Synthesis of Polyvinyltetrazole by Combination of Free Radical Polymerization and Click Chemistry for Adsorption of Pb (II) in Aqueous Solution

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Abstract

Polyvinyltetrazole (PVT) is produced from acrylonitrile (AN) monomer by using free-radical polymerization and Click Chemistry methods. The resulting polymer with a broad range of tetrazole group contents was conveniently synthesized through [3+2] azide-nitrile cycloaddition reaction of nitrile-containing polymer with sodium azide in DMF. The prepared PVT was characterized by[13]C-NMR, FT-IR and UV-Vis spectroscopies. Elemental analysis indicated that approximately 92% of the cyano groups on the polymer surface were converted to tetrazolyl groups. The PVT exhibited excellent adsorption form et al ions and the maximum adsorption capacity for Pb (II) was 2.39mmol/g which are much higher than corresponding literature results. 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 chelate were characterized by FT-IR, elemental analysis, gravimetry, scanning electronic microscopy (SEM), thermogravimetry analysis (TGA), UV-Vis spectroscopy, and atomic absorption techniques (AAS). All these analyses methods confirmed the presence of metal in the polymer-metal complex.

Keywords: Free Radical polymerization, Click Chemistry, Acrylonitrile, Heavy Metal Ions, Adsorption.

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Introduction

The by-product of the continuing dominance of heavy industry is ever-increasing reliance on dirty coal and a surge in greenhouse gas emissions. Heavy metal pollution is regarded as a global environmental problem which is threatening different organisms' survival[1-4].The removal of heavy metal ions from industrial wastewater has attracted much attention due to the hazardous effects of the heavy metal ions on different forms of life[5-7].Various techniques have been utilized to remove and recycle heavy metals from aqueous solutions such as chemical precipitation, ion exchange, electrochemical treatment and adsorption[8–10].The use of synthetic polymers with various functional groups for chelating toxic metal ions by adsorption is an interesting method for preventing environmental pollution[11-15].Functional polymers based on polyacrylonitrile are easily produced and the reactive pendant groups (nitrile groups) which can be modified by different kinds of reagents such as hydrazine, thiosemicarbazide, ethylenediamine and sodium azide through nucleophilic addition and cycloaddition reactions [16-19].The aim of this study is to synthesis tetrazol-containing adsorbent based on polyacrylonitrile by free radical polymerization and Click Chemistry as a synthetic strategy with high sorption capacity for metal ions in aqueous solutions compared to similar previous works[20-22].Lead ions represent a serious environmental problem since others are widely used in general applications and many industries. Therefore, in this work, we used the PVT as an adsorbent for the removal of Pb (II) ions from aqueous solutions in a series of batch adsorption experiments under different contact time and solution pH media.PVT and its lead (II) complexes were characterized by FT-IR,^{13}C-NMR, scanning electron microscopy (SEM), thermal gravimetry (TGA),elemental analysis, gravimetry, UV-Vis spectroscopy, and atomic absorption techniques.

Experimental

Melting points were measured with a digital melting point apparatus (Electrothermal, UK). The IR spectra were determined in the region 4000-400 cm^{-1} on a NEXUS 670 FT IR spectrometer (USA) by preparing KBr pellets. The metal adsorption capacity of the polymer was 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 thermal stability of polymers was studied by a Thermal Analysis METLLER STAR SW 10.0(Switzerland) by scanning up to 600°C with the heating rate of 10 °C/min. Elemental analysis of the polymer was carried out using a EURO EA 3000(Italy). The electron micrographs were obtained by using a scanning electron microscope (SEM) LEO 440i(UK).The gel permeation chromatography (GPC) measurements were conducted at 25°C with

aAgilent1100 instrument. The columns used were packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B from Polymer Laboratories) and THF was used as eluent at a flow rate of 1 mL/min. The ^{13}C-NMR spectra were recorded on Bruker Ultra shield 400 NMR at 400 MHz.

The monomer, acrylonitrile (Merck, Germany) was distilled under normal pressure and stored in the refrigerator. Benzoylperoxide, ammonium chloride, Lead (II) Nitrate [Pb (NO$_3$)$_2$.6H$_2$O], sodium azide and solvents were purchased from Merck or Aldrich and used without further purification.

