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Effective Removal of Heavy Metal Ions Zn^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+} from Aqueous Solution by Synthetic Superabsorbent Polymer

Mehdi Hosseinzadeh*[1], Farideh Mahmoodzadeh[2]

[1]*Marand Faculty of Technical and Engineering, University of Tabriz, Tabriz, Iran*

[2]*Halal Research Center of IRI, FDA, Tehran, Iran*

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Abstract

Heavy metal pollution is propagating throughout the world with the enlargement of industrial activities. The elimination of heavy metal ions from industrial wastewaters has drawn much attention because of the hazardous effects of the heavy metal ions on different organisms. According to these facts, poly (2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylate (PTCP) with multi cyanocyclopropane functionalities in the pendant group were prepared by reacting benzoyl peroxide with *p*-(2,2,3, 3-tetracyanocyclopropyl) phenylacrylate (*TCP*) monomer. (*TCP*) monomer was synthesized by reacting cyanogen bromide and malononitrile with *p*-acryloyloxybenzaldehyde at 0 °C in a short time. The synthesized PTCP homopolymer were examined in heavy metal ions adsorption such as Ni (II), Cu (II), Cr (III) and Zn (II) under competitive and non-competitive conditions in aqueous solutions at different pH. The high adsorption rate (<65 min) was seen. The synthesized polymer and its metal chelates were investigated by thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FT-IR), atomic absorption techniques (AAS), UV-vis spectroscopy and scanning electron microscopy (SEM).

Keywords: *Heavy metal ions, Phenylacrylate, Malononitrile, Cyanogenbromide, Radical polymerization.*

Corresponding author:Mehdi Hosseinzadeh, Marand Faculty of Technical and Engineering, University of Tabriz,Tabriz,Iran. E-mail:mh_1268@yahoo.com.Telefax: +98 4142266741.*

Introduction

In the last decade, innovative design and development of various specific polymers which can absorb metal ions in aqueous and non-aqueous media have been an enduring topic in material and polymer sciences [1-3]. In this context, the functional group(s) on their surface polymer such as, carboxylic acid, amine, thiol, nitrile, sulfonic and hydroxyl acid are of particular interest, mainly due to effective absorption of heavy metal ion[4-7].The presence of toxic and non-biodegradable of heavy metals ions in industrial wastewater have posed many serious environmental problems, even at low concentrations [8-9]. These heavy metals ions are found in various industry sources such as metal finishing, textile, electroplating, storage batteries and chemical manufacturing [10-11].

Toxic heavy metals ions such as zinc, copper, nickel, and chromium extensively concern in the treatment of industrial waste waters. Because nickel exceeding its critical level might bring about serious kidney and lung problems aside from skin dermatitis, pulmonary fibrosis and gastrointestinal distress, and it is well established that nickel is a human carcinogen [12].Zinc is an essential element for human health. It is significant for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can make high health problems, such as skin irritations, vomiting, nausea and anemia stomach cramps [13]. Copper does essential work in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as convulsions, vomiting, cramps, or even death [14].So these toxic heavy metals should be removed from the wastewater to protect the environment and the people live. Many approaches that are being used to remove heavy metal ions include electrolytic recovery, membrane processes, liquid-liquid extraction, precipitation, and sorption (ion exchange, adsorption). Among the above- mentioned approach, adsorption is commonly regarded as an economical and effective method for wastewater treatment [15-17].It was found that, functionalized polymers containing nitrile have been attracted much attention in the removal or adsorption of heavy metal ions. These groups can be introduced into or graft onto the backbone of polymer chains [18-19]. Polymers bearing such groups have stable complexes with various heavy metal ions.

In this study, we aimed to develop novel complexing polymer materials, which can be used in wastewater treatment. For this reason, *p*-hydroxybenzaldehyde reacts with acryloyl chloride and triethyamine for preparation of *p*-acryloyloxybenzaldehyde. Then *p*-(2,2,3,3-tetracyanocyclopropyl) phenylacrylate (*TCP*) monomer was prepared by the reactions of *p*-acryloyloxybenzaldehyde with cyanogen bromide and malononitrile. Finally, the *TCP* monomer was polymerized by free-radical polymerization technique to afford a poly-(2,2,3,3-tetracyanocyclopropyl) phenylacrylate polymer *(PTCP)*. The chemical structures of samples were investigated and applied as chelating agents for removal of Zn(II), Cr(III),Cu(II) and Ni(II), ion in competitive and non-competitive conditions, in aqueous solutions at different pH.

