# Synthesis and Adsorption Properties, Toward Some Heavy Metal Ions, of a New Polystyrene-Based Terpyridine Polymer

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**ABSTRACT:** A novel polymeric ligand having 2,2′:6′,2″-terpyridine as pendant group was prepared through a Williamson type etherification approach for the reaction between 4′-hydroxy-2,2′: 6′,2″-terpyridine and the commercially available 4-chloromethyl polystyrene. The chelating properties of the new polymer toward the divalent metal ions ($Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, and $Pb^{2+}$) in aqueous solutions was studied by a batch equilibration technique as a function of contact time, pH, mass of resin, and concentration of metal ions. The amount of metal-ion uptake of the polymer was determined by using atomic absorption spectrometry. Results of the study revealed that the resin exhibited higher capacities and a more pronounced adsorption toward $Pb^{2+}$ and that the metal-ion uptake follows the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. The adsorption and binding capacity of the resin toward the various metal ions investigated are discussed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2717–2724, 2012

**Key words:** 2,2′:6′,2″-terpyridine; adsorption properties; thermogravemetric analysis (TGA); FTIR; divalent metal ions

## INTRODUCTION

Heavy metals are commonly found in large quantities in industrial wastewaters. For this reason, the recovery of the metal ions present in these wastewaters is necessary for environmental protection and economical reasons. The most common metals found in wastewater are copper, cadmium, nickel, lead, and zinc, which are toxic at high concentrations.[1] The presence of heavy metals in the environment is of great concern because of their increased discharge, toxic nature, and other natural water adverse effects on receiving water.[2] The role played by toxic heavy metals in the aquatic environment has stimulated considerable activity and interest in the development of metal chelating polymers that found widespread use in the separation and monitoring of trace heavy metal ions from aqueous solutions.[3]

The chelating characteristics of these materials is largely dependent on the nature of the active chelating groups incorporated into the polymeric matrix and the type of intervening spacer groups connecting the active chelating ligands.[3] In addition, polymers bearing ligands with the ability to complex transition metals continue to attract the interest of researchers due to their ability to form tuneable and reversible supramolecular structures.[4] Moreover, polymers containing *N*-heterocyclic chelating ligands have become important macromolecular candidates in the field of metallo-supramolecular chemistry.[5] In the case of polymers containing terpyridine ligands, the literature provides a large variety of metallo-supramolecular systems that have different applications in different fields.[5] On the other hand, polymers-bound bipyridyl and terpyridyl complexes of metals such as Zn, Fe, Ni, Co, Cu, and Ru have been used to construct supramolecular step-growth polymers, block-copolymers, amphiphilic polymer assemblies, and polymers for self-healing materials among others.[4]

2,2′:6′,2″-Terpyridine and its derivatives are well-known metal complexing ligands.[6] Terpyridine-based lanthanide(III) chelates are among the best luminescent europium(III) chelates used as nonradioactive markers in a wide variety of routine and research applications.[7] In addition, terpyridine derivatives have also been used as building blocks for suprumolecular structures and nanotechnology as well as RNA cleavage agents.[8] Moreover, 2,2′:6′,2″-Terpyridines bearing well-defined π-conjugated substituents at the 4-position are known to exhibit interesting electronic and optical properties.[9]

There has been a number of publications pertaining to the synthesis of 2,2′:6′,2″-terpyridine derivatives. Jari Hovinen has prepared a number of 4-substituted 2,2′:6′,2″-terpyridine in high yields through the Mitsunobu reaction[7] by treating 2,6-di(pyridine-2-yl)pyridine-4(1H)-one with various protected primary alcohols in dry THF in the presence of triphenylphosphine and diisopropylazodicarboxylate. Vilar and coworkers[8] have prepared three new substituted terpyridine ligands functionalized with cyclic amines along with their corresponding platinum(II) complexes; the complexes have been shown to interact strongly with quadruple DNA. On the other hand, Garcia and his coworkers[10] have recently discovered that gold nanoparticles functionalized with iron(II) terpyridine complexes undergo upon laser flash excitation long-lived charge separation in both conventional organic solvents and ionic liquids. The photogeneration of long-lived transients upon irradiation of these functional gold nanoparticles has been applied to develop an integrated (light harvester plus catalyst) visible-light photocatalysts for $H_2$ generation from water that does not need methyl viologen as an electron relay. Moreover, Schubert and coworkers[11] have employed the click reaction of azido- and ethynyl-functionalized terpyridines to obtain a series of 1H-1,2,3-triazole-substituted terpyridines. They have also extended this protocol toward the synthesis of terpyridine-based macroligands via end group modification of ethynyl-functionalized polymers. Two of the (triazolylphenyl)terpyridine products were used in synthesis of homoleptic ruthenium(II) complexes. The combination of two orthogonal terpyridines within one-click reaction highlights the potential of this approach with respect to the preparation of new building blocks for supramolecular assemblies and functional materials. More recently, Li and Higuchi[12] have synthesized Dimethyl-substituted bis-terpyridines as novel ditopic ligand through aldol condensation, Michael-type bis-addition and Suzuki-type cross-coupling and prepared metallo-supramolecular coordination polymers by complexation of the bis-terpyridines with metal ions such as Ru(II), Fe(II), Co(II).