Radical Polymerization of Acrylonitrile

In a 10 mL-ampoule, benzoyl peroxide (3mg, 0.018 mmol), and acrylonitrile (1 mL, 15.28 mmol) were dissolved in Dimethyl formamide (DMF) (2 mL) to obtain a solution. The reaction mixture was purged with dry nitrogen for 10 min in an ice-water bath to eliminate the oxygen and water. The ampoule was placed in a water bath which was thermostated at 60°C and it was shacked for 12 hr. After the mentioned time, the reaction mixture was cooled to ambient temperature, and the ampoule was broken open. Then DMF (3 ml) was added into the ampoule to dilute the solution, and the resulting solution was totally precipitated in a large amount of methanol (200ml). The precipitate was collected and washed with 30 ml ethanol and dried under vacuum to give polyacrylonitrile (PAN) (0.71g,yield: 83%)**.**Intrinsic viscosity**[η]**=0.81dL/g (Concentration of 0.5 g/dL in acetone at 25°C).FT-IR (KBr): 2933(C-H)، 2246 (CN)، 1638(C=N).

Preparation of PVT

A total of 106 mgof PAN solid was dissolved with about 4 mL of DMF in a 10 mL-ampoule. The mixture was stirred in an oil bath equipped with a thermostat until it was well-distributed at 25°C. Subsequently, (156 mg, 2.4mmol) of NaN$_3$ and (128 mg, 2.3 mmol) of NH4Cl were added to the PAN 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 at 120°C for 10 h. The final obtained reaction mixture was poured into a 200 mL beaker with HCl (100 mL, 1.0mol/L) for a complete precipitate of the PVT. Then, the precipitate was collected and washed with 10 ml DMF and dried in air at room temperature to give PVT (yield:81%). Intrinsic viscosity,[η]=5.8dL/g (Concentration of 0.5 g/dL in acetone at 25°C).FT-IR(KBr):3100-2400 (tetrazolyl), 2921 (C-H)،1634 (C=N),1533(N=N),1364 (C-N).

Adsorption Feature of PVT

Effect of pH on adsorption

The effect of pH on the adsorption properties of polyvinyltetrazole and polyacrylonitrile to Pb (II) was carried out with Pb^{+2}ion by batch equilibration technique [23]. The polymer (100 mg) was stirred with excess metal salt (4 mmol) for 30 min at 25°C. The pH of the solution was set at 1- 7. Then the mixture was filtered, and the residual metal ion concentration in solution was determined by AAS or UV-Vis spectrophotometer at room temperature. The adsorption capacities, (mmol M^{2+}/g resin) in various conditions were calculated as follows (Eq. 1):

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

Where C_0 and C_f are the initial and final concentrations (mmol/l) of the 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).

Kinetic adsorption

The study of the PVT adsorption kinetics for Pb (II) was carried out by shaking the mixture of adsorbent (100 mg) and Pb (II) solution (30 mL,0.04mol/L, pH 5.0) in a 100-mL beaker at 25°C. The filtrates were collected at different times for the determination of ion concentrations by AAS. The kinetic curve was obtained by the plot of the adsorption capacities vs. adsorption time.

Isothermal adsorption

In investigating the effect of temperatures on the sorption capacity of PVT for Pb (II) ion**,** a total of about 100 mg of adsorbent was soaked in the 100-mLbeaker filled with Pb(II) solution (pH 5.0). The mixture was shaken for 60min at a different temperature. The filtrates were collected for the determination of ion concentrations by AAS. The Adsorption isotherm 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 Pb(II)loaded polymers 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) :

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

Results and discussion

Preparation and Characterization of PVT

The AN monomer was polymerized by free radical polymerization with benzoyl peroxide as an initiator to obtain the PAN (scheme1). Polymerization was carried out in DMF solution at 60°C. The AN monomer was quite reactive toward free radical polymerization and polymerized readily. The obtained polymer was soluble in ethylacetate, acetone, DMF, and DMSO, but was not soluble in methanol and diethyl ether. Chemical structures of the PAN were determined IR spectra (Figure 2a).

