COMPARATIVE STUDY ON THE SORPTION PERFORMANCES OF Cu(II), Co(II) and Cr(III) BIFUNCTIONAL CHELATING ION EXCHANGERS WITH HYDROXAMIC AND AMIDOXIME GROUPS FOR HEAVY METAL IONS

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ABSTRACT

Two new types of bifunctional chelating ion exchangers on the basis of ethylacrylate: acrylonitrile: divinylbenzene copolymers with hydroxamic acid and amidoxime groups have been evaluated for Cu(II), Co(II) and Cr(III)ions sorption from unbuffered diluted aqueous solutions. To model the retention and to compare the sorption capacity of bifunctional acrylic chelating sorbents for the tested cations the Langmuir and Freundlich isotherm equations have been used. The Langmuir maximum sorption capacities for the sorbent of type A were determined to be 2.081, 1.423 and 1.384 mmole/g for Cu (II), Co (II) and Cr (III), respectively. The increase of cross-linking degree for the bifunctional chelating ion exchanger of type B resulted in the decrease of its sorption capacity toward heavy metal ions under study. The negative values of ΔG in all cases indicate the spontaneous character of the sorption process. The kinetics of the Cu (II), Co (II) and Cr (III) sorption follow the Lagergren pseudo – first order model. The results are significant for the future development of the tested sorbents into beneficial materials for industrial and environmental applications.

Keywords: acrylic resins, hydroxamic acid, amidoxime groups, sorption, copper, cobalt, chrome.

1. INTRODUCTION

Chelating resins are complexing or specific ion exchange resins which are designed to have high selectivity for an ion or groups of ions. These types of ion exchange resins adsorb metal ions through a combination of ionic and coordinating interactions instead of the simple electrostatic interactions in conventional cation or anion exchangers. As a consequence, chelating resins offer a greater selectivity than the conventional resins /1/.

For the sorption of Cu (II), Co (II) and Cr (III) ions selected as study cations in the present work, there exists a wide range of commercial chelating resins carrying active functional groups of iminodiacetic acid, aminophosphonic acid, bispicolylamine, N – picolylamine, N – hydroxyethyl, hydroxamic acid, amidoxime.

Due to their particular stability and high complexing abilities, the hydroxamic acids have played a major role in inorganic analysis /2-5/. There are numerous literature data concerning different synthesis methods by means of which chelating resins with functional groups of hydroxamic resins have been prepared. Thus, by the reaction of methyl polymethacrylate with hydroxylamine in benzene, a chelating polymer containing 80% acryl hydroxamic acid, 14%acrylic acid and 6% methylacrylate has been obtained /6/. Several chelating resins with hydroxamic acid functional groups have been prepared by the conversion of carboxylic acid groups from Amberlite IRC – 50 on acid chloride /7/, or esther /8/, and the subsequent hydroxylamine treatment. Application of different methods of synthesis resulted in hydroxamic acid groups incorporation into polyacrylonitrile /9-11/, polyacrylic acid /12/, acrylamide /13/, or ion exchange resins /5, 14 - 17/. Five new poly(methacrylhydroxamic)acids (N–phenylpolymethacryl-hydroxamic acid, N–p–tolylpolymethacrylhydroxamic acid, N–m– tolyl-polymethacrylhydroxamic acid, N–p–Cl–phenyl polymethacrylhydroxamic acid, N–m–Cl–phenylpolymethacrylhydroxamic acid), synthesized according to proceedings described in /18/, have been used as chelating resins for sorption of copper, zinc, nickel, cobalt, iron and lead ions and chromatographic separation of these ions from binary, ternary and quaternary systems /19/.