Similarly, polymers containing 2,2′:6′,2″-terpyridine have also been synthesized by a number of research groups. In a series of article,[5,6,9,11,13–15] Schubert and coworkers have prepared a number of well-defined macromolecular polymeric ligands containing terpyridines end groups bearing different polymeric spacers with different properties.[5] They have employed a Williamson type etherification approach for the reaction between 4′-chloro-2,2′:6′,2″-terpyridine with a number of well-defined mono- and bis-hydroxy functionalized polymers; the resulting terpyridine functionalized polymers could be considered as key candidates for the preparation of

metallo-supramolecular polymers via metallo-terpyridine complexation. They have also synthesized systems with different geometries and studied the effect of the systematic variation of both the spacer unit and the linker in conjugated bis(terpyridines).[9] In addition, They have functionalized dextran with 6-(2,2′:6′,2″-terpyridin-4′-yloxy)-hexanoic acid using two different ratios of terpyridine to dextran, leading to terpyridine-functionalized dextran esters possessing different degrees of substitution. They studied the "intra- and intermolecular" complexation behavior of both functionalized biopolymers using Fe(II) metal ions as well as activated Ru(III) complexes and succeeded in obtaining water soluble comb-polymer when using a PEG- functionalized terpyridine Ru(II) moiety for complexation.[13] Moreover, the same research group described the synthesis and characterization of four metallo-polymers containing either Zn(II) or Ru(II) ions in the main chain and were also able to produce the first photovoltaic devices out of these materials.[14] Furthermore, Schubert and coworkers[15] have synthesized A series of rigid π-conjugated bis(terpyridines) bearing electron-acceptor spacer units in 4′-position by Pd-catalyzed Sonogashira cross-coupling reactions. These new bis-(terpyridines) were applied for the self-assembly reaction with Zn(II) ions to form metallo-homo polymers. They have also investigated the electro-optical properties of the materials and observed band gaps up to 2.08 eV and bright blue to orange photoluminescence with quantum yields of 18 to 66%; these properties were strongly dependent on the nature of the π-conjugated bis(terpyridine) system. Similarly, Chen et al.[16] have prepared a series of novel terpyridyl Zn(II))-based metallo-polymers, including metallo-homopolymers and metallo-alt-copolymer, containing carbazole pendants attached to the C-9 position of fluorene by long alkyl spacers by self-assembled reaction. The photo-physical properties of these polymers exhibited blue photo-luminescent emissions (around 420 nm) with quantum yields of 11–23% (in DMF) and the photo-luminescent results revealed that the formation of excimers were suppressed by the incorporation of carbazole pendant groups. On the other hand, Kimura et al., reported on the formation of metallo-supramolecular polymers within silicate channels by using tpy-terminated EO-PO-EO triblock copolymers as both structure-directing agents and monomers.[17] Additionally, Pefkianakis et al.,[18] have prepared free terpyridine end-functionalized semiconducting oligomers (distyrylanthracene, quinquephenylene, mono- and trifluorenes) and have employed atom transfer radical polymerization for the preparation of side-chain oligomeric and polymeric (oxadiazole)s using a terpyridine initiator which were then complexed with a Percec-type first-generation (G1)

dendronized terpyridine–Ru(III)Cl₃ monocomplex, having two dodecyloxy groups. They discovered that the existence of the organic semiconducting blocks in combination with the terpyridine–Ru(II)–terpyridine groups afforded hybrid metallo-semiconducting species presenting the optical features of both their components. Moreover, their thin-film morphologies were investigated through atomic force microscopy, revealing, in some cases, an organization tendency in the nanometer scale.