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 Ka to the carboxylic acid. In the preparation procedure of PVT, PAN was modified through [3+2] cycloaddition reaction of nitrile with the triazol group. There action usually requires high temperatures above 100°C (scheme1).
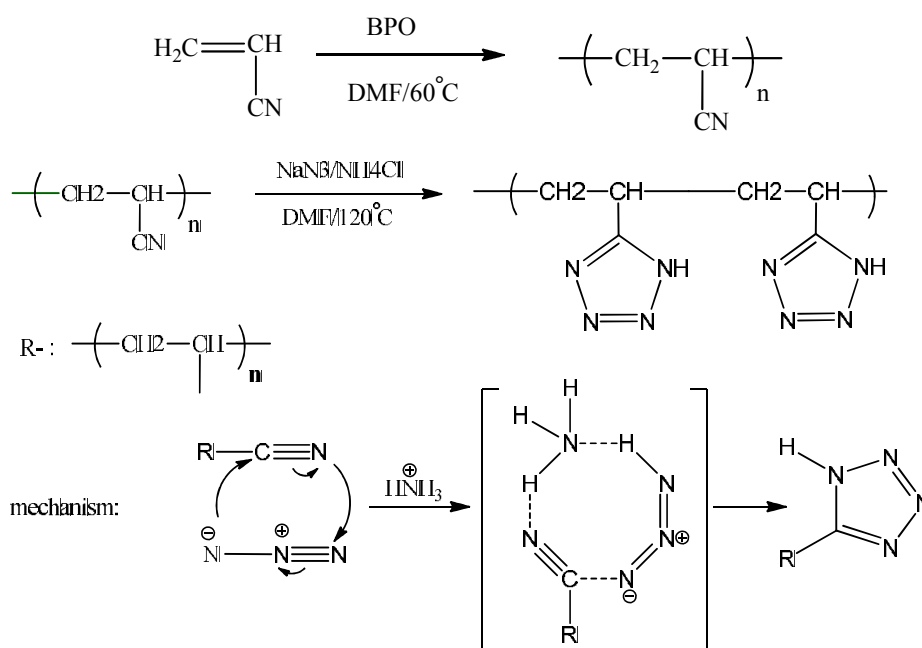
Scheme 1. Synthesisroute of PAN and PVT.

The chemical structure of the compounds was confirmed by ^{13}C-NMR, IR spectroscopy and elemental analysis techniques. Figure 1a and 1b displays the ^{13}C-NMR spectrum of PAN and PVT. The comparison of two spectrum showed that the signal at about 157 ppm assigned to the tetrazole carbon indicates the formation of tetrazolyl ring.
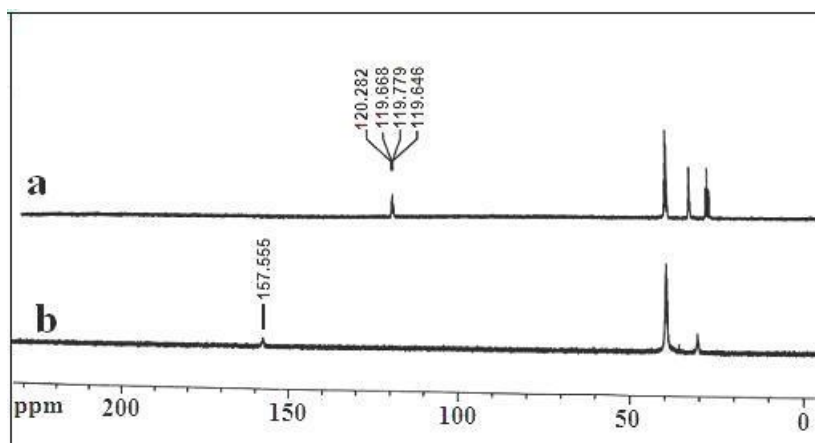

Figure1. Characterized ^{13}C-NMR spectra of (a)PAN and (b) PVT.

