Influence of Competing Agent on Heavy Metal Ions Removal Capacities of Amberlite IRC 748 - a Chelating Resin

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In this study, the removal of Cu(II) from synthetic wastewater was studied using a fluidized bed containing Amberlite IRC 748 – a chelating resin. Kinetic studies were performed as batch tests. The most chelator resins used industrially are in batch systems, where large volume of wastewater are stirred with the chelator resin beds before the beads are filtered off and regenerated, or under very slow conditions. There are some factors which have to be considered when a chelator resin is used industrially in wastewaters treatment. One of the most important factors is the presence of some metal chelating agents such as ethylenediamine derivatives capable to stabilize the metal ions in solution. These agents may compete with the binding sites of metal removal materials, thereby decreasing the effectiveness of these agents. For this reason in this paper are presented the effects of the competing chelating agent ethylenediaminetetraacetic acid (EDTA) on the copper ion removal capacities of IRC-748 in batch tests. In the conditions used the chelating resin adsoption capacity was changed in presence of EDTA.

Keywords: copper removal from wastewater, batch test, chelating resin, competing agent

Water, an important natural resource is sometimes contaminated with heavy metals which derived from acid mine drainage and from many industries, including those involving metal plating, mining, pickling and tanning. Water pollution due to the toxic metals has been a major cause of concern for environmental engineers. The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. Several episodes due to the heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity [1-5]. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain.

The main techniques, which can be used to reduce the heavy metal from wastewater include lime precipitation, adsorption into activated carbon, membrane processing, electrolytic methods, reverse osmosis. These methods have been found to be limited, since they often involve high operational costs and may be associated with the generation of secondary waste which present treatment problems, as the large quantity of sludge generated by precipitation processes. Ion exchange is a more attractive method for heavy metal removal from domestic and wastewater because the metals values can be recovered along with their removal from the effluents [6-12].

Chelating resins contain ionic grups which can form coordinative bonds with metals. In this case the donor atoms can be sulf atoms, nitrogen atoms, oxygen atoms or combination of these kinds of atoms. These types of bonds which can be formed in sorption process have both ionic and covalent characteristics.

The retain capacities of chelating resins are well known. Their most important characteristic is selectivity for heavy metals, and the weak acide nature of chelating bonds make regeneration to be more easy with mineral acid. The using of these materials to treat wastewaters is based on their property to retain heavy metals at low *p*H.

For these important properties of chelating resins, and because of the posibility of using them in heavy metals removal form wastewaters in this paper is presented the copper removal from synthetic wastewaters by Amberlite IRC 748 – a chelating resin in presence and in absence of one competing chelator ethylenediaminetetraacetic acid.

Experimental part

The chelating resin - Amberlite IRC – 748 (from Supelco USA Co.) was used in this study. Amberlite IRC 748 is generally used for the removal and recovery of heavy metals in plating rinses and for the purification of galvanizing solutions. They are also used for hardness removal from NaCl brine in membrane chlor-alkali plants with excellent selectivity for Strontium.

Stock solutions of 600 mg/L copper were prepared by dissolving the corresponding salt ($CuCl_2$) (Merck a.r. grade) in distilled water. EDTA 0.01M solutions were made from $Na_2H_2EDTA{\cdot}2H_2O$ (Merck a.r. grade) in distilled water.

In these experiments the resin was used in H - form. To bring Amberlite in H-form 5% HCl solution was used. After this solution was passed over resin bed, it was washed with distilled water until the regeneration agent was removed from the resin bed.

The batch tests were made by using a Heidolph RZR 2041 stirrer. For the determination of resin performance in kinetic terms, the adsorbtion of Cu(II) on this resin was monitored as a function of time. The quantity of resin used has varied between 0.1-2.5 g, and the speed rotation was 150 rpm (rotation per min). The solution volume used was 100 mL.

Metalic ion concentration in initial solution, and in solution after the retaining on the resin were determined by atomic absorbtion spectrometry by using a type AAS 1N Carl Zeiss Jena atomic absorbtion spectrophotometer. The next parameters: wavelenght λ = 324.75 nm, gap = 4, photomultiplication = 1, lamp current = 6 mA, work range 1 -100 A (absorbance units), time constancy = 0.5 s were

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used in copper concentration in solution determination.

