Synthesis of Functionalized Polymeric Adsorbent Selective to Cobalt

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ABSTRACT: Amino derivative of chloromethylated polystyrene resin was synthesized and functionalized by 1,10-phenanthroline (1,10-Phen) to yield a novel adsorbent, namely 4-methylamino-[N,N-bis(2,2$'$)-1,10-phenanthroline] polystyrene (**4-MABPPS**). The complete development of novel adsorbent along with its characterization is described in detail. The adsorption ability and selectivity of **4-MABPPS** were investigated for cobalt and zirconium ions so as to efficiently separate cobalt ion impurities from zircalloy cladding material of nuclear reactors. The experimental results showed selective uptake of cobalt by the adsorbent in the presence of zirconium. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4054–4060, 2012

Key words: chloromethylated polystyrene resin; 1,10-phenanthroline; adsorbent; adsorption

INTRODUCTION

A significant need exists for development of new materials to recover valuable and toxic metal ions from both the environmental and industrial process streams. A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentrations and exist in complex mixtures.

High-purity Zirconium and its alloys (Zircalloys) are required for cladding materials in nuclear reactors. Cobalt-60 is an activation product of stable [59]Co, which is a common impurity in zircaloy and aluminum fuel cladding and in uranium metal fuel.[1] The half-life of Co-60 ($t_{1/2}$ = 5.3 y) and its gamma emissions make it a principal contributor to potential dose effects in environment and hence it is essential to address this problem by developing a suitable separation technique for cobalt. In this article an attempt has been made to develop a functionalized polymer which can selectively adsorb cobalt ion in pr esence of zirconium.

Use of chelating resins seems to be a promising technique for selective separation of metal ion. The main criterion which determines the affinity of chelating resins for a given metal are ionic charge, hydrated ionic radius, and ligand bonding with exposed electron pairs on nitrogen and oxygen.[2] There has been a great deal of interest in the synthesis of free and substituted polyazamacrocycles due to their wide range of applications.[3] It has been demonstrated that macrocyclic ligands containing nitrogen and sulfur as donor atoms can behave as highly selective complexing agents for transition metal cations and heavy metal ions.[4,5]

These resins have been the subject to number of reviews.[6] Till date various synthetic methods have been developed for the synthesis of macrocyclic ligand systems incorporating 1,10-phenanthroline (1,10-Phen) moiety,[7–12] but most of them consists of multistep synthetic routes, which are time consuming and expensive. These methods also suffer from limitations like separation of side products and low yields. The 1,10-Phen forms highly stable complexes with transition metal ions such as Co, Ni, Cu, etc. and has been used for many years as a co-ordinating ligand group.[13,14] Compared to the more common 2,2$'$- bipyridine system, 1,10-Phen can form complexes with metal ions more rapidly.[3] The chemistry of synthetic aza-macrocycle and their metal complexes have been intensively investigated to correlate their structural properties, as well as reactivities with those of metalloporphyrins and corrins.[13] Preparation of macrocyclic ligand by condensation of 2,9-diamino- and 2,9-dichloro-1,10-phenanthroline in the presence of potassium carbonate and nitrobenzene as media has been already reported by Ogawa et al.[9]

This work deals with the development of comparatively simple and efficient process for the development
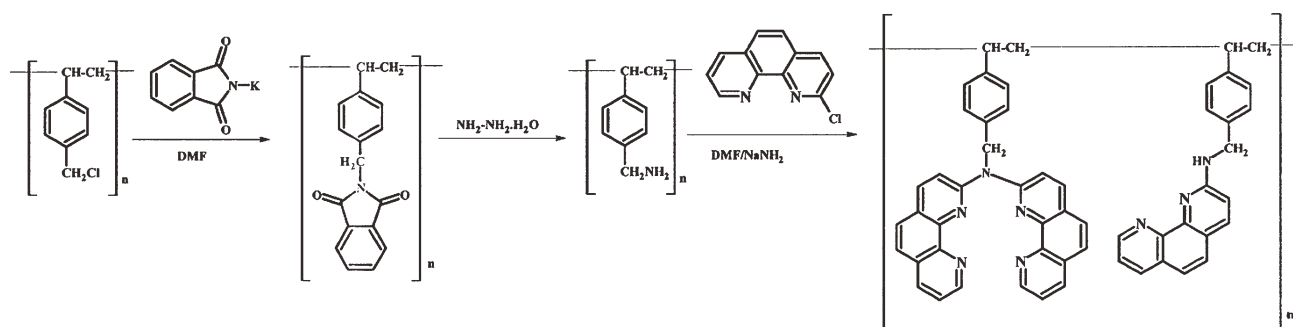
Figure 1 Synthesis of 4-MABPPS.

