Synthesis and Characterization of Polymer Metal Chelates Derived from Poly(2,2,3,3-tetra methyleneaminecyclopropyl)phenyl Acrylate

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ABSTARCT: The new method for the synthesis of *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate (*P*-TCP) was applied. In this method, *p*-acryloyloxybenzaldehyde was reacted with malononitrile and cyanogen bromide at 0°C in short time. Then, the *P*-TCP monomer was polymerized by free-radical polymerization to obtain a poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate with multicyanocyclopropane functionalities in the pendant group. The nitrile functions in pendant groups of the prepared polymer were reduced to primary amines using $NaBH_4$ and $NiCl_2$ salts at 65°C in dry ethanol for the preparation of poly(2,2,3,3-tetra methyleneaminecyclopropyl)phenyl acrylate (PTAP) as a new polymer. The PTAP was soluble in acetone and ethylacetate. The PTAP was examined for the removal of Cu(II), Ni(II), Zn(II), and Cr(III) ions from aqueous solutions under noncompetitive and competitive conditions at various pH. The adsorption rate was high (<60 min). The complexation of selected heavy metal ions by the PTAP is strongly dependent on the pH of medium and the adsorption of all selected metal ions was more favorable at the pH 7. Also the maximum sorption of the PTAP for selected metal ions under competitive conditions belongs to Cu(II) at pH 7. The k_d value is calculated for the prepared chelating polymer, and the result indicates approximately high values in the case of Cu(II) ion. The synthesized polymer and its metal chelates were characterized by FT-IR, ^{1}H NMR, thermogravimetric analysis, gravimetry, UV–vis spectroscopy, and atomic absorption spectrometry. Adv Polym Technol 2018, 37, 21685; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21685

KEY WORDS: Adsorption, Metal-Polymer Complexes, Malononitrile, Radical Polymerization

Introduction

In recent years, preparation of specific polymers either soluble or insoluble in water with various functional groups has been developed, which can adsorb metal ions in aqueous and nonaqueous media.[1,2] Environmental contamination by heavy metal ions is a serious problem. Toxic natures of heavy metals are generally refractory and cannot be degraded. Thus, safe and effective wastewater treatment containing heavy metal ions is always a challenge to industrialists and environmentalists, since cost-effective treatment are not available.[3] Another problem encountered in the removal of the metal ions is that the target species are usually in low concentration and in complex mixtures.[4] The most promising technique for removal of metal cations is their adsorption on organic and polymeric sorbents containing chelating functional groups. In general, functionalized polymers for metal ion complexation can be prepared either by derivation of a basic polymer with the desired ligand or by polymerization of the corresponding ligand derivative. The great deal of attention has been paid for polymer–metal complexes by many chemists, because not only they are excellent models for metalloenzymes but they have also led to developments in metal ion separation and recovery of metal ions.[5–8] Also increasing environmental concerns in wastewater treatment has led to the use of organic ligands anchored to solid supports or synthetic polymers in order to remove and recover important metal ions from aqueous solutions.[9] Among functionalized polymers, those containing amine and nitrile have attracted much attention. These groups can be introduced into or graft onto the backbone of polymer chains.[10–14] Polymers bearing such groups have stable complexes with various heavy metal ions. Recently, aminated polymers have been also used for the removal of metal ions such as Cu(II), Pb(II), and Fe(II) from aqueous solution, but with low metal sorption capacity.[15] Therefore, we attempted to prepare new complexing polymer materials with high sorption capacity, which can be used in wastewater treatment. In this work, the *P*-TCP was prepared by the reactions of *p*-acryloyloxybenzaldehyde with malononitrile and cyanogen bromide. Then, the *P*-TCP monomer was polymerized by free-radical polymerization method to obtain

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a poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate polymer with multicyanocyclopropane functionalities in the pendant group.[16] Finally, a new polymer with amine pendant groups, poly(2,2,3,3-tetramethyleneaminecyclopropyl)phenyl acrylate (PTAP), was synthesized by nitrile reduction of cyanide groups in poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate to amine for the first time.[17–19] The resulting polymer was characterized and used as chelating agents for the removal of Cu(II), Ni(II), Zn(II), and Cr(III) ion in competitive and noncompetitive conditions and their metal sorption capacities were measured by gravimetry, UV–vis spectroscopy, and atomic absorption techniques.

