New Polymeric Structures Designed for the Removal of Cu(II) Ions from Aqueous Solutions

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ABSTRACT: New polymeric structures obtained by chemical transformations of maleic anhydride/dicyclopentadiene copolymer with triethylenetetraamine, p-aminobenzoic acid, and p-aminophenylacetic acid were used for the removal Cu(II) ions from aqueous solutions. The experimental values prove the importance of the chelator nature and of the macromolecular chain geometry for the retention efficiency. The retention efficiency (η_r), the retention capacity (Q_e), and the distribution coefficient of the metal ion into the polymer matrix (K_d) are realized by evaluation of residual Cu(II) ions in the effluent waters, by atomic adsorption. Also are discussed the influence of pH, the thermal stability of the polymer, and their polymer–metal complex, as well as the particular aspects regarding the contact procedure and the batch time. Based on the polymers and polymer–metal complexes characterization a potential retention mechanism is proposed. All polymer supports as well theirs metal–complexes are characterized by ATD and FTIR measurements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1397–1405, 2007

Key words: polymer–metal-ion complexes; waste waters; Cu(II) removal; chelator

INTRODUCTION

The increased industrial use of heavy metals, in the last decades, has inevitably raised the risk of environmental contamination with nondegradable metallic pollutants. The diminishing of their content in the environment may be realized in two possible ways, either by decreasing their influx in the environment or by removing them from contaminated media.

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 complexing extractors, ion exchangers, or polymeric adsorbents with selectivity for a wide range of metal species.[4–8]

The selectivity of macromolecular polyligands for metal ions is an extensive subject.[9–15] 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:

- 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.
- Through a complexing process determined by the polychelator groups position in the macromolecular chain and by their relative distances.

This study is a preliminary 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) ions from aqueous solutions. The retention mechanism is suggested and discussed. Operational parameters such as chelator nature, pH value, and batch time were investigated.

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EXPERIMENTAL

Six polymeric structures were obtained from maleic anhydride/dicyclopentadiene copolymers (MA-DCPD) synthesized and characterized in our laboratory (64.65% mole MA, $M_n = 2860$, $I_D = 7$).

The reactants used for the chemical transformations were as follows: p-aminophenylacetic acid 99% and triethylenetetraamine (TETA) from Riedel De Häin AG, Seelze, Hannover; p-aminobenzoic acid from Reactivul, Bucharest; hexane (H) and N,N-dimethyl-formamide (DMF) from Fluka; diglycol-dibutyl-ether (DGBE) from Merck; diethyl ether (EE) from Reacti-vul. Acetic anhydride and sodium acetate (Reactivul, Bucharest) were used as anhydrization agents in the imidization step. $CuCl_2 \cdot 2H_2O$ (Fluka) was used to prepare the metal ion solutions. The pH was adjusted with 1N NaOH and 1N HCl solutions from Reactivul.

Applying the experimental procedure proposed by Patel and coworkers,[9] from chemical modification of MA-DCPD copolymer structure with p-aminophenyl-acetic acid were obtained the copolymer structures APA and APA1, in semiamide (amic) and imide form, respectively. Similarly, with p-amino-benzoic acid were obtained the copolymer structures ABA and ABA1, in semiamide (amic) and imide form respectively.

B and C copolymer structures are the result of the chemical changes induced by superficial crosslinking graft of TETA on AM-DCPD pearls.[16,17]

The retention capacity of the polymeric structures was studied on aqueous solutions with exact content of Cu(II) ions. Because the polymeric structures used for Cu(II) ions retention are not totally soluble in DMF (excepting polymer ABA), the following contact procedures are used:

(a) The contact between the polymer suspension and the Cu(II) ions solution (abbreviated "suspension")
(b) The polymer suspension was filtered and the filter liquor was mixed with the metal ion solution (abbreviated "liquor")
(c) The polymer suspension was filtered and the "pseudo solid" phase of polymer was contacted with the metal ion solution (abbreviated "gel")

The experimental set-up consists of a reactor, $V = 0.25$ L, provided with mechanical stirring and thermostat. To avoid the contact with the surrounding medium, the experiments were carried out in a sealed vessel. The stirring rate was maintained at 500 rpm and the temperature was kept at 22 $\pm$ 0.5°C. The batch time varied from 30 min to 4 h and the pH was 2–8. The volumetric ratio between the polymer solution and the metal ion solution was 0.6 as recommended in the literature.[10,14,18–20] A typical

procedure used for the preparation of the complex was as follows: a polymer solution (liquor) or suspension (10 mL, 1% in DMF) was added to the aqueous metal solution (copper (II) chloride (9 mL) 2.9 g/L or 2.82×10^{-2} mol/L), under stirring. The reaction mixture was maintained in these conditions for 2–4 h. The precipitated polymer–metal ion complex was separated by filtering, washed with warm water and ethanol, and dried at 60°C to avoid the destruction of the polymeric support.

