STUDY ON THE BEHAVIOR OF BIFUNCTIONAL ION EXCHANGER WITH HYDROXAMIC ACID AND AMIDOXIME GROUPS TO Cu(II) IONS SORPTION

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ABSTRACT

This article analyzes a bifunctional chelating sorbent that is characterized by two functional groups: one of hydroxamic acid and one of amidoxime. A study on copper ions sorption on these bifunctional changers was conducted with static laboratory methods such as PH influence; the retaining process, the distribution factor; the influence of the environment acidity, the concentration of the external solution and the time contact over the retaining of the metallic ions were analyzed; the kinetic properties were also observed, that is, the relative speed of the sorption process, the variation of the apparent Gibbs free energy. The analysis includes the presentation of the method used as well as the results of the procedures conducted in order to retain the metallic ions Cu(II) in comparison with the bifunctional acrylic resin. The procedures were conducted using optical microscopy scanning electron microscopy (SEM)) and X-ray photoelectron spectroscopy (XPS). The chemical analysis was conducted using the EDS procedure. The XPS and EDS analyses clearly showed the existence of copper in the ions changer Cu(II). This aspect definitely demonstrates the special properties of the bifunctional acrylic resin.

Keywords: chelating sorbent, bifunctional acrilic resin, Cu(II) ion exchanger, preconcentration, separation, hydroxamic acid, amidoxime, IR, OM, SEM, XPS .

1. INTRODUCTION

Both the growth of high-tech and the demographic explosion, two characteristics of the modern civilization, have generated a serious ecological lack of balance, genetic mutations, waste of certain raw material sources, etc. Under these circumstances, the general attention is focused on undertaking special measures such as creating new sorbtive materials or improving the performances of those already existing in order to eliminate or pre-concentrate certain metals from different environments.

The separation or pre-concentration methods represent the basics of some important techniques for the recuperation of some micro-components or elimination of some noxious components.

The chelating sorbents can be defined as matrix polymers that incorporate functional groups in order to create the formation of complex. The large range of the functional groups which can be incorporated in these polymers determines the various characteristic and analytic applications or the chelating sorbets.

The main advantage of these efficient methods of concentration and separation is that they enable the selective recuperation of some microelements with complex chemical compositions from natural or industrial samples.

Sometimes the Cu(II) ions can be found in natural or industrial noxious samples and have to be eliminated or pre-concentrated.

A new type of chelating sorbent has been created /1,2,3/. This sorbent is special because it includes in its composition two functional groups – the hydroxamic acid and the amidoxine. These transformers of bifunctional acrylic ions are characterized by complete capacities of low basic change. It was found that some fiber chelating sorbents which contain two functional groups – one acid and one base - have improved properties over similar monofunctional sorbents /4,5/.

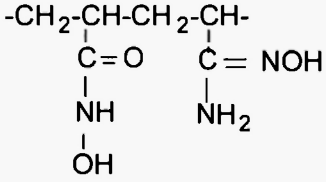
In this paper, the study on copper ions sorption on these bifunctional exchangers was conducted with static laboratory methods such as PH influence, the retaining process, the distribution factor; the influence of the environment acidity, the concentration of the external solution and the time contact over the retaining of the metallic ions were analyzed; the kinetic properties were also observed, that is, the relative speed of the sorption process, the variation of the apparent Gibbs free energy, etc.. This paper also presents the methodology and the results of the investigation procedure of retaining the metallic ions on the bifunctional acrylic resin using optical microscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS); chemical analysis used the EDS procedure. The XPS analysis and the EDS analysis revealed the existence of copper in the ion changer Cu(II). This unequivocally demonstrates the special properties of the bifunctional acrylic resin analyzed and the fact that the bifunctional acrylic resin has improved properties compared to the similar monofunctional sorbets.

2. EXPERIMENTAL

2.1 Study of Cu(II) Ions Sorption on Bifunctional Acrylic Resin of Type A

The chelating ion exchanger of type A has the following characteristic features:

- Functional groups of hydroxamic acid and amidoxime



- Cross – linking degree of 10% divinylbenzene at a dilution D = 0.25 (D = mL diluent / mL diluent + mL comonomers)
- Weak basic exchange capacity : 4.06 mequiv / g
- Diameter of beads : 0.3 – 0.8 mm
- Morphological structure : macroporous resin

The sorption of Cu(II) ions of this type of chelating ion exchanger was performed by batch method, as shown in the following

2.1.1. Reagents, methodology

In order to carry out the batch experiments, the following reagents have been used:

- Acrylic ion exchange resin with hydroxamic and amidoxime groups of type A;

- Cu(II) stock solution of 1 mg / mL : 0.9208g of $CuSO_4 \cdot 5H_2O$ were dissolved and diluted to 200 mL; the working solutions were prepared by the appropriate dilutions of the stock solution;
- Buffer solutions of CH_3COOH – CH_3COONa and NH_4Cl – NH_4OH.

The Cu (II) sorption on bifunctional ion exchange resin was studied by the batch method. Samples of about 0.05 g resin were equilibrated with 25 mL of aqueous solution containing Cu(II) known amounts. After 24 hours, with intermittent stirring, the phases were separated by filtration. The Cu(II) amount in filtrate was determined spectrophotometrically with rubeanic acid at λ = 390 nm(linear range = 1 – 5 µg / mL).

The absorbance measurements were performed on a UV–VIS spectrophotometer (V-530, Jasco Company).

In order to measure pH, a pH–meter of 230A model from the Orion Company was used.

Taking into account the fact that the major analytical features expressing the efficiency of chelating sorbents on a concentration / separation process depend upon the sorption conditions, the effects of the medium acidity, concentration of outside solution and contact time in the Cu(II) bifunctional acrylic ion exchanger of type A sorption systems were studied.

2.1.2. Initial pH influence

The Cu(II)retention percentage (R %) on new chelating exchanger of type A as a function of initial solution pH is plotted in Figure 1.

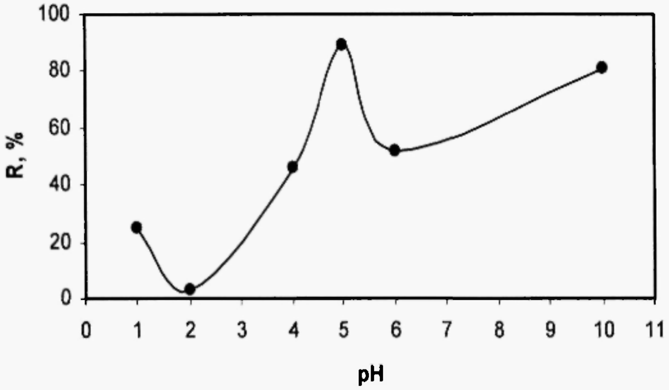
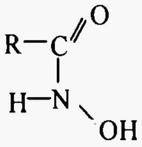


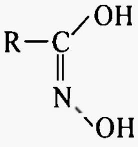
Fig. 1: Influence of initial pH on exchanger of type A – Cu(II) batch sorption system. C_0=80mg/L, 0.05g of resin, equilibration time of 24 hours.