Experimental

The thermal stability of polymers was studied by a Thermal Analysis METTLER STAR SW 10.0by scanning up to 600°C with the heating rate of 10 °C/min. Melting points were measured with a digital melting point apparatus (Electro thermal). The ^{1}HNMR spectra were recorded on Bruker 300 FT-NMR at 300 MHz(Urmia University, Urmia, Iran). The solution ^{1}H NMR spectra were obtained in acetone-d6 and/or CDCl3 as solvent using TMS as an internal standard.IR spectra were determined in the region 4000-400 cm^{-1} on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The electron micrographs were obtained by using a scanning electron microscope LEO 1430VP (Germany and UK).The metal adsorption capacities of polymer were measured by an AA-670 Shimadzu atomic absorption spectrometer and ANA77 (UV-Vis) spectrophotometer at room temperature in aqueous solution.

Cyanogen bromide and *p*-acryloyloxybenzaldehyde were synthesized based on reported references [20,21]. The *p*-Hydroxybenzaldehyde (Fluka, Switzerland) was recrystallized from water and dried under vacuum before use. Acryloylcholoride (Merck) was distilled in vacuum and used immediately. Sodium borohydride, Malononitrile, triethylamine and solvents were purchased from Merck or Aldrich and used without further purification. Zinc (II) nitrate [Zn $(NO_3)_2.6H_2O$], nickel (II) nitrate [Ni $(NO_3)_2.6H_2O$], chromium (III) nitrate [$Cr(NO_3)_3.3H_2O$] and Copper (II) nitrate [$Cu(NO_3)_2.3H_2O$] were provided from Fluka and used without further purification. All other reagents were purchased from Merck and purified according to the standard methods.

Synthesis of p-acryloyloxybenzaldehyde

A 200 ml round-bottom flask equipped with gas inlet/outlet, dropping funnel and magnetic stirrer, was charged with triethylamine (0.02mol, 2.02 g), *p*-hydroxybenzaldehyde (0.018mol, 2.2g), and diethylether (30 ml). Then, freshly distilled acryloyl chloride (0.02mol, 1.81 g) in dry diethylether (12 mL) was added drop wise to a solution at 0°C. The reaction mixture was stirred for 3hr at 0°C and additional 2hr at 25^{o}C. At the end of this time, Triethylamine hydrochloride was filtered off and rinsed with 27 mL ethyl acetate. Extractions were performed on the filtrate twice with 22 mL of HCl (1 N), once with H_2O (26 mL), and twice with saturated sodium bicarbonate (22 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 2.30 g of the *p*-acryloyloxybenzaldehyde (mp 13-16°C, yield: 70%).

Synthesis of p-(2, 2, 3, 3- tetracyanocyclopropyl) phenylacrylate (TCP) monomer

A10 mL teflon-faced screw cap tube was charged with butanol (10 mL) and magnetic stirrer. Then triethylamine (2 mmol, 0.202 g), malononitrile (2 mmol, 0.132 g), *p*-Acryloyloxybenzaldehyde (1mmol, 0.176g) was added to the screw cap. The reaction mixture was cold down to 0 - 4 °C then the cyanogen bromide (1 mmol, 0.106 g) was added slowly. Cream color solid precipitated during 15 minutes, after about 45 minutes the product was filtered ,washed with 20 ml ethanol and dried to give 0.362 g of the *TCP* (mp156-158°C , yield: 95%,).

Synthesis of poly-(2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylatepolymer (PTCP)

A 50 mL three-neck round-bottom flask equipped with a magnetic stirrer, septum, condenser, and gas inlet/outlet was charged with *TCP* **(**2.0 mmol, 0.574g), and ethylacetate (6 mL). This solution was de-aerated by bubbling highly pure argon for 20 minutes, and then benzoyl peroxide (3.0 mg, 0.018 mmol) was immersed to the flask. The solution was stirred for about 12 hour at 70^{o}C under argon protection. After the mentioned time the polymerization flask was opened and their viscous product was poured into cyclohexane (150 mL). The mixture was collected and washed with 25 ml ethanol and dried under vacuum to give poly-(2,2,3,3- tetracyanocyclopropyl) phenylacrylate (0.49g, yield: 88%)**.**

Determination of metal ion adsorption capacities

Non-competitive Adsorption

The complexation of the poly-(2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylate polymer was performed with Ni^{2+}, Cu^{2+}, $Cr^{3+}$and Zn^{2+}ions by batch equilibration technique in various pH values. The synthesized polymer (0.05 g) was stirred with excess metal salt (50 ml, 0.04mol/L) for 45 min. The pH of solution was fixed at 3- 7 by adding moderate 0.01 M HCl or NaOH. After being went away all-night, the pH of the solution was adjust again. Then the solution was filtered, and the remainder metal ion concentration in solution was determined by UV-Vis spectrophotometer or AAS at 25^{o}C. The adsorption capacities, q, (mmol M^{2+}/g resin) in various conditions was determined as follows (Eq. 1):

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

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

Competitive Adsorption

The above-remarked procedure was used, for adsorption of metal ions in competitive condition in the solution of four metal ions simultaneously. The concentration of the each metal ion was 0.04mol/L.