Figure 2a and 2b displays the FT-IR spectrum of PAN and the PVT polymers.The comparison of two spectrum showed that the nitrile peak is omitted and the formation of the broad medium band centered at 3100–2400 cm^{-1}was assigned to the tetrazolyl groups in PVT because of [3+2] cyclization reaction with azide. The broadening of this peak may indicate some hydrogen bonding on the part of the N-H bond with neighboring tetrazole groups. The band at 1634 cm^{-1}could be seen obviously due to the presence of C=N stretching vibration of the tetrazole ring and the new bands at 1533cm^{-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 C≡N groups and the formation of tetrazolyl groups. The number and weight average molar masses (Mn and Mw) of this polymer were determined by GPC were $1.076×10^5$ and $1.265×10^5$ g/mol, respectively, with a distribution index of 1.17.
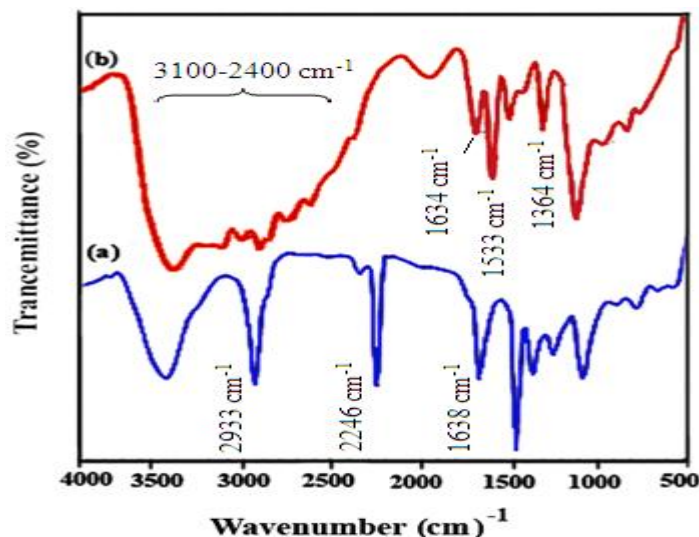
Figure2.FT-IR spectrum:(a) PAN,(b) PVT.

By comparing the FT-IR curve of the PVT(fig.3a) with its lead complex curve (Figure 3b) in figure 3, it can be seen that the C=N bonds of tetrazolyl groups in PVT, which would become stronger and shift to a higher frequency in the tetrazole salt, are probably responsible for the strong band which shifts from 1634 cm^{-1} in tetrazole to 1649 cm^{-1} in the tetrazolate ions[24].The stretching vibration band of N=N (1533cm^{-1}) was shifted to 1547cm^{-1} when PVT are associated with lead ions [25].
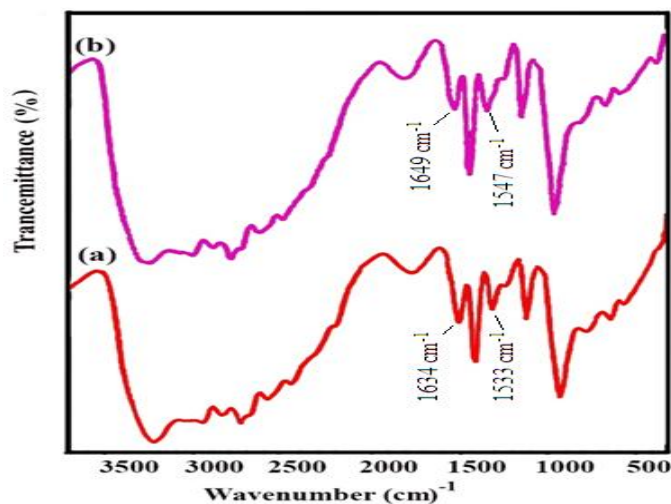

Figure3.FT- IR spectra of (a) PVT, (b) PVT-Pb complex (numbers represent pH in which maximum metal sorption was obtained).

The modified polymer (PVT) 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. The results of the elemental analysis of PVT are shown in Table1. As is known to us, the N content of the PAN is 24.94%. The C content of the PAN is 66.38%. The H content of the PAN is 5.49%. The N content of the PVT compared with the

N content of the PAN indicated the formation of the tetrazole groups. We can calculate the N content of PVT is 58.33% when the PAN was completely transformed to the PVT. The C content of PVT is 25%. The H content of PVT is 4.17%.The elemental analysis of PVT exhibits higher nitrogen content (56.61%) due to the formation of more tetrazole groups. Based on the chemical structure of PAN before and after reaction with azide, elemental analysis was used to calculate 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 PAN and PVT respectively; and N_c and N_r are themolar content of nitrile groups accessible and not accessible for reaction with NaN_3 in PAN, respectively. The calculated results were listed in Table 1.Over 92% of the cyano groups on the PAN were converted to tetrazole groups, determined according to elemental analysis results.

Table 1. Elemental analysis of polymers and the calculated group contents of PVT.

