REMOVAL OF Pb (II) IONS BY USING MODIFIED ANIONIC ION EXCHANGER, AMBERLITE IRA-400

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ABSTRACT

Amberlite IRA-400 is a strongly basic anion exchanger resin. In the present work, Amberlite IRA-400 is modified with disodium salt of ethylene diamine tetra acetic acid (Na3EDTA). The modified chelating cation exchanger is characterized by various instrumental techniques like TGA, FTIR and BDX. The resultant cationic ion exchange is used for removal of Pb (II) from aqueous solution using batch method. Various parameters such as effect of concentration, equilibrium time and effect of pH have been varied in order to get maximum removal of Pb (II) ions. Further sorption of Pb (II) ion on chelating ion exchange was confirmed by EDX. Ammonium nitrate, nitric acid, perchloric acid and acetic acid were tested as eluents. The studies indicate that promising use of modified chelating ion exchange for selective removal of Pb (II).

Key Words: Chelating ion exchanger, Pb (II) ion, Distribution coefficient, Ammonium nitrate, Amberlite IRA-400

INTRODUCTION

The problems of the ecosystem are increasing with developing technology. Heavy metals are considered high priority environmental pollutants. Because they are toxic for living beings and non-degradable biologically or chemically. These metals are toxic in both their chemically combined forms as well as the elemental form. Exposure to these contaminants present even in trace amount in the environment can prove to be harmful to the aquatic life and human health. Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis, nephritic syndrome and can interfere with enzyme activities. It can affect nerves and brain. Various treatment techniques have been applied to remove metal ions from contaminated waters such as chemical precipitation, adsorption and ion exchange, membrane technology and solvent extraction. However in some cases especially at low concentrations, the practical application of the methods can be ineffective economically unfavorable or technically complicated. Over the last few decades sorption has gained importance as an effective purification technique used in wastewater treatment and the removal of heavy metals is considered an important application of adsorption processes using a suitable adsorbent. A number of adsorbents such as polymeric materials, zeolites, activated carbon, clay minerals and biosorbents have been used in the adsorption process. However, the complexity of natural materials has made them unpredictable regarding the impact of existing conditions on the binding mechanism, capacity and affinity. In order to removal of heavy metal ions, ion exchange has been used more extensively than any other technique because it has been preferred...
by many researchers on account of the fast simple and higher preconcentration factors time and phase saving. Pollutant ions present in the stream are replaced by noncontaminant ions released from the ion exchange.

Amberlite IRA-400 is a strongly basic ion exchange available as a tertiary ammonium chloride form. In the present work Amberlite IRA-400(Cl\(^{-}\)) has been modified with disodium salt of Ethylene Diamine Tetraacetic Acid (Na\(_2\)EDTA). The modified amberlite IRA-400 reported here have two neutral, as well as two anionic coordinating sites. In this way it became potential chelate ion exchange. These coordinating sites have ability to bind to the metal ion through amine nitrogen and carboxylate oxygen. The modified resin has been characterrized by TGA, FTIR and EDX. The sorption behavior of Pb (II) on the modified resin was investigated at different pH values and its different concentrations. The selectivity order of Pb (II) ion towards modified resin has been obtained based on evaluation of distribution coefficient (K\(_d\)) in aqueous and various electrolytic media/concentrations.

**MATERIAL AND METHODS**

Amberlite IR-400(Cl\(^{-}\)), lead nitrate, ammonium nitrate, nitric acid, perchloric acid, acetic acid were procured from SD fine. Disodium salts of EDTA, Xylenol orange, K\(_2\)CrO\(_4\) indicator, Sodium nitrate, zinc sulphate Merck (India) were obtained from Merck (India). All chemicals were analytical reagent grade.

They were used without further purification. Double distilled water was used for all the studies. The pH adjustments were made with from pH 1 to pH 7 using nitric acid or sodium hydroxide solution.

**Physical measurements**

The FTIR spectra were recorded in the form of KBr pellets on shimadzu-8400s and pH of the samples were studied in aqueous solution using ANALAB and pH meter. The thermogravimetric analysis of the samples were carried out by using TGA-50, Shimadzu, thermogravimetric analyser instrument in air atmosphere with a heating rate of 10\(^\circ\)/min. The EDX of the samples were studied using EDX OXFORD 6587.