Sorption kinetic experiment

The kinetic for the sorption capacity of metal ions under non-Competitive conditions was investigated for poly-(2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylate polymer (PTCP). (0.05 g) PTCP were added to a series of solutions (50 ml, 0.04 mol/L), of Zn (II), Cu(II), Ni(II), and Cr(III) . Then the mixture was stirred at room temperature. The filtrates were sampled in particular time intervals for the determination of ion concentrations by AAS. The kinetic curve was offered by the plot in the adsorption capacities vs. adsorption time. The above-mentioned method was repeated for competitive adsorption conditions too.

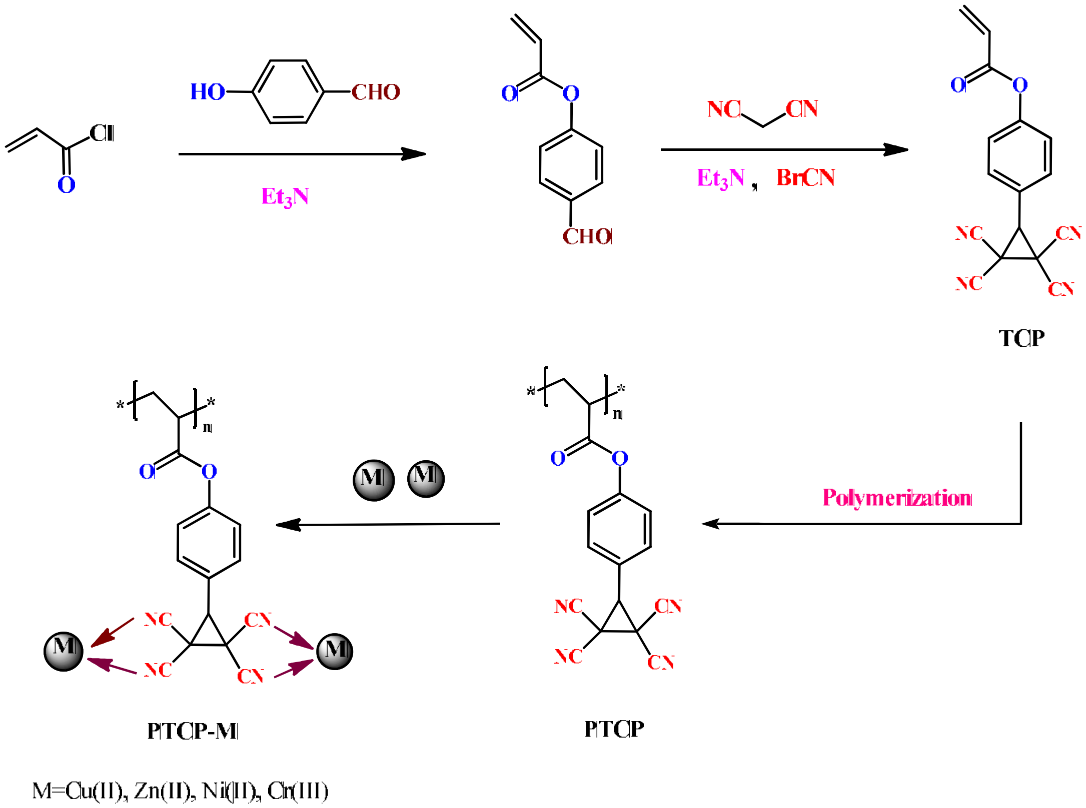
Desorption of metal ions in acidic medium

The polymer–metal complexes were placed in aqueous HCl solution (0.2 M, 30ml) in order to metal ion desorption at room temperature for 1h. At the end of this time, the mixture was filtrated and the final metal ion concentrations in the mixture were determined by AAS. The desorption ratio (D %) was calculated as follows (Eq. 2) :

$$D\% = \frac{\text{mmoles of metal ion desorbed to the HCl solution}}{\text{mmoles of metal ions adsorbed on to polymer}} \times 100 \qquad (2)$$

Results and discussion

In this study, for the removal of heavy metal ions, the *p*-acryloyloxybenzaldehyde was synthesized by the well-known Schotten-Baumann approach [21]. Then the *TCP* was prepared by the reactions of *p*-acryloyloxybenzaldehyde with cyanogen bromide and malononitrile in a short time. Finally, the *TCP* monomer was polymerized by free-radical polymerization technique to afford a novel poly-(2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylate polymer (PTCP) with multi cyanocyclopropane functionalities in the pendant group (Scheme 1).