In view of the wide interest in the activity and profile of terpyridines and terpyridine containing polymers and as part of our ongoing research on the synthesis and adsorption properties of chelate-forming polymers[1,3,19,20] we present, herein, the preparation of a novel polymeric ligand containing 2,2′:6′,2″-terpyridine through a Williamson type etherification approach for the reaction between 4′-hydroxy-2,2′:6′,2″-terpyridine and the commercially available 4-chloromethyl polystyrene. Because 2,2′: 6′,2″-terpyridine and its derivatives are well known as metal chelating agents the new polymer could be employed for the removal of heavy metal ions from the aquatic environment. The chelating properties of the new polymers toward the divalent transition metal ions ($Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, and $Pb^{2+}$) in aqueous solutions under different experimental conditions of contact time, pH, mass of resin, and concentration of metal ion are investigated.

## EXPERIMENTAL

### Reagents

Unless otherwise indicated, all chemicals used were of analytical grade and were used as received; chloromethylpolystyrene (Merrifield Polymer) cross-linked with 5.5% DVB; porous;16–50 mesh, 5.5 mmol Cl/g resin was purchased from Fluka (Buchs, Switzerland); ethyl picolinate was obtained from Acros Organics (Geel, Belgium); sodium hydride 60% dispersion in mineral oil was purchased from Aldrich (Milwaukee, WI). The following metal-ion salts were also used without further purification: copper(II) acetate dihydrate (98%), from Fluka, nickel(II) acetate tetrahydrate from BDH (Poole, England), zinc(II) acetate dihydrate from Riedel de Haen (Seelze, Germany), and lead(II) acetate trihydrate from S. D. Fine Chemicals (Mumbai, India).

### Instrumentation

Infrared spectra of the monomer, polymer, and metal chelates were recorded with a Nicolet Impact 400 Fourier transform infrared Spectrophotometer (Madison, WI) from 400 to 4000 cm$^{-1}$. KBr discs were used for all of the solid samples by the mixture of 1.0 mg of the sample with about 100 mg of KBr. NMR spectra were recorded with the aid of a Bruker-DPX 300 MHz spectrometers and are reported in ppm (δ) relative to TMS as an internal standard and with CDCl₃ or DMSO-$d_6$ as solvents. Atomic absorption data were obtained with the aid of a Varian Atomic Absorption spectrophotometer (Mulgrave, Victoria, Australia) model AA-250 plus. Samples were shaken using a GFL-1083 shaker thermostated water bath maintained at 25°C. A Metrohm pH meter model 525A was used for pH measurements. Elemental analyses were acquired with a Euro EA3000 CHNS-O elemental analyzer (Milian, Italy). A Brucker APEX (IV) mass spectrometer (Bremen, Germany) was used to obtain high resolution mass spectral data. The thermal stabilities of the polymer samples were studied by thermogravemetric analysis (TGA) with the aid of a Netzch STA 409 PG/PC thermal analyzer (Selb Bavaria, Germany). Measurements were performed at a heating rate of 20°C/min under dry nitrogen atmosphere purging at a flow rate of 50 mL/min in the temperature range of 20–1000°C.

### Synthesis of 1,5-bis-(2′-pyridyl)-1,3,5-tricarbonyl pentane (3)

Compound **3** was synthesized and characterized according to literature procedures outlined by Schubert and coworkers[21] that involved the slow addition of acetone (30 mmol) in dry THF (30 mL) to a solution of ethyl picolinate (55 mmol) and NaH (75 mmol) in dry THF (100 ml) under N₂ atmosphere (Scheme 1). The mixture was stirred at room temperature until a very vigorous reaction occurred and then heated to reflux for 6 h. The solvent was removed under reduced pressure, and the orange paste was treated with water (250 mL). The orange solution was filtered through celite, and the filtrate adjusted to pH 7 by drop-wise addition of dilute hydrochloric acid. The yellow solid was collected by filtration and washed with water then dried to give compound **3** as a yellow solid (80%), m.p. 103–105°C. NMR spectrum is in agreement with the proposed structure and similar to the literature.[21]

