Novel Tetrazole-Functionalized Absorbent based on poly (2,2,3,3 -tetracyanocyclo-propyl) phenylacrylate to remove heavy metal ions from aqueous solution

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ABSTRACT

The new method for synthesis of P-(2,2,3,3-tetracyanocyclopropyl) phenylacrylate (TCP) was applied. In this method p-acryloyloxybenzaldehyde was reacted with malononitrile and cyanogen bromide at 0°C in short time. Then the TCP monomer was polymerized by free-radical polymerization initiated with benzoyl peroxide in ethylacetate as solvent to obtain a polymer with multicyanocyclopropane functionalities in the pendant group. The prepared polymer was characterized by FT-IR, and ^{1}H-NMR spectroscopy. A novel Tetrazole-Functionalized polymer as absorbent (TFP), was made from poly (2,2,3,3-tetracyanocyclo-propyl)phenylacrylate (PTCP) through [3+2] azide-nitrile cycloaddition reaction of nitrile containing polymer with sodium azide in DMF. It was found that approximately 50% of the cyano groups on the polymer surface were converted to tetrazolyl groups, as estimated by elemental analysis. The obtained functionalized absorbent showed strong adsorption ability to the investigated heavy metal ions, Cr (III), Cu (II), and Zn (II), with the maximum adsorption capacities of 5.67,4.13, and 2.51mmol g^{-1}, respectively. The adsorption process was described as an ion exchange and chelation interaction mechanisms. The high adsorption rate (<40 min) was seen. The resulting polymer and its metal chelates were characterized by FT-IR, elemental analysis, gravimetry, UV-Vis spectroscopy and atomic absorption techniques (AAS).

KEYWORDS: *Adsorption, Click chemistry, Metal ions, Polymer complexes, Radical polymerization.*

J. Polym. Mater. Vol. **34,** No. 2, 2017

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1. INTRODUCTION

The by-product of the continuing of heavy industry is ever-increasing reliance on dirty coal and a surge in greenhouse gas emissions. Among this, heavy metal pollution has attracted much attention because of the hazardous effects of the them on different organisms' survival [1-5].Various methods have been utilized to remove and recycle heavy metals from aqueous solutions such as chemical precipitation, membrane separation, ion exchange, electrochemical treatment, adsorption [6–8].Among them, adsorption is one of the most simple and common methods. Functional groups on the adsorbent surface not only affect the adsorption selectivity but also dominate the adsorption mechanism. Adsorbents with carboxyl, phosphonic and sulfonic groups remove adsorbates through ion exchange [9,10],whereas those containing nitrogen such as amine, tetrazolyl, hydrazine, and imidazoline groups not only chelate cationic metal ions but also adsorb anionic adsorbates through electrostatic interaction [11,12]. In particular, tetrazolyl groups have been found to belong to the most effective groups for pollutant removal from aqueous solutions[13].

Tetrazoles are heterocyclic compounds with five membered ring constructed by one carbon atom and four nitrogen atoms. Tetrazolyl group has similar structural requirement and aqueous pKa value as carboxylic acid, and thus has become a widely known alternative to a carboxylate moiety but it shows a strong ability to chelate with transition metal ions compared to the carboxylic group[14–16]. As carboxylate O atoms and tetrazolyl ring N atoms have good coordination capacities[17-18]. Tetrazole-containing polymer could exhibit versatile coordination modes to construct transition metal ions with structural varieties and interesting performance. This polymer produces strong adsorption to Cu(II), Zn(II), Ni(II) and Zn(II) [19,20].The new adsorbents capable of coordinating with heavy metal ions would be expected from the introduction of tetrazolyl groups into ligands. Therefore, we attempted to prepare new complexing polymer materials, which can be used in wastewater treatment. In this work, we prepared *p*-(2,2,3,3-tetracyano-cyclopropyl) phenylacrylate (TCP) by the reactions of *p*-acryloyloxybenzaldehyde with malononitrile and cyanogen bromide[21], then we researched the modification of TCP via a combination of radical polymerization and Click Chemistry[22,23] by translation of cyano into tetrazolyl group using the [3+2] cyclization reaction of nitrile with triazo group to prepare a chelating polymer with new functional groups for metal ion sorption. The resulting polymer (TFP) were dispersed in aqueous solutions of various metal ions and their metal sorption capacities were measured by gravimetry, UV-Vis spectroscopy and atomic absorption techniques.