The content of Cu(II) ions in the effluent and in the washing waters was determined by means of an atomic adsorption spectrophotometer (PerkinElmer AAS3-1988).

The polymers and metal ions–polymer structures were characterized by IR spectroscopy, on a Shimadzu FTIR 8000 infrared spectrophotometer as potassium bromide pellets, and by X-ray diffraction, Shimadzu XRD 600; differential thermal analysis (DTA) was performed on a Shimadzu DTG-TA-51H analyzer, under air, at a heating rate of 10°C min^{-1}; porosity analysis was recorded on a Hg porosymeter (Pascal 240/140).

RESULTS AND DISCUSSION

The efficiency of the employed materials as well as the discussions regarding the complexing–chelating mechanisms are 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).[18] These parameters are defined by the following equations:

$$\eta_r = \frac{\Delta C}{C_0} = \frac{C_0 - C_f}{C_0} 100 \, (\%) \tag{1}$$

$$Q_e = \frac{m_c}{E_{Me} m_p} \, (E_{Me}/\text{g polym}) \tag{2}$$

$$K_d = \frac{m_c V}{m_{Cu} m_p} \, (\text{mL/g}) \tag{3}$$

where C_0 is the initial metal ion concentration, [g/L], C_f is the metal ion concentration in the effluent [g/L], m_p is the polymer weight [g], V is the volume of the polymeric solution in the reactor [mL], m_c is the amount of metal ion retained by the polymer [mg], and m_{Cu} is the amount of metal ion in the reaction medium [mg].

Polymer characterization

The six polymeric structures differ not only by the nature of the active chelator sequences but also by the transformation degree and by the crosslinking degree (Table I).

TABLE I
Characteristics of Polymer Substrates

Chelator groups	Polymer	Transf. degree	Crosslink. degree
$-NH_2$; $-NH-$; $-COOH$; $-\overset{O}{\underset{\|}{C}}-N-\overset{O}{\underset{\|}{C}}-$	A	–	14
$-\overset{O}{\underset{\|}{C}}-NH(CH_2CH_2NH)_2CH_2CH_2NH-\overset{O}{\underset{\|}{C}}-$	B	63.74	50.1
(diimide structure) N(CH_2CH_2NH)_2CH_2CH_2N	C	97.40	52.3
$-NH-$; $-COOH$	APA	–	10.12
$-\overset{O}{\underset{\|}{C}}-NH-\bigcirc-(CH_2)_nCOOH$	APA I	31.86	17.67
(imide)-N-$\bigcirc$-(CH_2)_nCOOH	ABA I	43.61	15.67

Crosslinked structures appear both in amic and imidic generating processes, because of interchain reactions involving functional groups. For all proposed polymeric structures, the reticulation degree was evaluated as "insoluble fraction". A–C series, APA, APA1, ABA1 copolymers are characterized by gel fraction, while ABA does not develop a gel fraction (Table I).

IR spectra provide qualitative and quantitative data regarding the structure of the polymeric supports and of their polymer–metal ion complexes. The conversion of the anhydride group to the semiamide and the respective imide forms can be evaluated.[21]

Theoretical adsorption peaks at 1780 and 1860 cm^{-1} are typical for the anhydride unity. Copolymers AM-DCPD undergo a shift to 1782 cm^{-1} and, respectively, 1865 cm^{-1}. Following the reaction with the amine derivative, the characteristic adsorption bands corresponding to amide I band (1655 cm^{-1}) and amide II (1550 cm^{-1}) appear at the same time with the peak specific for the carboxylic group (1705 cm^{-1}) (Table II and Fig. 1). Because we used the same amount of polymeric component for preparation of KBr pellets, the

evaluation of the cycling degree, and subsequently the imidization process, is possible by measuring and comparing the specific surface under the amic peak.[21]

The polymeric supports were characterized by DTA. DTA diagrams are represented in Figure 2 and all data obtained are presented in Table III. Being partial transformation compounds of copolymer AM-DCPD, the conversion does not amount to 100% because of sterical hindrance at the main chain level. On the other hand, a complete transformation degree would promote totally insoluble compounds with reduced moistening capacity even in organic solvents: closed pores. The transitions registered in the temperature range 20–150°C, characterized by weight losses of 0.3–20% are assigned to chemical reactions finishing off. The basic structure MA-DCPD shows two transitions with peaks at 228.9°C and, respectively, at 340°C. The first weight loss range was assigned to the loss of the solvent traces. The second range, characterized by a significant exothermic effect, accompanied also by a high weight loss, was attributed to the destruction of the copolymer reactive functional groups. For the derived