Scheme 1. Synthesis of poly-(2, 2, 3, 3- tetracyanocyclopropyl) phenyl acrylate.

Synthesis of poly (2,2,3,3- tetracyanocyclopropyl) phenylacrylate (PTCP)

The chemical structure of *p*-acryloyloxybenzaldehyde, the *TCP* monomer and PTCP were investigated by ^{1}H-NMR, and IR spectroscopy techniques as shown in Figure 1 and 2.The comparison of FTIR spectrum showed that the aldehyde peak is omitted (Figure 1a) and nitrile groups appeared in about (2261-2263) cm^{-1}region(Figure 1b, 1c)).This result indicated successful polymerization of TCP monomer. The above- mentioned polymers were further characterized by means of ^{1}HNMR spectroscopy as shown in figure 2. The successful formation of tetracyanocyclopropane ring is verified by the appearance of new chemical shift at 5.04 ppm assigned to the cyclopropyl proton.

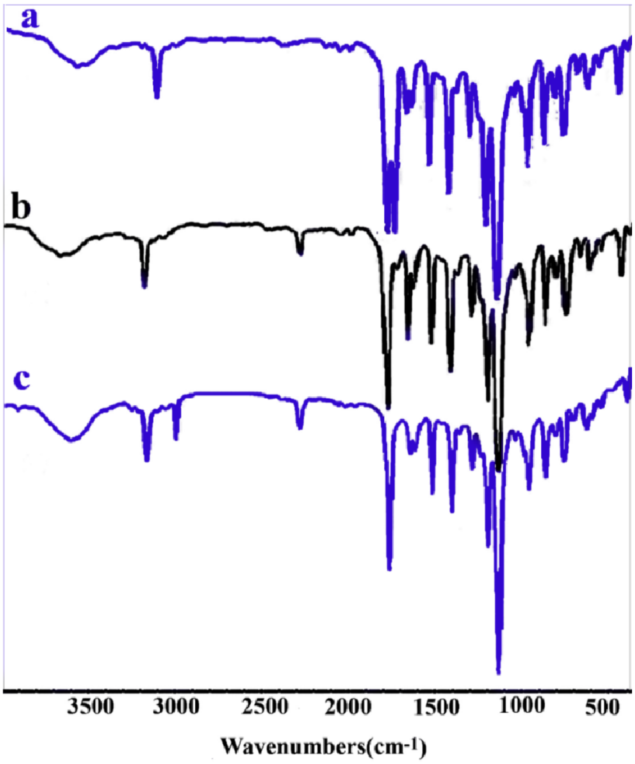


Figure 1. FT-IR spectrum: *p*-acryloyloxybenzaldehyde (a), *TCP* monomer (b)and PTCP (c).

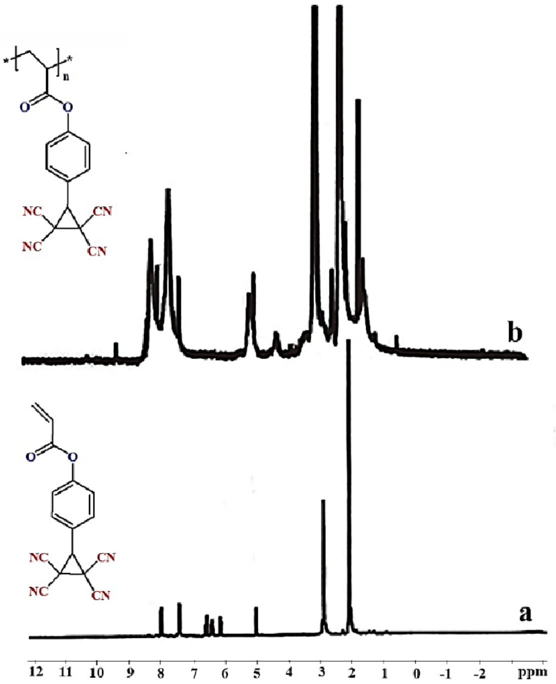


Figure2. Characterized ^{1}HNMR spectra of *TCP* monomer (a)and PTCP (b).

