Synthesis and application of cross-linked graft copolymer from poly(vinyl alcohol) and malic acid

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A novel polymeric sorbent has been synthesized by graft copolymerization of crosslinked polyvinyl alcohol with malic acid, and characterized by FTIR, TGA and swelling studies. A suitable and interesting method has been developed for the extraction and separation of lead ion with the graft copolymer. The lead ion uptake capacity of the polymer has been evaluated vis-a-vis varying pH and metal ion concentration. Pb(II) ion has been isolated quantitatively from various synthetic mixture containing metal ions (Cd(II), Zn(II), Ni(II), Hg(II)) commonly found in battery and electroplating waste. The synthesized material has also been tested for analyzing real samples such as solder, lead concentrate and electroplating waste.

Keywords: Analytical chemistry, Cross-linked copolymers, Polymers, Graft copolymers, Solid phase extraction, Lead

Lead is considered to be poisonous because it can affect the nervous system and gastrointestinal track through co-coordinating with S and N sites of the enzyme. The upper limit as recommended by world health organization (WHO) is less than 10 ng/L. Many industries such as electroplating, pigment and battery discharge hazardous heavy metal ions such as lead, cadmium and mercury. Several conventional techniques chemical precipitation, solvent extraction, ultra filtration, complex formation by polymer, membrane separation, ion exchange and adsorption are available for removal of lead ion from aqueous solution. Removal of lead ions using sorbents (solid phase extraction) deserves particular attention because these materials are efficient and easy to handle, and in several cases can be regenerated. Reproducibility of metal ion binding capacity and enhanced sensitivity make the polymer suitable for solid phase extraction. Commercially available polymers generally lack selectivity. Recently a group of researchers have reported in synthesis of new polymers having selective metal ion binding capacity. Solid phase extraction of lead ion from aqueous solutions using polymers has also been reported. While PVA itself has poor metal ion binding capacity, sorption properties of PVA can be enhanced by grafting with suitable binding sites. PVA is cheap and its physico-chemical properties can be enhanced by simultaneous cross-linking and grafting.

The present work highlights a new procedure for separation of lead(II) form aqueous solution using chemically synthesized novel graft copolymer of cross-linked PVA. The synthesized material and the developed method have been tested in synthetic mixture containing metal ions commonly found in solder, lead concentrate and electroplating waste.

Experimental

Poly(vinyl alcohol) (PVA) (Burgoyne Burbidges, India mol. wt. = 16100, degree of hydrolysis = 98.5-99.0 mol %, viscosity = 30 cps) was used, Glutaraldehyde (SD Fine Chem. Ltd, India), lead nitrate (Merck, India) and sulfuric acid (Merck, India, 98 % sp. gravity = 1.84), malic acid (MA) (Aldrich, Germany), ceric ammonium sulfate (CAS) (Himedia Laboratories Pvt. Ltd. Mumbai, India) were used as received.

Fourier transform infrared (FTIR) spectra of the polymer were recorded on a Shimadzu FTIR spectrometer (model No. 8400s) using KBr pellets. Thermal analysis was conducted using a Stanton Red Craft thermal analyzer (STA-780) in air at a rate of 10 °C/min. The amount of metal ion was measured on a atomic absorption spectrophotometer (AAS, Shimadzu, AA 6300) and complexometrically. An Elico L1-120 pH meter, thermostat and chromatographic column (i.d. = 0.8 cm) were used.

Graft copolymerization of PVA was carried out in a two-necked round-bottomed flask at 70 °C. A definite amount of PVA (0.5 g) was dissolved in warm water (20 mL), and then malic acid (0.3 g) was added gradually. After warming the solution for 15 minutes, conc. sulphuric acid (2 mL) and CAS (0.2 g) were added and stirred magnetically for 1 h. Nitrogen atmosphere was maintained throughout the graft polymerization. The grafted product (PMA-g-PVA) was precipitated by using acetone. The product was then re-dissolved in water for cross-linking.
Glutaraldehyde (0.1 g) was mixed to cross-link the grafted product and stirred for 1 h. Quenching with hydroquinone arrested the cross-linking reaction. The precipitated cross-linked graft copolymer (X-PMA-g-PVA) was separated by filtration and washed several times with 1:10 H₂SO₄ (v/v). The unreacted PVA was separated by prolonged (24 h) extraction with water in a Soxhlet apparatus. Finally, the sample was extracted with acetone for 72 h to dissolve all other impurities. The colorless product was dried under vacuum at 100 °C for 72 h to a constant weight. The dried solid was grounded and screened through a set of sieves to obtain particles of size ranging between 0.14-0.26 mm for further experiments.