TABLE II
IR Spectral Data for Polymers

Polymer	—COO (1680)[a]		—NH— (820)[a]		(1780)[a]		(1860)[a]	
	h	A	h	A	h	A	h	A
B	1683		808.11		1775.4		1868	
	1.52	37.95	1.229	162.61	1.46	33.72	1.25	31.16
C	1685.6		804.26		1772.4		1868	
	1.40	34.68	1.169	158.34	1.30	29.8	1.25	31.16
ABA	1652		864		–		1845.7	
	1.73	162.94	1.233	82.87	–		1.36	59.94
ABA1	1685		804		–		1868.8	
	1.50	37.03	1.282	190.05	–		1.37	31.4
APA	–		813		1774.3		1845.7	
	–		1.176	60.55	1.63	77.53	1.31	27.6
APA1	1685		804		–		1868.8	
	1.50	37.03	1.289	190.0	–		1.37	31.4

h and A are the height and specific area of the peak.
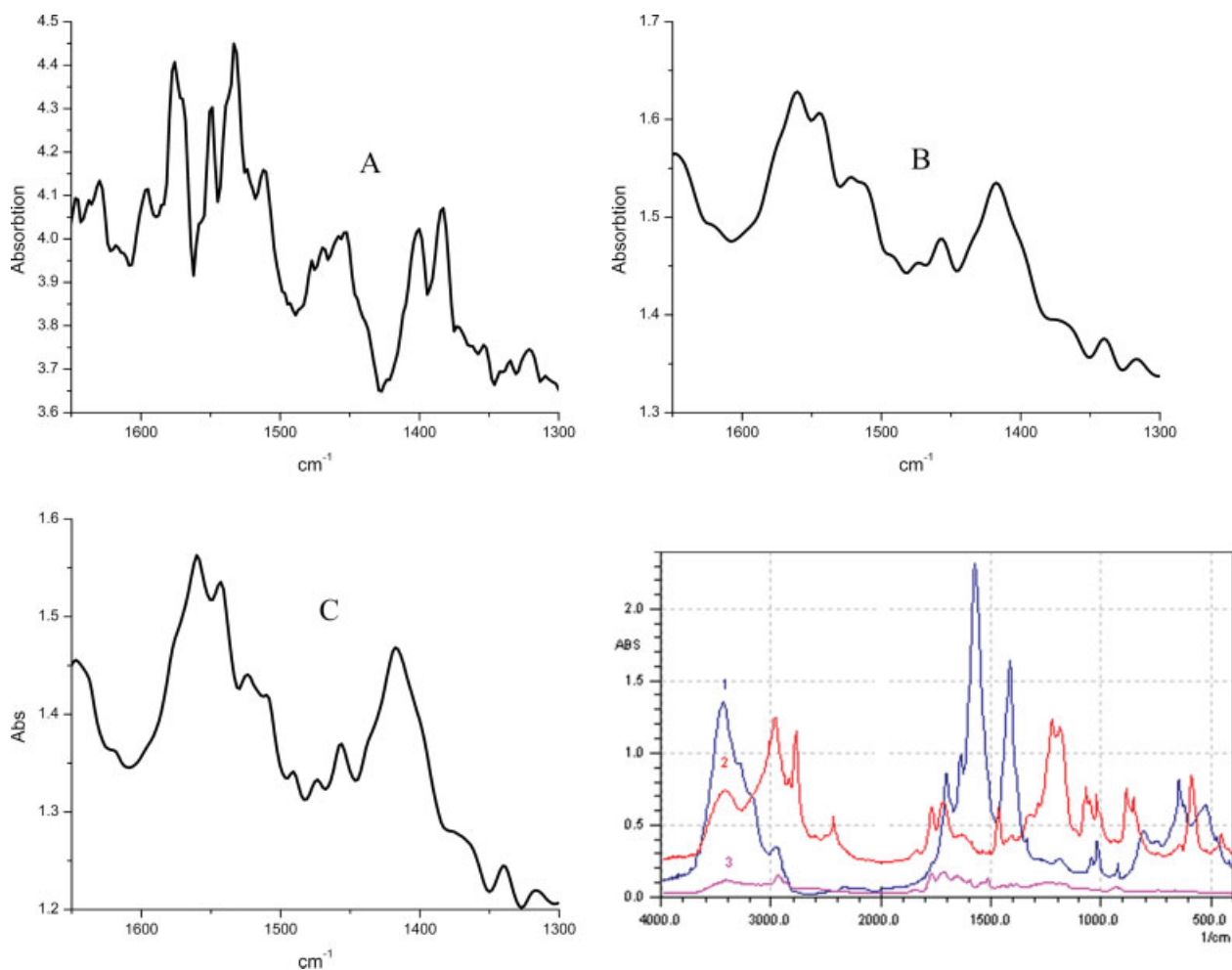[a] Theoretical values.