Many research studies are focused on the chelating resins carrying amidoxime groups. One of the most important applications of these sorbents is the recovery of uranyl ions from seawater /20-25/. Literature data mentioned that amidoxime groups formed stable complexes with different metal cations and, consequently, the polymers with amidoxime groups can be successfully used for the preconcentration of heavy metals from aqueous solutions. However, there is a small number of studies concerning the sorption of heavy metal ions on amidoxime resins. For example, Inuline modified with a group of amidoxime forms stable complexes with Cu(II) /26/. The complexing of copper, lead and zinc ions on Duolite ES – 346 (cross-linked copolymer of polystyrene–divinylbenzene with amidoxime group) is favoured by the pH increase /27/. Some resins based on divinylbenzene cross-linked with polyacrylamide have been successfully applied to the determination of metal traces from natural waters /28, 29/. The metallic ions of palladium /30/, hydrargyrum /31/, or gold /32/ have been retained selectively on some chelating sorbents on the basis of polyvinilic alcohol or polyacrylonitrile with amidoxime groups.

Taking into account the findings that some fibrous chelating sorbents containing two types of functional groups – carboxylic acid and amidoxime – possess improved properties as compared to the similar monofunctional sorbents (an increased degree of hydrophilie, higher selectivity toward some metallic ions, increased rate of sorption) /33, 34/, the retention of copper, cobalt and chrome ions on a new type of chelating resins, namely bifunctional acrylic ion exchange resins with groups of hydroxamic acid and amidoxime has been studied.

2. EXPERIMENTAL

2.1. Materials

Four types (A, B, C and D) of chelating ion exchange resins with hydroxamic acid and amidoxime groups have been used in this study. The synthesis of these products involved two stages /35-37/. First of all, some precursors of the chelating ion exchangers were obtained by suspension copolymerization of ethylacrylate (EA) and acrylonitrile (AN) with divinylbenzene (DVB), using benzoyl peroxide as initiator and benzine or toluene as diluent [D= 0.25, D= mL diluent / mL diluent + mL copolymers], Figure 1.

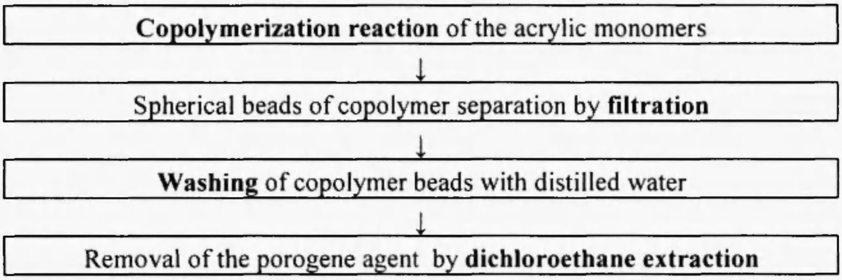


Fig. 1: Schematic representation of the synthesis of ethylacrylate: acrylonitrile : divinylbenzene – precursors of the acrylic ion exchangers

The EA / AN / DVB copolymers were subsequently converted into the sorbents under study by the aminolysis reaction with hydroxylamine chlorohydrate, in the presence of sodium ethoxylate as catalyst, Figure 2.