Experimental

INSTRUMENTS

Melting points were measured with a digital melting point apparatus (Electrothermal, Rochford, UK). The IR spectra were determined in the region 4,000–400 cm^{-1} on a NEXUS 670 (Waltham, Massachusetts, USA) FT-IR spectrometer by preparing KBr pellets. The ^1H NMR spectra were recorded on Bruker 300 FT-NMR (Karlsruhe, Germany) at 300 MHz (Urmia University, Urmia, Iran) and obtained on solution in acetone-d_6 or $CDCl_3$ as solvent using tetramethylsilane (TMS) as an internal standard.

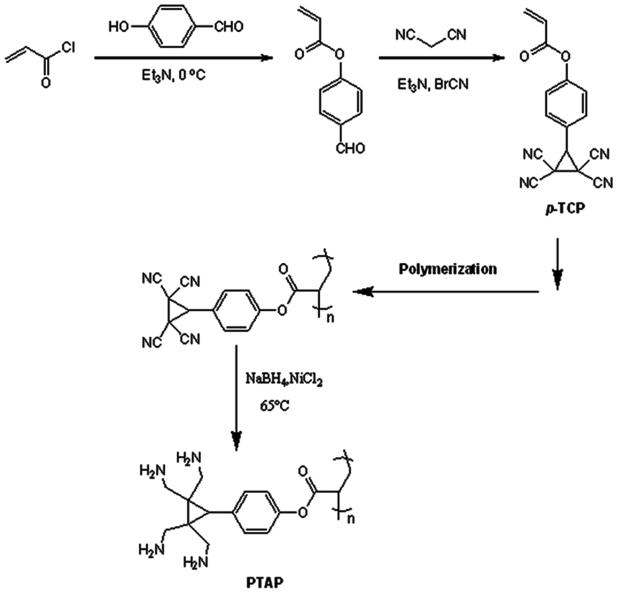
The metal absorption capacities of polymers were measured using an AA-670 Shimadzu atomic absorption spectrometer (Tokyo, Japan) and ANA77 (UV–Vis) spectrophotometer (Japan) at room temperature in aqueous solution. The thermal stability of polymers was studied by a Thermal Analysis METTLER STAR SW 10.0 (Schwerzenbach, Switzerland) by scanning up to 600°C with the heating rate of 10°C/min.

MATERIALS

The reagent grade chemicals were purified by distillation or recrystallization before use. *p*-Hydroxybenzaldehyde (Merck) was crystallized from water containing a small amount of sulfuric acid and dried under vacuum. Acryloylcholoride (Merck) was distilled and used immediately. Cyanogen bromide was synthesized based on reported reference.[20] Malononitrile, sodiumborohydride, triethylamine, and solvents were purchased from Merck or Aldrich and used without further purification. Copper (II) nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], nickel (II) nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], zinc (II) nitrate [$Zn(NO_3)_2 \cdot 6H_2O$], and chromium (III) nitrate [$Cr(NO_3)_3 \cdot 3H_2O$] were provided from Fluka and used without further purification.

PREPARATION OF *p*-ACRYLOYLOXYBENZALDEHYDE

The procedure of *p*-acryloyloxybenzaldehyde synthesis was illustrated in Scheme 1. Briefly, into a 100-mL round bottom flask equipped with inlet and outlet of nitrogen gas, magnetic stirrer, and dropping funnel, freshly distilled acryloyl chloride (1.81 g, 0.02 mol) in dry diethylether (10 mL) was added dropwise to a solution of *p*-hydroxybenzaldehyde (2.2g, 0.018 mol), triethylamine (2.02 g, 0.02 mol), and diethylether (30 mL) with stirring at 0°C. The resulting solution was stirred for 2 h at 0°C and additional 1 h at room temperature. Triethylamine hydrochloride was filtered off and rinsed with 25 mL ethylacetate. Extractions were performed on the filtrate twice with 20 mL of HCl (1 N), once with H_2O (25 mL), and twice with saturated sodium bicarbonate (20 mL). The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The solvent was evaporated by reduced pressure, concentrated, and the resulting liquid was placed in a refrigerator (–5°C) to crystallize. The obtained white crystals were collected and washed with cold water and were dried to give 2.31 g of the *p*-acryloyloxybenzaldehyde (yield: 73%, mp 14–16°C).



