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THE FRIENDLY MATERIALS FOR ENVIRONMENTALLY PROTECTION

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Abstract: *A common approach for achieving new polymer materials, characterized by metal ions selectivity, presumes the use of cyclic chelators. That supposes multistep synthesis and a prior knowledge of how the cycling process can affect the binding and the selectivity. There are two general ways to obtain polymer– metal ions complexes:*

1. *by retention of the metal ion in a fix cage. The density of the fix cages and the accessibility of the metal ions to the functional groups determine the retention efficiency. The metal ion retention is a consequence of a sterical effect.*
2. *through a complexing process determined by the polychelator groups position in the macromolecular chain and by their relative distances.*

This study is a report regarding the possibility to develop new polymer materials designated for waste waters treatment. This article presents the possible use of several new polymeric structures for the removal of Cu(II) and Cr (III) ions from aqueous solutions. The retention mechanism is suggested and discussed. Operational parameters such as chelator nature, pH value, and batch time were investigated.

1. Introduction

In recent years, synthesis of metal complex forming polymers has gained considerable interest owing to their attractive applications in diverse fields such as water and waste-water treatment, hydrometallurgy, removal of nuclear waste, catalysis of organic syntheses and initiation of polymerization. The complexation of metal ions with polymer matrices containing functional ligands results in superior properties compared with the simple compound counterparts. Functionalized multidentate ligand resins are often used for these applications. Conventional technologies for waste water treatment, such as precipitation, coprecipitation, and concentration, are quite satisfactory regarding the removal of the pollutants, but solid residues containing toxic compounds are produced and their final disposal is generally done by land filling, with high costs and the probability of groundwater contamination.

New technologies such as membrane separation, electrodialysis, and selective adsorption were developed [1-3]. Selective adsorption presumes the synthesis of new metal complexion extractors, ion exchangers, or polymeric adsorbents with selectivity for a wide range of metal species [4-7]. The selectivity of macromolecular polyligands for metal ions is an extensive subject [8-14].

Most commercially significant chelators contain polystyrene (PS) anion-exchange matrices. One of the drawbacks of these ion exchangers is their poor selectivity and slow kinetics toward metal ions. One factor contributing to such behavior is the hydrophobicity or low water wettability of the PS backbone, which lowers the reaction rate with aqueous agents

Copolymers of MA have been commonly used for the synthesis of water-soluble materials, such as thickeners in paints and coatings, industrial emulsifiers and flocculating agents, [15-18] and carriers of biological substances [19]. The copolymerization of MA with vinyl monomers and their subsequent hydrolysis have also led to copolymers exhibiting remarkable selectivity toward divalent metal-ion.

From the theoretically point of view, the AM-S system has attracted a special interest. The development of the radical polymerization of this substrate led to products with alternant structure equimolar composition, irrespective of the composition of the initial substrate. The reaction rate of this process is the highest for the equimolar composition of the substrate [20].

MA-DCPD copolymers are interesting from the application point view, primarily due to the reactive MA units (sensitive to reactions with water, alcohols and amines), and then due to the unsaturation induced to the final polymer structure by the presence of DCPD units. Such compounds can be used in the field of ion exchangers, self-crosslinkable chelating supports, thermosetting resins, polymeric networks able to stabilize optical devices [21-25].

However, many research workers have used CMS for improving and modification of tailor made polymers (block-copolymers, graft copolymers, dendrimers etc). Also, another concern is related to controlling intramolecular architecture; in this respect, stepwise polymerization (including living radical polymerization, with or without separating the intermediary macromers) has gained an increasing importance.

2. Experimental

We were synthesized few polymeric structures from maleic anhydride (MA) – styrene (S) - vinyl benzyl chloride (VBC) and respectively, MA–VBC–dicyclopentadiene (DCPD) figure 1 [21-25]. The terpolymers were obtained by precipitation technique using as reaction medium toluene (T) and initiator 2, 2'- bisazoisobutironitril (AIBN). We are working in micro reactors with magnetic stirring at 80°C, for two hours. After separation by simple filtration, washing with anhydrous toluene, we drying the polymer a 60°C and we use that in complexation procedure.

