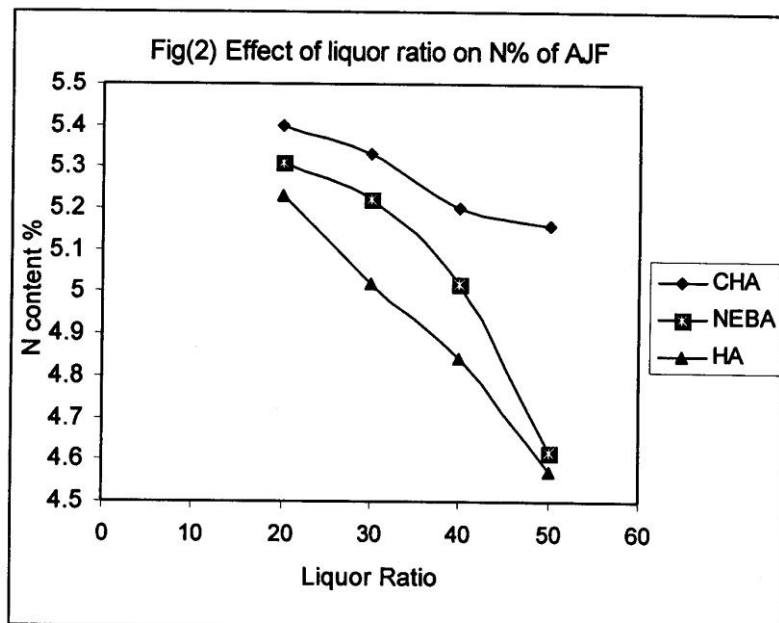
Fig(1)Effect of amine concentration on N% of AJF

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

Fig(2) Effect of liquor ratio on N% of AJF

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

Fig(3) effect of Amination time on N % of AJF

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

Fig(4) Effect of amination temperature on N% of AJF
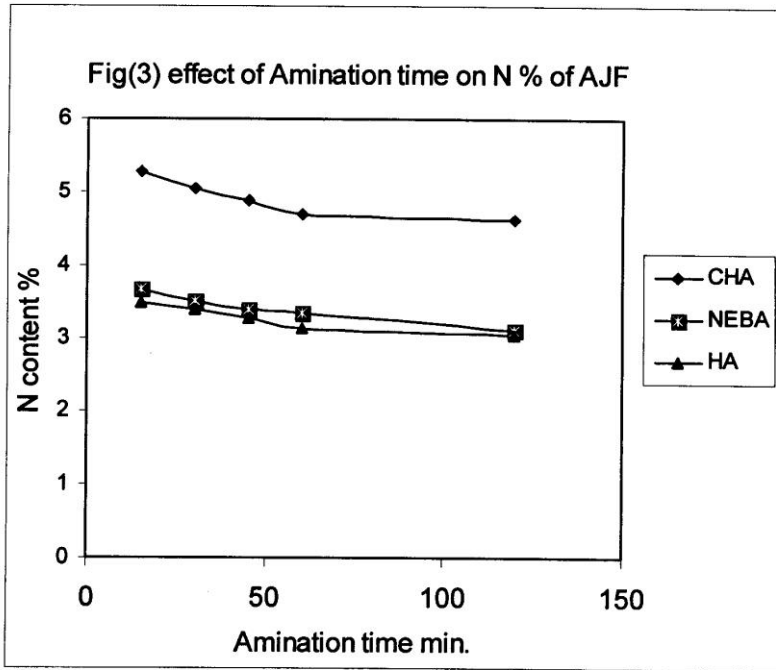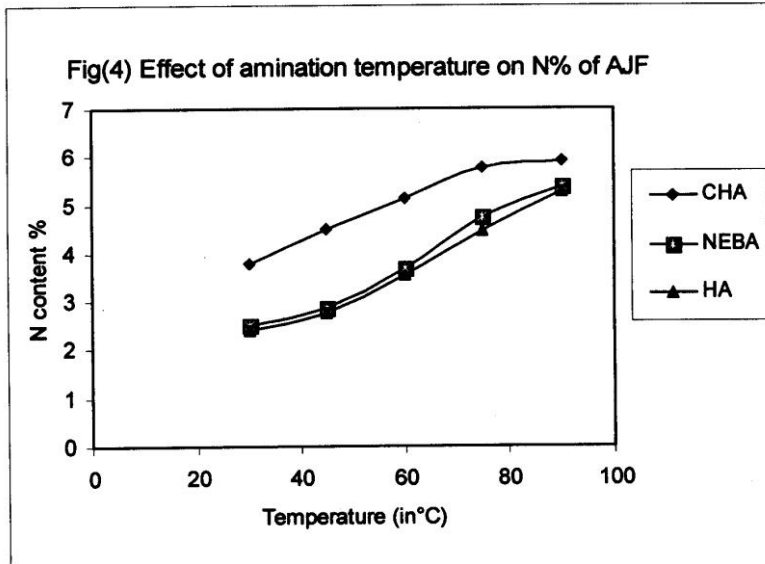
L.R= 1:20, Time 15 min. and amine Concentration = 8 mol/l