Retention by batch method was carried out by mechanical agitation (90-100 rpm) at a temperature of 27 ± 2 °C. To determine the retention of metal ion, 0.013 g of the prepared polymer (X-PMA-g-PVA) was taken in a 100 mL beaker with 10 mL metal ion solution. The concentration of lead ion in aqueous solution was kept within 207 to 1242 mg/L. The pH of the solution was varied from 1-6. The absorbed metals were eluted (desorbed) sequentially with the selective stripping (eluting) agents. All the experiments were performed at least in triplicate at room temperature (27 °C). The adsorption capacity (Q, mg/g), percentage of recovery (R) and cross-link density (q) were calculated from the following relationships: Q = W₃/W₂; R = 100 W₃/W₁; q = Mₓ/Mₑ, where W₁ = metal adsorbed (mg), W₂ = adsorbent added (g), W₃ = metal ion eluted (g), Wₑ = metal ion originally bound in the polymer (g), Mₓ = mol. wt. of the repeating unit, Mₑ = average molecular mass between consecutive cross-links. The samples were immersed in purified water and weighted in definite time interval for 72 h and swelling was calculated by the equation, Swelling (%) = (Mₑ-Mₐ) ×100, where Mₑ = mass of the swelled polymer and Mₐ = mass of the dry polymer.

Results and discussion

The traces of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Fig. 1) of the synthesized polymer indicates three-step weight loss: First step (40–140 °C, ≈ 60 %), second step (100–250 °C, ≈ 10 %) and third step weight loss (250–490 °C, ≈ 30 %) of the polymer occurred mainly due to removal of water, carbon dioxide and nitrogen respectively. IPDT (integral procedure decomposition temperature) was calculated from TGA curves as IPDT (°C) = A.K. (Tᵢ-Tᵢ) + Tᵢ; where A= (S₁+S₂)/ S₁+S₂+S₃, K= (S₁+S₃)/S Tᵢ = initial temperature (40 °C), Tᵢ = final temperature (490 °C), S₁, S₂ and S₃ indicate the specified area of the TGA curve. The IPDT value of the prepared polymer was found to be 470 °C, which is higher than the reported value for PVA (350 °C). The higher IPDT value indicates better thermal stability of the grafted polymer.

Figure 2 shows swelling behavior of the cross-linked graft copolymer (X-PMA-g-PVA), which was measured in redistilled water at various temperatures. Swelling of hydrogels was found to decreases with increase in temperature, and a maximum extent of swelling was achieved at 27 °C. In fact, the diffusion of water molecules in the copolymer network tend to increase as the temperature increased due to better swelling of copolymer molecules. As a result the absorbed water molecules migrate back in the solution. The time required to reach equilibrium decreases with increasing temperature. At low temperature, hydrogen bonding between hydrophilic

![Fig. 1—TGA and DTA of the grafted copolymer (X-PMA-g-PVA).](image1)

![Fig. 2—Swelling of the cross-linked polymer (X-PMA-g-PVA).](image2)
groups of cross-linked polymer and surrounding water molecule leads to enhanced swelling. However, hydrophobic interaction among hydrophobic groups is strengthened and hydrogen bonding becomes weaker as temperature increases. This may induce shrinking of hydrogels due to interpolymer chain association through the hydrophobic interaction.

Thus, X-PMA-g-PVA showed temperature responsive swelling behavior based on the association/dissociation of hydrogen bonding. FTIR spectral data of cross-linked grafted copolymer of PVA shows all characteristic peaks of PVA and two new peaks at 1725 cm\(^{-1}\) and 1030 cm\(^{-1}\). These two new bands are probably due to carbonyl stretching frequency of carboxylic group and ether linkage respectively. The presence of carboxylic group and ether linkage in the FTIR due to grafting of PMA and cross-linking of PVA chain respectively confirms the formation of cross-linked graft polymer (X-PMA-g-PVA).