of 1,10-phenanthroline bound polymeric adsorbent by reacting 2-chloro-1,10-phenanthroline (2-ClPhen) with an amino containing polymer i.e., amino methylated polystyrene (AMPS). The 1,10-phenanthroline moiety is loaded on to the polymer matrix which acts as an adsorbent for selective separation of Co(II) and Zr(IV).

EXPERIMENTAL

Materials

Chloromethylated polystyrene (CMPS) was obtained from Ion Exchange (I), Mumbai, India having chloride ion content 4 mmol g^{-1}. All the solvents and reagents [methanol, N,N-dimethyl formamide (DMF), phosphorous oxychloride 1,10-phenanthroline, iodomethane etc., the metal salts; cobalt chloride hexahydrate, zirconium oxychloride octahydrate, and concentrated hydrochloric acid] required for synthesis and adsorption study were procured from S.D-fine chemicals, Mumbai. The reagents such as thorine indicator, hydrazine sulfate, and hydroxyl amine hydrochloride required for the quantitative analysis of metal ions were procured from Merck, Mumbai. All the chemicals procured were of analytical grade and were used as they are supplied.

Synthesis of polymeric adsorbent (4-MABPPS)

Preparation of amino methylated polystyrene resin (Amps) (III)

AMPS (**III**) (Fig. 1) was prepared by the conventional Gabriel reaction[15] by reacting potassium–phthalimide (2.77 g, 0.015 mol) with CMPS (**I**) resin [2.50 g, 0.01 mol with respect to chlorine content in (**I**)]. The reaction was carried out in DMF as reaction media at 100°C for 3 h. Initially an intermediate phthaloyl-loaded resin (PLR) (**II**) was obtained with 100% conversion [3.65 g, 0.01 mol with respect to phthaloyl group content in (**I**)]. This (**II**) on hydrazinolysis at 50°C for 6 h gave (**III**), which was filtered and washed thoroughly with water and methanol successively. The resin was dried at 70°C for 3 h. (2.40 g, 0.0098 mol, Yield: 98.47%). This method of

hydrazinolysis offered a milder and more efficient method for deprotection of phthaloyl group than base hydrolysis.[15]

Preparation of 2-ClPhen (IV′)

2-ClPhen was prepared from 1,10-Phen (I') in three steps.[7–12]

Step 1. 1,10-Phenanthroline methyliodide (**II′**): (**II′**) was prepared by reaction between (**I′**) (5.94 g, 0.03 mol) and methyl iodide (11.35 g, 0.08 mol) in nitrobenzene as reaction media at room temperature for an interval of 10 h. The yellow crystalline product obtained was filtered and washed with benzene till material was free from nitrobenzene. The yield of the product was 9.97 g, 0.029 mol (97.8%).

Step 2. 1-methyl-1,10-phenanthroline-2-one (MPO) (**III′**): To an ice-cold aqueous solution of potassium ferricyanide (19.7 g, 0.06 mol), saturated solutions of sodium hydroxide (500 mL of 6M) and (**II′**) (9.97 g, 0.029 mol), were added dropwise simultaneously and then excess NaOH being added until no further precipitation took place. The yellow precipitate was refluxed with benzene to give a product. The light brown solid, obtained on removal of the benzene, crystallized from benzene (Yield: 5.967 g, 0.028 mol, 91%).

Step 3. 2-Chloro-1,10-phenanthroline (**IV′**): (**III′**) (7.23 g, 0.026 mol) and phosphorus pentachloride (8.67 g, 0.034 mol) in phosphorus oxychloride media were refluxed for 8 h. After removal of excess phosphorus oxychloride by distillation under reduced pressure, ice cold water was added and the solution was basified with ammonia. The pale brown precipitate was crystallized from hot water as cotton white needles (Yield: 6 g, 0.019 mol, 88.73%).