Results and discussion

To establish the influence of one competing chelating agent such as ethylenediame derivatives capable to stabilize the metal ions in solution experiments were done by using a solution formed by Cu(II) and Na_2H_2-EDTA in different molar ratio.

This competing chelating agent was choosen because it has a structure (fig. 1a) which contains the same donor atoms as Amberlite IRC-748 (fig. 1b), consequently they can bond copper atoms in the same fashion as in case of Amberlite IRC-748.

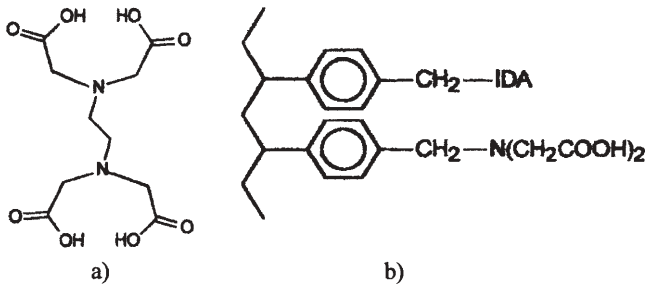

Fig. 1. a) EDTA structure; b) Amberlite IRC-748 structure

From this picture it can be seen that both EDTA and Amberlite IRC-748 contain atom donors like: the amine nitrogen and the oxygen atoms of two carboxylic acid ligands.

The interaction of copper with EDTA and Amberlite IRC-748 are presented in the next two reactions:

$$2Cu^{2+} + (HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2 \longrightarrow$$

$$\longrightarrow Cu(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2Cu + 4H^+$$

$$2Cu^{2+} + (HOOCCH_2)_2NCH_2PCH_2PCH_2N(CH_2COOH)_2 \longrightarrow$$

$$\longrightarrow Cu(OOCCH_2)_2NCH_2PCH_2PCH_2N(CH_2COO)_2Cu + 4H^+$$

in the last reaction P = $-C_6H_4-CHCH_2CH_3$

The copper ions are bonded in a bidentate fashion through the two oxygen atoms of two carboxylic acid ligands of the EDTA and iminodiacetic acid groups of Amberlite IRC-748.

Kinetic studies of Amberlite IRC-748 were performed as batch tests, with the samples removed from the shaker between 1 min and 540 min.

The Amberlite IRC-748 sample (0.2000±0.0001 g) was weighed into a glass vial with a screw top. A total of 100 mL of the cooper 600 mg/L was added to each vial via a volumetric pipet, and the vials were capped. The initial *p*H was 4.3, and the temperature was 22 °C. Each sample was then filtered, and tested for metal ion concentration. The same experiments were conducted in presence of a 1±0.0001 g Amberlite IRC-748 quantity.

The quantity of heavy metal uptake by resins was calculated at different times, and experimental data are presented in figure 2.

Metal uptake for the different ion exchangers can be calculated as the difference between the heavy metal concentration from initial solution and heavy metal concentration after reaching the equilibrium using the following equation :

$$Q = \frac{(C_i - C_f)V}{m} \quad (1)$$

where: Q = is the metal uptake at equilibrium, mg/g;

C_i = is the initial metal ion concentration, mg/L;

C_f = is the metal ion concentration remained in solution at different times, mg/L;

V = solution volume, L;

m = resin mass (g).

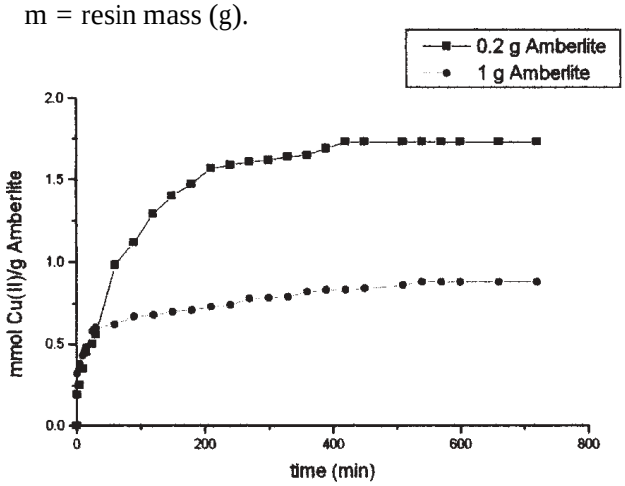

Fig. 2. Adsorption isotherm of Cu(II) onto Amberlite RC-748 at *p*H 4.3 and 22°C as function of time for 0.2 g Amberlite and 1 g Amberlite bed resin used

From this figure it can be seen that equilibrium adsorption of copper onto Amberlite IRC-748 is reached in approximately 7 hours. This value indicates that it has a longer ion diffusion path, and so the metal ions must penetrate more deeply into the imidoacetic surface of Amberlite IRC-748 in order to reach its chelating ligands.