The Pb(II) retention at varying \(pH\) (1-6) was studied (Fig. 3). The retention capacity of the polymer was increased with the increase of \(pH\), reaches maximum at \(pH\) 4.7 and then decreases with the further increase of \(pH\).

The lead ion reaches the exchange site mainly through the ion exchange process. The presence of exchangeable H\(^+\) ion favors the ion exchange process (ion exchange capacity = 4.0 meq H\(^+\)/g). At lower \(pH\) (< 4.7) the polymer is in protonated form and it can act as a mono-dentate ligand and hence, the exchange capacity is low. As a result, there is lesser retention of Pb(II) ion (\(pH\) 1.5), while at higher \(pH\) (> 4.7), the lead ion undergoes hydrolysis and interferes with the exchange process. Thus the optimum \(pH\) for lead ion retention is 4.7.

![Fig.3—Pb (II) retention at varying pH. [Sorbent dose: 1.3 mg/L; sorbate dose: 207 mg/L; time: 1 h; temp.: 27 °C].](image)

The chelating process of a metal ion by a polymeric sample may be carried out by long range attractive electrostatic interactions and once the metal ion is condensed on the polymer surface, its site is fixed by the polymer ligands. The most accepted mechanism of carboxylic type complex is as shown in below (I), where M represent bivalent metal ion. The carboxylic groups can act as mono- and bidentate ligands depending on the \(pH\) values.

![I](image)

The effect of sorbate dose on retention of lead ion was studied (Fig. 4). The lead ion uptake capacity of the sorbent increases sharply with the increase of metal ion concentration. The lead ion retention capacity of the resin was 14.0 mg/g at low level of the sorbate (207 ppm) and reaches 50.2 mg/g at 1000 ppm of lead, which is higher than for commercially available polymeric resin (Amberlite IRC-50, Tulsion T-335 and Amberlite IR-406).

Ion exchange separation was carried out with a chromatographic column (i.d. = 0.8 cm, bed ht = 8 cm) washed with 2 M of HCl. The binary and ternary metal ion solution (10 mL) containing ions were passed through the column at a constant flow rate of 1 mL/min. After extraction, the metal ions were eluted sequentially with suitable eluents and the amounts of metal ions were determined by AAS with a detection limit in ppm range.

Each binary mixture was prepared by using an aliquot of standard solution of Pb(II) (2.30 mg/L) and

![Fig. 4—Effect of sorbate dose on metal ion retention. [Sorbent dose = 1.3 mg/L; \(pH\) = 4.7; time = 1 h; temp.: 27 °C].](image)
NOTES

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one of the other metal ions at desired pH (Table 1). At pH 4.7, Hg(II), Ni(II), Cd(II) and Zn(II) were co-extracted quantitatively along with Pb(II) from their respective binary mixture. Pb(II) was eluted first from the column with the help of 0.01 M HNO₃ (mixture A) and then Hg(II) recovered with 0.05 M H₂SO₄. Similarly, the other metal ions were separated by using different eluents as shown in the table. The relative standard deviation (RSD) values indicate the better results than those reported earlier.

Separation of Pb(II) ions from ternary mixtures (Fig. 5) as indicated in Table 1 (E&F) also shows good results.

The sorption–desorption cycle was repeated five times with the same adsorbent in batch and column processes. During the five sorption–elution cycles, the resin could be loaded and regenerated without any loss in its metal ion retention capacity. Thus, the resin could be used in a continuous separation process to remove the undesirable metal ions.

In order to assess the possible analytical applications, the polymeric resin was used to separate lead ion from multi-component mixture containing lead with different metal commonly associated with ores, alloys and industrial sample (Table 2).