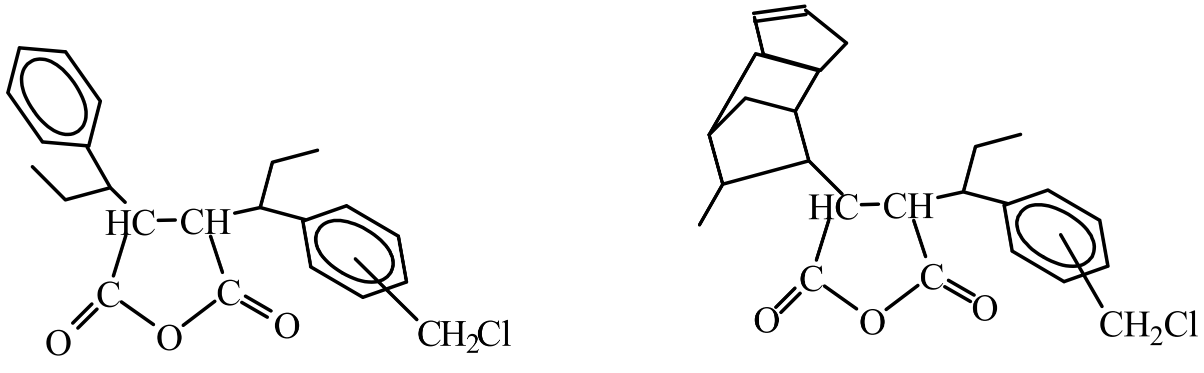


Fig. 1. Structure of chelatizant polymer structure

The reactants used: MA, S, VBC (mixture m/p=4/6), DCPD, AIBN, from MERCK, and T from REACTIVUL Bucharest are used after preliminary purification procedure: recrystallization (MA, AIBN), rectification at normal or reduced pressure (S, VBC, and T).

The retention capacity of the polymeric structures was studied on aqueous solutions with exact content metal ions. $CuCl_2 \cdot 2H_2O$ and $CrCl_3$, both from Fluka, was used to prepare the metal ion solutions. Initial concentrations of synthetic waters were 2,9g/l (Cu (II)) and 2,6g/l (Cr (III)). The chose of these values are based on the fact that are the similar values in damages waters.

The pH was adjusted with 1 N NaOH and 1 N HCl solutions from Reactivul Bucharest.

Chelating procedure involves the following characteristics:
- the ratio metallic ion solution/ polymer=2:1
- working pH =8.5 (that is a value established in our anterior studies [26].
- contacting procedure: dissolution of polymer in alkaline water and dropping in metallic ion solution.
- contact time: =2 hours.

The precipitated polymer-metal ion complex was separated by filtering, washed with warm water and ethanol and dried at 60º C in order to avoid the destruction of the polymeric support.

The efficiency of the employed materials as well as the discussions regarding the complexing – chelating mechanisms is based on the following parameters: the retention efficiency (**η_r**), the retention capacity (**Q_e**) and the distribution coefficient of the metal ion into the polymer matrix (**K_d**) [15]. These parameters are defined by the following equations:

$$\eta_r = \frac{\Delta C}{C_0} = \frac{C_0 - C_f}{C_0} 100 \quad [\%] \tag{1}$$

$$Q_e = \frac{m_C}{E_{Me}\, m_p} \quad [E_{Me} / \text{g polym}] \tag{2}$$

$$K_d = \frac{m_c V}{m_{Cu}\, m_p} \quad [\text{ml/g}] \tag{3}$$

Where: C_0 = the initial metal ion concentration, [g/l]; C_f= the metal ion concentration in the effluent [g/l]; m_p = the polymer weight [g]; V = the volume of the polymeric solution in the reactor [ml]; mc = the amount of metal ion retained by the polymer [mg]; m_{Cu} = the amount of metal ion in the reaction mixture [mg].

The polymers and metal ions-polymer structures were characterized by IR-spectroscopy, on a Shimadzu FTIR 8000 infrared Spectrophotometer as potassium bromide pellets; by X-ray diffraction and elemental analysis.

3. Results and discussions

Table 1 and 2 summarized the experimental data obtained from the two class of polymer substrate used from retention of metallic ions.