Figure 1 IR spectra for polymers: (a) A, B, C; (b) 1: APA1; 2: ABA; 3: APA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
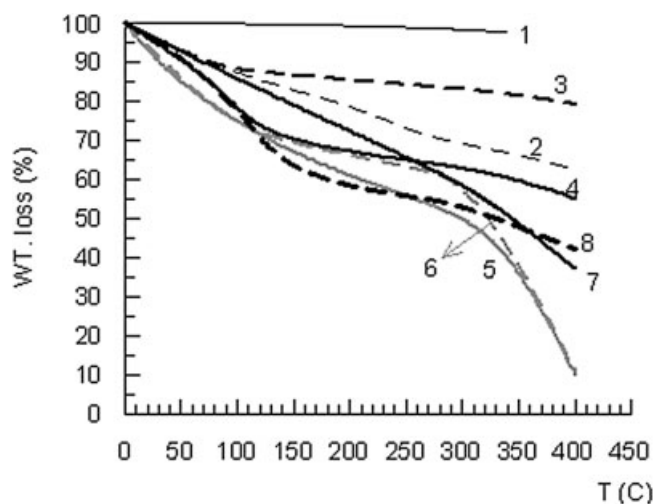
Figure 2 Weigh loss obtained by TGA curves of polymers structures: 1: MA-DCPD copolymer; 2: A; 3: B; 4: C; 5: ABA; 6: ABA I; 7: APA; 8: APA I.

structures of amic and imidic kind, at least a degradation transition is noticed at intervals intermediary to those existing in the copolymer (Table III). These transitions are assigned to destruction at the functional groups of the substituent. Structures C, APA1, and ABA1 possess the best thermal resistance because of the small amount of carboxylic groups (the main cause of weight loss) as a consequence of the imidic cycles closing reactions.

Porosity analysis offered information concerning the microstructure of polymeric materials. Polymer B exhibits a large pore distribution, with an average dimension of 11.96 μm and a specific surface area of 3.151 m^2/g. In the case of polymer C, the maximum of the distribution shifts to 7.62 μm, the specific surface area is 2.998 m^2/g, and the density is four times bigger than that of polymer B.

Characteristics of the chelating process

Influence of the contact procedure

Figure 3 presents the residual concentration of Cu(II) ions (mE/L) and the evolution of the retention process for these contact procedures, for polymers B and C [Fig. 3(a)], and APA and APA 1 [Fig. 3(b)].

The best results for the contact procedure were obtained for "suspension". This may be explained by the fact that the decay of the hydrophobic organic material in direct contact with water is avoided by forming a homogeneous suspension. Consequently, all further experiments were carried out in this manner.

Influence of the batch time

Generally, the complexing processes of metal ions are determined by interface diffusion phenomena. It would be expected that the access to all functional chelator groups will be favored by a higher contact time but the experimental results proved a decrease of the retention efficiency with the increasing of the batch time for more than 2 h.

Several batch times ranging from 30 min to 4 h were experimented to establish the optimum reaction time. The best retention efficiency was obtained for a time of 2 h (Fig. 4).

The diminishing of η_r at higher times may be explained, in a first approach, by a shift in the complexing equilibrium, as a direct consequence of the structural–conformational changes of the polymer chains after the coordination process.

Influence of pH

The dependence of the retention capacity versus pH and the nature of the chelator groups are presented in Figure 5. In all cases a maximum of the retention efficiency is situated at pH = 7. At higher pH values a flat area [Fig. 5(a,b)] or a dropping of the retention efficiency [Fig. 5(c)] follows. The retention efficiency of

TABLE III
Thermogravimetric Analysis Data for Polymer Materials

| Cod	Decomp. temp. (°C)		Peak temp., T_s (°C)	Mass loss (%)
	T_i	T_f		
AM-DCPD	27.13	272.77	228.9	0.359
	272.77	352.3	340.00	2.05
A	27.86	71.53	49.936	6.936
	71.53	164.45	108.85	7.591
	168.04	236.32	204.28	6.513
	236.32	293.68	271.85	2.622
	293.68	348.96	345.00	9.452
B	28.21	103.46	67.72	10.999
	103.46	131.91	114.58	1.615
	131.91	281.82	230.71	2.887
	281.87	324.73	347.9	2.552
C	28.09	77.78	58.85	7.989
	77.78	110.54	95.27	9.606
	110.54	161.17	128.09	10.42
	161.17	307.42	286.64	6.007
	307.24	331.06	286.64	2.502
	331.06	346.35	339.74	1.747
ABA	28	284.7	269.00	24.664
	284.7	320.48	298.00	21.929
	320.48	349.46	340.24	5.87
ABA1	27.11	101.96	70.474	20.474
	101.96	230.72	114.74	9.946
	230.72	302.15	279.97	7.113
	302.15	348.44	318.13	5.304
APA	27	274.3	106.94	15.803
	274.3	317.49	297.83	24.433
	317.49	354.56	330.6	6.247
APA1	26.34	122.71	96.63	15.732
	122.71	204.15	115.98	22.422
	204.15	291.96	263.44	6.846
	291.96	316.17	304.16	1.476