As can be seen, the percentage of Cu(II) retention on acrylic exchanger with hydroxamic and amidoxime groups reached maxima values (80 – 90 %) on unbuffered solutions(pH =5) and ammoniacal solutions of pH =10. In this context, the subsequent investigations were carried out on solutions containing Cu(II)at pH =5.

The explanation of pH effect is based on the two tautomeric forms in which the hydroxamic acid exists in solution.



Keto form



Enol form

The keto form predominates in an acid medium and the enol form in an alkaline medium. They are known to form complexes with a large number of metal ions. On the other hand, the amidoximes exist predominantly in the syn – hydroxyamino form that is stabilized by an intramolecular hydrogen bond, and these compounds behave as bases in water. The amidoximes may coordinate as a non-ionic group, but they generally undergo metal–assisted hydroxyl proton dissociation upon coordination.

All these observations permitted us to affirm that on Cu(II)retention at pH = 5 the metallic ion predominates, complexing with the functional groups of the tested sorbent.

2.1.3. Influence of Cu(II) concentration in initial solution

The influence of initial solution concentration on batch retention process of Cu(II) by the acrylic bifunctional sorbent is illustrated in Figure 2

As can be seen, the amount of Cu(II) retained from a solution of pH = 5 increases with an increase in metallic ion initial concentration.

On the other hand, increasing the amount of Cu(II) results in the decreasing of the retention percentage value (▲). This behaviour suggests that the chelating ion exchanger with hydroxamic and amidoxime groups can be efficiently used for quantitative recovery of Cu(II) from diluted solutions.

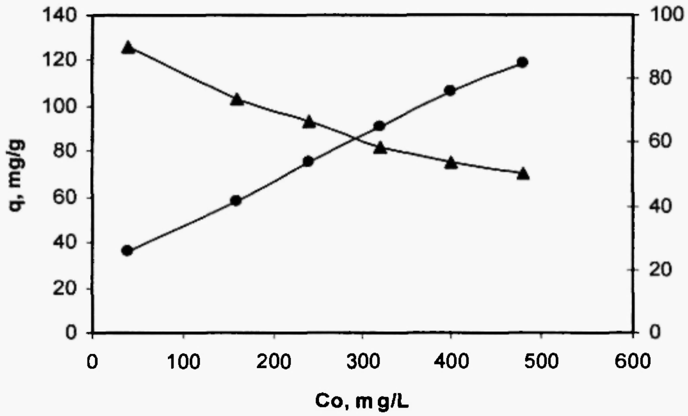


Fig. 2: Effect of initial concentration on Cu(II) retention process by bifunctional resin.

(●) q, mg /g; (▲) R, %, pH =5, temperature =25^{0}C, time = 24 hours.

2.1.4. Influence of contact time

The experiments performed on solutions containing 80 μg Cu(II)/ mL at pH = 5 indicated that for the equilibrium achievement a phases contact time of 4 hours is necessary (Figure 3.).

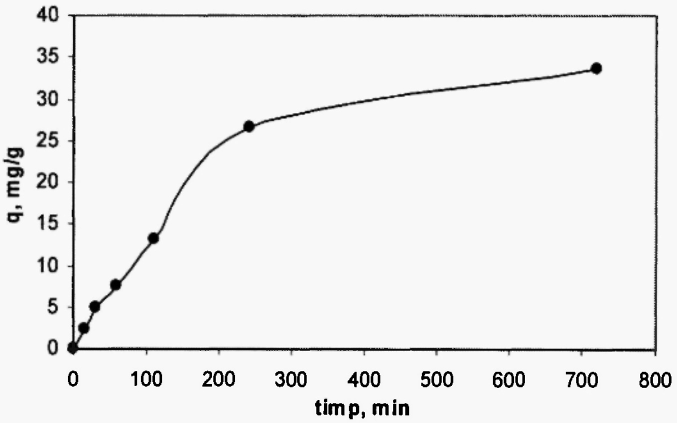


Fig. 3: Influence of phase contact time (0.05 g of sorbent)

It can be seen that the sorption process is relatively slow. After a range of 2- 4 hours, the amount of retained Cu(II) ions exceeded slightly 50%.

In order to calculate the rate constant of Cu(II) retention process value, the experimental data were processed according to the Lagergren equation:

$$\lg (q_0 - q) = \lg q_0 - K' \cdot t / 2.303$$

where q and q_0 represent the amounts of Cu(II) retained at time t(minutes)and equilibrium, respectively and K' is the constant of rate.

Table 1 records the results obtained by the application of the Lagergren equation.

Table 1

Data processing according to Lagergren equation

t, min	$\lg(q_0-q)$	The regression equation	R^2
15	1.521	$y = - 0.0017x + 1.5301$	
30	1.488	$q_0 = 35.72$	0.9974
60	1.451	$K' = 3.44 \times 10^{-3}$ min^{-1}	
120	1.293		
240	1.100		
720	0.324		

Usually, the kinetic properties of sorbents are expressed by the relative rate of sorption process. This parameter is characterized by means of the half – exchange time ($t_{0.5}$) notion, being the time in which an exchange degree F equal to 0.5 is reached. The ratio between the ion amount retained at time t (mg/g) and the amount of ion (mg) taken up per gram of sorbent at equilibrium is named degree of equilibrium achievement F.

The experimental data processing and the F – t (min) plot lead to the value of 120 minutes for half exchange time ($t_{0.5}$)

These kinetic data lead to the conclusion that the Cu(II) retention on the chelating ion exchanger of type A is a mass–transfer process, the rate controlling reaction step being the metallic ion diffusion inside the exchanger beads. This fact reconfirms the possibility of resin application to Cu(II)separation and preconcentration.

2.1.5. The characterization of the sorption process

The dependence between the equilibrium concentrations of ions on the sorbent phase and the solution phase, respectively, q = f(C) is plotted by the sorption isotherms. The sorption isotherm of Cu(II) on the bifunctional resin, at 25°C and for initial concentrations ranged between 40 and 560 μg / m L is presented in Figure 4. The isotherm is nonlinear of Langmuir type, specific to a monolayer adsorption on a surface containing a finite number of active and equivalent energetically sites. The equation describing the process is of the following form:

$$q = K_L \cdot q_0 \cdot C_e / (1 + K_L \cdot C_e)$$

where q is the amount of Cu(II) sorbed on acrylic bifunctional resin (mmole/g); K_L is an affinity parameter expressing the strength of sorbed ion – sorbent bond (L/mole); C_e represents the solution concentration at equilibrium (mmole / mL) and q_0 is the maximum capacity of sorption (at saturation), mmole/g.