Fig(5) Effect of pH on Cu(II) removal by AJF
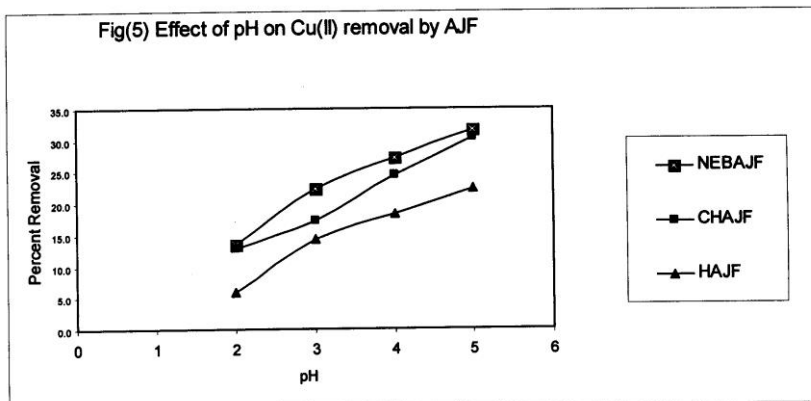
Adsorbent 2g/l , Temp.=30°C , Time= 2 Hrs. and [Cu(II)] =200mg/l

Fig(6) Effect of Cu(II) ion concentration removal by AJF
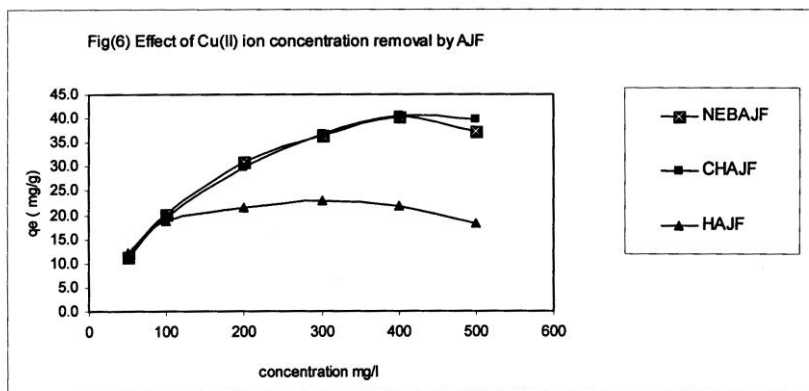
Adsorbent 2g/l , Temp.=30°C , Time= 3 Hrs. and pH=5

Fig(7) Effect of Adsorbent concentration on Cu(II) removal by AJF
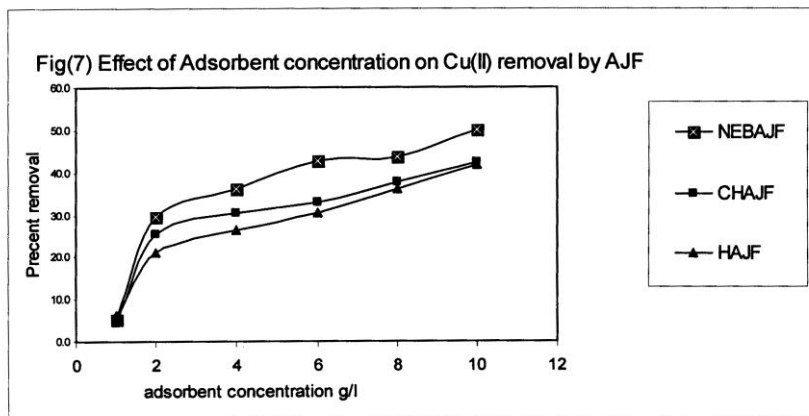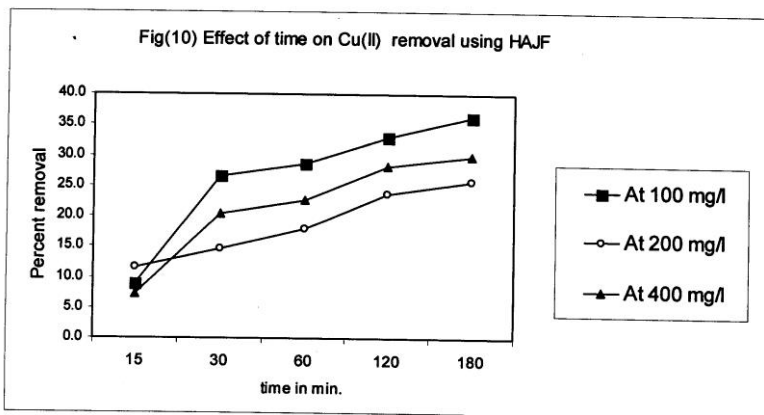