Synthesis of 4-MABPPS (IV)

The novel adsorbent **4-MABPPS** (**IV**) was prepared by reaction between **IV′** (8.58 g, 0.04 mol) and **III** (2.455 g, 0.01 mol with respect to amino content in AMPS) in presence of sodamide (NaNH$_2$) (1.17 g, 0.03 mol) in DMF media. The reaction was carried out with continuous stirring at 110°C under an inert

atmosphere of nitrogen for duration of 5 h. The loaded resin **4-MABPPS (IV)** was washed with water and methanol successively. The resin was dried at 70°C for 3 h. This being a solid phase synthesis no impurities remained with the product. The conversion of AMPS to **4-MABPPS** projected to partly monofunctionalization and partly bisfunctionalization. The total yield is 4.121 g. (62.39%).

Characterization of synthesized polymer

The newly synthesized adsorbent 4-methylamino-[N,N-bis(2,2$^{'}$)-1,10-phenanthroline] polystyrene **(4-MABPPS)** and intermediate reactants were characterized by Solid state ^{13}C-NMR and ^{1}H-NMR (Bruker/Advance AV 500WB spectrophotometer, Biospin, Switzerland), FTIR (Perkin–Elmer Fourier Transform-2000), EDX (JEOL, JSM-6380LA), and X-RD (Rigaku, MiniFlex) to confirm the presence of matrix as well as chelating moiety on the substrate.

Equilibrium adsorption study of cobalt and zirconium ion by 4-MABPPS in different pH range

Equilibrium adsorption studies were carried out to generate an equilibrium relationship between the adsorbed amount of cobalt on the adsorbent and the residual concentration of the solution, in the form of an adsorption isotherm. These studies were carried out to check the maximum adsorption capacity of cobalt ions of synthesized polymeric adsorbent. The equilibrium adsorption studies were conducted in Erlenmeyer flasks. Known amounts of resin (0.05 g) were taken in these flasks, and solutions of known concentrations (1–100 ppm) of metal salts (cobalt chloride and zirconium oxychloride) were then added into these flasks. Batch equilibrium study was conducted in de-ionized water in the range of 1–8 pH using HCl and NaOH solutions. The Erlenmeyer flasks were then kept in a shaker incubator for 24 h at 30°C to attain equilibrium. The three samples at each pH of the residual concentrations of metal salts were analyzed by UV-vis spectroscopy for confirming the reproducibility of observations and also to determine moles of cobalt adsorbed per kg of adsorbent.

Selective separation of cobalt ion by ion exclusion

4-MABPPS adsorbent was placed in a Plexiglas column, 20 cm long, and 1.2 cm in diameter. The top and the bottom zones of the column were packed with glass beads and nonadsorbing cotton. The air bubbles in the resin bed and associated channeling were removed by passing de-ionized water. The 1000 ppm solutions each of cobalt and zirconium were prepared. The two solutions were mixed in a ratio of 1 : 1 and this mixture was used as a feed

solution for adsorption. The flow rate was 2 cm^3 min^{-1} was maintained during adsorption studies. Samples were collected at regular time intervals (1 min initially and later 10 min) at the exit of the column for 2 h and analyzed by UV spectrophotometer. Once the column was saturated, as indicated by leakage of cobalt in the effluent of the column, the solution flow was replaced by 6M HCl. The adsorbed cobalt on the polymer bed was desorbed with a downward flow of HCl at the rate of 4 cm^3 min^{-1}. Samples were also collected during the desorption stage and were analyzed by UV spectrophotometer as described below.

Quantitative analysis of zirconium during adsorption studies

Totally, 0.5 mL of 20% hydroxyl amine hydrochloride solution was added to the samples removed during adsorption studies, so as to remove interference of any ferric, stannic or chromic ions present. Further, 0.5 mL of conc. HCl and 1 mL of 0.2% thorine solution was added. The solution was further diluted to 10 mL with deionized water. The resulting solution was heated to 75°C and maintained at 75–80°C for 5 min to develop color. The solution was cooled to room temperature and was analyzed at 555 nm against de-ionized water as blank on UV-vis spectrophotometer (Chemito Spectroscan UV 2700).