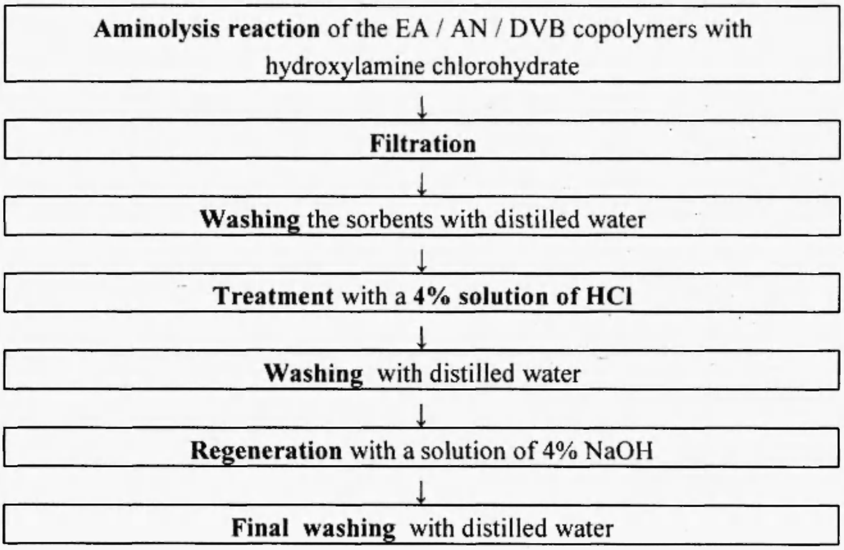


Fig. 2: Scheme of bifunctional chelating ion exchanger preparation

Stock solutions of copper sulphate ($1.57 \cdot 10^{-2}$ mole/L), cobalt nitrate ($2 \cdot 10^{-2}$ mole/L) and chromium nitrate ($5 \cdot 10^{-3}$ mole /L) were prepared and standardized gravimetrically. All working solutions were diluted with distilled water as required.

2.2. Sorption Studies

The studies of Cu(II), Co(II) and Cr(III) ions sorption on the tested chelating ion exchangers were performed by batch method. For this purpose, samples of about 0.05 g of bifunctional chelating ion exchanger were equilibrated for 24 hours at 18°C with 25 mL of each aqueous solution containing defined amounts of metal ions. The mixture was then filtrated and the solution was analyzed for the cation content. The content of the metallic ions in the filtrate was determined spectrophotometrically as follows: Cu(II) with rubeanic acid (λ = 390 nm), Co(II) with R – Nitroso Salt (λ = 550nm) and Cr(III) with complexone III (λ = 550 nm). The amount of metal ion sorbed on the bifunctional chelating ion exchangers was calculated from the difference between the initial and final concentrations of the solution.

2.3. Apparatus

The optical micrographs of the tested sorbents were performed on the Omnimet 3 equipment, manufactured by Buehler Ltd., equipped with Nikkon Epiphot digital photo camera. Scanning Electron Microscopy was carried out on a JSM -5600 model.

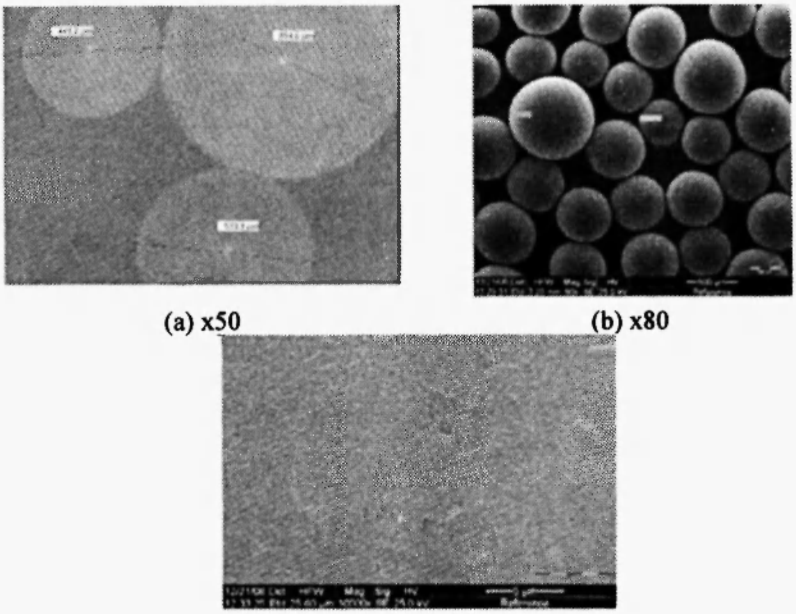
The absorbance was measured on a UV – VIS spectrophotometer (V – 530, Jasco Company).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Tested Sorbents

The synthesized bifunctional chelating ion exchange resins are of types A, B, C and D, respectively. They are based on ethylacrylate: acrylonitrile: divinylbenzene copolymers with hydroxamic acid and amidoxime groups. Due to the fact that the basic copolymers contain an amount of ethylacrylate being much higher than the acrylonitrile amount, the presence of hydroxamic groups predominated in the sorbents under investigation /38/.

The tested chelating ion exchangers benefit from the macroporous structure of the resin, Figure 3.