EXPERIMENTAL

Materials and instruments

Melting points were measured with a digital melting point apparatus (Electrothermal,UK). IR spectra were determined in the region 4000-400 cm^{-1} on a NEXUS 670 FT IR spectrometer (USA) by preparing KBr pellets. The ^{1}HNMR spectra were recorded on Bruker 300 FT-NMR (Germany) at 300 MHz (Urmia University, Urmia, Iran). ^{1}H NMR spectra was obtained on solution in acetone-d_6 and/or $CDCl_3$ as solvent using TMS as internal standard. Elemental analysis of the polymer was carried out using a EURO EA 3000 (Italy).

The metal absorption capacities of polymers were measured by an AA-670 Shimadzu atomic absorption spectrometer (Japan) and ANA77 (UV-Vis) spectrophotometer (Japan) at room temperature in aqueous solution. Viscosity value was obtained by using a Cannon-Fenske viscometer. 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 vaccume. Acryloylcholoride (Merck) was distilled and used immediately. Cyanogen bromide and *p*-acryloyloxybenzaldehyde were synthesized based on reported references[24,26]. Malononitrile, ammonium chloride, sodium azide, triethylamine and solvents were purchased from Merck or Aldrich and used without further purification. Copper (II) nitrate [Cu $(NO_3)_2.3H_2O$], Zinc (II) nitrate [$Zn(NO_3)_2.6H_2O$] and chromium (III) nitrate [$Cr(NO_3)_3.3H_2O$] were provided from Fluka and used without further purification.

Preparation of TCP

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

FT-IR (KBr): 3031(ar-CH), 2262(CN),1739(C=O), 1629(C=C), 1154-1212(C–O) cm^{-1}; ^1H NMR (acetone-d_6) δ6-7 (m, 2H, $=CH_2$), 6-7 (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).

Polymerization of TCP

A representative polymerization procedure of the TCP was as follows: A solution of TCP **(**0.574g, 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 which was thermostated at 70°C and it was shaked for 12 hr. 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) phenylacrylate (PTCP) (0.517g,yield: 90%)**.**

FT-IR (KBr):2859, 2926 (aliph-CH), 2262 (CN),1739 (C=O), 1154-1212(C–O) cm^{-1};^1H NMR (acetone-d_6) 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).

Preparation of Tetrazole-Functionalized absorbent (TFP).

The synthesis reaction of TFP with ammonium chloride as catalyst and in the presence of sodium azide was performed in a stirred oil bath equipped with a thermostat. A total of 345mg (1.2mmol) of PTCP solid was dissolved with about 4 mL of DMF in a 6 mL ampoule. The mixture was stirred until it was well-distributed at ambient temperature. Subsequently, 312mg (4.8mmol) of NaN_3 and 128 mg (2.4mmol) of NH_4Cl were added to the PTCP solution with stirring. The ampoule was immediately put into an oil bath with stirring when the oil bath was heated to 120°C. Then the temperature of the oil bath was held in 120°C for 12 h. The final obtained reaction mixture was poured into a 100 mL beaker with HCl (50 mL, 0.5 mol/L) for a complete precipitate of the modified polymer. Afterwards, the product was soaked with distilled water for 2 h and washed repeatedly for elimination of DMF. The expected compound was dried in air until a constant weight at room temperature to give (0.501g) of polymer TFP. n_{inh} =0.26 dL/g (Concentration of 0.5 g/dL in acetone at 25 °C).The preparation routes of procedures were depicted in Scheme 1.

FT-IR (KBr):3100-2400 (tetrazolyl), 2221 (CN),1723(C=O ester),1597(C=N),1507(N=N), 1457(C=C phenyl), 1364 (C-N), 1172-1268 (C-O ester).