The maximum quantity of Cu(II) uptake was 2.20 mmol Cu(II)/g Amberlite IRC-748 for 0.2 g Amberlite bed resin used, and 0.88 mmol Cu(II)/g Amberlite IRC-748 for 1 g Amberlite bed resin used.

The most simple adsorbtion isotherm is based on the assumption that every adsorbtion center is equivalent and the capacity of the particles to bond some components is independent of how many adiacent centers are occupied or not with sorbat. Dates obtained from copper retaining on Amberlite IRC-748 are correlative with Langmuir and Freundlich models in function of the next equations:

$$Q = K_F \cdot C_e^{1/n} \quad (2)$$

or

$$Q = \frac{K_L \cdot C_e}{1 + a \cdot C_e} \quad (3)$$

where: K_f and 1/n are adsorbtion isotherm parameters (capacity and intensity);

K_L and a are Langmuir model parameters.

These models are made in linear form by logaritmation.

$$\log Q = \log K_f + n \log C_e \quad (4)$$

$$C_e/Q = 1/K_L + (a/K_L)C_e \quad (5)$$

For the determination of adsorbtion isotherms synthetic solutions with 600 mg/L, 160 mg/L, 80 mg/L and 40 mg/L copper concentrations were used. The solution volume used was 100 mL, the Amberlite quantity used was 0.2 g, the contact time was 600 min, and the temperature was 22°C. Results obtained are presented in table, figure 2 and 3.

From the figures 3 and 4 it can be seen that in case of Cu(II) adsorption on Amberlite IRC-748, the correlation parameter between experimental and the date obtained by Freundlich linearized isotherm is R^2 = 0.9888, and for

Table 1
LANGMUIR AND FREUNDLICH PARAMETERS FOR COPPER REMOVAL

Copper conc. mg/L	C_e (mmol/L)	Q (mmol/g)	C_e/Q (g/L)	logC_e	logQ	Parametrii Freundlich	Parametrii Langmuir
600	5.1559	2.1464	2.402	2.515	0.3317	K_F = 0.0971	K_L= 1.6237
160	1.1132	0.7031	1.583	1.849	-0.1529	1/n = 1.6076	a = 1.4033
80	0.3686	0.4455	0.827	1.369	-0.3511	R^2 = 0.9888	R^2 = 0.9040
40	0.1635	0.2334	0.701	1.016	-0.6319		

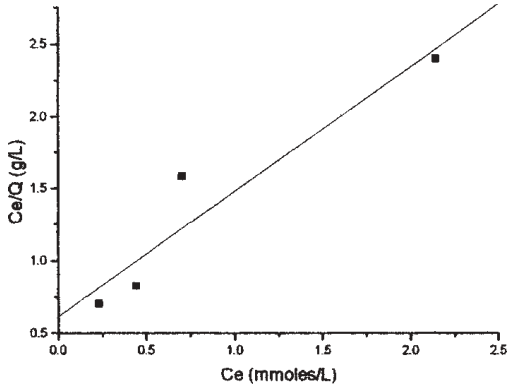

Fig. 3. Lagmuir linearized isotherm for Cu(II) adsorption on Amberlite IRC 748

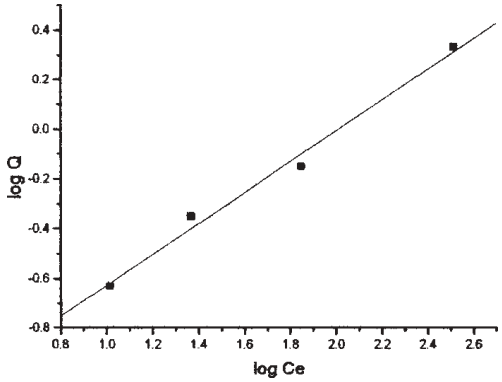

Fig. 4. Freundlich linearized isotherm for Cu(II) adsorption on Amberlite IRC 748

Langmuir isotherm is R^2 = 0.9040. This fact leads to the conclusion that Cu(II) adsorption on Amberlite IRC-748 in H form may be the best described by Freundlich isotherm:

$$Q = 0.0971 \cdot C_e^{1.6076} \quad (6)$$

Results obtained in case of contact between a solution formed by 80 mL Cu(II) 0.01M and 20 mL EDTA 0.01 M with 0.2 g Amberlite IRC-748 are presented in figure 5. In this case the solution *p*H was 2.4, and temperature 22°C.