(a) x50

(b) x80

(c) x10000

Fig. 3: The optical micrographs (a) and SEM micrographs (b, c) for the beads of acrylic bifunctional chelating ion exchanger of type A

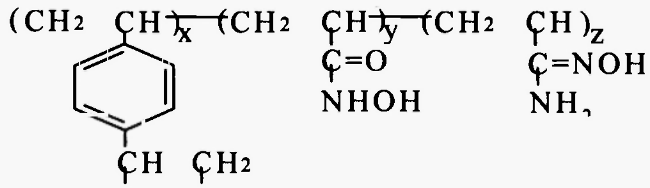
The macroporous structure avoids excessive swelling and shrinking of the resin beads, thus minimizing breakage caused by osmotic shock. The higher surface area of this structure also means that chelating resins have higher resistance to organic fouling. They exhibit good values of the weak basic exchange capacity /38/. These capacities decreased significantly on degree of cross-linking increase, Table 1.

The results of some preliminary studies on Cu(II) sorption by the bifunctional chelating ion exchangers of type C and D were not very encouranging.Under these circumstances, only types A and B have been tested for Cu(II), Co(II) and Cr(III) sorption. It was found that the maximum retention of the tested cations took place in solutions with initial pH in the range 4–5 /39-42/. To compare the Cu (II), Co(II) and Cr(III) sorption performances, the experiments were carried out in unbuffered solutions of pH $\simeq$ 4 for Cr(III) and pH $\simeq$5 Cu(II) and Co(II), respectively. These solutions were obtained by the simple dilutions of initial solutions. Literature speciation data indicated that at pH 4 approximately 20 and 50% occurs as

Cr(III), whereas both copper and cobalt exist in solutions of pH below 5 in their double charged form [Cu(II) and Ni(II)] /43/.

Table 1

Characteristic features of the tested bifunctional chelating ion exchangers

Chemical structure				
Diameter of beads, mm	0.3 – 0.8			
Morphological structure	Macroporous resin			
Type	A	B	C	D
Cross – linking degree, %DVB at a dilution D = 0.25	10	15	10	15
Exchange capacity				
mequiv/g	4.06	1.75	3.90	0.93
mequiv/mL	1.38	0.78	1.20	0.60

3.2. Sorption Modelling

To describe the equilibrium distribution of the cations between the sorbent phase and the aqueous solution phase, two different sorption models, Langmuir and Freundlich, were used.

* *Langmuir isotherm.*

The most widely used isotherm for modelling of the sorption equilibrium data is represented by the Langmuir two parameter equation /44/:

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

where q is the amount of cation sorbed per unit weight of sorbent at equilibrium(mmole/g); C is the equilibrium concentration of cation remaining in the solution (mmole/L); q_0 and K_L are Langmuir constants related to the sorption capacity and energy of sorption, respectively.

The Langmuir isotherms obtained under unbuffered batch studies of each metal ion are shown in Figure 4 and Figure 5.

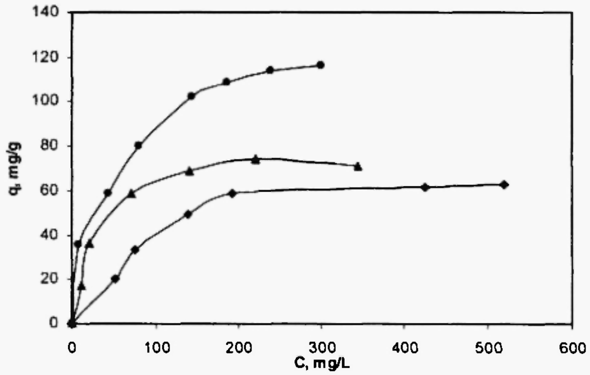


Fig. 4: Langmuir isotherms for the sorption of Cu(II) (●), Co(II) (▲) and Cr(III) (♦) ions on the acrylic ion exchanger with hydroxamic and amidoxime groups of type A