Analyzing the experimental results (see table 1 and 2) we relieve a distinct comportment for two material classes. So, defining the selectivity such a difference of the retention efficiency of Cu (II) to Cr (III), is evident than the polymer support AM-VBC-S are an affinity from chromium ion (see table 1, A1, B1, C1, C2, C3). The polymer supports with DCPD, as inert sequence, are affinity from Cu ions (see table 1, AD2, BD2. BD4, CD2).

In the both cases, interactions of metal ions with polymers are mainly due to the electrostatic forces. But other weak interaction may appear as trapping metal ion in bulk polymer.

When interchain complexes are predominant, it is normally recognized the existence of polymer domain with near constant concentration ligands, since the distance between them are kept in a narrow range for a given polymer chain. This is responsible that the chelating reaction appears as one-step reaction.

For relative low ligand amounts in the solution, complexed metal ions may coexist with free, uncomplexed ones.

Table 1. Experimental dates from AM-VBC-S polymers

	AM		VBC		S		η (%)		Q (EMe/g poly)		K (ml/g)	
	x	X	x	X	x	X	Cu	Cr	Cu	Cr	Cu	Cr
A1	0.330	**0.535**	0.330	**0.050**	0.330	**0.390**	82.63	**99.93**	11.195	**27.870**	220.0**0**	**266.48**
A2	0.125	**0.307**	0.500	**0.406**	0.375	**0.250**	**99.98**	99.91	**13.328**	27.430	**262.46**	263.22
A3	0.375	**0.440**		**0.353**	0.125	**0.180**	**99.96**	99.91	**13.838**	28.487	**272.50**	272.37
A4	0.450	**0.135**		**0.730**	0.050	**0.100**	**99.96**	99.91	**13.927**	28.670	**274.25**	274.00
B4	0.050	0.033	0.450	0.387	0.500	0.548	99.11	91.89	14.230	27.171	282.70	259.79
B1	0.125	**0.450**	0.375	**0.275**		**0.250**	76.49	**99.94**	10.814	**29.100**	213.00	**278.22**
B2	0.375	0.342	0.125	0.132		0.500	99.45	99.80	14.600	30.170	287.00	283.00
C4	0.500	**0.384**	0.450	**0.410**	0.050	**0.179**	99.38	**99.93**	13.750	**28.480**	271.00	**272.30**
C1		**0.415**	0.375	**0.366**	0.125	**0.195**	97.17	**99.98**	13.480	**28.570**	265.00	**273.17**
C2		0.465	0.125	0.090	0.375	0.418	97.17	99.98	13.260	26.560	261.00	265.63
C3		0.476	0.050	0.024	0.450	0.500	70.46	99.86	9.930	27.720	195.6	277.17

x, X= molar fraction of monomer in starting substrate and, respectively, in polymer

Another hand, the capacity of polymer complexing agents is influenced by sterical and statistical factors. Usually there is not only intramolecular, but also intermolecular complexation because the coordination number of metal ions is greater than two. By consequence, the sterical hindrance may be modified the complexation capacity from polymer to polymer.

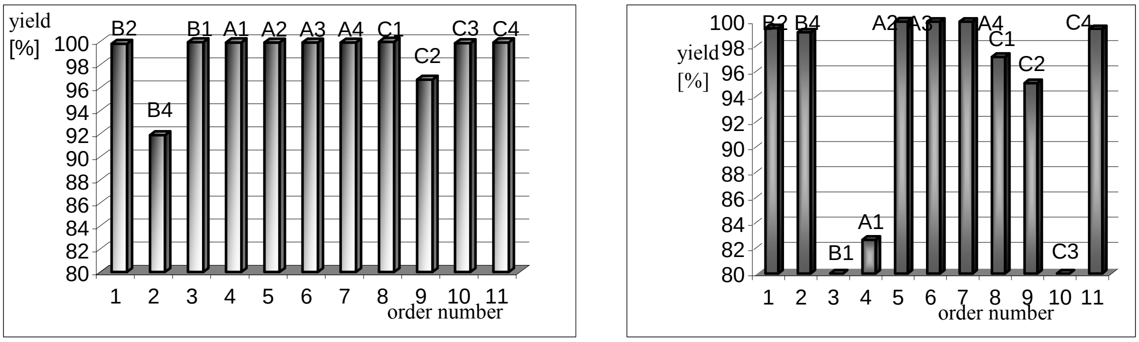
Table 2. Experimental dates from AM-VBC-DCPD polymers