(a)

(b)
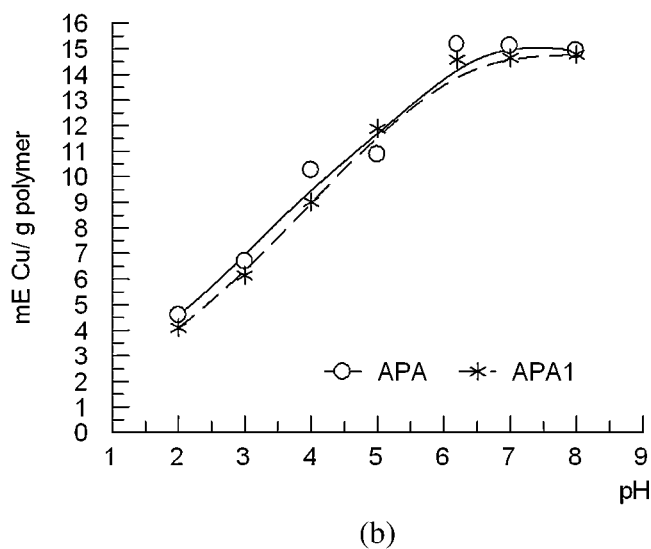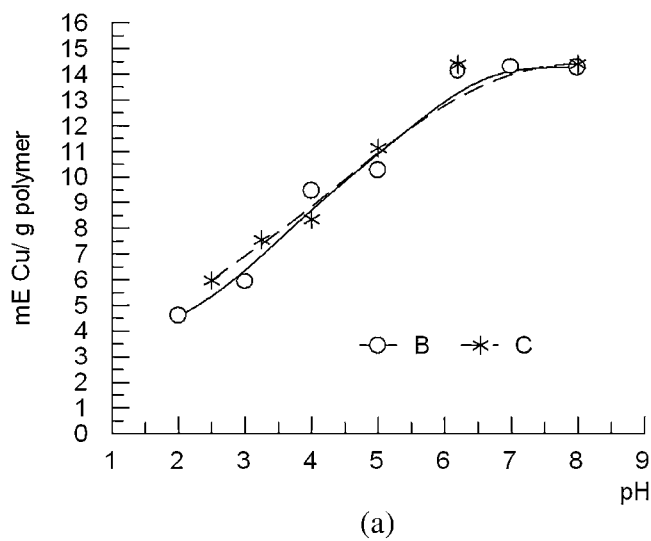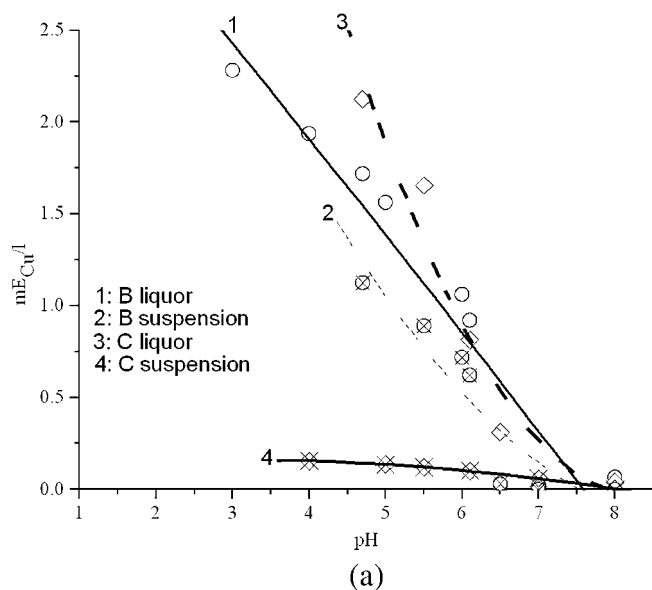
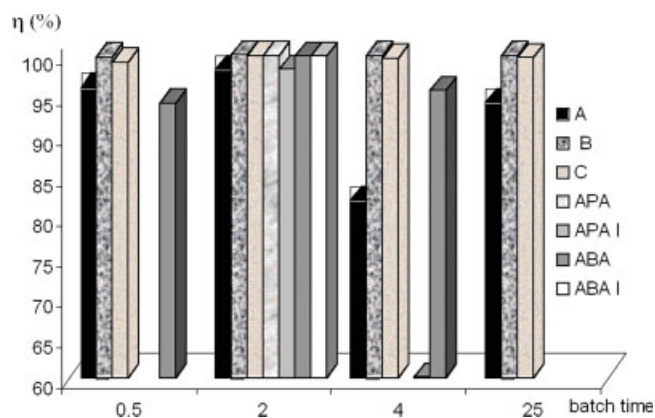**Figure 3** Residual profile of Cu(II), batch time = 2 h.