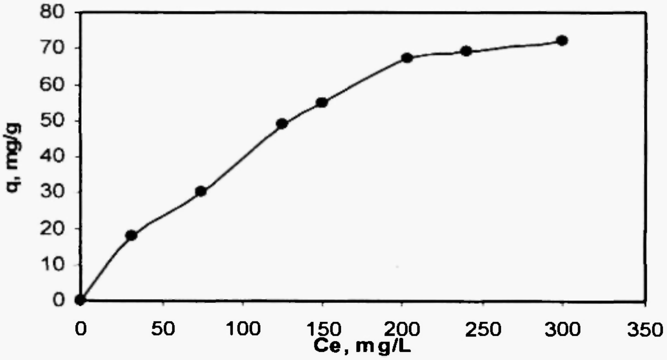


Fig. 4: Sorption isotherm of Cu(II) on the bifunctional resin of type A (temperature =25^{0}C; 0.05 g of resin; pH =5).

The Langmuir equation may be arranged in the linear form:

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot q_0 \cdot C_e}$$

Hence, a plot of $1/q$ versus $1/C_e$ is linear with the intercept equal to $1/q_0$ and the slope equal to $1 / K_L \cdot q_0$. The plot of $1/q$ versus $1/C_e$ for Cu (II) sorption on the resin under study is shown in Figure 5.

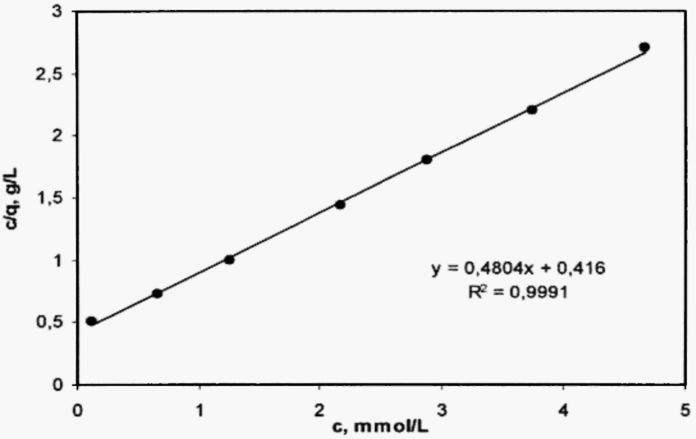


Fig. 5: Linear Langmuir plot of Cu(II) cation retention on chelating ion exchanger under study.

The q_0 and $K_L$values derived from this linear Lamgmuir plot are given in Table 2

Table 2
Values of Langmuir constants

q_0(mmole/g)	K_L(L/mole)	Equation of linear regression	R^2
2.081	1156.06	$y = 0.4804x + 0.416$	0.9991

Also, the experimental data were statistically processed by linear regression. The equation of $y = ax + b$ type and the obtained value of the correlation coefficient, R^2 are given in Table 2, too The results in Table 2 allow the conclusion that the experimental data of Cu(II) sorption on ion exchange resin with hydroxamic acid and amidoxime groups fit well the Langmuir model with two parameters (q_0 and K_L), R^2 being 0.9991.

As can be seen, the maximum capacity of sorption and Langmuir constant of sorption exhibit high values, reflecting strong interactions between the Cu(II)ions and the resin functional groups.

On the basis of the Langmuir sorption constant, the variation of Gibbs free energy (ΔG) for the retention of Cu(II) ions on acrylic resin with hydroxamic acid and amidoxime groups was determined with the aid of the following equation:

$$\Delta G = - RT \ln K_L$$

where R is the gas constant (8.31 J / mole) and T represents the absolute temperature.

The negative value of this parameter (ΔG = - 17.463 KJ / mole) points out the existence of a spontaneous process of sorption, based on the complexes formation.

The experimental results concerning the dependence between the equilibrium concentrations of ions in the resin phase and in the aqueous solution phase, respectively, have also been processed by means of the Freundlich model. This type of isotherm describes the sorption process from diluted solutions by the equation $\lg q = \lg K_F + (1/n) \lg C$, where K_F and n are the Freundlich constants relating to all factors affecting the retention process: the sorption capacity (K_F) and energy of sorption (n), respectively. The sorption is favourable for $1 < n < 10$.

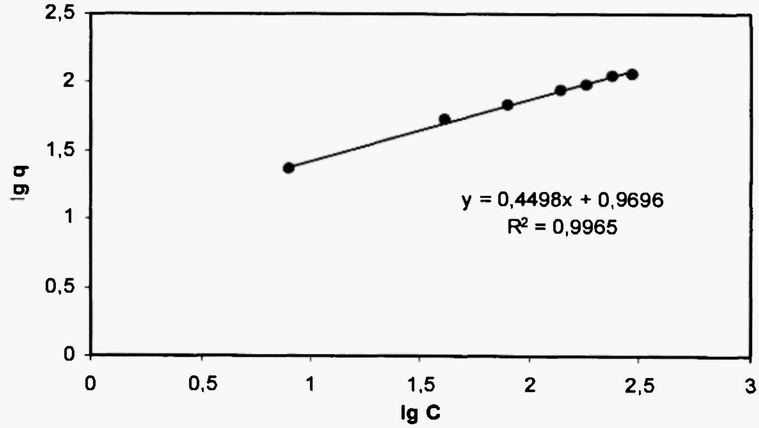


Fig. 6: Freundlich plot of Cu(II) sorption on the bifunctional acrylic resin of type A.

The plot of Freundlich equation for the tested sorption system is shown in Figure 6

Table 3 records the K_F and n values derived from the Freundlich plot given in Figure 6.

Table 3

Freundlich constants for Cu(II) sorption on the tested chelating ion exchanger

Equation of linear regression	N	K_F	R^2
y = 0.4498x +0.9696	2.2232	9.3299	0.9965

Referring to Figure 6 and Table 3 it may be noticed again that by introducing hydroxamic acid and amidoxime groups into the synthesized copolymers, favourable conditions for selective retention of Cu(II) ions were created.

The results in Table 2 and 3 allow the conclusion that obtained data fit better to the Langmuir model (higher value for R^2).

In order to characterize the sorption process selectivity, the Hall method /8/ has been applied. In this context, the value of the separation factor (K_R) has been calculated by means of equation $K_R= (1 + K_L \cdot C_0)$, where K_R is the separation factor; K_L is the Langmuir sorption constant (L/ mole) and C_0 represents the initial cation concentration (mole / L).