Determination of adsorption capacity for single metal ion

The complexation of the TFP was carried out with Cu (II), Zn(II) and Cr(III) ions by batch equilibration technique[25]. The TFP (50 mg) was stirred with excess metal salt (0.04

mol/L) for 60 min at 25°C. The pH of solution was set at 1-7. Then the mixture was filtered, and the residual metal ion concentration in solution was determined by AAS and UV-Vis spectrophotometer at room temperature. The adsorption capacities, q, (mmol M^{2+}/g resin) in various conditions was calculated as follows(Eq. 1):

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

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 lit) and W is the weight of polymer (0.05 g).

Adsorption selectivity

The adsorption selectivity of the polymer was investigated under competitive conditions, and the above mentioned procedure was applied,but the solution contained all three metal ions. The concentration each metal ion was 0.04 mol/L.

Contact time experiment

In investigating the effect of time on the sorption capacity of TFP for metal ions**,** To a series of Cu(II) as well as Zn(II) and Cr(III) solutions (0.04mol/L,50 ml) the TFP (0.05 g) were parallelly added, and then the solutions were stirred at 25°C.The filtrates were collected at different times for the determination of ion concentrations by AAS. The kinetic curve was obtained by plot of the adsorption capacities vs. adsorption time.

Desorption of metal ions in acidic medium

For metal ion desorption, aqueous HCl (1M) was used. The TFP–metal complexes in which adsorption was carried out in pH = 5 were immersed in HCl(1M) solution with a magnetic stirrer at 25°C for 1h. 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):

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

RESULTS AND DISCUSSION

Synthesis of TCP monomer

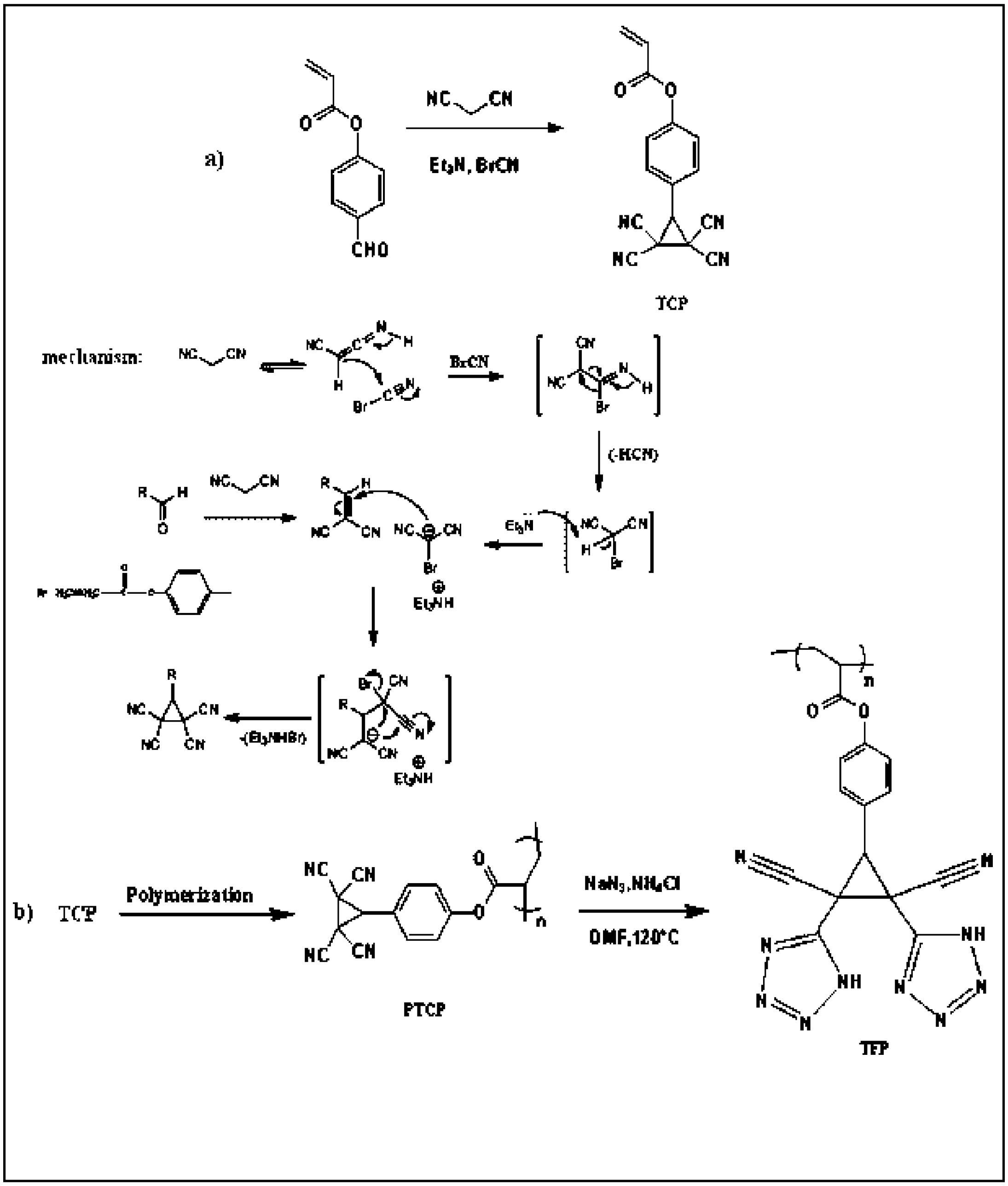
The *p*-acryloyloxybenzaldehyde was prepared by the well-known Schotten-Baumann method [26].Then the TCP was prepared by the reactions of *p*-acryloyloxybenzaldehyde with malononitrile and cyanogen bromide in short time (sheme 1a)[21]. The chemical structure of the compounds was confirmed by ^{1}H-NMR, and IR spectroscopy techniques. Figure 1a and 1b displays the FT-IR spectrum of *p*-acryloyloxybenzaldehyde and the TCP monomer. The comparison of two spectrum showed that the aldehyde peak is omitted and the formation of nitrile groups took place in about 2262 cm^{-1}.The ^{1}H-NMR spectrum of the TCP monomer was shown in figure 2a. In this spectrum the signal at 5.02 ppmassigned to the cyclopropyl proton indicates the formation of tetra cyanocyclopropane ring.