Scheme 1. Synthesis of *P*-TCP and PTAP.

FT-IR (KBr): 3031 (ar-C–H), 1743 (C=O ester), 1702 (C=O aldehyde), 1596 (C=C alkene), 1152–1209 (C–O ester), 980 (C–H alkene) cm^{-1}.

PREPARATION OF *P*-TCP

Into a 10-mL Teflon-faced screw cap tube equipped with magnetic stirrer, butanol (10 mL) was added. Then, *p*-acryloyloxybenzaldehyde (0.176 g, 1 mmol), malononitrile (0.132 g, 2 mmol), and triethylamine (0.202 g, 2 mmol) were also added. The solution was cold down to 0–4°C, and then the cyanogen bromide (0.106 g, 1 mmol) was added gently. Cream color solid precipitated during 10 min, after about 30 min the solution was filtered off, washed with 15 mL ethanol and dried to give 0.362 g of the *P*-TCP (yield: 100%, mp 155–158°C).

FT-IR (KBr): 3131 (ar-C–H), 2262 (CN nitrile), 1739 (C=O ester), 1629 (C=C alkene), 1154–1212 (C–O) cm^{-1}; ^{1}HNMR (acetone-d_6) δ 2.04–2.07 (m, 2H, $=CH_2$), 2.86 (m, 1H, =CH–CO–), 5.02 (s, 1H, cyclopropyl), 7.42 (d, 2H, $J = 8.7$ Hz), 8.00 (d, 2H, $J =$ 8.7 Hz) ppm.

POLYMERIZATION OF THE *P*-TCP

A representative polymerization procedure of the *P*-TCP was as follows: A solution of *P*-TCP (0.574 g, 2.0 mmol) in ethylacetate (4 mL) was placed in a polymerization tube. Then, benzoylperoxide (3.0 mg, 0.018 mmol) was added under nitrogen atmosphere. The polymerization tube was placed in an oil bath that was thermostated at 70°C and it was shaken for 12 h. After the mentioned time, the polymerization tube was opened and their viscous product was poured into cychlohexane (100 mL). The precipitate was collected and washed with 30 mL ethanol and dried under vacuum to give poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate (0.517 g, yield: 90%).

FT-IR (KBr): 2859, 2926 (aliph-C–H), 2262 (CN), 1739 (C=O ester), 1154–1212 (C–O ester) cm^{-1}, ^1H NMR (acetone-d_6) δ 1.29–2.86 (m, 3H), 4.84 (s, 1H, cyclopropyl), 6.99–7.30 (m, 2H, aromatic), 7.6–8.01 (m, 2H, aromatic) ppm.

PREPARATION OF PTAP

In a 50 mL conical flask which was mounted over a magnetic stirrer, a mixture of poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate (0.459 g), nickel (II) chloride (1.6 mmol), and dry ethyl acetate (20 mL) was added. Then, sodium borohydride (0.302 g, 8.0 mmol) was added very cautiously while the solution was stirred vigorously at 65°C. The progress of the reaction was monitored by thin-layer chromatography (TLC) using benzene: ethyl acetate (90:10, v/v) as eluent. After completion of the reaction (controlled by TLC), the reaction mixture was filtered through a celite pad after 15 min. The nickel boride precipitate was washed with ethanol (20 mL). Then, the filtrates were combined and diluted with water (100 mL) and extracted with ethyl acetate (2 × 30 mL). The extract was dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator under reduced pressure to give the PTAP (0.418 g, yield: 91%).

FT-IR (KBr): 3389 (NH_2), 2859, 2926 (aliph-C–H), 1725 (C=O ester), 1457 (C=C phenyl), 1172–1268 (C–O ester) cm^{-1}.

DETERMINATION OF AMINE GROUP CONTENT

The following procedure[21] was used to determine the amount of amine group in the polymeric product. The polymer (0.05 g) was equilibrated with HCl (20 mL, 0.1 N) by stirring for 24 h in a sealed flask, followed by filtration and washing the residue with distilled water to remove unreacted HCl and titration of filtrate with NaOH (0.1 N) in the presence of phenolphthalein indicator was carried out.