### Synthesis of 2,6-bis-(2′-pyridyl)-4-pyridone (4)

Compound **4** (Scheme 1) was also synthesized and characterized according to literature procedures.[21] A solution of compound **3** (10 mmol) and ammonium acetate (4.0 g, excess) in ethanol (50 mL) was heated to reflux for 6 h, after which the dark brown solution was concentrated to half volume. The solution was cooled, and the white precipitate formed was collected by filtration and washed well with diethyl ether. Recrystallization from ethanol yielded white
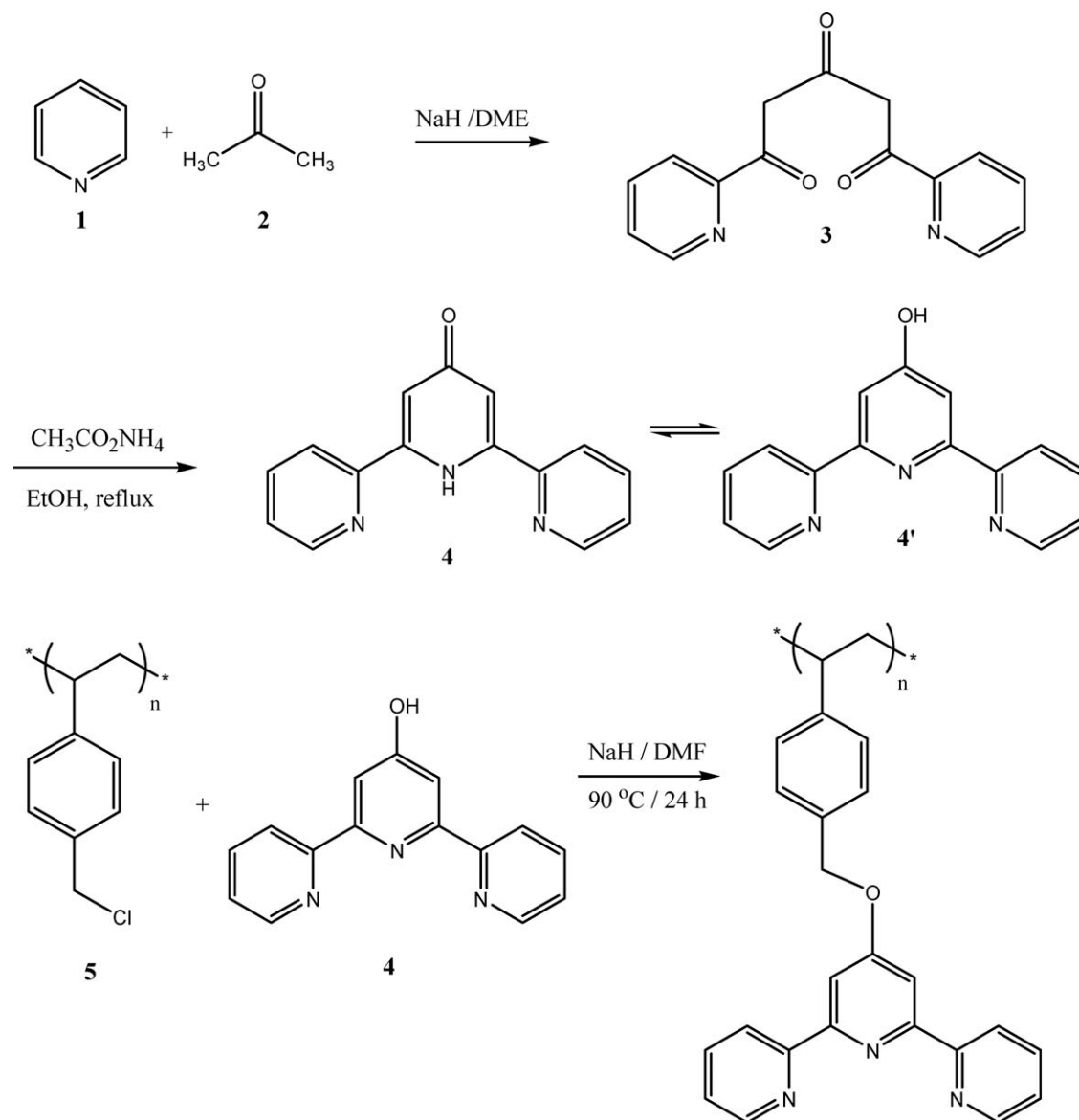
**Scheme 1** Synthesis of the tyrpyridine-based polymer.

needles of compound **4** (80%), m.p. 166–168°C. HRMS (EIMS) $m/z$: Calcd. for $C_{15}H_{11}N_3NaO$ [M + Na]$^+$ 272.07998. Found 272.07943. $^1$H and $^{13}$C spectra are in agreement with the proposed structure and are similar to the literature spectra.[21]