Samples	C (%)	H (%)	N (%)	Group contents in PVT (mmol g⁻¹)		Conversion of nitrile (%)
				Nitrile	Tetrazole	
PAN	66.38	5.49	24.94			
						92.7
PVT	32.21	4.64	56.61	0.4	5.1	

UV–Vis spectra of PVT

The UV-Vis spectra of PAN and PVT are shown in Figure4. The PAN exhibits a weak absorption at λ_{max} of 288 and 318 nm, whereas the PVT exhibit much stronger absorption at around 286 nm, indicating the presence of n→π* absorption due to the tetrazole rings [26]. These results show the presence of aromatic tetrazole groups in the polymer formed after the reaction of PAN with sodium azide and ammonium chloride.
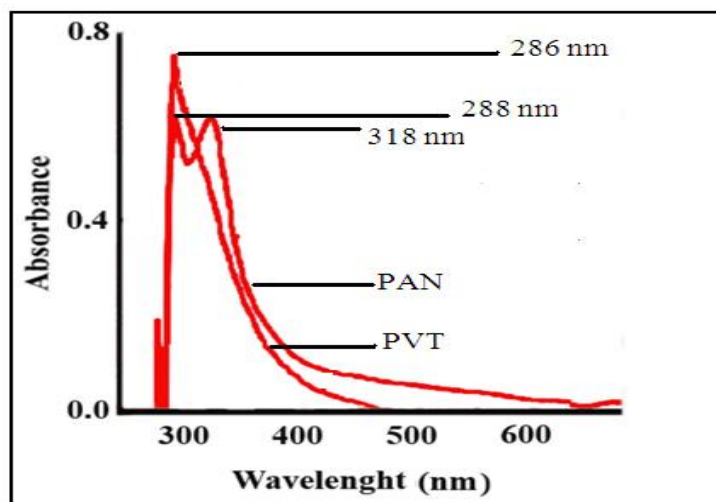
Figure4. UV–Vis absorption spectra of (a) PAN,(b) PVT. The PVT and PAN solutions had the same concentration of 2 mg polymer in 1 mL DMF.

Effect of pH and sorption mechanism

Figure 5 a presents the effect of pH values on the sorption of Pb (II) by the PAN and PVT. The resulting polymers were brought in to contact with aqueous solutions of Pb (II) in the range of pH 1-7.The metal sorption capacity of the polymers was measured with atomic absorption and UV-Vis spectroscopy methods at different pH values.

From the comparative experimental results (figure 5), it could be seen that the sorption capacity of PVT is higher than that of PAN. The chelating interaction and electrostatic attraction of Pb (II) with tetrazolyl groups are reasons that result in the removal of Pb (II) while the weak chelating interaction between Pb (II) and cyanide groups occurred in PAN.

An abrupt increase in the adsorption capacity by the PVT was observed in figure 5 when the pH increased from 1.0 to 4.0, and the plateau values were approximate 5.0for this case. This adsorption trend might be related to the property of the tetrazolyl groups.

H-tetrazole (TZH) is an amphiprotic compound, has a two-step protonation as follows (Eq. 3):

$$\Leftrightarrow \quad TZH_2TZ^+HTZ^- \quad \Leftrightarrow$$
$$PK_{a1}=0.8\pm0.1 \quad (3)$$
$$PK_{a2}=4.73\pm0.1$$
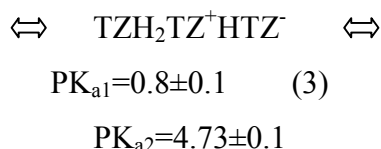
At low pH value, tetrazolyl groups occurred in the protonated form and the active sites of the PVT were less available for metal ions due to greater repulsive forces. Moreover, high concentration of H^+ ions could compete with metal ions and further lead to the decrease in metal adsorption. At intermediate pH (1to4), TZH_2^+ was deprotonated and favored the coordination-bond formation, and consequently, PVT began to adsorb metal ions via chelation interaction [Scheme 2a].

At pH > 4, tetrazolyl became a negative five-membered ring due to the dissociation of tetrazolyl groups, thus the electrostatic attraction of PVT to metal ion sharpened by an ion exchange mechanism [scheme 2b].