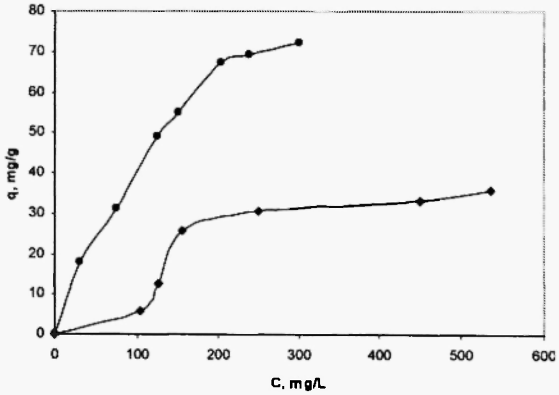


Fig. 5: Langmuir isotherms characteristic to the following sorption systems: Cu(II) – chelating ion exchanger of type B (●); Cr(III) – bifunctional ion exchange resin of type B (♦)

The validity of the Langmuir equation assumes that the uptake of Cu(II), Co(II) and Cr(III) ions on bifunctional chelating ion exchangers occurs via formation of a monolayer coverage of the sorbate at the outer surface of the sorbent, without any interaction between the sorbed ions. The Langmuir equation can be linearised as:

$$\frac{1}{q}=\frac{1}{q_0}+\frac{1}{K_L \cdot C} \qquad (2)$$

The linear form (2) can be used for the linearisation of experimental data by plotting 1/q against 1/C. The Langmuir constants can be evaluated from the slope and the intercept of linear equation.

Table 2 presents a comparison of the constants obtained from the linear Langmuir plots for each ion metal on the bifunctional chelating ion exchangers of type A and B. It is significant from Table 2 that the values of the maximum capacity of sorption, q_0 (maximum amount of sorbed ion required to give a complete monolayer on the surface) for the acrylic chelating ion exchanger of type A show a decreasing trend of 2.081 to 1.423 and 1.384 mmole/g, with the following order: Cu(II)>Co(II)>Cr(III). On the other hand, Langmuir sorption capacities for Cu(II) and Cr(III) ions on the chelating ion exchanger of type B follow the same order, being smaller than the values corresponding to the sorbent of type A. This last trend indicates that the increase of cross-linking degree to 15% DVB for bifunctional ion exchanger of type B will reduce its sorption capacity toward heavy metal ions that were studied.

K_L is a measurement of the relative sorption affinity, being the Langmuir constant related to the energy of sorption. Its high values recorded in Table 2 involve strong bonds between the sorbed cations and the sorbent and indicate the existence of a complexation mechanism. Further investigations are neccessary in order to correlate the sorption affinity with the stability constants of the formed complexes. These investigations will be focused on the fraction in which both hydroxamic acid and amidoxime groups are involved in the chelating process. As compared to the sorbent of type B, the K_L values for the chelating ion exchange resin of type A are significantly larger, confirming the higher accessibility of this material against the tested cations.

Table 2

Quantitative description of Cu(II), Co(II) and Cr(III) sorption on the bifunctional chelating ion exchangers of type A and B by means of Langmuir isotherm

	q_{0}, mmole/g		K_L, L/mole		K_R		ΔG, KJ/mole	
Cation	Type A	Type B	Type A	Type B	Type A	Type B	Type A	Type B
Cu(II) pH =5	2.081	2.071	1156.06	313.85	0.58	0.75	-17.463	-13.975
Co(II) pH =5	1.423		1574.00		0.44		-17.922	
Cr(III) pH · 4	1.384	0.796	699.00	547.40	0.41	0.47	-15.948	-15.352

Also, Table 2 lists the values of the separation factor (K_R) defined by Equation (3) /45/:

$$K_R = \frac{1}{1 + K_L \cdot C_0} \qquad (3)$$

where K_R is the separation factor (dimensionless parameter); K_L is the Langmuir constant (L/mole) and C_0 is the initial cation concentration(mole/L).

Values of the separation factor express the essential features of Langmuir isotherm, the sorption being favourable for $0<K_R<1$. Referring to the values of the separation factor from Table 2 it is obvious that by introducing the hydroxamic acid and amidoxime groups into the ethylacrylate : acrylonitrile : divinylbenzene copolymers, favourable conditions ensue for Cu(II), Co(II) and Cr(III) ions sorption. The K_R values result in a selectivity sequence (Cu(II)>Co(II)>Cr(III)) similar to that previously reported.