DETERMINATION OF METAL ION ADSORPTION CAPACITIES

Noncompetitive Adsorption

The complexation of the PTAP was carried out with Cu(II), Ni(II), Zn(II), and Cr(III) ions by batch equilibration technique at various pH values [11]. The PTAP (0.05 g) was stirred with excess metal salt (0.04 mol/L, 50 mL) for 60 min. The pH of solution was set at 3–7. After being left overnight, the pH of the solution was set again. Then, the mixture was filtered, and the residual metal ion concentration in solution was determined by atomic absorption spectroscopy (AAS) or UV–Vis spectrophotometer at room temperature. The adsorption capacities (q, mmol M^{2+}/g resin) in various conditions were calculated as follows (Eq. (1)):

$$q = \frac{(C_0 - C_f) \times V}{W} \tag{1}$$

where C_0 and C_f are the initial and final concentrations (mmol/L) of metal ion in the aqueous solution, respectively, V is the volume of metal ion solution (0.05 L), and W is the weight of the PTAP polymer (0.05 g).

Competitive Adsorption

The above-mentioned procedure was applied for adsorption of metal ions in competitive condition in the solution of fourmetal ions simultaneously. The concentration of each metal ion was 0.04 mol/L.

CONTACT TIME EXPERIMENT

The influence of contact time on the sorption capacity of PTAP for metal ions under noncompetitive conditions was investigated. To a series of Cu(II), Zn(II), Ni(II), and Cr(III) solutions (0.04 mol/L, 50 mL), the PTAP (0.05 g) was added parallelly, and then the solutions were stirred at 25°C. The filtrates were sampled in specific time intervals for the determination of ion concentrations by AAS. The kinetic curve was obtained by plot of the adsorption capacities versus adsorption time. The abovementioned procedure was also repeated for competitive adsorption conditions.

DESORPTION OF METAL IONS IN ACIDIC MEDIUM

For metal ion desorption, aqueous HCl (0.2 M) was used. The polymer–metal complexes were immersed in aqueous HCl solution (0.2 M) with a magnetic stirrer at 25°C for 1 h. After that, the mixture was filtrated and the final metal ion concentrations in the solution were determined by AAS. The desorption ratio (D %) was calculated as follows (Eq. (2)):

$$D\% = \frac{\text{m moles of metal ion desorbed to the HCl solution}}{\text{m moles of metal ions adsorbed on to polymer}} \times 100 \tag{2}$$

Results and Discussions

SYNTHESIS OF *P*-TCP MONOMER

The *p*-acryloyloxybenzaldehyde was prepared by the well-known Schotten–Baumann method.[22] Then, the *P*-TCP was prepared by the reactions of *p*-acryloyloxybenzaldehyde with malononitrile and cyanogen bromide in short time (Scheme 1). The chemical structure of the compounds was confirmed by ^1H NMR

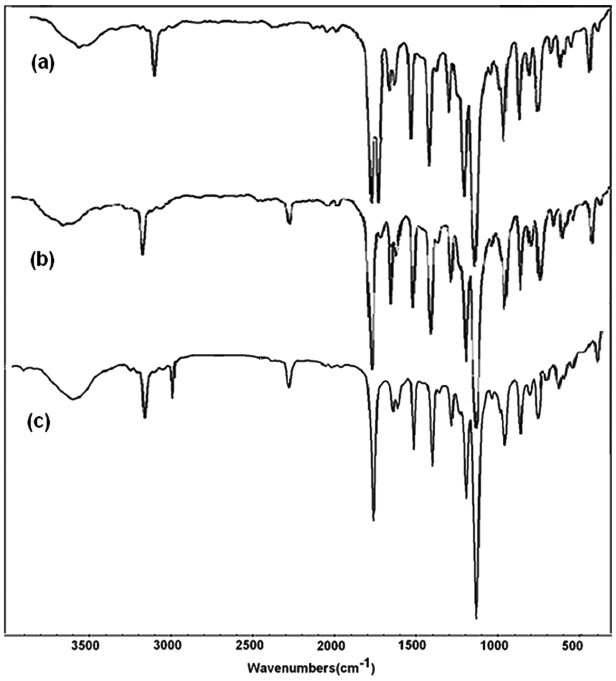


FIGURE 1. FT-IR spectrum: (a) *p*-acryloyloxybenzaldehyde, (b) *P*-TCP monomer, and (c) poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate.

and IR spectroscopy techniques. Figures 1a and 1b display the FT-IR spectrum of *p*-acryloyloxybenzaldehyde and the *P*-TCP monomer. The comparison of two spectra showed that the aldehyde peak is omitted, and the formation of nitrile groups took place at about 2262 cm^{-1}. The ^1H NMR spectrum of the *P*-TCP monomer is shown in Fig. 2a. In this spectrum, the signal at 5.02 ppm assigned to the cyclopropyl proton indicates the formation of tetracyanocyclopropane ring.