Figure 4 Retention efficiency pertaining to the nature of the polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
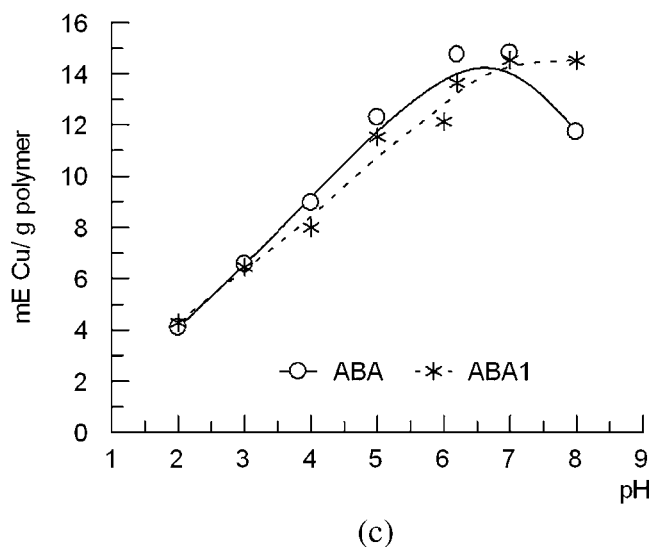
(a)

(b)

(c)

Figure 5 Retention profile of polymer ''suspension'' substrates, batch time = 2 h.

the organic molecules is limited, at acid pH values, by the precipitation of metal hydroxide. At the same time, the aminic/amic groups are protonated, leading to an electrostatic repulsion of the polymeric support for the Cu(II) ions. The gradual increase of the pH towards basic values determines a drop of these repulsive forces due to the decrease in the number of protonated chelator groups. Moreover, at pH = 7, the hydrolysis of unchanged anhydride groups from the main chain is favored and consequently the "density" of the chelator groups increases.

The analysis of the retention curves from Figure 5(c) shows the special behavior of ABA polymer, which presents a lesser retention capacity because of a specific retention mechanism by electrostatic interactions.

Influence of the polymer structure and the retention mechanism

The nature of the ligand groups and their density in the polymer skeleton influence the retention capacity for metal ions. To prove the high retention efficiency of the proposed polymers, quite concentrated Cu^{2+} solutions were used (industrial waste waters have usually concentrations 10 times lower).