Synthesis and Characterization of TFP

The TCP monomer was polymerized by free radical polymerization with benzoyl peroxide as initiator to obtain the PTCP with multicyanocyclopropane groups. Polymerization was carried out in solution at 65°C. The 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 PTCP were determined by^{1}HNMR (Figure 2b), and IR spectra (Figure 1c). The obtained polymer was soluble in ethylacetate, acetone, DMF, and DMSO, but was not soluble in methanol, diethyl ether and water.

Tetrazoles are heterocyclic compounds with a five-membered ring consisting of one carbon atom and four nitrogen atoms. A tetrazolyl group has similar structural requirements and aqueous pKa to carboxylic acid. In the preparation procedure of TFP (scheme1b), PTCP was modified through [3+2] cycloaddition reaction of nitrile with triazo group. The reaction usually requires high temperatures above 100°C.

The FT-IR spectrum of the TFP (figure 3a), reveals that a strong peak at 2240 cm^{-1}, attributed to the CN stretching vibration in PTCP became weaker in TFP because of [3 + 2] cyclization reaction with azide. A broad medium band centered at 3100–2400 cm^{-1}was assigned to the tetrazolyl groups in TFP. The broading of this peak may indicate some hydrogen bonding on the part of the N-H bond with



Scheme 1. Synthetic route for the preparation of a) TCP and b) TFP

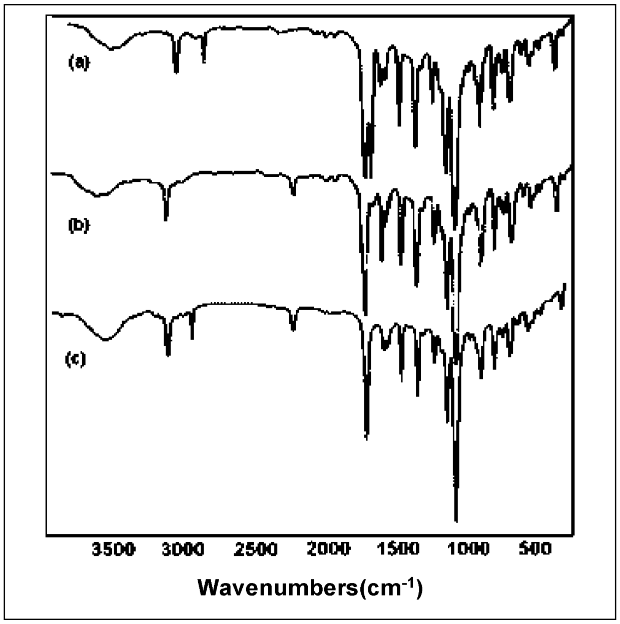


Fig 1. FT-IR spectrum: (a) p-acryloyloxybenzaldehyde, (b)TCP monomer and (c) PTCP

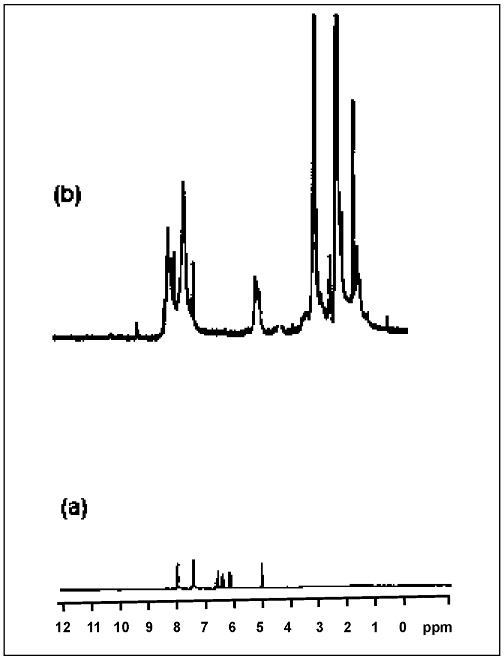


Fig 2. Characterized ^{1}HNMR spectra of (a) TCP monomer and (b) PTCP

neighbouring tetrazole groups. The band at 1597 cm^{-1} could be seen obviously due to the presence of C=N stretching vibration of the tetrazole ring and the new bands at 1507cm^{-1}and 1364 cm^{-1}were attributed to the stretching vibration of N=N and C- N of tetrazole ring, respectively. These results suggested the translation of CN groups and the formation of tetrazolyl groups.

The modified polymer (TFP) was characterized by the usual methods in polymer chemistry in order to verify the conversion of nitriles to tetrazole moieties. Elemental analysis was used to estimate the chemical conversion of nitrile into tetrazole groups by solving (Eq. 3):

$$\begin{cases} M_n=14(N_c+N_r) & (3) \\ M_t=\dfrac{14(N_r+4N_c)}{100+14\times 3N_c}\times 100 \end{cases}$$

Where Mn and Mt are the mass percentage of nitrogen in PTCP and TFP polymer, respectively; and N_c and N_r are the molar content of nitrile groups accessible and not accessible for reaction with NaN_3 in PTCP, respectively.

The calculated results were listed in Table 1. The conversion of nitrile groups was up to 50% which indicates that the conversion is not complete. This was understandable because of the hindrance of nitril groups and the heterogeneous reaction which was usually difficult. Considering the value of inherent viscosity, can be estimated that the molecular weight of TFP is relatively low.

By comparing the FT-IR curve of the TFP(fig.3a) with its chromium complex curve (fig3b) in figure 3, it can be seen that the stretching vibration bands of free N–H bonds of the tetrazolyl ring (3399 cm^{-1}) disappeared after chromium ions sorption by the polymer. The C=N bonds of tetrazolyl groups in TFP, which would become stronger and shift to a higher frequency in the tetrazole salt, are probably responsible for the strong band which shifts from 1597 cm^{-1} in tetrazole to 1635 cm^{-1} in the tetrazolate ions[27].