Quantitative analysis of cobalt (II) ion during adsorption studies

Totally, 0.5 mL of ethylene diamine was added to the samples taken during adsorption studies to form the required complex. The pH was adjusted to 10 with addition of sodium hydroxide solution. The solution was further diluted to 10 mL with deionized water. The solution was shaken and analyzed at 365 nm on UV spectrophotometer for absorbance.

Positron annihilation lifetime spectroscopy (Pals) measurements of 4-MABPPS before and after adsorption studies

PALS give hindsight about the void space occupancy of the metal ions. Reduction of free volume is attributed to the adsorption of metal ions on adsorbent. Free volume reduction is a direct indication of a particular metal ion onto the adsorbent.

PALS measurements was carried out using a 20 μCi ^{22}Na positron source in the form of NaCl folded in kapton foil, which was incorporated into the powder sample kept on a small glass tube. The source-sample assembly was placed between two plastic scintillation detectors coupled to fast–fast coincidence system with a time resolution of 235ps as measured with ^{60}Co source in ^{22}Na energy window setting. Data
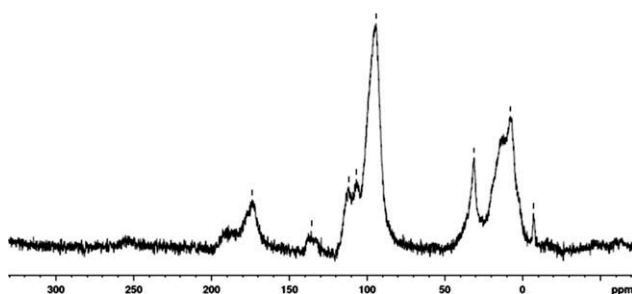
Figure 2 Solid state 13C NMR of 4-MABPPS.

analysis was carried out using PATFIT program in BARC, Mumbai.

RESULTS AND DISCUSSION

Synthesis of 4-MABPPS

Initially, AMPS was prepared by the conventional Gabriel reaction. This method gave 100% conversion of chloro group to amino group, confirmed by IR, NMR, and EDX. The newly synthesized adsorbent 4-methyla-mino-[N,N-bis(2,2´)-1,10-phenanthroline] polystyrene (**4-MABPPS**) was obtained with almost 62.39% conversion which is comparatively high as compared with reported methods.[16] The polymer matrix contains 3.72 mmol g^{-1} of 1,10-phenantroline moiety on resin matrix which is good enough to acts as an adsorbent for selective separation of Co(II) from Zr(IV).

Characterization of the synthesized 4-MABPPS

The synthesized **4-MABPPS** is characterized by ^{13}C-NMR (see supporting information for characterization of intermediates). The comparison of spectra of the AMPS and **4-MABPPS** is shown in Figure 2. Both spectrum shows common peaks from about 2–45 δ ppm indicates the presence of aliphatic methine (CH) and methylene (CH$_2$) carbons lying along the polymer main chains. The peak at 82–124 δ (ppm) shows the presence of aromatic carbons of polystyrene. The peak obtained at 170–198 δ (ppm)
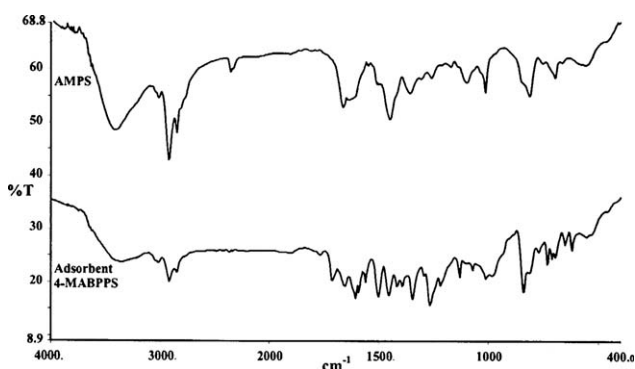

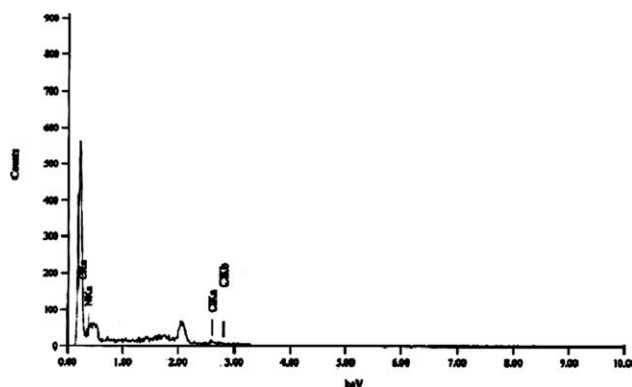**Figure 3** The comparison of Infrared spectra of AMPS and 4-MABPPS.