POLYMERIZATION OF THE *P*-TCP MONOMER

The *P*-TCP monomer was polymerized by free radical polymerization with benzoyl peroxide as initiator to obtain the poly(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate with multicyanocyclopropane groups. Polymerization was carried out in solution at 65°C. The *P*-TCP monomer was quite reactive toward free radical polymerization and polymerized readily. The free radical initiator did not attack the cyclopropane ring during polymerization. Chemical structures of the poly-(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate were determined by ^{1}HNMR (Fig. 2b) and IR spectra (Fig. 1c). The obtained polymer was soluble in ethylacetate, acetone, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), but was not soluble in methanol and diethyl ether.

The reduction reaction of poly(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate with sodium borohydride was carried out to obtain the PTAP polymer. The total synthetic procedure of reaction is shown in Scheme 1.

The prepared amine-containing PTAP polymer was insoluble in water. The obtained polymer was examined for complexation ability of several metal ions.

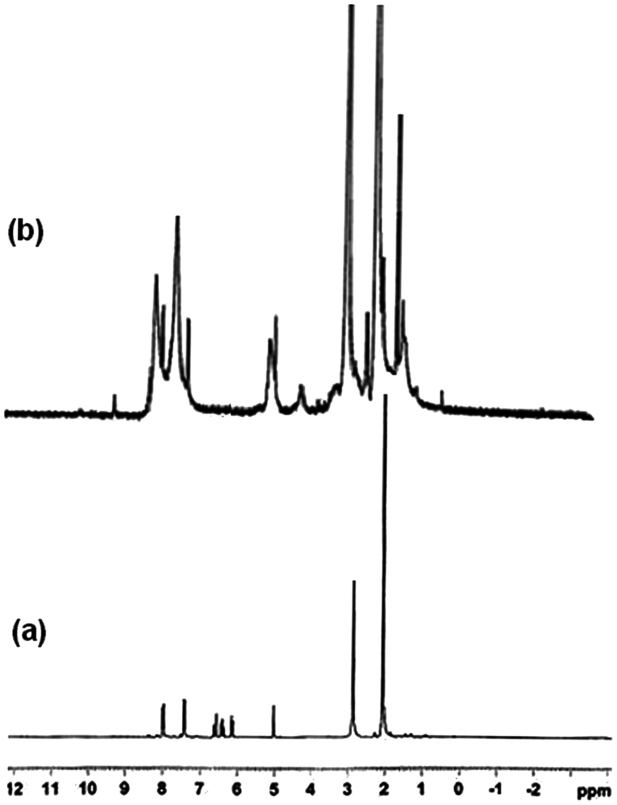


FIGURE 2. Characterized ^{1}HNMR spectra of (a) *P*-TCP monomer and (b) poly(2,2,3,3-tetracyanocyclopropyl)phenyl acrylate.

Figure 3 shows the FT-IR spectrum of PTAP with its metal complexes. The FT-IR spectrum of the PTAP (Fig. 3a) reveals that the nitrile peaks have disappeared completely and instead the absorption peaks of amine groups at higher frequency of about 3389 cm^{-1} was appeared.

By comparing the FT-IR curve of the PTAP (Fig. 3a) with its metal complexes curves (Figs. 3b, 3c, 3d, and 3e), it can be seen that the peak at 3389.5 cm^{-1} of N–H stretching was displaced toward higher wavenumber after metal ions sorption by the polymer. Meanwhile, the peak at 1375.7 cm^{-1} of C–N bending was displaced toward lower wave numbers. These changes occurred may be due to combination of nitrogen atoms in N–H with metal ions to form chelate complexes.