Cod	AM		VBC		DCPD		η (%)		Q (EMe/g poly)		K (ml/g)	
	x	X	x	X	x	X	Cu	Cr	Cu	Cr	Cu	Cr
AD	0.330	0.545	0.330	0.409	0.330	0.024	96.78	98.76	14.66	24.58	259	264.16
AD2	0.375	0.660	0.125	0.280	0.500	0.043	92.66	67.44	8.75	31.05	459	333.71
AD1	0.125	**0.520**	0.375	**0.320**		**0.140**	**99.98**	99.90	**15.42**	25.311	**272.2**	272.03
BD2	0.375	**0.348**	0.500	**0.488**	0.125	**0.140**	**99.96**	77.47	**15.381**	19.58	**271.5**	210.45
BD1	0.125	**0.490**		**0.430**	0.375	**0.061**	99.91	**99.98**	14.56	**23.94**	257.1	**257.29**
BD4	0.050	0.135		0.760	0.450	0.081	99.91	88.94	15.52	22.69	274	243.93
CD4	0.500	**0.384**	0.450	**0.461**	0.050	**0.128**	99.91	**99.93**	15.22	**24.87**	268.7	**267**
CD1		0.535	0.375	0.428	0.125	0.014	98.25	98.245	15.05	24.72	265.7	265.72
CD2		0.694	0.125	0.224	0.375	0.060	98.16	94.42	15.03	23.76	265	255.36

x, X= molar fraction of monomer in starting substrate and, respectively, in polymer

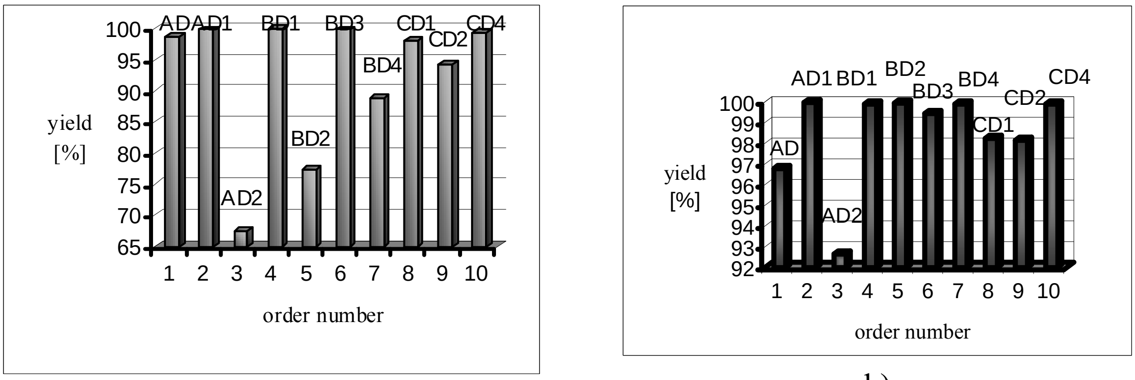
We talk in this case than two different polymer structures regarding the monomer constitutive units: AM-VBC-S and AM-VBC-DCPD. In fact, if we regard attentive the dates in the tables 1 and 2, we are many polymer material different by percent of monomer units in the final structure.

From polymer materials based of the MA-VBC-S copolymers, the selectivity is determined by molar ratio MA/VBC (figure 2). We observe an affinity for Cr (III) in the seria: C1>B1>A1>C4 with maximum selectivity value forC1: S /VBC ≅1.87, MA/ VBC≅1.13 and affinity for Cu (II)in the seria: A2>A3≅>A4, with maximum selectivity value A2: S /VBC ≅0.61, MA/ VBC≅0.76