Figure 4 ED-X of 4-MABPPS.

is due to C=O suspension stabilizer, used in chloro-methylated polystyrene synthesis. The peak at 128–142 δ (ppm) appearing in **4-MABPPS** confirms the presence of phenanthroline moiety on the polymer matrix which is not present in AMPS spectrum.[17,18]

The comparison of Infrared spectra of AMPS and **4-MABPPS** is shown in Figure 3, spectrum of **4-MABPPS** revealing a sharp peak for polynuclear aromatics resulting from isolated C—H out of plane bending at 840 cm^{-1}, C—N stretch at 1018 cm^{-1}, the sharp peak at 1450 cm^{-1} indicating the presence of scissoring frequency of —CH$_2$—N— (tertiary amines). The presence of heteroaromatic C=C and C=N ring stretching vibrations shows four sharp peaks in the region 1600–1300 cm^{-1}, and aromatic C—H stretch at 3040 cm^{-1}. Adsorbent shows comparatively very small peak for NH stretch at 3412.79 cm^{-1} due to monofunctionalized and incomplete conversion, whereas AMPS shows more intense NH$_2$ stretch at 3413.11 cm^{-1}.[19] Thus IR spectroscopy results complement the NMR indicating the structural confirmation of **4-MABPPS**.

Energy Dispersive X-ray (EDX) spectrum of **4-MABPPS** is present in Figure 4. It shows presence of 14.03% of nitrogen element in the synthesized adsorbent confirming required loading of 1,10-phenanthroline in the polymer matrix.

The X-ray Diffraction (XRD) of **4-MABPPS** (Fig. 5) shows broad diffraction peak at an angle 2θ = 20° due to mesoporous structure in AMPS and **4-MABPPS** with differed percent crystallite 47.93 and 56.96%, respectively. The change in percent crystallite also confirms the grafting of 1,10-Phen in polymer matrix. The XRD pattern of the functionalized adsorbent suggests a significant degree of short range ordering of the structure without much change in the structural orderness of the synthesized materials after functionalization.[20]

Effect of pH on rate of adsorption

Figure 6 shows adsorption trend of cobalt ion at varying pH by **4-MABPPS** adsorbent. The lines shown in
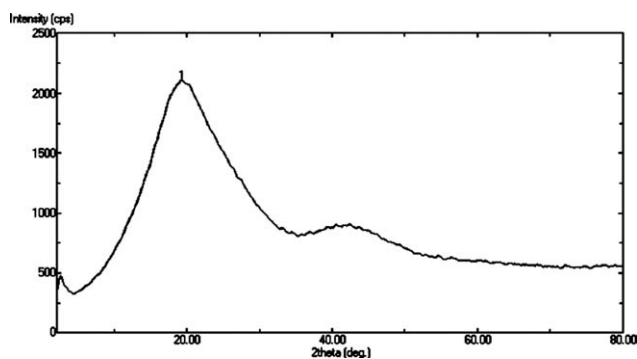
Figure 5   X-RD of 4-MABPPS.

Figure 6 are the curves obtained by fitting the adsorption data into the Freundlich isotherm equation.

$$q = K_F C_e^{1/n}$$

where K_F is a constant which indicates the relative adsorption capacity of the adsorbent (mol kg^{-1}); $1/n$ an empirical constant related to the magnitude of the adsorption driving force and also indicative of the intensity of the adsorption. Table I shows the value of K_F and $1/n$ which indicates favorable adsorption of cobalt ion in acidic pH. The maximum adsorption capacity for cobalt was estimated to be 1.85 mol kg^{-1} of resin at pH 4.