Both polymers B and C have good retention efficiency (Q_e = 14.30 and 14.40 respectively; K_d = 486 and 677 respectively). For these polymers the complex polymer–metal ion structure involves, probably, majority the nitrogen ions from TETA [Fig. 6(a)]. The presence of TETA sequences in their structure favors new conformational binding possibilities: they trap
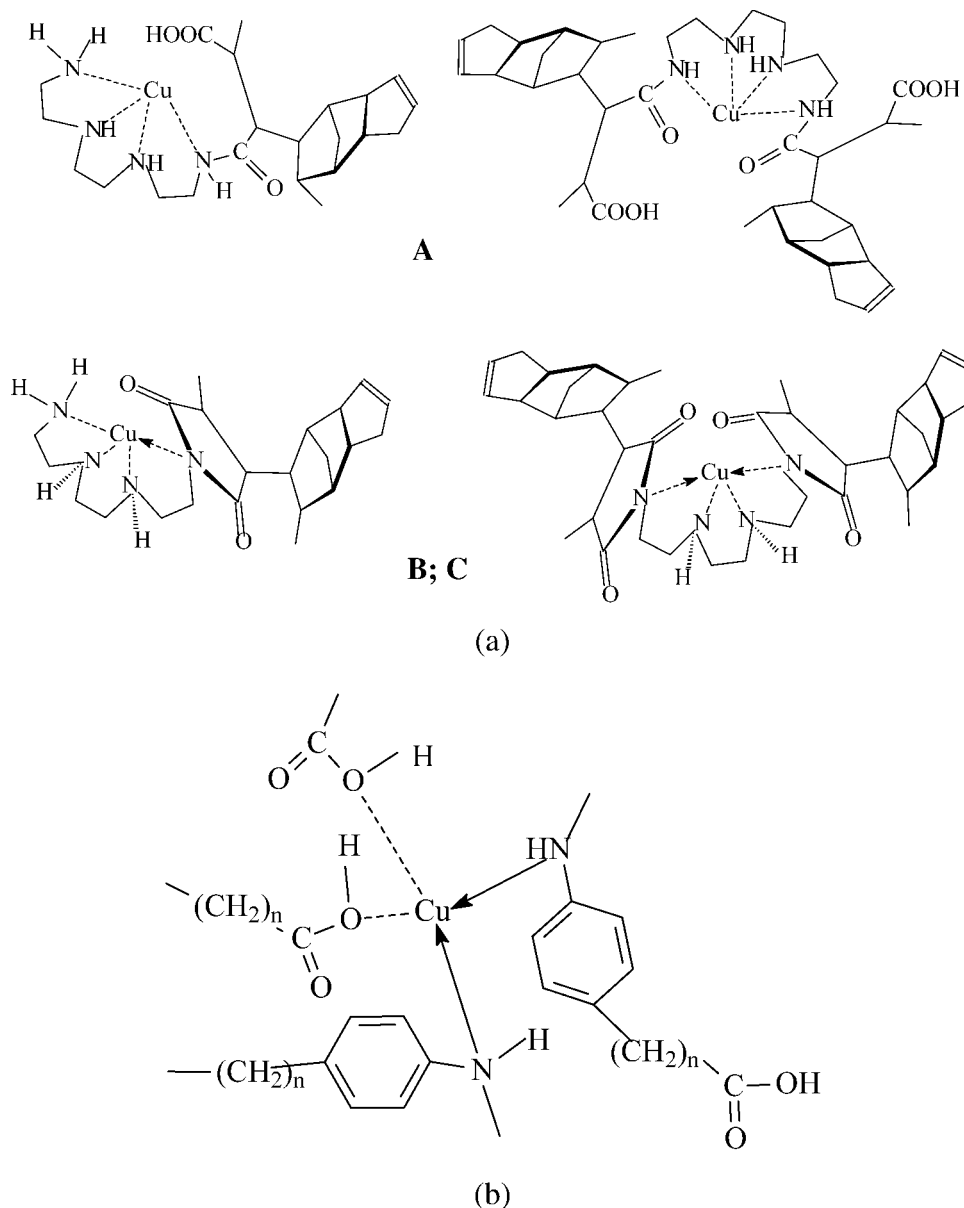

Figure 6 Possible complexing geometries: (a) A, B, and C polymers; (b) APA, APA1 (n = 1); ABA, ABA1 (n = 0).
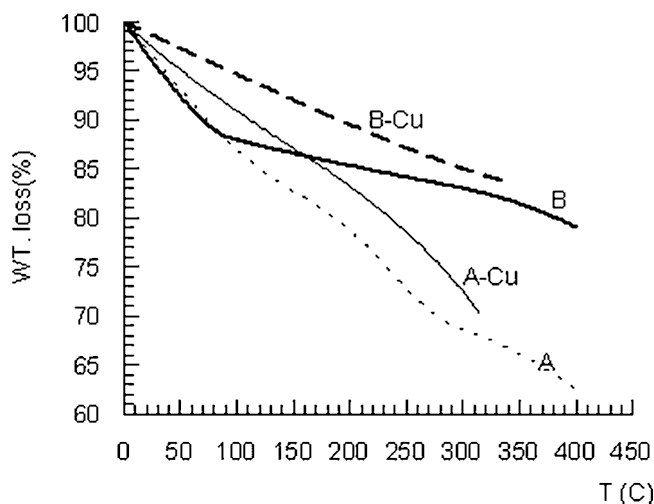
Figure 7 Weigh loss obtained by TGA curves for polymers and polymer–Cu complexes.

the metal ion into a pseudoclosed structure, which is a stable chelator structure [Fig. 6(a)] specific for each metal ion.[14] On the other hand, the presence of amine groups in their structure determines a good affinity for Cu(II) ions. Polymer C has a better retention capacity than does polymer B, though the imidization degree is higher. The increase of the crosslinking degree (from 50.1 to 52.3) and transformation degree (from 63.74 to 97.40), determines a favorable arrangement of the chelator groups.

The advance of the imidization process determines the increase of the superficial density of the network with preestablished dimensions.

As a consequence, for these two polymers, B and C, the chelating process may be explained by a double mechanism of complexing by trapping in a stable cage and by chemical coordination.