Metal ion sorption capacity of poly (2,2,3,3- tetracyanocyclopropyl)phenylacrylate

Non-competitive conditions

The complexion of heavy metal ions by a chelating ligand is powerfully dependent on the pH of the medium.This effect can be remarked particularly the formation of the coordination bond between metal ions and nitrogen. The resulting 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 polymer was measured with UV-Vis spectroscopy and atomic absorption methods. The results are shown in Tables 1. The adsorption of all selected metal ions on the polymer was more favorable at the pH value of 7. The high adsorption at pH=7 reveals that metal ions interaction with nitrile groups is favorable due to their protonated form. At low pH value, high concentration of H^+ can react with nitrile 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^{2+} in pH=7 and Zn^{2+} in pH= 3, which was approximately 1.7mmol/g and 0.25 mmol/g, respectively.

Table 1. Adsorption capacity of poly (2,2,3,3- tetracyanocyclopropyl) phenylacrylate for single metal ions and its distribution coefficient at different pH: metal salt (0.04 mol/L) , polymer (50 mg).

Polymer complex	Metal salt	pH	Metal sorption capacity (mmol/g)
L-Cu	$Cu(NO_3)_2.6H_2O$	7	1.7
		5	1.1
		3	0.36
L-Ni	$Ni(NO_3)_2.6H_2O$	7	1.35
		5	0.99
		3	0.35
L-Zn	$Zn(NO_3)_2.3H_2O$	7	0.61
		5	0.39
		3	0.25
L-Cr	$Cr(NO_3)_2.3H_2O$	7	0.72
		5	0.47
		3	0.26

L= PTCP

Competitive conditions

It is being estimated that in the existence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. The selectivity of chelating polymers for metal ion competing for the active sites in the PTCP composite. It is being estimated that in the existence of different metal ions, one metal ion could be selectively adsorbed by a chelating agent. 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 non-competitive conditions. In this study, metal ion sorption of the polymer under competitive conditions as a function of pH for Cr

(III), Zn (II), Cu (II) and Ni (II) ions were determined. The results are presented in figure 3. The maximum sorption of the polymer for Ni(II), Cu (II) , Cr(III) and Zn(II) ions under competitive conditions is belongs to Cu (II) at pH=7.

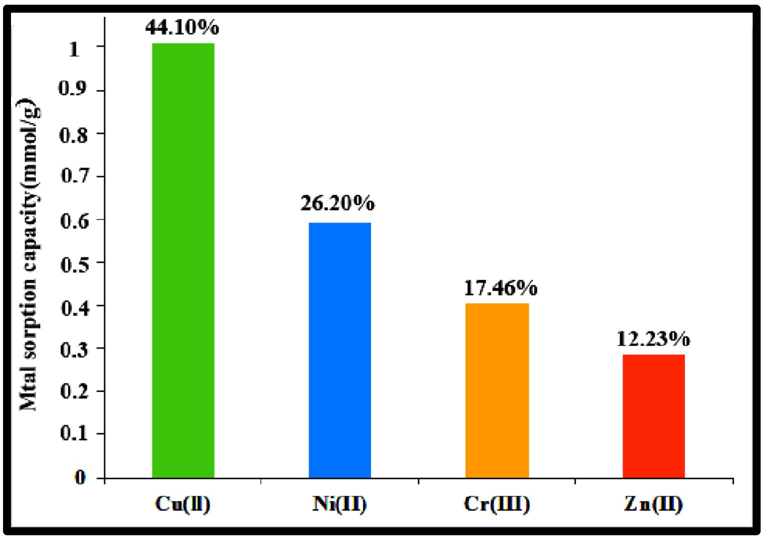


Figure 3. The adsorption capacities and selectivity (%) of poly (2,2,3,3- tetracyanocyclopropyl) phenylacrylate under competitive conditions at pH = 7. (Total metal ion ads. Cap=2.29 mmol/g).

Effect of contact time

To achieve the adsorption rates of metal ions under non-competitive conditions, the influence of time on the sorption capacity of the PTCP for these metal ions was investigated and the results are shown in Figure 4. The results confirmed that the rate of metal sorption by PTCP was rapid and reached a constant value after about one hour.