The variation in selective adsorption of cobalt by **4-MABPPS** varies with pH and it attains maxima at pH 4. This is partly because of hydrogen ions themselves are strongly competing adsorbates and the solution pH influences the ionization of surface functional groups. The synthesized chelating polymer adsorbent with 1,10-Phen groups have strong complexing properties. The adsorption of Co(II) ion on the resin is clearly very favorable at pH 4. At low pH an excess of hydrogen ions can compete effectively with Co(II) for binding sites, resulting in a lower level of Co(II) uptake. At pH values below 2, hydrogen ions are likely to compete with Co(II) ions
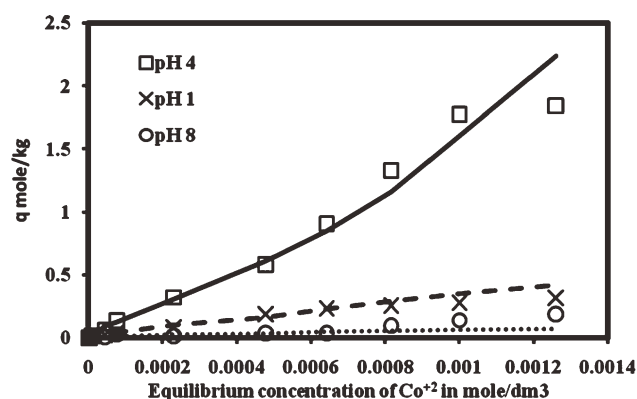
TABLE I
Freundlich Adsorption Parameters

pH	K_F	$1/n$
1	64.45	0.74
4	762.04	0.784
8	4.46	0.603

and at pH values above 6, Co(II) ions might precipitate due to the presence of hydroxyl ions as hydroxyl complexes Co(OH)$_2$. Co(II) metal showed strong affinity towards the resin at pH 4 at which maximum amount of Co(II) was adsorbed. The retention of Co(II) by resin decreases markedly from 5 to 8. Hence all experiments were performed using solution of pH 4. Batch adsorption study of Zr shows maximum 12% adsorption as compared with 76% of Co on resin matrix in acidic pH.

Column studies on 4-MABPPS adsorbent

The 1000 ppm solutions each of cobalt and zirconium were prepared. The two solutions were mixed in a ratio of 1 : 1 and this mixture was used as a feed solution for adsorption. The pH of the solution was 4. Column studies were carried out on the **4-MABPPS** adsorbent to investigate the adsorption behavior of cobalt and zirconium. The concentration of cobalt and zirconium are shown in Figure 7 as dimensionless concentration (C/C_0) versus number of bed volumes of solution that has been passed through the column. At the experimental conditions the break point of cobalt occurred after 20 min whereas for zirconium it occurred within 5 min. Also, the breakthrough fronts of cobalt and zirconium are well separated suggesting possible separation of cobalt and zirconium. The uptake by the polymer from the acidic solution was found to be maximum for cobalt (77.50%), and least for
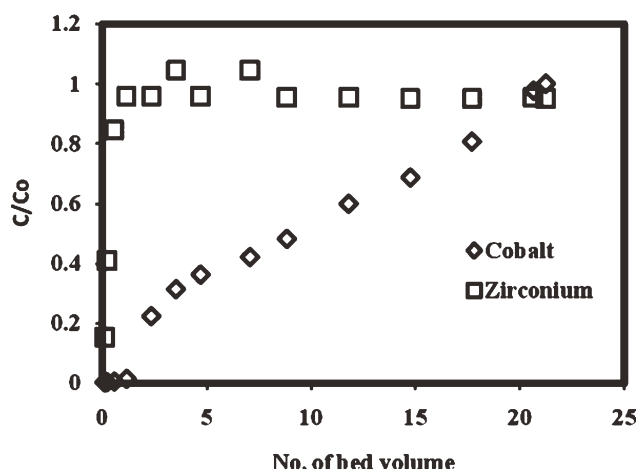

Figure 6   Freundlich Adsorption Isotherm of Co+2 on 4-MABPPS adsorbent.

Figure 7   Column study of Co+2/Zr+4 ions on 4-MABPPS adsorbent.