The stretching vibration band of N=N (1507cm $^{-1}$) was shifted to 1533cm^{-1} when TFP are associated with chromium ions [28].

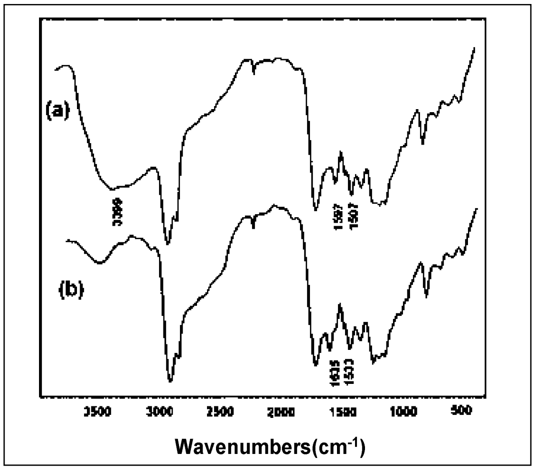


Fig 3. FT-IR spectra of (a) TFP, (b) TFP-Cr complexe (numbers represent pH in which maximum metal sorption was obtained).

Sorption behaviors

The resulting TFP polymer was brought in to contact with aqueous solutions of metal ions in the range of pH 1-7. The metal sorption capacity of the TFP polymer was measured with atomic absorption and UV-Vis spectroscopy methods at different pH values, as shown in Figure 4. An abrupt increase in the adsorption capacity was observed when the pH increased from 1.0 to 4.0, and the plateau values were approximately 5.0for all cases. This adsorption trend might be related to the property of the tetrazolyl groups.

Table1. Elemental contents of polymers and the calculated group contents of TFP

N content (%)		**Group contents inTFP (mmol g^{-1})**		**Conversion of nitrile (%)**
PTCP	**TFP**	**Nitrile**	**Tetrazole**	**53.3**
19.8	**38.7**	**7**	**8**	

H-tetrazole (TZH),is an amphiprotic compound, has a two step protonation as follows (Eq. 4):

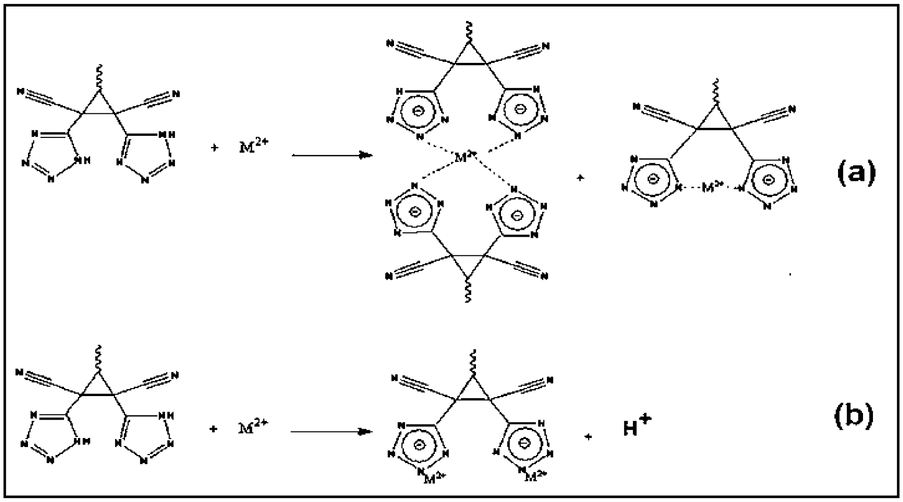
$$TZH_2^+ \quad TZH \quad TZ^-$$
$$PK_{a1}=0.8\pm0.1 \qquad (4)$$
$$PK_{a2}=4.73\pm0.1$$

At low pH value, tetrazolyl groups occurred in the protonated form and the active sites of the TFP were less available for metal ions due to greater repulsive forces. Moreover high concentration of H^+ ions could compete with metal ions and further lead to the decrease in metal adsorption. At intermediate pH (1to4), TZH_2^+ was deprotonated and favored the coordination-bond formation, and consequently, TFP began to adsorb metal ions via chelation interaction [Scheme2a].