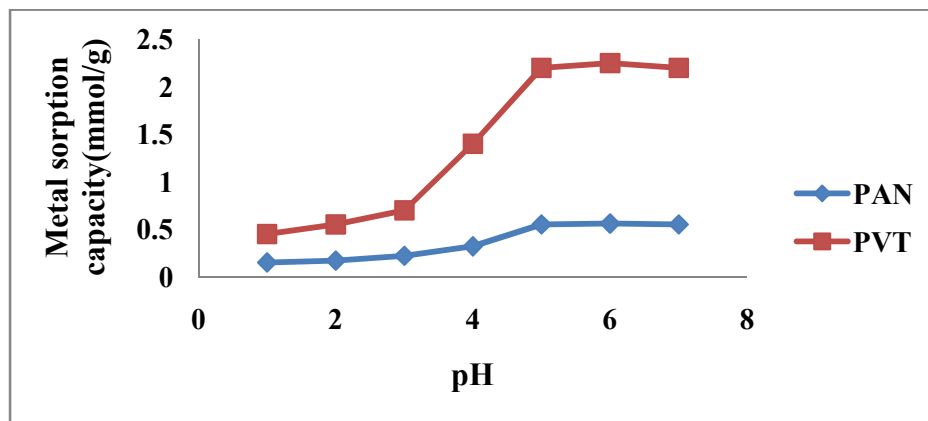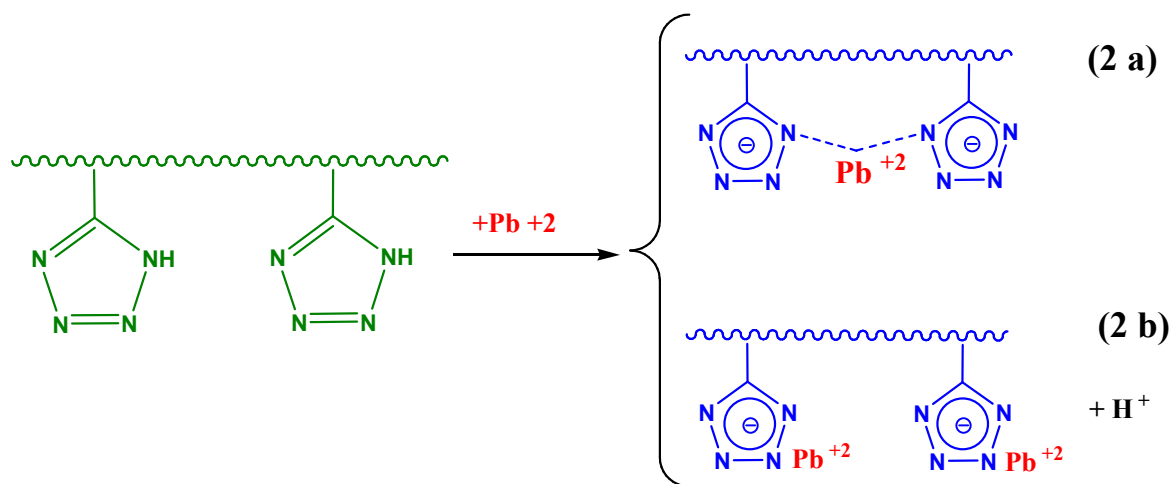The adsorption of Pb (II) on the polymer was more favorable at the pH value of 5 (Figure 5).

Figure 5. Effect of pH on the sorption of Pb(II) onto PAN and PVT [initial metal concentration 0.04mol/L, polymer (0.1 g)].

Scheme 2. Adsorption mechanism of PVT for lead ions.

The comparative experiments between PVT and other reported adsorbents were investigated to illustrate the excellent adsorption performance of PVT. The maximum adsorption capacity of PVT for lead ion was obviously higher than that of other presented adsorbents. The results are shown in Table 2.

Table 2. Comparison of the maximum Pb(II) sorption capacity of on PVT with other sorbents.

Adsorbents	Sorption capacity (mmol/g)	Reference
Polyvinyltetrazole	2.39	This work
polyvinyltetrazole-grafted PS resin	1.52	[21]
5-aminopyridine-2-tetrazole-functionalized polystyrene	1.35	[22]
Activated Carbons (PSW-P-500)	0.36	[27]
Commercial 732-CR resin	1.92	[28]
Cassava starch 5- chloromethyl-8- hydroxyquinoline	0.22	[29]
Rhodamine 6g-actinated carbon	0.20	[30]
Triethylene-tetramine grafted magnetic chitosan	1.78	[31]

Desorption of Pb(II) from PVT

Desorption of Pb (II) from the chelating PVT 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=5 were placed in the medium containing 1MHCl for 2 h. The amount of desorbed metal ion was measured in solution. The result shows that Pb (II) has a desorption ratio up to 92%.