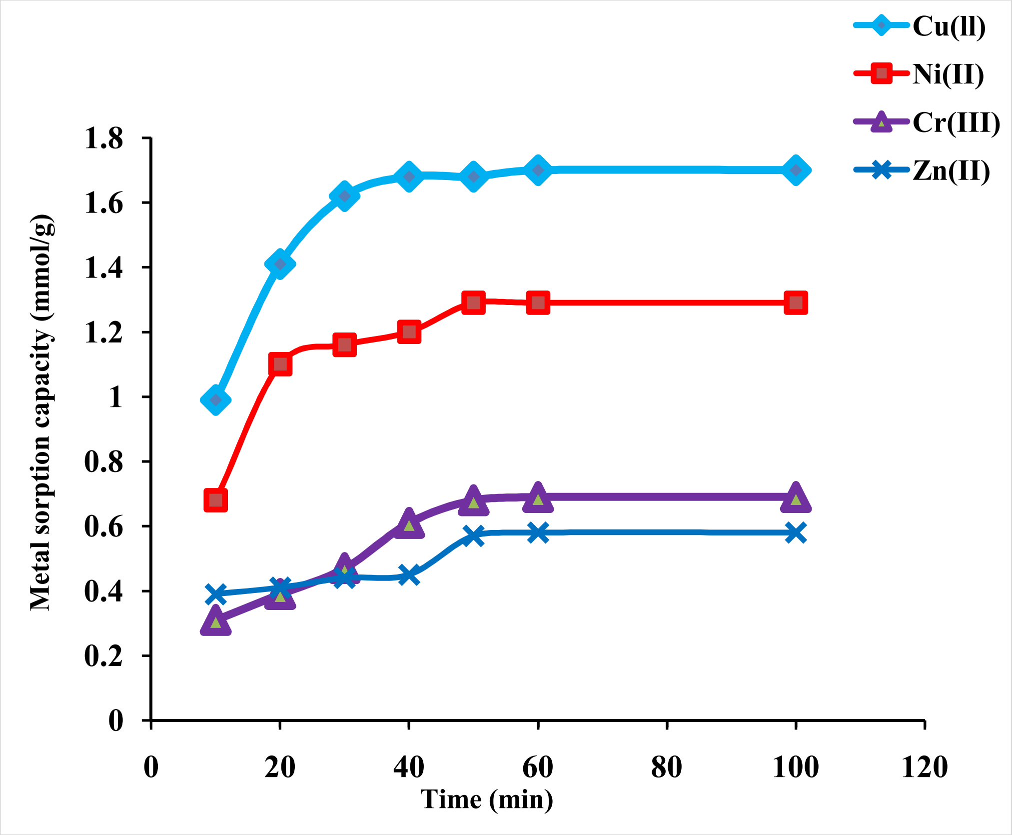


Figure 4. Effect of time on the sorption of metal ions Cu(II),(Ni(II) , Cr(III)) and Zn(II) by PTCP under non-competitive conditions (metal ions initial concentration 0.04mol/L,pH=7).

The sorption rates for Ni (II), Cu (II), Cr (III) and Zn (II) ions under competitive conditions from multi-component metal solutions were determined for the PTCP too and results were presented in Figure 5.The maximum sorption capacity for Cu (II) on PTCP is 2.52, 1.68and 3.6 times higher than that of Cr (III), Ni (II) and Zn (II), respectively. It is well established that Ni (II) and Cu (II) sorption on the PTCP in the mixed metal salt solution is slower compared with results obtained in single-component solutions, likely due to the challenger between metal ions for the active sites on the PTCP polymer.