Variation of Gibbs free energy (ΔG) for the retention of Cu(II), Co(II) and Cr(III) ions on acrylic ion exchangers with hydroxamic acid and amidoxime functional groups was determined in Table 2 from the K_L Langmuir sorption constant with the aid of Equation(4) /46/:

$$\Delta G = - RT \ln K_L \qquad (4)$$

where R is the gas constant and T is the absolute temperature.

The negative values of ΔG in all cases under study point to the spontaneous character of the sorption process (a high affinity of bifunctional chelating ion exchangers toward the tested cations).

* *Freundlich Isotherm*

The Freundlich isotherm is represented by Equation (5) /47/:

$$\lg q = \lg K_F + (1/n) \lg C \qquad (5)$$

where q is the amount of cation sorbed per unit weight of chelating ion exchanger at equilibrium; C is the equilibrium concentration of cation left in solution; K_F (sorption capacity) and $1/n$ (sorption intensity) are the Freundlich constants. If sorption is favourable, then $1/n<1$ or $n>1$, meaning that the forces within the surface layer are repulsive. On the other hand, a value for 1/n below one indicates a Langmuir–type isotherm, because it becomes more and more difficult to adsorb additional sorbate species at higher sorbent at constant /48/.

The plots of Eq. (5) for the tested systems of batch sorption are shown in Figures 6 and 7. The linear plots in these figures indicate that the retention of the investigated cations on the types A and B of chelating sorbents based on ethylacrylate : acrylonitrile : divinylbenzene copolymers with hydroxamic acid and amidoxime functional groups may be also expressed by the means of the Freundlich isotherm model.

Table 3 records the K_F and 1/n values derived from the slope and the intercept of the linear Freundlich plots given in Figure 6 and Figure 7. The empirical values of the Freundlich constants point out again that the sorption process is strongly dependent on the nature of metal ion and the type of sorbent. The highest K_F value has been found to be 9.323 for Cu(II) ions on the bifunctional chelating acrylic resin of type A. The numerical values of 1/n <1 indicated that the sorption capacity is only slightly suppressed at lower equilibrium concentrations. Saturated acrylic materials with sorbed materials were no evident by this isotherm; thus infinite coverage is predicted mathematically, indicating multilayer sorption on the surface /49/.

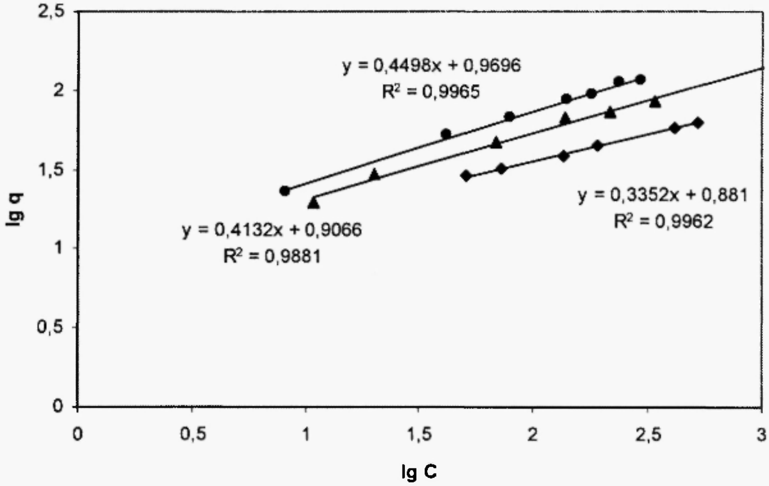


Fig. 6: Freundlich plots of Cu(II) (●), Co(II) (▲) and Cr(III) (♦) sorption on the bifunctional chelating ion exchanger of type A