Values of the separation factor express the essential features of Langmuir isotherms, the sorption being favourable for $O<K_R<1$.

For the retention process of Cu(II) on the acrylic bifunctional resin, the separation factor K_R is equal to 0.58. Under these conditions, it is obvious that the new chelating ion exchanger with hydroxamic acid and amidoxime groups of type A is a good sorbent for Cu(II)ions.

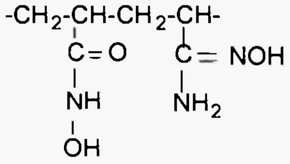
2.2. Study regarding the Cu(II) retention on the acrylic bifunctional resin of type B

In order achieve an efficient and rapid removal of the toxic metallic ions from different complex matrices, the synthesis of many chelating resins types has been tried.

The products obtained by the aminolysis reaction of ethylacrylate / acrylonitrile / divinylbenzene copolymers with sodium ethoxylate are new chelating ion exchangers with hydroxamic acid and amidoxime groups and different morphologies. The sorbent of type B is a macroporous resin with a cross–linking degree of 15%, giving to the structure a higher rigidity. The reaction was performed in the presence of benzene as diluent at a dilution D = 0.25(D =mL diluent / mL diluent + mL comonomers). The main features of the chelating ion exchanger of type B are presented in Table 4 /6/.

Table 4

Characterization of the tested sorbent

Functional groups	Capacity of exchange		Diameter of beads (mm)
	mEq/mL	mEq/g	
	0,78	1,75	0,3-0,8

2.2.1. Reagents, methodology

- Stock copper aqueous solution of 847.2 mg /L concentration was prepared from $CuSO_4 \cdot 5H_2O$. The used concentrations of the metal cation were in the range of 10 – 180 µg /mL;
- The pH of the solutions were adjusted with buffer solutions of mixtures of CH_3COOH –CH_3COONa 2M concentration and 0.2M mixture of NH_4Cl + NH_4OH;
- The absorbance measurements were performed with a V530 Jasco Company spectrophotometer;
- The optimum conditions of Cu(II) sorption were investigated by batch method described in the previous chapter. For the Cu(II) determination, the spectrophotometric method with rubeanic acid, previously presented, was used.

2.2.2. Influence of the pH's initial solution

Due to the fact that the quantity of ethylacrylate is higher than the acrylonitrile quantity, the presence of hydroxamic groups predominated in the chelating ion exchanger under study. For this reason, one of the most important factors affecting the Cu(II) sorption on this type of resin is the pH value.

Figure 7 presents the variation of the Cu(II) sorption percentage (R %) as function of medium pH, adjusted with buffer solutions. We noticed that the solution of pH =5 has been obtained by a simple dilution of the initial solution, without the use of buffer solution.

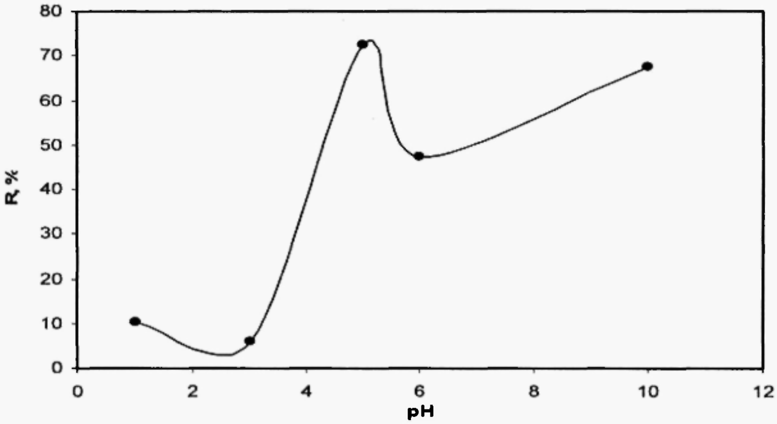


Fig. 7: Cu(II) retention on the acrylic bifunctional resin of type B as function of initial ph (0.05 g of resin; C_0= 67.77μg / mL; equilibration time = 24 hours).

As can be seen, the Cu(II) retention percentage has high values (R=70%) for unbuffered solutions of pH=5 and ammoniacal solutions of pH =10. The resin of this type behaves almost in the same manner as the chelating ion exchanger of type A.

From the literature data it is known that the stability constants of Cu(II)complexes with hydroxamic acid are considerably large compared to other metallic ions. Under the influence of the ligand field Cu(II) ($3d^5$) will receive stabilization due to the tetrahedral distorsion of octahedral symmetry according to the Jahn–Teller effect. The structure of the hydroxamic acid metal complexes is the following:

2.2.3. Influence of Cu(II) concentration on initial solution

Figure 8 presents the effect of Cu(II) initial concentration on its retention by bifunctional acrylic ion exchange resin of type B. The experiments were performed in unbuffered solutions oh pH =5, the contact time being 24 hours.

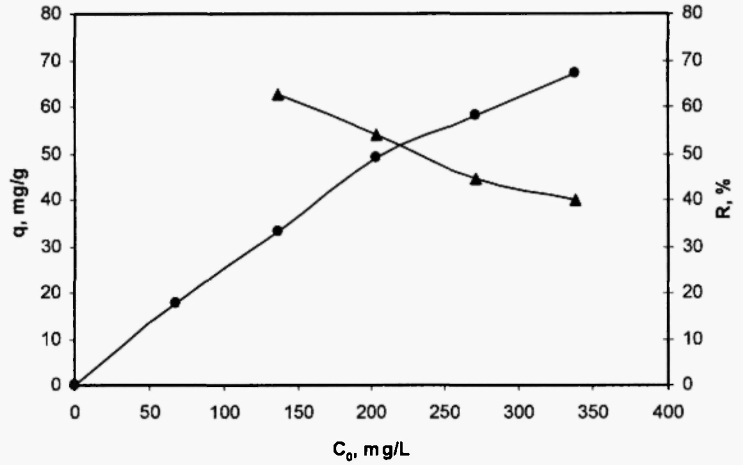


Fig. 8: The influence of Cu(II) initial concentration (●)q, mg/g; (▲)R%.

By contacting with solutions of different Cu(II) concentrations, the resin of type B behaviour is similar to that of type A resin: initial concentration increasing results in the amount of retained Cu(II) increase and the decrease of Cu(II) sorption percentage. Also, it may be noticed that by comparison with the resin of type A, the retention capacity of type B resin is smaller. This fact is probably due to its rigid structure, determined by the higher degree of cross-linking (15%).

2.2.4. Influence of phase contact time

The effect of phases contact time is illustrated in Figure 9. The experiments were carried out on solutions of pH =5 containing 67.77 μg Cu(II)/ mL. As can be seen, the retention process of Cu(II) on the chelating ion exchanger is slow. The sorption equilibrium is reached after at least 6 -8 hours.