## Polymer preparation

The new polymer was prepared, according to Scheme 1, by treating 10.0 g (0.04 mol) of compound **4** in dry DMF (50 mL) with 1.45 g of NaH (0.060 mol) under $N_2$ atmosphere. The mixture was stirred at room temperature for 30 min and then 5.05 g of the commercially available 4-chloromethylpolystyrene polymer (**5**) (0.033 mol) was added. The reaction mixture was heated at 90°C for 24 h. The reaction mixture was then cooled and the polymer was col-

lected by filtration and washed with DMF (50 mL) and with diethyl ether (2×50 mL). Further purification of the resin was achieved by soxhlet extraction with methanol for 24 h. The resin was then dried in a vacuum oven at room temperature for 24 h and sieved through mesh size 35–60 (0.25–0.50 mm$^2$). Satisfactory elemental analyses were obtained. Calculated for $[C_{24}H_{19}N_3O]n$: %C 78.88, %H 5.24, %N 11.50; found : %C 77.84, %H 5.35, %N 9.56.

## Adsorption of the metal ions on the polymer

We employed batch equilibrium technique to investigate the metal chelating characteristics of the polymer for each metal ion; duplicate experiments involving dry 0.1000 g of 35–60 mesh resin samples were suspended in 35 mL of sodium acetate- acetic
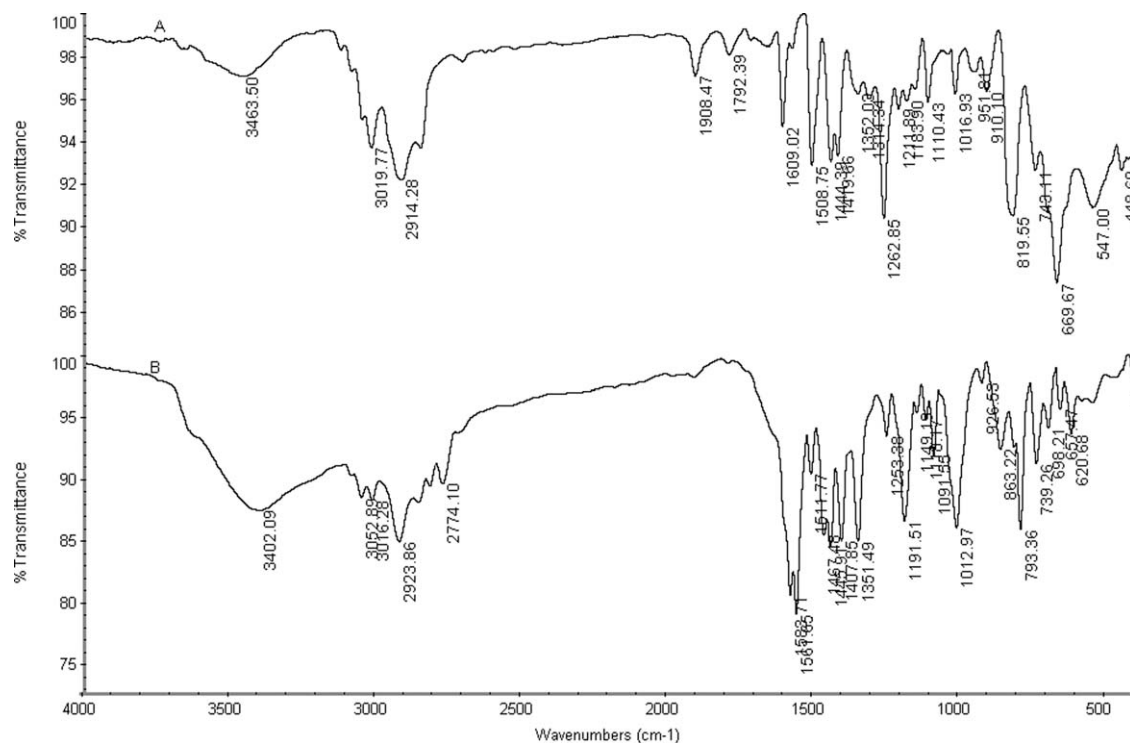
**Figure 1** A: IR spectrum of chloromethylpolystyrene. B: IR spectrum of resin.