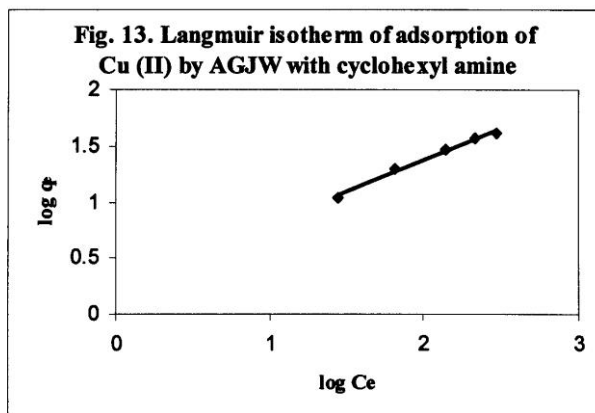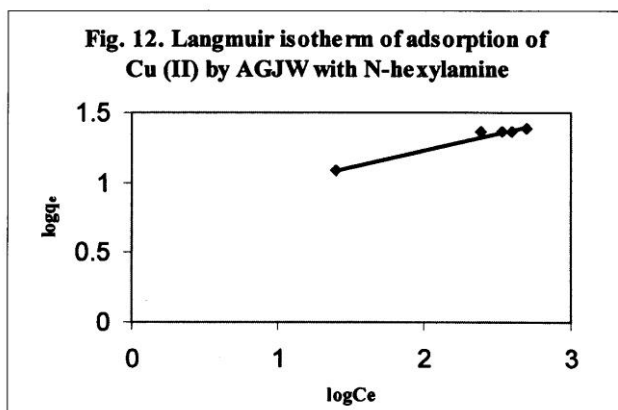Temp.=30°C , Time= 3 Hrs. pH=5 and [Cu(II)] =200mg/l and
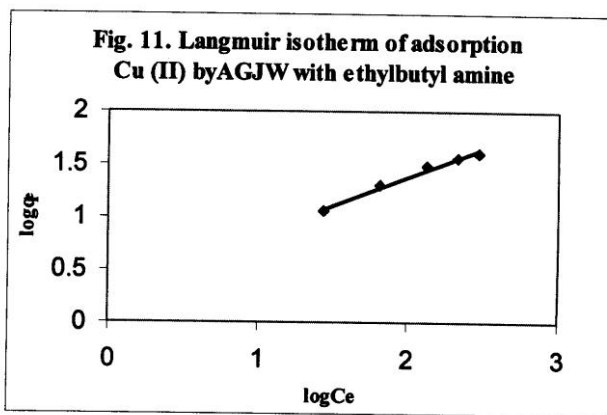
Fig.(8) Effect of time on Cu(II) removal using NEBAJF

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

Fig(9) Effect of time on Cu(II) removal using CHAJF

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

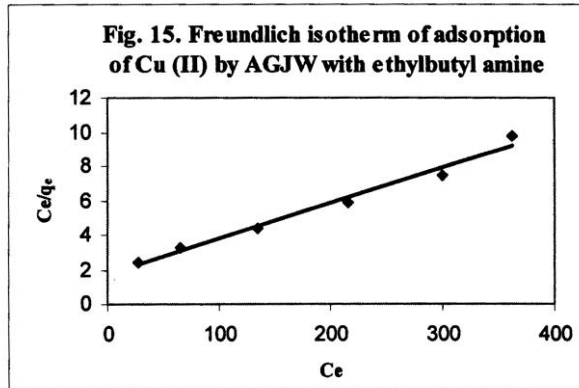Fig(10) Effect of time on Cu(II) removal using HAJF

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

Fig. 11. Langmuir isotherm of adsorption Cu (II) byAGJW with ethylbutyl amine

Fig. 12. Langmuir isotherm of adsorption of Cu (II) by AGJW with N-hexylamine

Fig. 13. Langmuir isotherm of adsorption of Cu (II) by AGJW with cyclohexyl amine

Fig. 14. Freundlich isotherm of adsorption of Cu (II) by AGJW with cyclohexyl amine

Fig. 15. Freundlich isotherm of adsorption of Cu (II) by AGJW with ethylbutyl amine

Fig. 16. Freundlich isotherm of adsorption of Cu (II) by AGJW with N-hexylamine

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