This finding is in good agreement with the constant of sorption rate value, calculated by means of Lagergren's equation, Table 5.

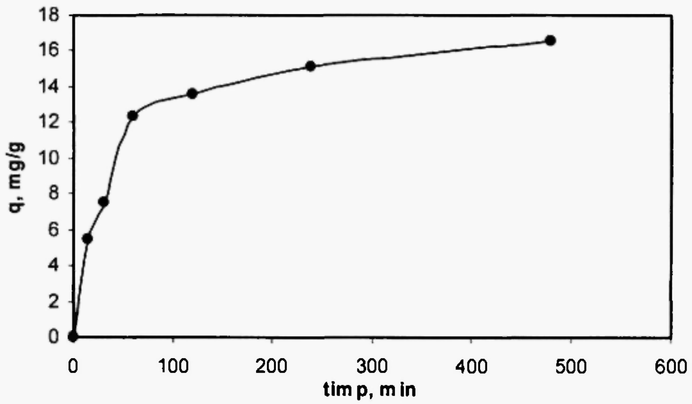


Fig. 9: Influence of phases contact time on Cu(II) sorption process by the type B acrylic ion exchanger (0.05 g of resin; C_0= 67.77 μg / mL ; pH =5).

Table 5

Experimental data processing according to the Lagergren equation

t, min	$lg(q_0-q)$	The regression equation	R^2
15	1.053	y = - 0.0022x + 1.0797	
30	1.018	q_0=17.90	0.9961
60	0.942	$K'=2.48\times10^{-3}min^{-1}$	
120	0.720		
240	0.517		
480	0.027		

2.2.5. The sorption constants

For a more complete description of Cu(II) retention process on bifunctional acrylic ion exchange resin, the Cu(II) equilibrium distribution between the resin phase and aqueous solutions of variable initial concentrations has been investigated. The obtained data were plotted as sorption isotherms, shown in Figure 10.

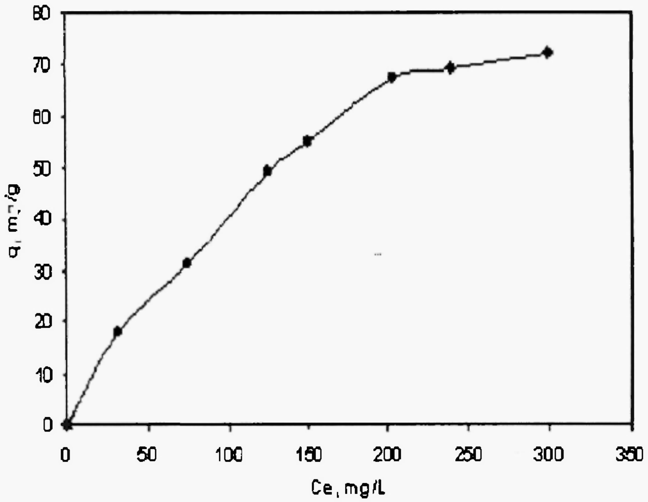


Fig. 10: Isotherms of Cu(II) sorption on the acrylic bifunctional resin of type B
(●) – unbuffered solutions of pH =5;

It is obvious that the resin has a similar behaviour in both reaction media, the sorption isotherms being of the Langmuir type.

The experimental data were processed (Table 6.) by means of a linear Langmuir equation ($C_e / q = C_e / q_0 + 1/K_L \cdot C_e$),, where q is the amount of retained Cu(II), C_e is the Cu(II) concentration in solution at equilibrium; K_L (affinity parameter expressing the strength of sorbed ion – sorbent bond) and q_0 (maximum capacity of sorption) are the Langmuir constants.

Table 6

Characterization of the type B resin – Cu(II) sorption system on basis of Langmuir model

pH	Equation of regression	R^2	q_0 (mmole/g)	K_L (L/mole)	ΔG (kJ/mole)
5	y = 0.4827x + 1.5385	0.9937	2.071	313.85	- 13.975

The experimental data were also statistically processed by linear regression. The regression equations are of y = ax +b type and the obtained values of the correlation coefficients, R^2, are given in Table 6. The results evidence that the experimental data fit the Langmuir model well with two parameters (q_0 and K_L).

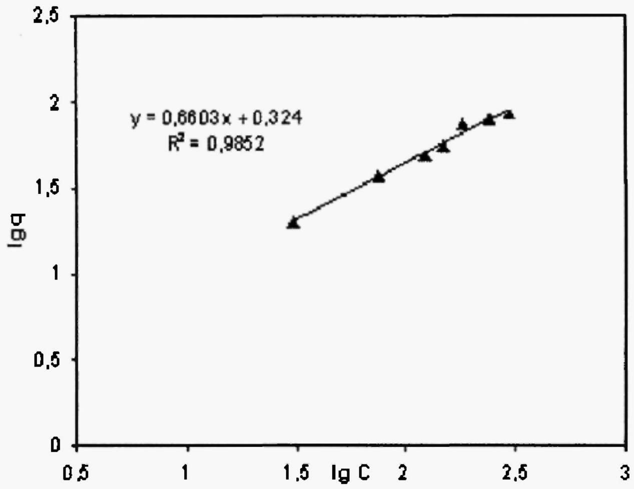


Fig. 11: Freundlich plots of Cu(II) sorption at pH =5(▲) by the type B chelating ion exchanger

The analysis of the Langmuir constants values leads to the conclusion that the chelating ion exchanger with hydroxamic acid and amidoxime groups of type B exhibits a high affinity toward Cu(II) ions.

The negative value of the Gibbs free energy indicates the spontaneous character of the sorption process.

The description of the Cu(II) sorption process according to the Freundlich isotherm model is presented in Figure 11 and Table 7.

Table 7

Freundlich constants

	Equation of linear regression	n	K_F	R^2
pH = 5	y = 0.6603x +0.324	1.5144	2.1086	0.9852

As can be seen from Table 7, in case pH =5 under study, 1 <n <10, indicating favourable conditions of Cu(II) sorption.

2.3 Comparative experimental results

Table 8 presents systematic results of the experimental studies concerning the Cu (II) ions sorption on the acrylic resin type A and B:

Table 8

Comparative experimental results

	Type A	Type B
Degree of cross – linking (%DVB)	10	15
Total weakly basic capacity of exchange - mequiv / cm^3 - mequiv / g	 1.38 4.06	 0.78 1.75
The maximum percentage of retention at pH =5 (unbuffered solutions)	80 – 90%	≈70%
The constant of sorption rate, K', min^{-1}	3.44x10^{-3}	2.48x10^{-3}
The retention process quantitative analysis on the Langmuir isotherm basis: • q_0, mmole/g sorbent • q_0, mg/g sorbent • K_L, L / mole	 2.081 132.226 1156.06	 2.071 131.591 313.85

The experimental results carried out on the type A and type B resins revealed that the type A resin has a superior behavior in the sorption process, compared to the type B resin. Therefore, the investigation was continued only on the type A resin.