acid buffer solutions of pH 7 for 4 h and were left to equilibrate. To this mixture, 15 mL of metal-ion solution containing a total of 15.0 mg metal ion were added. After being shaken for a definite period of time at 25°C, the mixture was filtered and the amount of metal ion remaining in the filtrate was determined by atomic absorption spectrometry (AAS) using standard solutions for calibration. The effect of contact time on the rate of metal-ion uptake was studied under similar experimental conditions where the contact time was varied from 1 to 24 h at 25°C after being equilibrated with distilled water. Similar experiments were performed, in buffer solutions in which the pH was varied between 2.0 and 8.0 at fixed contact time of 6 h to evaluate the effect of pH on the extent of metal ion uptake.

The effect of amount of polymer on the metal-ion uptake was also studied using the same general procedure by shaking a suspension of 0.1, 0.2, 0.3, 0.5, 0.7, or 1.0 g of the dry polymer in 25 mL of the acetate buffer solution at pH 6.0 for 2 h. To this mixture, 25 mL of buffer solution containing 25 mg of metal-ion were added. The mixtures were then shaken at 25°C for 6 h, filtered, and the amount of metal ion remaining in solution was determined by AAS. Similar experiments were carried out to assess the effect of metal-ion concentration on the rate of metal ion uptake; buffer solutions containing 0.100 g of dry polymer and variable amounts of metal ions at 25°C and a fixed contact time of 6 h were employed for this purpose.

## RESULTS AND DISCUSSION

### Preparation and characterization of polymer

The polymer was prepared by reacting compound **4** with the chloromethylated polystyrene (**5**). Elemental analysis gave 6.83 mmol N/g resin which corresponds to almost 100% yield of chloromethyl group substitution and indicates total chlorine displacement. The polymer is insoluble in all organic solvents; this makes it difficult to use certain spectroscopic techniques, such as NMR for characterization. Structure of the resin was also confirmed using FTIR. In the spectrum of the resin, the absorption bands observed around 3060–3020 $cm^{-1}$ and 2930 $cm^{-1}$ region have been attributed to the stretching vibration of the aromatic C—H and to the C—H of the methylene groups connecting the aromatic rings with the terpyridine, respectively. In addition, the disappearance of the strong absorption band at 1263 $cm^{-1}$ [Fig. 1(A)] associated with chloromethyl group indicates the reaction between —$CH_2Cl$ and compound **4**.[22] Moreover, the appearance of a strong absorption band at 1191.5 $cm^{-1}$ [Fig. 1(B)] indicates an ether group that resulted from the reaction between the monomer and the chloromethyl group of the commercially available resin.

### Thermal stability of the polymer

The thermal stability of the polymer was investigated by TGA under dry nitrogen. The relative
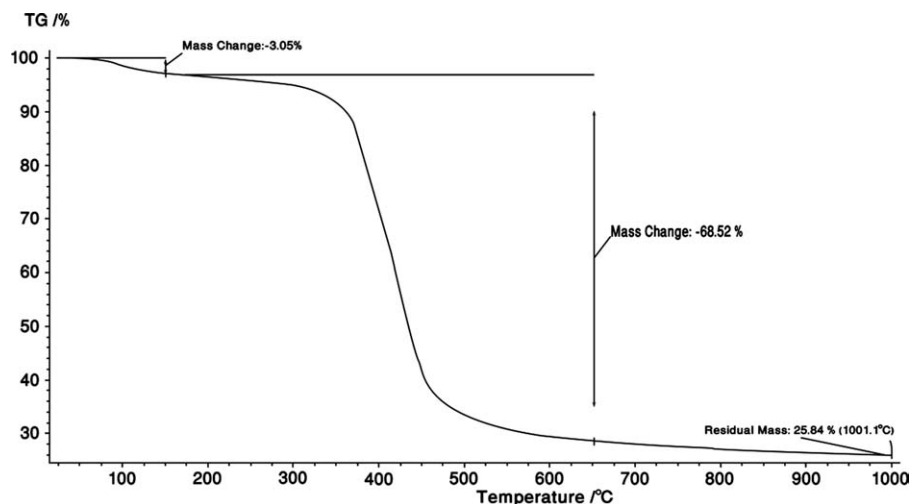
**Figure 2** TGA thermogram of resin 2. TG % is the mass percentage of the polymer sample remaining after heating the polymer to a certain temperature.

thermal stability of the resin was evaluated by comparing the weight loss in the temperature range 200–1000°C. Displayed in Figure 2 is the TGA thermogram of the resin. The first stage of decomposition was the desorption of water molecules. Thus, within 140°C, the resin has lost about 3.05% of its weight. Beyond this temperature the resin displayed one-stage degradation with a fast loss of mass starting from ∼ 200°C to 650°C with an additional 68.5% weight loss which corresponds to the loss of the terpyridyl moiety. The residual mass percentage remaining after the resin was heated to 995°C was about 26%. These results show that the prepared resin has good thermal stability.