Effect of Contact time

The adsorption kinetics of Pb (II) was investigated to determine the adsorption behavior. Figure 6 shows the adsorption kinetic curve of the lead ion at pH 5. The adsorption increased sharply within 40 min and then the curve became gentle and turned into a straight line at the end. Overall, the adsorption equilibrium was reached within 60 min.
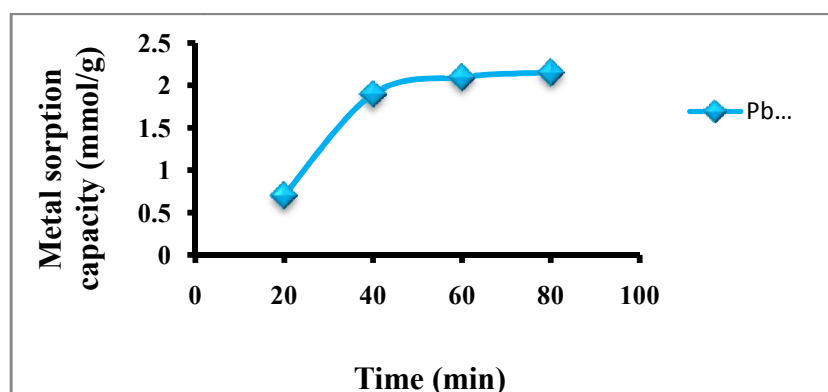

Figure 6. Effect of time on the sorption of metal ion Pb (II*)* by the PVT (metal ion initial concentration 0.04mol/L, pH=5).

Effect of temperature

The effect of temperature on the adsorption reaction for metal ions is regarded as one of the important characteristics that can decide the efficiency of adsorption. Figure 7 shows that the decrease of the adsorption capacities accompanied with the increase of temperature from 25°C to 55°C.That may be as a result of the weakening of the adsorption reaction between the metal ions and tetrazole groups of the polymer.
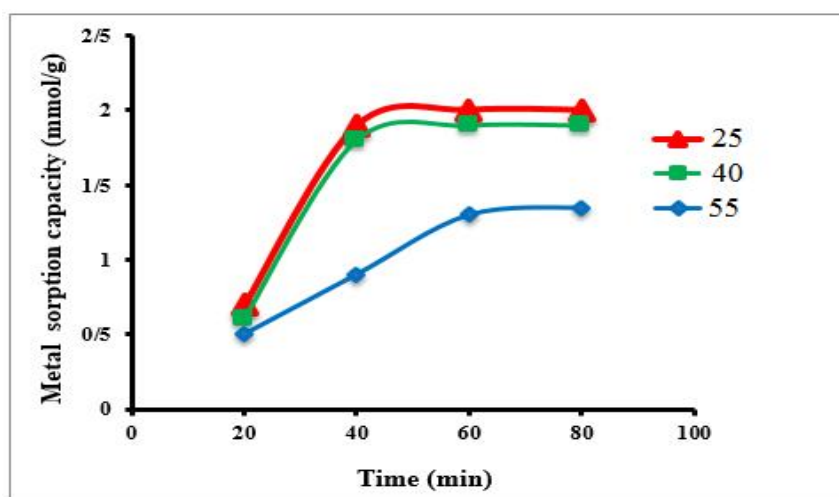

Figure 7. Adsorption isotherms of Pb (II) on PVT at different temperatures. (pH= 5.0,60 min).