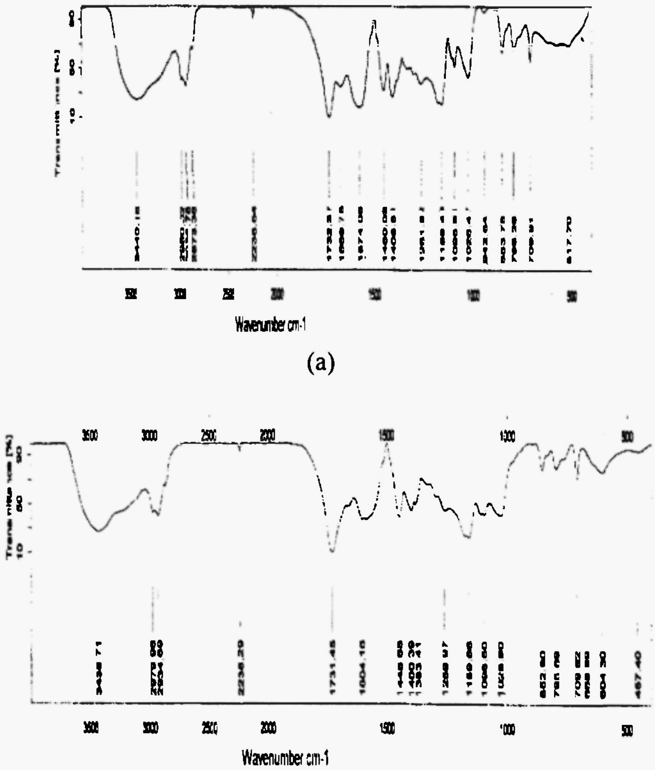
3. INVESTIGATIONS

3.1. Study of Metallic Ion Retention on the Bifunctional Acrylic Ion Exchange Resin by IR Spectroscopy

3.1.1. IR investigation

The study of molecular spectra IR can supply qualitative data of high utility concerning the sorption mechanism of metallic ions on solid matrices with complexing properties.

In the acrylic ion exchange resin with hydroxamic acid and amidoxime groups instance, the vibration spectra of the resin complexed with Cu(II) ,Figure 12 b, by comparison with uncomplexed spectrum (Figure 12. a) have been studied /6/.The spectra were recorded to an IR spectrometer of FT – IR type, VERTEX 70.



(a)

(b)

Fig. 12: IR spectrum of the acrylic resin before (a) and after (b) Cu(II) sorption

Starting with the research works carried out by the scientific team involved in the synthesis of this new type of resin, the identification of the absorption bands in the spectra of the samples under study has been carried out by comparison with the literature correlation tables (Table 9).

Table 9

The major spectral attributions of the absorption bands

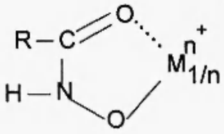
Absorption bands		Group
Bifunctional acrylic resin	Bifunctional acrylic resin + Cu(II)	
3440 broad band	3438	- OH and – NH
1732.37 narrow band	1731.45	$> C = O$
1669.75 broad band	–	$- C = N -$
1620	–	$- NH_2$
1574.06 broad band	–	$= NH$
1406.64 narrow band	1400.39 broad band	$- CH_2$
1026 – 1200 narrow bands	1028 – 1200	$- C – N$
942.64	–	$= N –O -$

3.1.2. Results and discussion

Analyzing the changes of vibration bands from IR spectra of the acrylic resin in metallic ion absence and presence, respectively, the following conclusions may be drawn:

- The broad band at 3440 cm^{-1} is attributed mainly to the group – OH which is presents both in hydroxamic acid and amidoxime groups. The change of this band might be determined by hydroxyl group involvement in the bonding of metallic ions.
- The broadening of band with the frequency of 1732.37 cm-1 is indicated in the instance of the retention of two metallic ions. This band is attributed to the valence vibrations of the >C =O bond that is present in the hydroxamic acid group only.
- As can be seen, the vibration of –C=N– bond, characteristic of the amidoxime group, has completely disappeared in the case of the presence of metallic ions, leading to the conclusion that this group is involved in Cu(II) bonding too.
- Also, there are major changes of the bands from 1026 – 1200 cm^{-1} range, due to the –C–N– bond that is present both in hydroxamic acid and amidoxime groups.

- In this context of upper assertions, the metallic ions can form with both functional groups, hydroxamic acid and amidoxime, respectively, complex combinations of the following type :

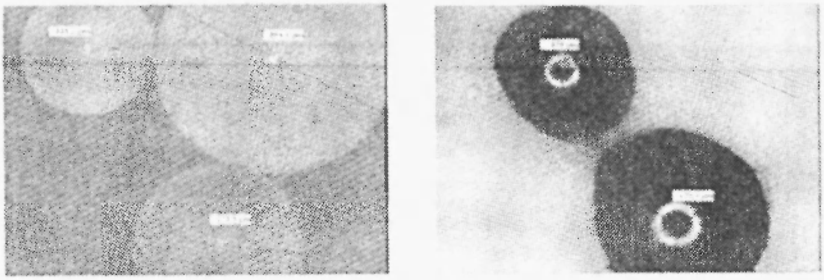


3.2. Optical microscopy investigations of Metallic Ions Retention on the Bifunctional Acrylic Resin

Optical microscopy with OMNIMET 3 equipment, made by BUEHLER Ltd. USA, equipped with a NIKKON EPIPHOT digital photo-camera, was performed.

3.2.1. Results and Discussion

The two types of samples were enclosed onto a plasticine support. The transparent sample of reference (a) was investigated in the bright field (BF), the contrast being in comparison with the plasticine support. The milky background of micrograph is due to this fact. The Cu(II) ions samples – samples (b) - were tested in dark field (DF).



(a) (b)

Fig. 13: Optical micrographs, x50

For both types of samples the investigations indicate a sufficiently large dispersion spectrum of bead size ranged from 300 – 900μm, with a relatively regular micro-geometry, Figure 13.

Note: The existence of a central bright point – at the reference sample – and central bright circle – at the samples Cu(II) –results from the optical effect of the operating bright field, BF and dark field, DF, respectively.

As can be seen, the micrographs indicate clearly the loading of exchanger beads with metallic ions.