At pH > 4, tetrazolyl became a negative five membered ring due to the dissociation of tetrazolyl groups, thus the strong adsorption of TFP to metal ions happened by an ion exchange mechanism [scheme2b].

The adsorption of all selected metal ions on the polymer was more favorable at the pH value of 5 (Fig4).

The highest and lowest metal sorption obtained for Cr(III) in pH=5 and Zn(II) in pH= 1, which was approximately 5.67 mmol/g and 0.31 mmol/g, respectively.



Scheme 2. Adsorption mechanism of TFP for metal ions

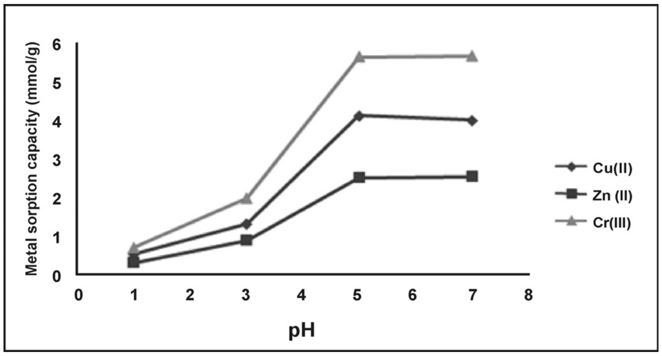


Fig 4. Effect of pH on the sorption of single metal ions [Cu(II), Zn(II) and Cr(III)] onto TFP [initial metal concentration 0.04mol/L, polymer (0.05 g)].

Desorption of metal ions from chelating polymer

Desorption of the adsorbed metal ions from the chelating TFP was also studied in a batch experimental setup. The chelating polymer beads which was loaded by the maximum amounts of the respective metal ions in pH=5 were placed in the desorption medium containing 1M HCl for 2 h. The amount of desorbed metal ion was measured in solution and the results were summarized in table 2. The results shows that all metal ions have desorption ratio up to 93%.

Table 2. Percent of desorption for single metal ions

Percent of desorption			
Polymer	Cu(II)	Zn (II)	Cr (II)
TFP	94.2	93.697.1	

Effect of Contact time

The adsorption kinetics of three metal ions were investigated to determine the adsorption behavior. Figure 5 shows the adsorption kinetic curves of three metal ions at pH 5. The adsorption increased sharply within 40 min and then the curves became gentle and turned into a straight line at the end. Overall, the adsorption equilibrium was reached for the three ions within 60 min.

Adsorption selectivity

The competitive adsorption among Cr (III), Cu(II) and Zn(II) was examined in a ternary system. As shown in figure 6, TFP polymer have good adsorption selectivity for Cr(III) with the coexistence of Cu(II) or Zn(II). This indicated that the tetrazolyl groups on the polymer had a relatively stronger affinity for Cr(III) ions than Cu(II) and Zn(II) ions at pH 5. Normally, Cr(III) ion is more easily adsorbed than other metal ions. This could be applied to the separation of Cr(III) in aqueous systems containing Cu(II) or Zn(II).