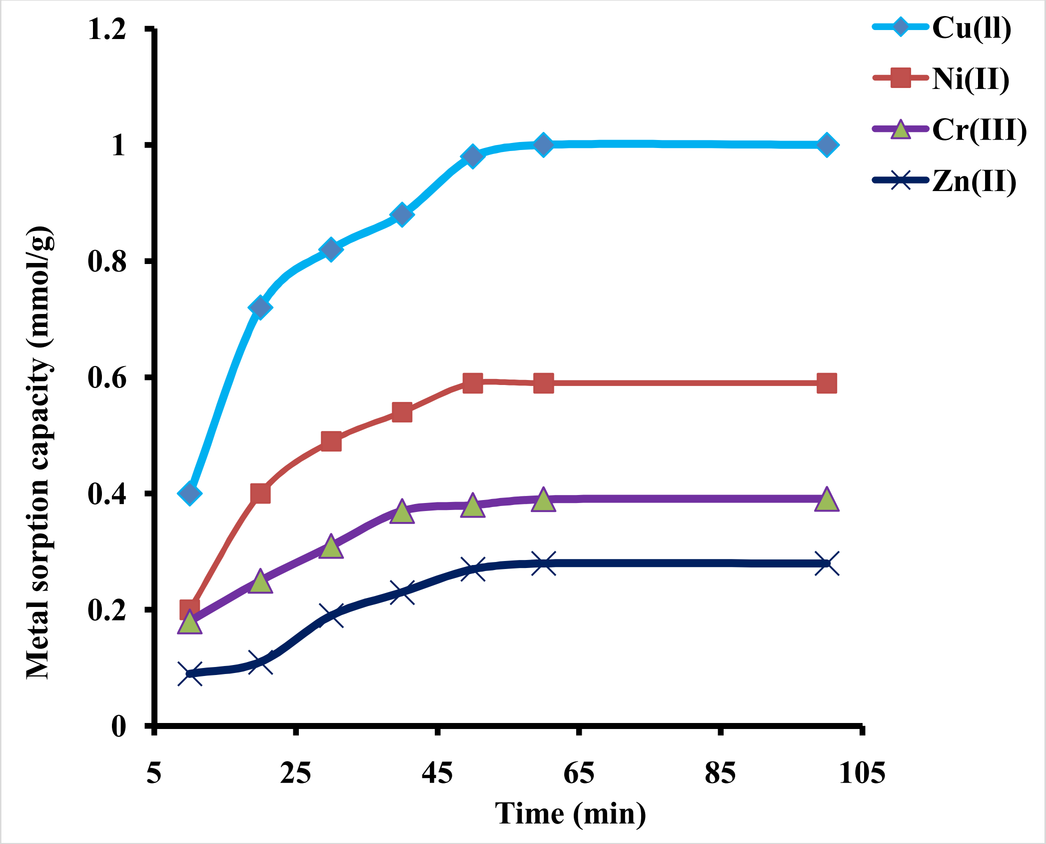


Figure 5. Effect of time on the sorption of metal ions (Ni(II), Cu(II), Zn(II) and Cr(III)) by PTCP under competitive conditions (metal ions initial concentration 0.04mol/L,pH=7).

*Desorption of metal ions from chelating poly*mer

Desorption of the adsorbed metal ions from the chelating PTCP was also studied in a batch experimental setup. The chelating polymer beads which were loaded by the maximum amounts of the respective metal ions in 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 were summarized in Table 2. The results show that all metal ions have desorption ratio up to 90%.

Table 2. Percent of desorption for single metal ions.

	Percent of desorption			
Polymer	Ni(II)	Cu(II)	Zn(II)	Cr(III)
PTCP	93.3	95.8	92.3	98.0

Thermal Gravimetry Analysis

The thermal degradation analysis of PTCP and its copper complex were performed with aheating rate of 10 ºC per minute in N2 atmosphere. The decomposition behavior of prepared polymers is shown in Figure 6. The thermo grams indicated that PTCP decomposed with three steps at 25 -210 ° (7 % mass change)C could be attributed to the loss of adsorbed and bounded moistures, 230-370 ºC (49% mass change)due to the degradation of grafted functional groups and 440-600 ºC(27.5% mass change), attributed to the degradation of the remaining polymer chains respectively. The weight loss pattern of PTCP and its copper complex with maximum metal sorption up to about 150°C was approximately the same, but between 180°C and 600°C polymer was decomposed stronger than the copper-polymer complex. There remained mass PTCP-Cu complex (31 wt%) at 600 ºC corresponds to the formation of copper oxide.