### Rates of metal-ion uptake by the polymer

The adsorption of various divalent metal ions ($Ni^{+2}$, $Cu^{+2}$, $Pb^{+2}$, and $Zn^{+2}$) on the newly synthesized polymer was investigated by a batch equilibrium technique as a function of contact time at fixed pH of 7.0. Depicted in Figure 3 are the results for the dependence of the metal ion uptake on contact time. These results indicate fast rates of equilibration; the rates of metal-ion uptake increase in the first 1 h and reach a steady state after 6–12 h. It is interesting to note that, during the first 30 min, over 60–70% of the metal ions are taken by the polymer. Various classes of chelating polymers reported in the literature exhibited a wide range of rates of metal ion uptake. In general, the adsorption rates are governed by several factors such as the nature of active chelating groups and repeating units, structural properties of the polymer (porosity, surface area, size, and molar mass), the concentration of metal-ion, the amount of polymer used, and the concentration of other ions that may compete with the metal ion of

interest[3]; this makes rate comparisons a subject of great uncertainty.[19] Typical phenol–formaldehyde polymers such as poly(8-hydroxyquinoline-5,7-diyl-methylene)[19] achieve adsorption equilibrium after 7 to 10 h. However, relatively, shorter equilibration times were observed in chelating polymers containing oxime groups. Ebraheem and Hamdi[23] have reported fast equilibration times of 1 h for Cu(II), Zn(II) and Ca(II) and 5 h for Ni(II) and Cd(II) with poly(salicylaldoxime-3,5-diylmethylene).

Results also revealed that the metal-ion uptake follows the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} >$. This difference in metal-ion uptake capacities observed among the metals by the resin can be attributed to a combination of factors including metal-ligand stability constants, metal ionic radii, and stereochemical configuration of active chelating sites among others.[20] Apparently, the formation constant of $Pb^{2+}$ ions-polymer is higher than those of other metal ions; this behavior has been previously observed by
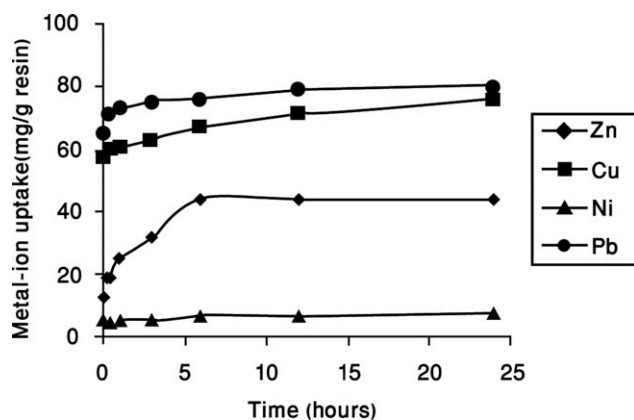


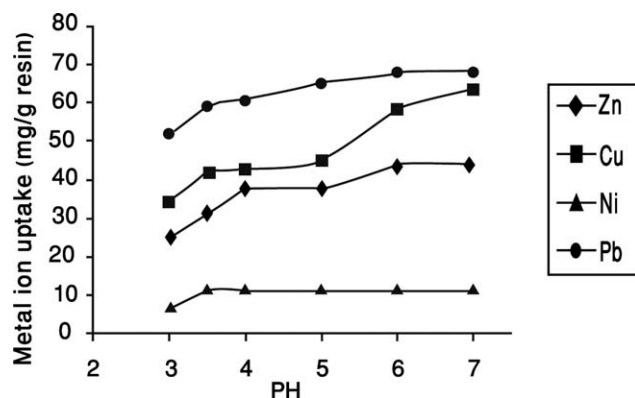**Figure 3** Metal-ion uptake by resin as a function of contact time.