Figure 5 shows that in case of using 20 mL EDTA 0.01M the equilibrium is reached after 360 min for 0.2 g Amberlite bed used, and the maximum quantity of Cu(II) uptake for Amberlite IRC-748 is 1.79 mmol/g Amberlite IRC-748 for a bed of resin of 0.2 g, and 0.73 for a quantity of resin by 1 g. It can be seen that in the case of solution formed for Cu(II) and EDTA, the maximum quantity of Cu(II) uptake for the Amberlite IRC-748 decreases.

The same experiments were performed using a solution formed by 50 mL Cu(II) 0.01M and 50 mL EDTA 0.01M. The quantity of resin was the same (0.2000±0.0001 g), (1±0.0001 g), and the temperature was 22°C.

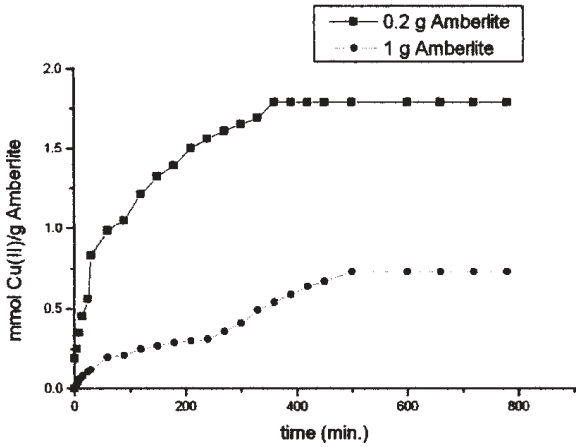

Fig. 5. Adsorption isotherm of Cu(II) of EDTA onto Amberlite RC-748 at *p*H 2.4 and 22°C as function of time for 0.2 g Amberlite and 1g Amberlite bed resin used

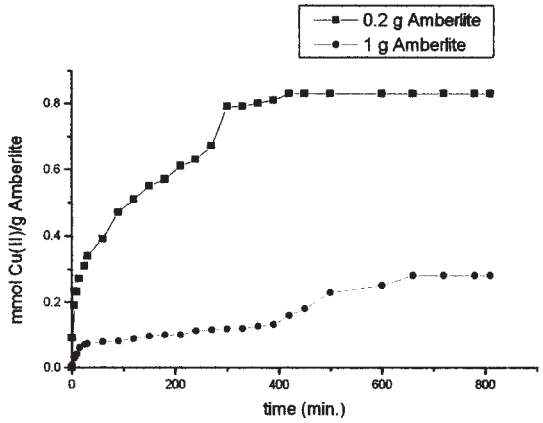

Fig. 6. Adsorption isotherm of Cu(II) in presence of EDTA (Cu(II): EDTA=1:1) onto Amberlite RC-748 at *p*H 2.4 and 22°C as function of time for 0.2 g Amberlite and 1g Amberlite bed resin used

Results obtained from these experiments are presented in figure 6.

In this case the equilibrium was reached after 420 min for 0.2 g Amberlite used, and after 540 min for experiments coonducted in presence of 1 g Amberlite. The maximum quantity retained by Amberlite IRC-748 in presence of a high quantity of EDTA was low (0.83 mmol Cu(II)/g Amberlite IRC-748 for 0.2 g Amberlite, and 0.28 mmol Cu(II)/g Amberlite for 1 g Amberlite).

Conclusion

On the basis of the strong affinity of Cu(II) ions for the hexadentate EDTA ligand [13, 14] it was obtained that the chelating capacity of Amberlite IRC-748 under static conditions, and in presence of high levels of EDTA decreased probably because of the fact that the bonds formed between copper ions and donor atoms of EDTA are much stronger and they cannot be broken for participate to other interactions with donor atoms of Amberlite IRC-748.

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