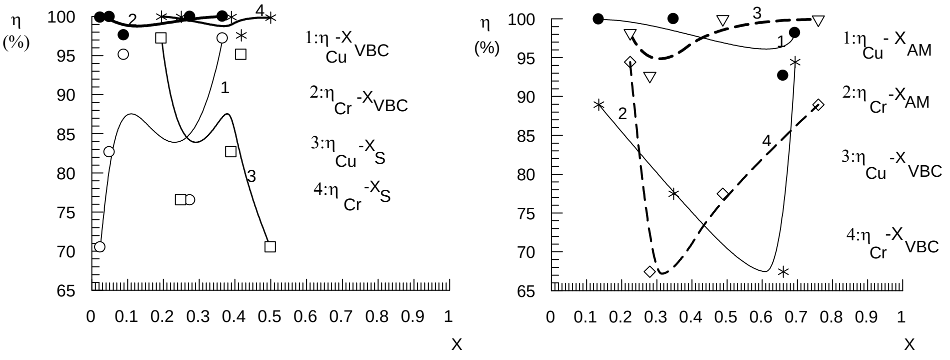
a) b)

Fig. 2. Removing of the a) Cr (III) ions and b) Cu(II) ions using the the MA-VBC-S polymers



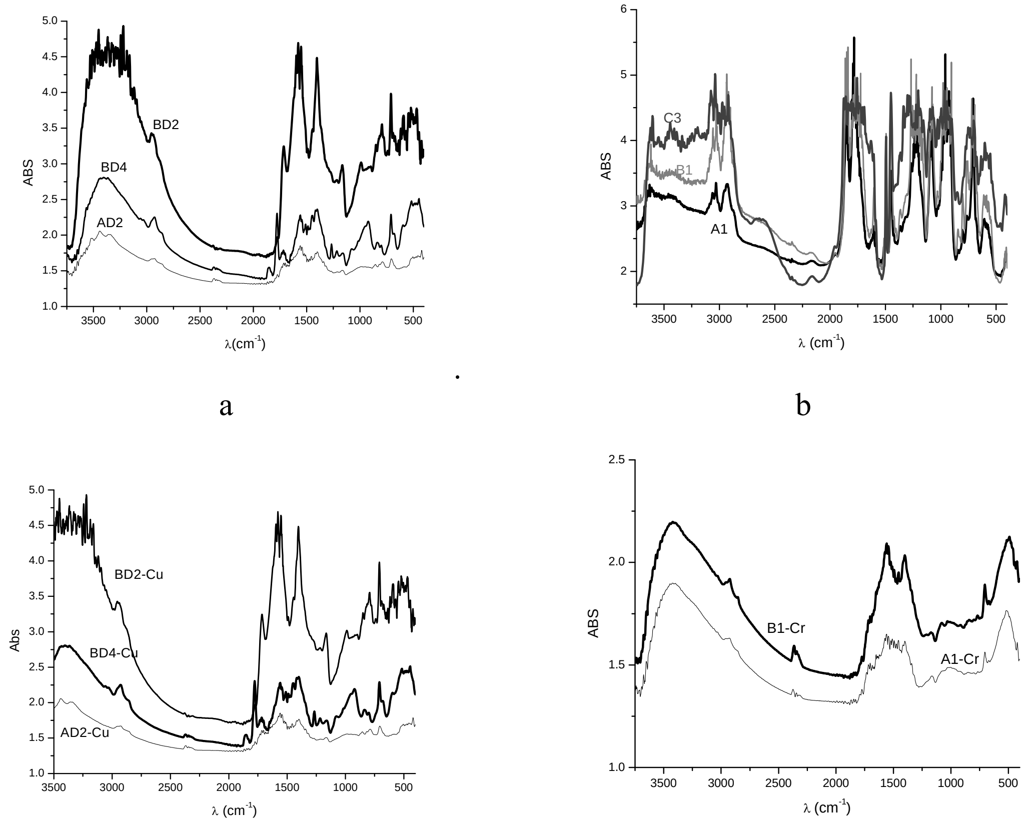
a) b)

Fig. 3. Removing of the a) Cr (III) ions and b) Cu(II) ions using the the MA-VBC-DCPD polymers



a b

Fig. 4. The variation of retention efficiency by rapport of polymer composition from: a) MA-VBC-S; b) MA-VBC-DCPD polymers



a b

c d

Fig. 5. IR spectra for polymer supports (a) MA-VBC-DCPD; b) MA-VBC-S) and its complexes (c); (d).