3.3. XPS analysis

The analysis of elements and characterization of superficial layers has been performed by X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA). The used apparatus was a PHI 549 SAM/AES/XPS with ultra – high vacuum chamber (10^{6} torr), equipped with double cylindrical mirror analyzer (DCMA) and X-ray primary source of high energy (12536 eV) of Mg - K_α type.

After the general spectrum recording, a high-resolution scanning was performed at the energy of 25 eV for Cls, Cu2p, and Ols peaks. The positions of elements reported to the sharp binding energy Cls of the hydrocarbon side from carbon spectrum for the energy of 284.6 eV.

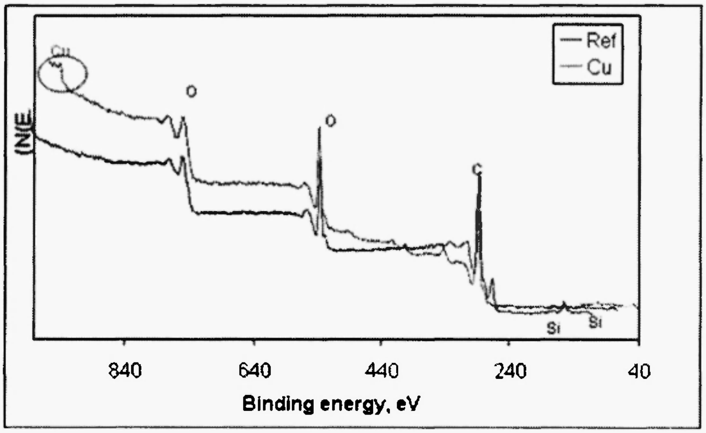


Fig. 14: The XPS general spectra obtained on the surface of analysed elements.

The quantitative analysis is based on the empirical atomic factors of sensitivity from speciality literature /7/. The results of three up-positioned XPS spectra are given in Figure 14; the plots are functions of type number of emitted photoelectrons as function of binding energy, N = f (binding energy), where "N" is the number of photoelectrons emitting at a given energy. Each peak corresponds to the emission characteristic of the analysed element. From spectra analysis the existence is obvious of carbon (binding energy = 284.6 eV being energy of reference) and copper (binding energy = 933.6 eV); also the peaks of oxygen, nitrogen and silicon existence can be noticed.

The interest peaks, C1s, Cu2p, and of the spectra from Figure 14 were performed at high resolution and are recorded in Figures 15(a) and 15(b).

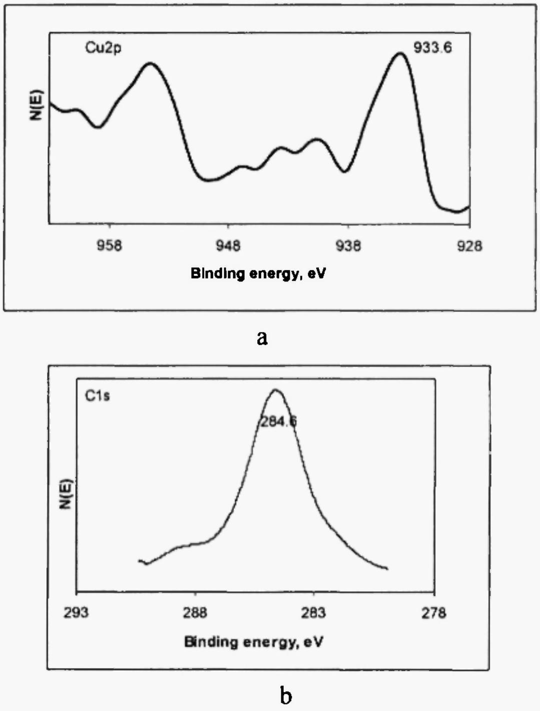


Fig. 15: High resolution XPS spectrum for the Cu(II) sample
(a) the peak for Cu(II) (b) the peak for C

The reference sample high resolution XPS spectrum is identical with the C-peak from the Cu(II) sample, Fig. 15b.

The XPS chemical analysis results of samples surface is shown in Table 10. The existence of copper on the Cu(II) samples can be noticed.

The analysis of the high resolution XPS spectra for the two types of samples (with reference for carbon), leads to the conclusion that most carbon has a bond of C – C type, the binding energy being of 284.6 eV.

Table 10

The surface chemical composition of the sample by XPS analysis

Sample	Content of elements, atomic percentage					
	C	O	N	Si	Cu	0
Reference	70.6	19.4	2.1	7.8	0	0
Cu^{+2}	63.8	29.7	2.8	0.0	0.7	0

Taking into account the positioning mode of peaks from the high resolution XPS spectra for Cu^{2+} samples, it is obvious that the ions of Cu(II) are in the oxidized and non-metallic form, the binding energies being of 933.6 eV; the bond being of M^+ type.

3.4. SEM investigations

These samples were investigated using a JSM-5600 Scanning Electron Microscopy (SEM), equipped with an EDS/EDX analyzer for microanalyses.

Taking into account the fact the samples are dielectric, a gold micro-coating of about 100Å thickness was carried out over the samples in order to solve the question of the electric conductivity. The working parameters: 25 KV, nitrogen protecting atmosphere.

For both types of samples micrographs were performed – with magnifications of x200 and x10000, respectively – and two chemical microanalyses, Figure 16.

The SEM micrographic investigations for all two of samples indicate the same type of morphology, without significant differences between the analyzed samples and the characteristic previously enunciated to the investigation by optical microscopy: an enough large dispersion spectrum of bead size, with a relative regular micro–geometry, Figure 16. The magnification x10000 emphasizes the existence of bead porosity, the pores of nanometric scale.

The plots of chemical composition, Figure 16, resulted from data base; the composition range is according to Table 11

The existence of the presence of copper on samples of Cu(II) can be noticed.