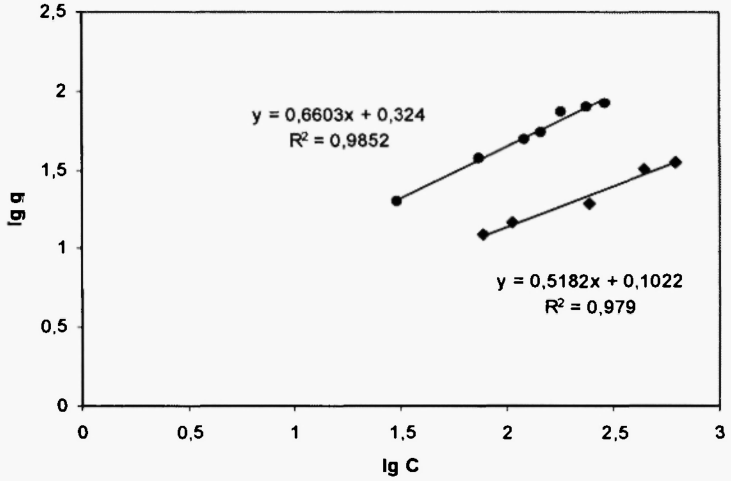


Fig. 7: Freundlich plots of Cu(II) (●) and Cr(III) (♦) sorption on the bifunctional chelating ion exchanger of type B

Table 3

Comparison of the constants obtained from the Freundlich isotherms for the sorption of Cu(II), Co(II) and Cr(III) onto acrylic chelating ion exchangers with hydroxamic acid and amidoxime functional groups.

	Type A			Type B	
	Cu(II)	Co(II)	Cr(III)	Cu(II)	Cr(III)
K_F	9.323	8.064	7.686	2.108	1.265
1/n	0.448	0.413	0.331	0.660	0.518

3.3. Goodness of Fit of Models

To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. The regression equations of y = ax +b type and the obtained values of the correlation coefficients R^2 are given in Table 4. Obviously, it can be seen that the sorption data were better fitted to the Langmuir isotherm since the coefficients of correlation for the Langmuir isotherm were higher than that for the Freundlich isotherm.

Table 4

Statistical analysis

Sorption system	**Langmuir isotherm**		**Freundlich isotherm**	
	Linear regression equation	**R^2**	**Linear regression equation**	**R^2**
Sorbent of type A – Cu(II) (pH =5)	y = 0.4804x + 0.416	0.9991	y = 0.4998x + 0.9696	0.9965
Sorbent of type B – Cu(II) (pH =5)	y = 0.4827x + 1.5385	0.9937	y = 0.6603x + 0.324	0.9852
Sorbent of type A – Co(II)	y = 0.7026x + 0.4463	0.9945	y = 0.4132x + 0.9066	0.9881
Sorbent of type A – Cr(III)	y = 0.7224x + 1.033	0.9994	y= 0.3352x + 0.881	0.9962
Sorbent of type B – Cr(III)	y = 1.256x + 2.294	0.9970	y = 0.5182x + 0.1022	0.9790

3.4. Kinetic Investigations

The macroporous structure characteristic to the tested sorbents enhances their kinetic performance as it allows more rapid diffusion within the resin. Usually, the kinetic data are treated with the aid of the Lagergren equation /50/:

$$\lg (q_e - q_t) = \lg q_e - k' \cdot t / 2.303 \qquad (6)$$

where q_e and q_t are the amounts of cations (mg/g) sorbed at equilibrium and any time, t, respectively and k' is the constant rate of sorption.

Plots of lg $(q_e - q_t)$ against t resulted in straight line relationships, Figure 8, indicating that the sorption process is of pseudo – first order with regard to the concentration of each sorbed metal ion.