METAL ION SORPTION CAPACITY OF PTAP

Noncompetitive Conditions

The complexation of heavy metal ions by a chelating ligand is strongly dependent on the pH of medium. This effect can be observed especially in the formation of the coordination bond between nitrogen and metal ions. The resulting PTAP polymer was brought in to contact with aqueous solutions of metal ions in the range of pH 3–7. The metal sorption capacity of the PTAP polymer was measured with atomic absorption and UV–vis spectroscopy methods. The findings are shown in Table I. The adsorption of all selected metal ions on the polymer was more favorable at the pH value of 7. The high

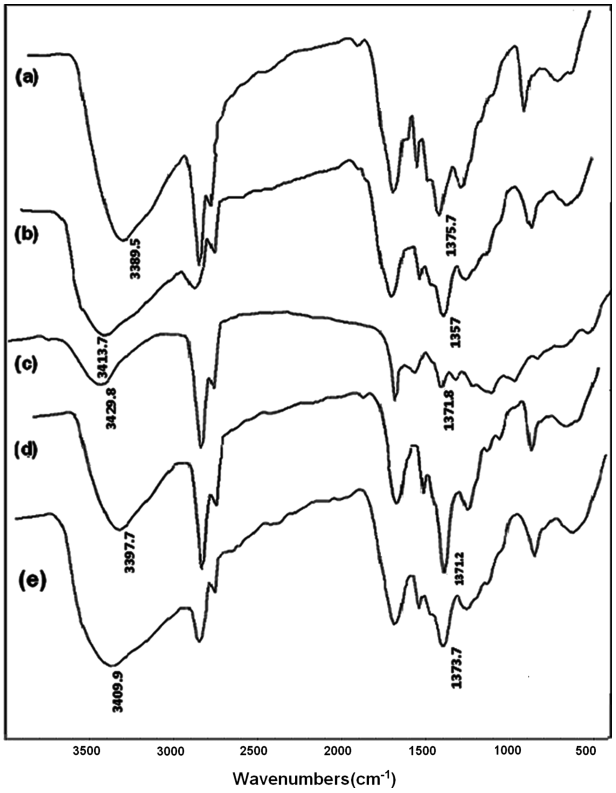


FIGURE 3. FT-IR spectra of (a) PTAP, (b) PTAP-Cu, (c) PTAP-Ni, (d) PTAP-Zn, and (e) PTAP-Cr (numbers represents the pH in which maximum metal sorption was obtained).

TABLE I
Adsorption Capacity of PTAP for Single Metal Ions and Its Distribution Coefficient at Different pH: Metal Salt (0.04 mol/L), Polymer (50 mg), and Amine Group Content in Polymer 6.36 (mmol/g)

Polymer Complex	Metal Salt	pH	Metal Sorption Capacity (mmol/g)	k_d (mL/g)$\times 10^3$
L-Cu	$Cu(NO_3)_2 \cdot 6H_2O$	7	2.61	70
		5	1.87	49
		3	0.91	46
L-Ni	$Ni(NO_3)_2 \cdot 6H_2O$	7	1.92	50
		5	1.48	38
		3	0.62	16
L-Zn	$Zn(NO_3)_2 \cdot 3H_2O$	7	0.95	25
		5	0.72	18
		3	0.51	13
L-Cr	$Cr(NO_3)_2 \cdot 3H_2O$	7	1.23	32
		5	0.85	22
		3	0.59	21

L = PTAP.

adsorption at pH 7 reveals that metal ions interaction with amine groups is favorable due to their unprotonated form.[23] At low pH value, high concentration of H^+ can react with amine groups to form protonation. In other words, H^+ can compete with metal ions for adsorption sites and reduce adsorption capacity. The highest and lowest metal sorption obtained for Cu(II) at pH 7

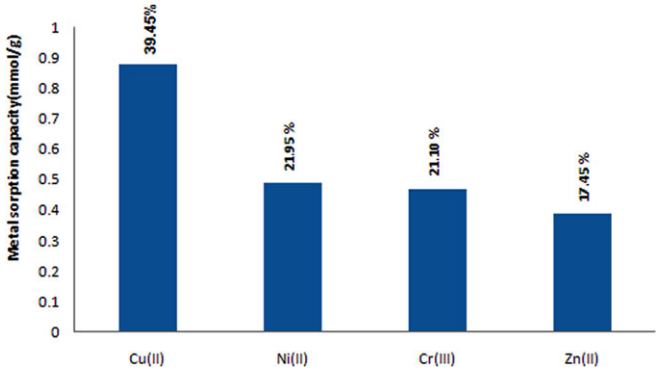


FIGURE 4. The adsorption capacities and selectivity (%) of PTAP under competitive conditions at pH 7. (total metal ion adsorption capacity = 2.23 mmol/g).

and Zn(II) at pH 3 was approximately 2.61 and 0.51mmol/g, respectively.