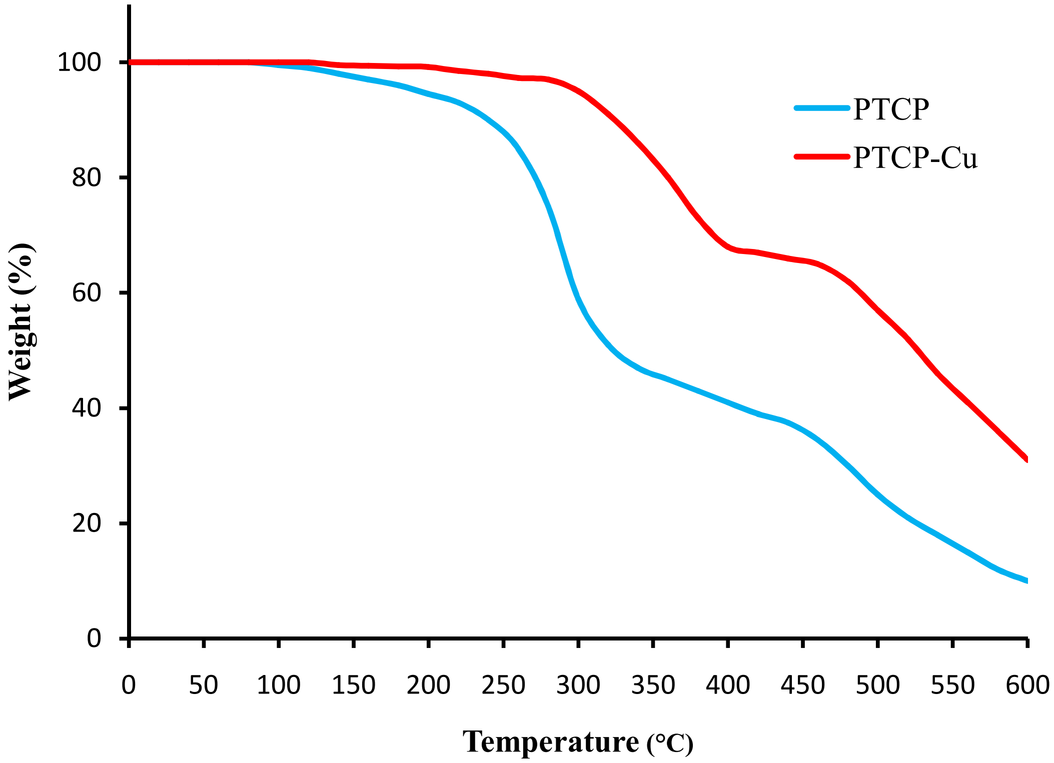


Figure 6. TGA Curves of PTCP and PTCP-Cu complexes.

Comparison with Other Adsorbents

The comparative experiments on the adsorption of selected metal ions with those of other published results are given in Table 3.The comparative results indicate that the removal efficiencies of the prepared polymer were higher or comparable, in some cases, than that of other presented adsorbents.

Table 3. Comparison of the maximum adsorption capacities of selected metal ions among different adsorbents.

Adsorbents	Cu(II)	Ni(II)	Zn(II)	Cr(III)	Ref.
CPAN-M	1.92	-	1.58	-	[22]
PAN carbon fiber	0.33	-	-	-	[23]
Raw polyacrylonitrile nano fiber	1.17	-	-	-	[24]
PTAP	2.61	1.92	0.95	1.23	[25]
CSMA–HPCA	2.75	-	1.92	-	[26]
PTCP	1.70	1.35	0.61	0.72	This study

Scanning electron micrographs

The scanning electron micrographs of the PTCP and PTCP-Cu show that there is a strong change in morphology of PTCP in comparison with PTCP-Cu complexes. PTCP had rougher surface but after complexation with copper ions, the surface becomes smoother (Figure 7).

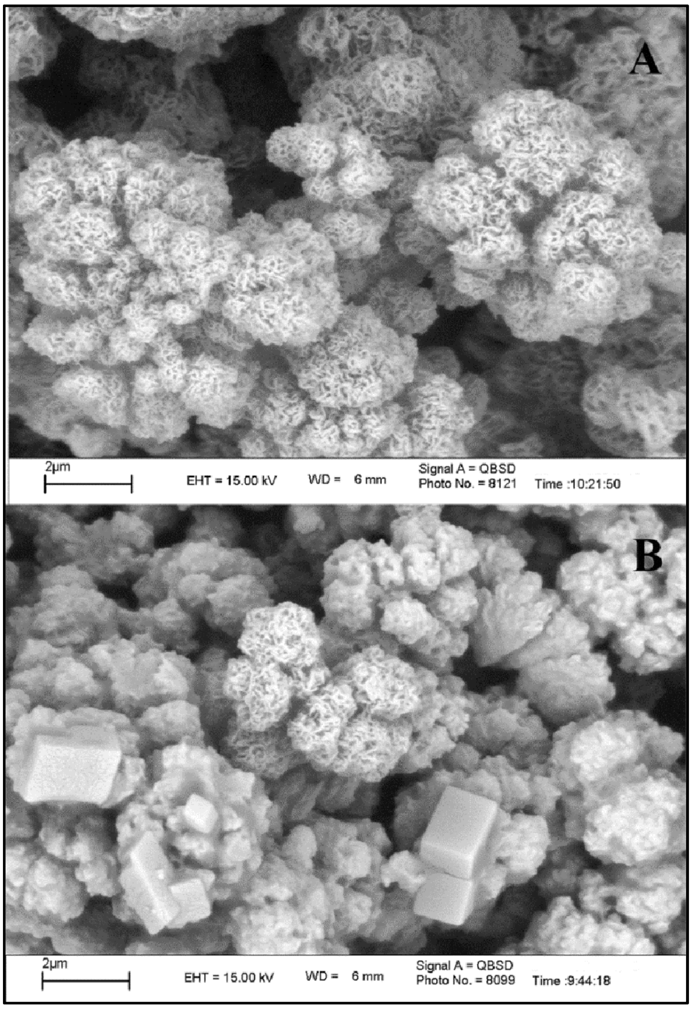


Figure 7. SEM Images of PTCP (A) and PTCP-Cu (B).

Conclusion

We developed novel chelating polymer carrying four nitrile groups in each repeating cyclopropane ring and were used for the adsorption of selected metal ions under non-competitive and competitive conditions. The prepared polymer beads have high metal removal efficiency and are repeatedly re-generable. This work suggests that the present polymer can be more useful for the adsorption of heavy metal ions from effluents discharged by industries and can have great potential applications in environmental protection.

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