**Figure 4** Effect of pH on metal-ion uptake by the resin.



**Figure 6** Effect of initial amount of metal ions on metal ion uptake by resin.

other research groups.[24] In addition, the ionic radius for $Cu^{+2}$ is 71 pm and for $Zn^{+2}$ it is 88 pm; the stability of the chelate is expected to be less favorable for ions of larger size which is consistent with earlier investigations.[1] Moreover, variation of contact time showed a maximum loading capacities of the different metal ions for the polymer of 80, 75, 44 and 7 mg/g resin for $Pb^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Ni^{2+}$, respectively. These are relatively large amounts and indicate that this polymer can be efficiently used to remove heavy metal ions, especially lead, from the aquatic environment.

The pH dependence of metal ion uptake by the new polymer was studied in the pH range 4.0–7.0 for a fixed contact time of 6 h. At higher pH values, hydrolysis of the metal ions investigated becomes significant and may compete with polymer chelate formation. Typical pH-binding capacity profiles are displayed in Figure 4. Results reveal that metal-ion uptake increased with pH of the medium and approached a steady state at about pH 6.0. This behavior could be explained by the nature of the chelating group; at low pH values the nitrogens of the terpyridyl group may get protonated which leads to less metal ion uptake. Therefore, at higher
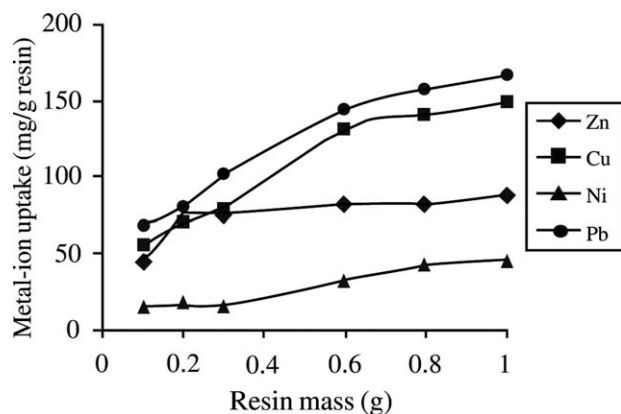
pH values the amine group lone pairs will be more available for binding to metal ions and the divalent metal ions compete favourably toward donor sites compared with hydrogen ions, in accordance with our recent work.[20] These findings are in agreement with the pH-profiles of most chelating polymers with N,O binding sites.

### Effect of the polymer mass and metal-ion concentration on the metal ions uptake

The batch equilibration technique was employed to investigate the effect of resin's mass on the rate of metal-ion uptake; different masses (0.1, 0.2, 0.4, 0.6, 0.8, or 1.0 g) of the dry resin were suspended in 25 mL of the acetate buffer solution at pH 6.0 for 2 h. Then, 25 mL of buffer solution containing 25 mg of metal ion was added at 25°C under continuous shaking for 6 h. Figure 5 shows the dependence of ion uptake on mass of resin. Results clearly reveal that extent of metal ion uptake increases with the increase of the mass of the polymer. This may be explained by the increase of the polymers sites available for adsorption and/or chelation which is in agreement with our recent findings.[25]

The effect of metal-ion concentration on metal-ion uptake was studied by suspending 0.100 g of the dry polymer in 25 mL of the acetate buffer solution at pH 6.0 for 2 h followed by the addition of 25 mL of buffer solution containing different amounts of metal-ion.[20] The dependence of metal ion uptake capacity on the amount of metal ion is displayed in Figure 6. Results reveal that the metal-ion uptake capacity of the resin increases with the increase in the initial metal ion concentration; similar results similar results have been reported in the literature.[1,26]

### CONCLUSIONS

A new polymer containing 2,2′:6,6″-terpyridine as pendant group was prepared through a Williamson type etherification approach from the reaction



**Figure 5** Effect of amount of polymer on the metal-ion uptake.

between 4′-hydroxy-2,2′: 6′,2″-terpyridine and the commercially available 4-chloromethyl polystyrene. The chelating properties of this polymer toward some divalent heavy metal ions in aqueous solutions were investigated using a batch equilibration method under different experimental conditions of contact time, pH, mass of resin, and metal ion concentration. The investigation has revealed polymer the metal-ion uptake follows the order: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. In addition, the pH-binding capacity profiles showed that the metal-ion uptake of the resins increased with increasing pH and reached a maximum at pH 7.0. The investigation has also revealed that this newly synthesized polymer can be utilized to remove heavy metal ions, especially, lead from the aquatic environment.

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