Competitive Conditions

It is hoped that in the presence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. The selectivity of chelating polymers for metal ion, besides pH, is mainly influenced by the presence of other metal ions competing for the active sites in the modified polymer. For that reason, it is almost impossible to generalize the order of metal sorption selectivity or to predetermine the amount of the adsorbed metal ions on the basis of the results obtained under noncompetitive conditions. In this study, metal ion sorption of the PTAP under competitive conditions as a function of pH for Cu(II), Ni(II), Zn(II), and Cr(III) ions were determined. The results are presented in Fig. 4. The maximum sorption of the PTAP for Cu(II), Ni(II), Zn(II), and Cr(III) ions under competitive conditions belongs to Cu(II) at pH 7. High selectivity for Cu(II) over Ni(II) and Cr(III) was 1.8:1 and over Zn(II) was 2.2:1 at pH 7.

EFFECT OF CONTACT TIME

To obtain the adsorption rates of metal ions under noncompetitive conditions, influence of time on the sorption capacity of the PTAP for these metal ions was studied and the results are shown in Fig. 5. The results indicate that the rate of metal sorption by polymer was rapid and reached a constant value after about 1 h.

The sorption rates for Cu(II), Ni(II), Zn(II), and Cr(III) ions under competitive conditions from multicomponent metal solutions were also determined for the PTAP and results are presented in Fig. 6.

The maximum sorption capacity for Cu(II) on PTAP is 1.8, 4.2, and 3.2 times higher than of Ni(II), Zn(II), and Cr(III), respectively. It is obvious that Cu(II) and Ni(II) sorption on the PTAP in mixed metal salt solution is slower compared with results obtained in single component solutions, probably due to the competition between metal ions for the active sites on the PTAP polymer.

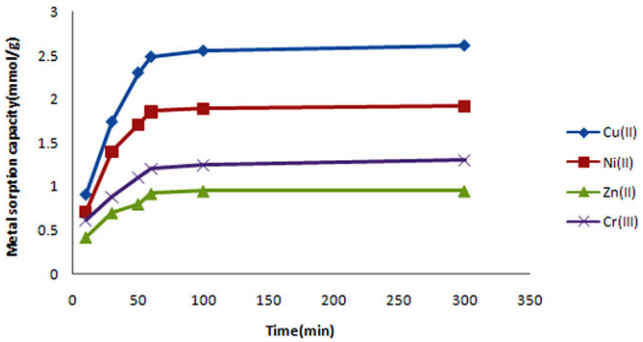


FIGURE 5. Effect of time on the sorption of metal ions (Ni(II), Cu(II), Zn(II), and Cr(III)) by PTAP polymer under noncompetitive conditions (metal ions initial concentration 0.04 mol/L, pH 7).

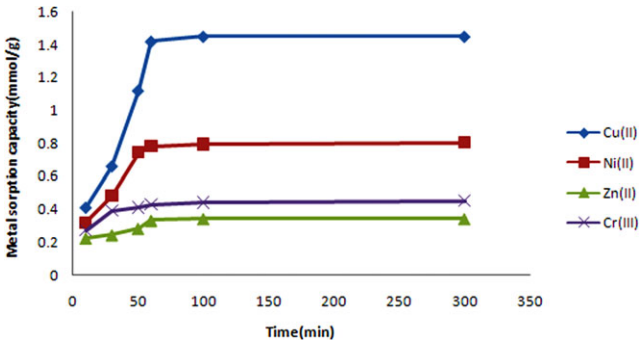


FIGURE 6. Effect of time on the sorption of metal ions (Ni(II), Cu(II), Zn(II), and Cr(III)) by PTAP polymer under competitive conditions (metal ions initial concentration 0.04 mol/L, pH 7).

DETERMINATION OF THE EQUILIBRIUM DISTRIBUTION COEFFICIENT (k_d)

The distribution coefficient k_d is determined according to Eq. (3):

$$k_d = \frac{Amount\ of\ metal\ ion\ in\ adsorbent}{\text{Amount of metal ion in solution}} \times \frac{V}{m} \qquad (3)$$

where V is the volume of the solution (mL) and m is the weight of adsorbent (g).