For series APA/APA1 and ABA/ABA1 polymers, the complexing process involves both oxygen from the carboxylic groups and nitrogen ions from the amic groups and imide groups respectively [Fig. 6(b)]. The ligands of these materials are highly rigid sequences comparative with TETA determining a complexing geometry, which involves minimum two neighbor chains. The flexibility of the chelator sequences in APA and ABA polymers, with amic structures, explains the higher retention yield [Fig. 6(b)].

Though ABA is totally soluble in DMF and might provide the maximum of the retention efficiency, the best results were obtained for APA due to the presence of the methylene groups from the p-phenyl acetic acid, which improve the flexibility of the chelator groups.

The calculated values of the retention parameters suggest that polymer APA presents the best retention capacity and the higher value for the distribution coefficient in the polymer matrix ($Q_e = 15.145$ mE$_{Cu}$/g polymer; $K_d = 650$ mL/g). The decrease in the retention

capacity for APA1 and ABA1 polymers, imide forms, ($Q_e = 14.63–14.85$ mE$_{Cu}$/g polymer; $K_d = 111–287$ mL/g) is a consequence of the macromolecular chain higher rigidity due to the closure of the imide ring.

The high value for Q_e at low acid pH for polymer APA suggests a nonideal retention mechanism characteristic for carboxylic groups. In this case the dominant species for the complexing process is the ionic pair: polymer–metal ion.[4,22]

Physical characteristics for polymer–metal complexes

Thermal analysis, the results of which are depicted in the Figure 7, provides information regarding the thermal stability of the polymer–metal complexes. The weight losses (6–14%) in the range of 30–190°C are due to desorption of the coordination water. In the second range, 190–300°C, the losses, 2–9%, suggest a degree of decarboxylation of the support up to 20%. The weight losses, in the third range, 300–347°C, represent the total decarboxylation degree of the support.

Complementary information regarding the complexing ways and the complexes structures are provided by X-ray diffraction. Figure 8 presents the X-ray spectra for A–C polymers. All cases present a shift for CuCl$_2$ characteristic maxima, explained by the metal trapping in an amorphous polymer structure. The influence of the polymer structure is obvious. It may be noticed that at the same time with the increasing of the microstructural organization degree through consecutive amide-imidization reactions (from A to C), the diffraction spectra present well-definite peaks. The best diffraction spectrum is for the complex obtained on the crosslinked structure of the C polymer.

Because usually the polymeric structures are amorphous materials (Fig. 8), we may declare that the polymer–Cu(II) complex crystallinity is determined mainly by the metal ion presence. So, the insertion of a metal ion in an amorphous structure with low organizing
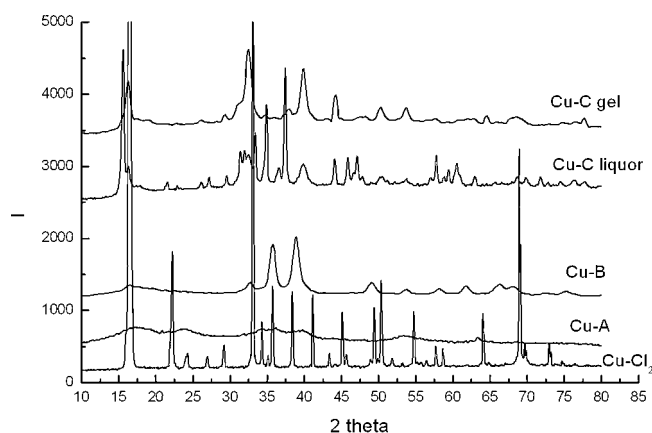

Figure 8 X-ray diffraction spectra for A and B polymers and polymer–Cu complexes.

degree determines probably a new supramolecular organization form, which tries to copy the organization of the basic inorganic crystal.

CONCLUSIONS

Six new polymeric structures, derived from MA-DCDP copolymers, were proposed for metal ions removal from aqueous solutions.

The experimental values for the retention capacity and distribution coefficient in the polymeric matrix point out the importance of the nature of the chelator groups and macromolecular chain geometry. Polymer APA, characterized by a rigid structure, showed the best retention properties towards Cu(II) ions, by involving a minimum two neighbor polymeric chains.

The chelating process was explained by a double mechanism of complexing: trapping in a stable cage and chemical coordination.

Experimental studies carried out on aqueous solutions with Cu(II) ions content, in the limits of industrial waste waters, established the best operating parameters for the retention of copper ions: contact procedure, batch time, and pH values.

The best results for the contact procedure were obtained when the polymer suspension was added in drops, under stirring, to the metal ion solution for a batch time equal to 2 h. Good results were obtained for pH = 7.

These experimental results might be the start for a new clean method of treatment for residual waters with metal ions content.

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