The synthesized resin acts as cation exchanger with high exchange capacity, good chemical and thermal stability. The exchange bed may be used for more than five cycles with only a little loss of exchange capacity. The developed method may be applied for the selective extraction and separation of lead ion from real samples such as solder, lead concrete and electroplating waste. The proposed method is highly efficient, cost effective, simple and rapid. The cross-

![Fig. 5—Elution of Zn(II), Cd(II) and Pb(II). (RSD 3.2 ± 0.03 %, confidence level: 97 %).](image-url)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb(II) (%)</th>
<th>Rel. error (%)</th>
<th>Std. dev. (%)</th>
</tr>
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<tr>
<td>Solder</td>
<td>Pb: 42.0</td>
<td>Pb: 40.25</td>
<td>-1.72</td>
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<tr>
<td></td>
<td>Sn: 57.9</td>
<td></td>
<td></td>
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<tr>
<td>Lead concentrate</td>
<td>Pb: 72.4</td>
<td>Pb: 75.4</td>
<td>-1.54</td>
</tr>
<tr>
<td></td>
<td>Zn: 02.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni: 0.95</td>
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<td></td>
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<tr>
<td>Electroplating waste</td>
<td>Cd: 16.0</td>
<td>Pb: 11.58</td>
<td>-1.85</td>
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<tr>
<td></td>
<td>Pb: 12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu: 08.0</td>
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<tr>
<td></td>
<td>Ni: 60.1</td>
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<table>
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<tr>
<th>Mixture</th>
<th>Cations Added (mg)</th>
<th>Recovered (mg)</th>
<th>Recovery (%)</th>
<th>RSD</th>
<th>Eluent (mL)</th>
</tr>
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<tr>
<td>A</td>
<td>Pb(II) 2.30</td>
<td>2.20</td>
<td>99</td>
<td>4.20</td>
<td>0.010 M HNO₃(70)</td>
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<tr>
<td></td>
<td>Hg(II) 2.15</td>
<td>1.90</td>
<td>85</td>
<td>2.80</td>
<td>0.050 M H₂SO₄(30)</td>
</tr>
<tr>
<td>B</td>
<td>Pb(II) 2.30</td>
<td>2.19</td>
<td>97</td>
<td>3.60</td>
<td>0.010 M HNO₃(70)</td>
</tr>
<tr>
<td></td>
<td>Ni(II) 2.18</td>
<td>2.05</td>
<td>92</td>
<td>1.80</td>
<td>0.005 M H₂SO₄(40)</td>
</tr>
<tr>
<td>C</td>
<td>Pb(II) 2.30</td>
<td>2.12</td>
<td>95</td>
<td>3.20</td>
<td>0.010 M HNO₃(70)</td>
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<tr>
<td></td>
<td>Cd(II) 2.20</td>
<td>1.80</td>
<td>88</td>
<td>1.60</td>
<td>0.005 M H₂SO₄(50)</td>
</tr>
<tr>
<td>D</td>
<td>Pb(II) 2.30</td>
<td>2.15</td>
<td>92</td>
<td>3.30</td>
<td>0.010 M HNO₃(70)</td>
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<td></td>
<td>Zn(II) 2.10</td>
<td>1.45</td>
<td>78</td>
<td>1.30</td>
<td>0.005 M H₂SO₄(45)</td>
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<tr>
<td>E</td>
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<td>2.20</td>
<td>99</td>
<td>3.20</td>
<td>0.010 M HNO₃(70)</td>
</tr>
<tr>
<td></td>
<td>Cd(II) 2.20</td>
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<td>Zn(II) 2.10</td>
<td>1.45</td>
<td>78</td>
<td>1.30</td>
<td>0.005 M H₂SO₄(45)</td>
</tr>
<tr>
<td>F</td>
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<td>2.20</td>
<td>99</td>
<td>4.10</td>
<td>0.010 M HNO₃(70)</td>
</tr>
<tr>
<td></td>
<td>Ni(II) 2.18</td>
<td>2.05</td>
<td>92</td>
<td>1.94</td>
<td>0.005 M H₂SO₄(40)</td>
</tr>
<tr>
<td></td>
<td>Hg(II) 2.15</td>
<td>1.90</td>
<td>85</td>
<td>2.54</td>
<td>0.050 M H₂SO₄(30)</td>
</tr>
</tbody>
</table>

Table 1—Separation of Pb(II) ion from synthetic mixtures. [Column: int. dia. = 0.08 cm, bed ht. = 8 cm, flow rate = 1mL/min, pH = 4.7 and temp. = 27 °C]

Table 2—Determination of lead ion in real samples. [Column = 0.8 × 8 cm; Flow rate = 1.0 mL; pH = 4.7]
linked grafted X-PMA-g-PVA shows a higher Pb(II) uptake capacity as compared to commercially available polymeric resin.

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