The k_d value can be used as a valuable tool to study metal cation mobility. High values of the distribution coefficient indicates that the metal has been retained by the solid phase, while low values of the k_d indicates that a large fraction of the metal remains in solution. Table I shows the k_d value for adsorption of single metal ions sample. These findings prove that the k_d value is approximately high in the case of Cu(II) and Ni(II) ions, so the synthesized chelating resins can be a good candidate for the removal of these metal ions from aqueous solutions. The prepared polymer does not show a good tendency for removing Zn(II) ion from aqueous solutions at pH 3.

TABLE II
Percent of Desorption for Single Metal Ions

	Percent of Desorption			
Polymer	Ni(II)	Cu(II)	Zn(II)	Cr(III)
PTAP	97.3	98.8	95.3	96.0

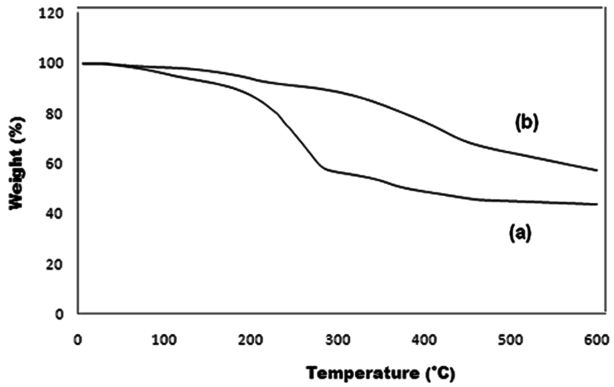


FIGURE 7. TGA curves of (a) PTAP and (b) PTAP-Cu complex (numbers represent pH in which maximum metal sorption was obtained).

DESORPTION OF METAL IONS FROM CHELATING POLYMER

Desorption of the adsorbed metal ions from the chelating PTAP polymer was also studied in a batch experimental setup. The chelating polymer beads that was loaded by the maximum amounts of the respective metal ions at pH 7 were placed in the desorption medium containing 0.2 M HCl for 1 h. The amount of desorbed metal ion was measured in solution and the results are summarized in Table II. The results show that all metal ions have desorption ratio up to 95%.

THERMAL GRAVIMETRY ANALYSIS

The thermal gravimetry analyses of the prepared PTAP polymer and its copper complex were performed with heating rate of 10°C min^{-1} in an N_2 atmosphere (Fig. 7). The thermogravimetric analysis (TGA) curve of the PTAP shows three-step decomposition. The first stage, ranges between room temperature to 150ºC, could be attributed to the loss of adsorbed and bounded moistures. The second stage of mass loss starts at about 200ºC and continues up to 380ºC due to the degradation of grafted functional groups. The last stage from 380 to 600ºC could be attributed to the degradation of the remaining polymer chains.

For comparison, the TGA curve of the PTAP and its copper complex with maximum metal sorption is shown in Fig. 7. The weight loss pattern of polymer and its copper complex was approximately same up to 200ºC, but between 200 and 470ºC the polymer was decomposed more than the polymer–Cu complex. The remaining mass polymer–Cu complex (55—60 wt%) at 600ºC corresponds to the formation of copper oxide.

Conclusions

We prepared new polymer containing four amino groups in each repeating cyclopropane ring. The polymer was soluble in ethylacetate and acetone but was not soluble in water and diethyl ether. Final polymer formed complexes with Cu(II), Ni(II), Zn(II), and Cr(III) in aqueous medium under competitive and noncompetitive conditions. The adsorption of all metal ions in completely acidic medium was moderate and it was favored at the pH value of 7.

The PTAP tended to adsorb the Cu(II) ions more than the others under competitive conditions. The adsorption rate of polymer was fast and the largest fraction of the adsorbed metal ion was attached to the polymer within 60 min. The k_d value is calculated for the prepared chelating polymer, and the result indicates approximately high values in the case of Cu(II)ion. All the complexes showed a change in the chemical shift in FT-IR spectra due to the metal ion complexation with the PTAP polymer. Thermal gravimetry study on copper–polymer complex confirmed the presence of metal in the resulting polymer.

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