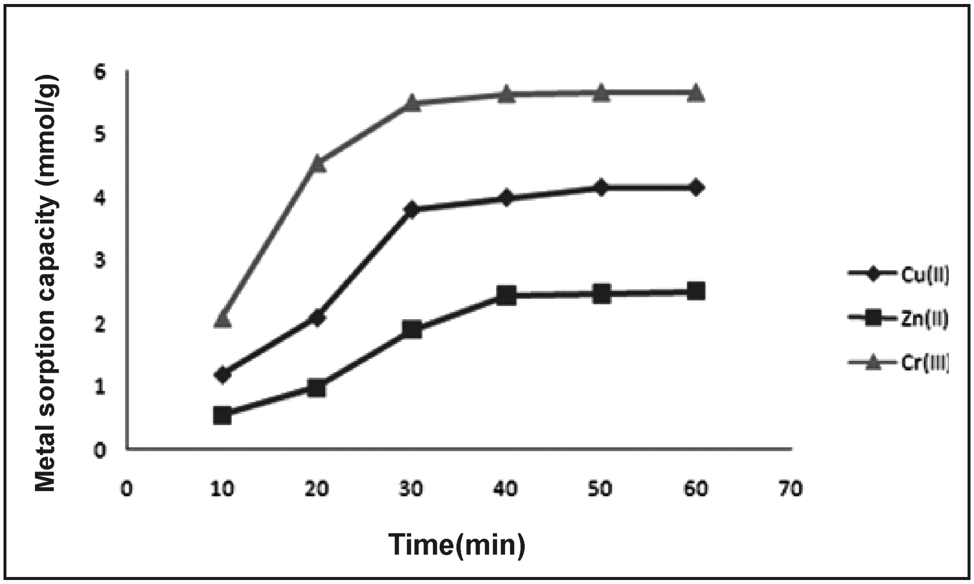


Fig 5. Effect of time on the sorption of metal ions Cu(II), Zn(II) and Cr(III)) by the TFP(metal ions initial concentration 0.04mol/L,pH=5).

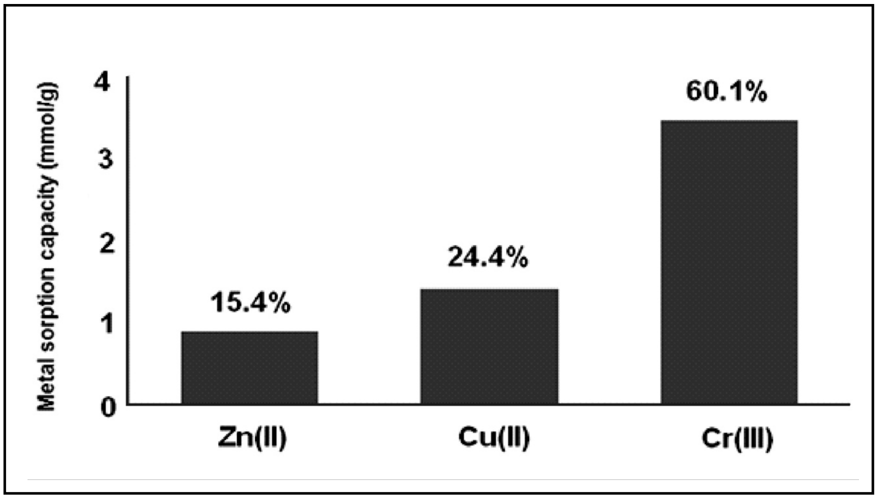


Fig6.The adsorption capacities and selectivity (%) of TFP under competitive conditions at pH = 5. (total metal ion ads.cap=5.72mmol/g)

In this condition TFP adsorbed the heavy metals in the following order: Cr(III) > Cu(II) >Zn(II). This affinity order was the same as that in the single metal adsorption studies.

CONCLUSION

A new tetrazole-functionalized absorbent (TFP) was successfully made from poly (2,2,3,3-tetracyanocyclopropyl) phenylacrylate by [3+2] azide-nitrile cycloaddition reaction in a small cyclopropane ring. FT-IR and elemental analysis confirmed the successful formation of the tetrazolyl groups in polymer. The resulting polymer and its adsorption behaviors for Cu(II), Zn(II) and Cr(III) ions were investigated in aqueous medium. The adsorption of all metal ions in completely acidic medium was moderate, and it was favored at the pH value of 5 to7. The adsorption behavior suggests that the adsorption was happened by an ion exchange and chelation interaction mechanisms. The chromium-TFP complexe showed a change in FT-IR spectra due to the metal ion complexation with the absorbent. A desorption rates for Cr(III) onto polymer were very rapid than Cu(II) and Zn(II). It was observed that the TFP was more selective for Cr(III) in the mixed solution. The adsorption–desorption processes demonstrated that the absorbent was suitable for reuse in the removal of heavy metal ions in aqueous medium.

Acknowledgements

The authors wish to acknowledge financial supports from the University of Urmia.

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Received: 20-12-2016

Accepted: 60-03-2017