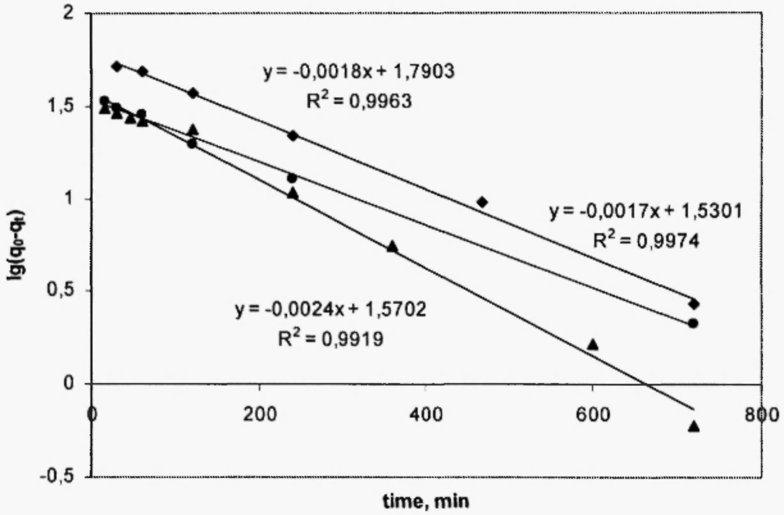


Fig. 8: Lagergren plots of Cu(II) (●), Co(II) (▲) and Cr(III) (♦) sorption on the bifunctional chelating ion exchanger of type A

The rate constants of sorption (k'), calculated from the slopes of these plots are summarized in Table 5.

Table 5

Kinetic data for the sorption of Cu(II), Co(II) and Cr(III) onto acrylic chelating ion exchangers with hydroxamic acid and amidoxime groups of type A

	Cu (II)	**Co(II)**	**Cr(III)**
Sorption rate constant, k', min^{-1}	$3.44\ 10^{-3}$	$3.61\ 10^{3}$	$4.14\ 10^{-3}$
Sorption half life, $t_{1/2}$, min^{-1}	201.4	191.6	167.3

Moreover, the half-life of sorption ($t_{1/2}$) at 18°C is calculated in Table 5 from k' values by use of the equation (7) /51/:

$$t_{1/2} = 0.693/k' \qquad (7)$$

According to the results in Table 5, the rate constant sequence is of Cr(III)>Co(II)>Cu(II). The different constants of sorption rate for these metal ions can be attributed to their different ionic sizes. On the other hand, the Cu(II) ions are sorbed faster on the chelating ion exchanger of type A (k'= $3.44 \cdot 10^{-3}$ min^{-1}) than the more cross- linked resin of type B (k'=$2.48 \cdot 10^{-3} min^{-1}$).The variation of the half – life ($t_{1/2}$) values for the sorption of these ions by the bifunctional chelating ion exchanger with hydroxamic acid and amidoxime groups of type A corresponds to the following order: Cu(II) >Co(II)>Cr (III).

The obtained kinetic results suggest that the retention of the tested cations on the bifunctional chelating ion exchangers is a process of mass transfer, the rate-controlling reaction step being the diffusion of metal ions inside the resin beads. This finding confirms the potential applicability of the chelating ion exchangers on basis of ethylacrylate : acrylonitrile : divinylbenzene copolymers with hydroxamic acid and amidoxime functional groups under study in separation and concentration of Cu(II), Co(II) and Cr(III) ions from unbuffered diluted solutions.

4. CONCLUSIONS

1. Bifunctional chelating ion exchangers prepared by the aminolysis reaction of some ethylacrylate :acrylonitrile : divinylbenzene copolymers exhibit reasonable sorption properties with major importance for their future development into beneficial materials for industrial and environmental applications.
2. The Langmuir and Freundlich isotherms were used to model the Cu (II), Co (II) and Cr (III) sorption equilibrium. The results indicated that the Langmuir model has a better correlation with experimental than the Freundlich model.
3. The values of the Langmuir maximum capacity of sorption, q_0 for the acrylic chelating ion exchanger with hydroxamic acid and amidoxime functional groups of type A show a decreasing trend of 2.081 to 1.423 and 1.384 mmole/g, with the folowing order: Cu(II)>Co(II)>Cr(III).
4. The increase of cross – linking degree for the bifunctional ion exchanger of type B results in a decrease of its Cu(II) sorption performance.
5. The high values of K_L constant involve strong bonds between the sorbed

cations and the sorbent and indicate the existence of a complexation mechanism.

6. The negative values of ΔG in all cases under study point on the spontaneous character of the sorption process (a high affinity of bifunctional chelating ion exchangers toward the tested cations).
7. The kinetic data were represented by the Lagergren pseudo – first order equation.

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