SEM analysis

Scanning electron micrographs (SEM) was utilized to study the morphology of the PVT and its metal complex (prepared in pH 5).Figure8 shows that there is a strong change in the morphology of polymer surface from PVT beads in comparison with its lead complex. It was observed that the presence of more lead ions in the polymer causes the surface smoother [23].
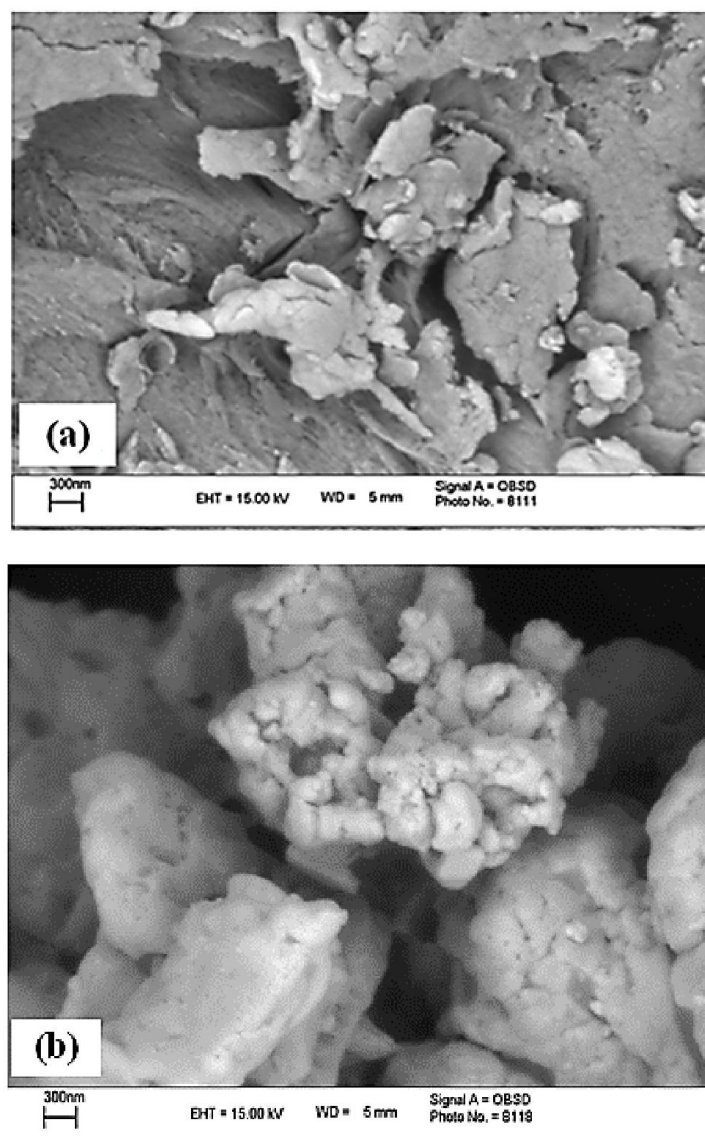
Figure 8. SEM images of (a) PVT, (b) PVT-Pb complex (numbers represent pH in which maximum metal sorption was obtained).

Thermogravimetry analysis

Thermal gravimetry analysis PVT and its lead complex curves (prepared at pH 5) are shown in Figure 9. It is interesting that the PVT show an extremely fast weight-loss at 267°C, indicating an explosive decomposition of the polymers containing more tetrazole groups due to the formation of a large amount of nitrogenous gaseous product [32].The second stage of mass loss starts at about 400 ºC and continues up to 600 ºC attributed to the degradation of the remaining polymer chains. The weight loss pattern of PVT and its complex up to about 220°C was approximately the same, but between 230°C and 600°Cpolymer was decomposed stronger than the polymer-Pb complex. There remained mass polymer-Pb complex (37wt %) at 600 ºC corresponds to the formation of lead oxide.
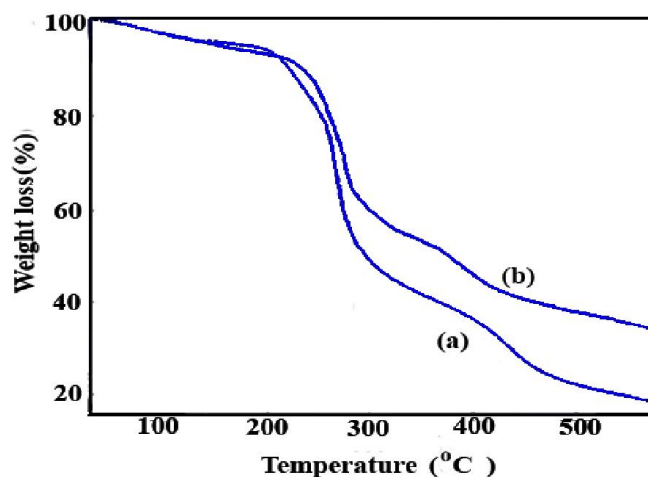
Figure 9. TGA Curves of (a) PVT, (b) PVT-Pb complex (numbers represent pH in which maximum metal sorption was obtained).

Conclusion

Polyvinyltetrazole have been successfully prepared via a combination of free radical polymerization and Click Chemistry and was used for the adsorption of Pb (II) from aqueous solutions. The obtained results showed rapid and effective favored adsorption method for the adsorption of lead ions. Using this resin for the removal of heavy metal ions is green, low cost, simple and clean technology method and has approximately high efficiency and maybe can provide a strategic approach to remove heavy metal ions from effluents discharged by industries.

Acknowledgement

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