From polymer materials based on the DCPD, the selectivity is determined by molar ratio AM/VBC (see figure 3). So the affinity for Cr(III) in the seria BD1>AD≅BD3 with maximum selectivity value for BD1: VBC /DCPD ≅6.51, AM/ VBC≅2.35, respectivelly affinity for Cu(II): AD1, BD2, with maximum selectivity value for AD1: VBC /DCPD ≅6.51, AM/ VBC≅2.35

Increasing or diminish of these composition are as consequence an equalize tendency from retention efficiency of both ions. This is due, probably, one hand by decreasing of COOH density. Consequently, appear the interchain statistic cage, favourable by dimension and electrostatic charge of ions. On the other hand, increasing the number a COOH chelators groups affect the dimension and distribution of electric cage.

Probably, underlined by sterical hindrance imposed by DCPD structure, in this case are formed the large cage with favourite equitable adsorption of the two ions. So, the DCPD units are only an electrical spacer and conformational orientation role.

Analysing the evolutions presented in figure 4 we observe in the same type of polymer material an optimum content of comonomers in the structure: from MA-VBC-S these value is $X_{VBC}=X_S$ =≈0.26, and respectively MA-VBC-DCPD $X_{VBC}=X_{MA}$ ≈0.43.

In order to describe the coordination of metal ions on the polymer supports by complexation theories it will be necessary to consider some particular aspects. So, for polymer materials characterized by low wettability (MA-VBC-DCPD) the binding of the metal ion is predominant an inter-chain. Increasing the wettability by S sequence we decrease the sterical hindrance, and by consequence the binding of the metal ion is preferred a chain level, so favourable for Cu (II), characterized by a large ionic radius (1.86Å).

IR spectra provide qualitative data regarding the structure of the polymeric supports and of their polymer-metal ion complexes (figure 5).

We remark in the same analysed cases disappearance of peaks characteristic for MA, situated at 1855 and 1784 cm^{-1}.

X ray spectroscopy offers information regarding the degree of crystallization and them nature (figure 6). As by excellence the polymers are amorphous materials, the crystallinity of polymer-ion complexes is a consequence of the presence of the metal ions. This impose a particular organization of ligands which are followed by apparition a crystalliform zones. We can observe the pronounced tendency for crystalline organization to the Cu polymer complete.

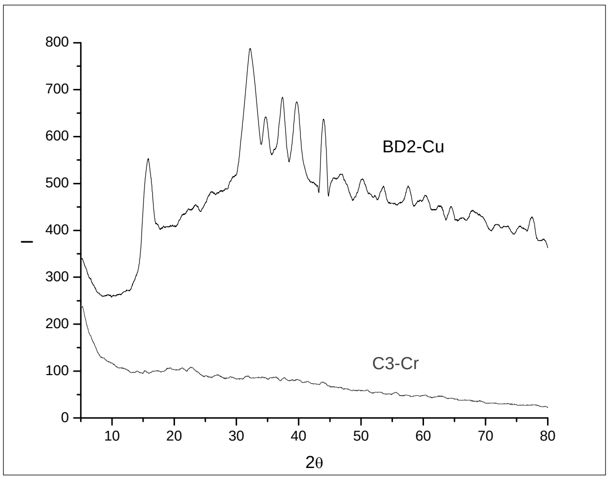


Fig.6. X-ray exemplificative spectra from polymer-ion complex

4. Conclusions

All polymer materials prepared by ternary copolymerization of MA, VBC, S, DCPD could be used for the removal of Cr (III) and Cu (II) ions. The results showed that the retention efficiency is strongly influenced by the nature and conformation of polymer material. We can spike to the selectivity for the two polymer series:

AM-VBC-S from Cr (III)
AM-VBC-DCPD from Cu (II).

In order to describe the coordination of metal ions on the polymer supports by complexation theories it will be necessary to consider some particular aspects. So, for polymer materials characterized by low wettability (MA-VBC-DCPD) the binding of the metal ion is predominant an inter-chain. Increasing the wettability, by S sequence, we decrease the sterical hindrance, and by consequence the binding of the metal ion is preferred a chain level, so favourable for Cu (II), characterized by a large ionic radius (1.86Å).

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