4-MABPPS adsorbent	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	R (nm)
Before adsorption study	0.125	11.06 ± 1.08	0.37 ± 0.003	73.84 ± 0.97	1.80 ± 0.02	15.09 ± 0.21	0.27
After adsorption study	0.125	8.09 ± 1.22	0.37 ± 0.003	81.01 ± 1.12	1.74 ± 0.02	10.90 ± 0.20	0.26

zirconium (20.47%). The reason behind the selective adsorption of cobalt ions in the presence of zirconium ions is the vacant space formed due to two chelating phenanthroline rings of the polymeric adsorbent. The aliphatic tertiary nitrogen atom of **4-MABPPS** is attached to bulky polymeric chain, hence the deformation of the other two bonds of nitrogen that is attached to phenanthroline rings are restricted and thus these rings prefer to lie in one plane. The space formed due to two phenanthroline rings loaded on polymer matrix leads to a cavity which is likely to have the similar cavity size as that of the ionic size of cobalt (0.74 Å). Since the size of zirconium is 0.98 Å which is larger than that of cobalt, it may not adsorb on the polymer matrix due to the unavailability of sufficient space on the polymer matrix. It would only be possible for both nitrogen atoms on the functional group to serve as donors for a single ion if the cation has suitable ionic radius, so that the nitrogen donors can interact with available orbitals without undue strain. Many divalent, first row transition metal ions appear to satisfy these criteria.[21] However, because the functional group is attached to a polymeric matrix, which would, to a greater or lesser extent, restricts its ability to interact freely with ions,[22] one would expect the stability of the resulting complexes to be strongly sensitive to the cationic radius. Collectively, all these reasons explain selective adsorption of cobalt on **4-MABPPS** adsorbent in presence of zirconium.

Positron annihilation lifetime spectroscopy (Pals) measurements of 4-MABPPS before and after adsorption studies

Table II shows the positron annihilation lifetime ($\tau_{n,n=1,2,3}$) and intensity ($I_{n,n=1,2,3}$) in the **4-MABPPS** before and after cobalt ion adsorption. The shortest lived components (τ_1, I_1) is attributed to the annihilation of *para* positronium (*p*-Ps), intermediate-lived component (τ_2, I_2) corresponds to the direct annihilation of positron in the bulk of the sample. The longest lived component (τ_3, I_3) is attributed to the *pick-off* annihilation of *ortho* positronium (*o*-Ps) at the free volume surface.

The free volume size (R) of the sample was calculated from *pick-off* lifetime (τ_3) using the Tao-Eldrup equation[23,24] as follows

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\frac{2\pi R}{R + \Delta R}\right)^{-1} \quad (1)$$

Here, τ_3 is measured in ns and R (radius of the spherical free volume) is in nm. The ΔR (=0.166 nm) is the electron layer thickness inside the wall of the spherical free volume. The result (Table II) shows that the size of the free volume has not significantly changed after the cobalt ion adsorption. However, the *pick-off* intensity (I_3) is seen to be reduced, which obviously indicates that the free volume sites have been reduced due to the cobalt ion adsorption. The fractional free-volume (f) can be calculated using the following relation[24]

$$f = cI_pV_f,$$

where c is the normalization constant and V_f (=4/$3\pi R^3$) is the free volume. The c value was not measured in this work, but as it is a constant, the fractional free volume (f) must be proportional to the product ($I_p \times V_f$), which shows that the fractional free volume has decreased with the adsorption of cobalt ions. For quantitative analysis, if we take the literature value[25] of $c = (0.325$ nm$^3)^{-1}$ as calculated in the PVA matrix above the glass transition temperature, we get $f = 3.80\%$ and 2.47% before and after the cobalt ion adsorption, respectively.

PALS give a hindsight about the void space occupancy of the Co(II) ions. Reduction of free volume is attributed to the adsorption of Co(II) ions on adsorbent. Thus free volume reduction is a direct indication of Co(II) ions onto the adsorbent.

CONCLUSIONS

A novel 4-methylamino-[*N*,*N*-bis(2,2$'$)-1,10-phenanthroline] polystyrene (**4-MABPPS**) adsorbent has been synthesized with high purity using amino methylated polystyrene resin and 2-chloro-1,10-phenanthroline.

The experimental results showed that complete separation of cobalt from zirconium is possible using the synthesized polymeric adsorbent. Cobalt can be adsorbed on **4-MABPPS** resin followed by its removal in highly acidic medium by immobilized chelating 1,10-phenanthroline moiety loaded on polymeric matrix.

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