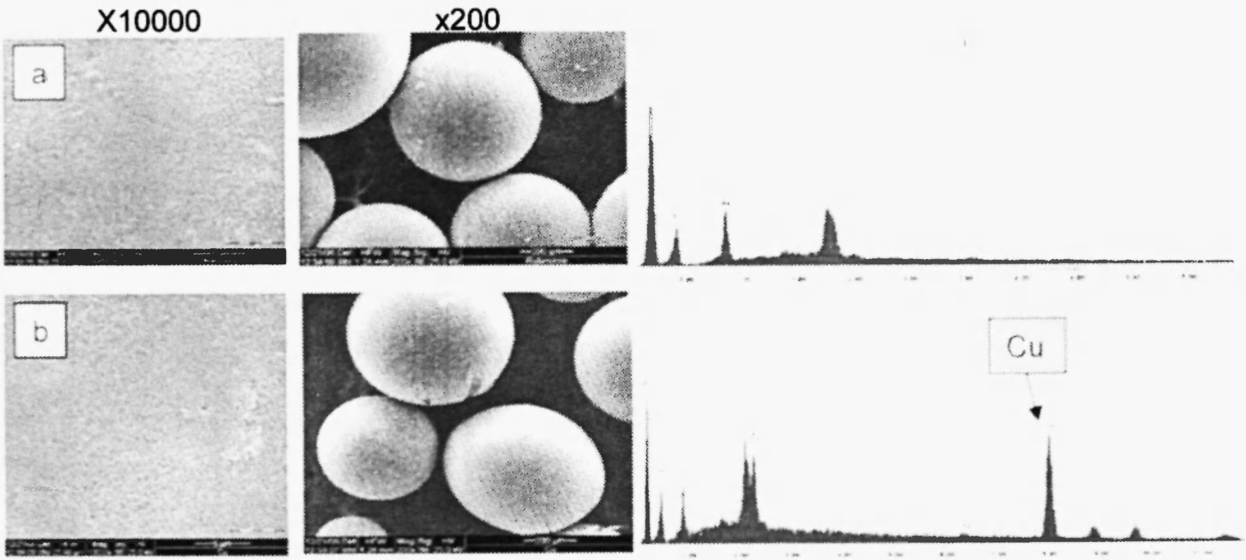


Fig. 16: SEM micrographs and chemical composition spectrum for the reference sample (a) and the Cu(II) sample (b).

Table 11

Chemical composition of samples by EDS analysis

For the reference samples:		% weight	% atomic
	C	69.85-70.80	77.38-78.25
	O	19.37-21.46	16.08-17.74
	Na	08.04-09.83	04.62-05.68
For Cu (II) samples:		% weight	% atomic
	C	52.83-62.54	75.56-79.00
	O	12.97-15.95	13.92-15.12
	Cu	17.82-28.60	04.25-07.73
	Fe	00.62-00.76	00.17-00.23
	S	03.09-04.24	01.46-02.21

Remarks:

- On Cu(II) samples there are traces of Fe and S, and on reference samples there are traces of Na. The cause of their appearance could not be defined;
- the peaks corresponding to gold from the plots of chemical analyses are due to the preliminary technological covering, the reason for which is mentioned;
- by comparing the values of samples chemical composition by XPS analysis (Table 10) and EDS analysis (Table 11) an apparent nonconcordance is obvious. This is due to the analysis principle: XPS analysis is a surface analysis (*thin film distribution*), while the EDS analysis supplies volumic information (*tower distribution*). Consequently, the superficial distribution for copper appears differently.

4. CONCLUSIONS

The researches carried out in order to establish a superior capitalization of the sorptive potential of new types of materials with uses in analytical separatology of high performance allowed the following general conclusions to be reached:

- In order to test the sorptive capacity of the acrylic bifunctional ion exchange resins, the retention of some heavy metal ions, namely Cu(II) has been studied. The experimental determinations carried out on two types of resin revealed that type A have a superior behavior in the sorption process, in comparison with type B.

- The retention of Cu(II) ions on ion exchange resin of type A is maximum (80 – 90%) at pH =5 (unbuffered solutions).
- By studying the influence of medium acidity on the sorbent of type B - Cu(II) sorption system it is obvious that the retention percentage has high values (R ~70%) in unbuffered solutions at pH =5
- The correlation of the experimental results with literature data leads to the idea that the complexing reaction between Cu(II) ion and functional groups is prevalent on the sorption mechanism at pH =5.
- The study of Cu(II) initial concentration influence suggests that bifunctional ion exchange resin of type A can be used in the quantitative recovery of the metallic ion from diluted solutions.
- In solutions containing 80mg Cu(II) /L, the sorption equilibrium at pH =5 is reached after a phases contact time of almost 4 hours ($t_{0.5}$=2h).
- The dependence between the equilibrium concentrations of Cu(II) ions on sorbent and solution phases has been described by means of Langmuir and Freundlich isotherms models.
- The characteristic sorption constants have been calculated on the basis of Langmuir isotherms: q_0=2.081mmole/g; K_L=1156.06 L/mole. These values define a sorption process by complexation, indicating strong bonds between the sorbed ion and the sorbent.
- The negative value of Gibbs free energy (ΔG = - 17.463 kJ / mole) indicates a spontaneous process of sorption.
- The processing of experimental data on the basis of the Freundlich model leads to the following values for the characteristic constants: K_F = 9.3239 and n = 2.2232, respectively. The favourable retention of Cu(II) ions on the bifunctional acrylic resin is reconfirmed.
- To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. The obtained results allow the conclusion that the experimental data fit the Langmuir model better (higher values for R^2).
- The effect of medium acidity, cation concentration and phase contact time on) Cu(II) retention by the ion exchanger of type B has been investigated.
- As in the case of the resin of type A, by contacting the ion exchanger of type B with solutions of different metallic ion concentrations, it can be

seen that to initial concentration increasing the amount of sorbed Cu(II) increases and the Cu(II) recovery percentage decreases.

- Although the sorption rate expressed as time variation of Cu(II) retained amount is high, especially in the first stages of the process, the sorption is almost quantitative after at least 6 – 8 hours.
- The interaction between Cu (II) ion and the sorbent of type B at pH =5 has been described by means of Langmuir and Freundlich isotherms of sorption.
- The sorption isotherms of Langmuir type for both reaction media verified the monomolecular layer adsorption corresponding to the Langmuir model.
- The saturation capacity of sorption, q_0, derived from the linear Langmuir plot has a lower value for the resin of type B than the ion exchanger of type A. This behaviour is probably due to its rigid structure, determined by the higher degree of cross-linking.
- The values of Langmuir constants and Gibbs free energy indicate a spontaneous process of sorption and high affinity of the acrylic resin against Cu(II) ions.
- By processing the experimental data on basis of Freundlich model it can be seen that $1< n < 10$ both at pH =5 (n= 1.5144) and pH = 10 (n=1.4940). Thus, it may be noticed that by introducing hydroxamic acid and amidoxime groups into acrylic copolymer favourable conditions for selective retention of Cu(II) were created.
- The analysis of these IR spectra reconfirmed the sorption mechanism by complexing.
- The XPS analysis and the EDS analysis revealed the existence of copper in the ion changer Cu(II)
- Cu(II) was found in the oxidized and nonmetallic form.
- The binding energies are 933.6 eV for the ion exchange resin with Cu(II). The bond is of M^{n+} type.
- The carbon has bonds of C – C type, the binding energy binding being 284.6eV.
- The beads are porous, the pores being of nanometric scale.

ACKNOWLEDGEMENTS

The authors acknowledge the support given by Dr. V. Neagu and Dr. I. Bunia from "P. Poni" Institute of Macromolecular Chemistry Iaşi, Romania

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