**Functionalization of Amberlite IR-400**

Amberlite IRA-400(Cl\(^{-}\)) is a strongly basic, clear gel, anion exchange resin. It is cross linked copolymer of polystyrene and divinylbenzene. In order to introduce chelating property and obtained effective sorption of metal ion. It is modified as 5.0g Amberlite IR-400 resin in Cl\(^{-}\) form was treated with 100ml of aqueous solution of 0.01M EDTA. The contents were left for 24 hours with intermittent shaking to ensure the complete replacement of Cl\(^{-}\) ions with Na\(_2\)EDTA. The resin was separated from the solution and washed several times with demineralized water until the supernatant liquid was found free from adhering ions. Finally the resin was dried in an oven at 60 \(^\circ\)C (Fig. 1).

![Chemical structure of Amberlite IR-400(Cl\(^{-}\)) and reaction details](image-url)

**Fig. 1:** Functionalization of amberlite IR-400(Cl\(^{-}\)) resin
Distribution studies

Equilibrium time determination
10ml metal ion solution was shaken with 100 mg of exchanger in stoppered conical flasks at 30°C for different time intervals (1.0, 2.0, 3.0, 4.0, 5.0 and 6.0). The supernatant liquid was removed after every prescribed time interval and the metal ion concentration evaluated by EDTA titration. A plot of the fractional attainment of equilibrium U(t) versus time(t) gives an idea about maximum equilibrium time.

Evaluation of distribution coefficient (Kd)
Distribution coefficient (Kd) is a measure of the fractional uptake of metal ions in solution competing for H⁺ ions in case of a cation exchange material. Almost all ion exchange reactions being reversible at equilibrium, the favoured direction of an exchange reaction is determined by the relative affinity of the ion exchanger for the ions entering into the exchanger matrix. The distribution studies for Pb(II) metal ion was carried out by batch method. 10ml metal ion solution (0.001-0.01M concentrations) was shaken with 0.1g of the modified resin in stoppered conical flask at room temperature for different time intervals (1 hour, 2 hours...24 hours). The metal ion concentration before and after sorption was determined by EDTA titration. Distribution coefficient (Kd) was evaluated using the expression \( K_d = \frac{(I-F)}{F} \times \frac{V}{W} \text{ (ml.g}^{-1}) \) where I = total amount of the metal ion in the solution initially F = total amount of the metal ion left in the solution after equilibrium V = volume of the solution, W = weight of the exchanger.

Kd was also evaluated at various pH range with concentration possessing maximum Kd value. Distribution studies were carried out in both aqueous and various electrolyte media like NH₄NO₃, HNO₃, HClO₄ and CH₃COOH of 0.02M and 0.2M concentration. Results have been presented in Table 1.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>0.001</th>
<th>0.002</th>
<th>0.003</th>
<th>0.004</th>
<th>0.005</th>
<th>0.006</th>
<th>0.007</th>
<th>0.008</th>
<th>0.009</th>
<th>0.01</th>
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<tbody>
<tr>
<td>Kd (mlg⁻¹)</td>
<td>74.19</td>
<td>292</td>
<td>590.0</td>
<td>650.0</td>
<td>740.0</td>
<td>780.0</td>
<td>836.84</td>
<td>349.0</td>
<td>173.94</td>
<td>124.12</td>
</tr>
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</table>

Elution studies
For elution studies 0.1g modified amberlite ion exchanger was packed in a glass column (30cm×1cm) washed thoroughly with double distilled water and flow rate adjusted to 0.5ml min⁻¹. The metal ion solution (0.007M, 10ml) was loaded onto the column. The metal ion loaded was eluted with reagents like NH₄NO₃, HNO₃, citric acid and HClO₄ of 0.02 and 0.2M concentration. The percentage metal recovered (metal eluted) was calculated in terms of % elution expressed as % E = (Cₑ/C₀)×100 where Cₑ is the concentration of the metal ion in the eluted solution and C₀ is the concentration of metal ion loaded onto the column (Table 2).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentrations</th>
<th>0.02 M</th>
<th>0.2 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td></td>
<td>385.71</td>
<td>25.92</td>
</tr>
<tr>
<td>HNO₃</td>
<td></td>
<td>112.5</td>
<td>61.90</td>
</tr>
<tr>
<td>HClO₄</td>
<td></td>
<td>41.67</td>
<td>25.50</td>
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<tr>
<td>CH₃COOH</td>
<td></td>
<td>112.5</td>
<td>30.77</td>
</tr>
</tbody>
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RESULTS AND DISCUSSION

Structural studies
Amberlite IRA-400(Cl⁻) resin is a strongly basic, clear gel and anion exchange resin. Chloride ion is associated with tertiary nitrogen of amine group by electrostatic bond. When amberlite IRA-400 (Cl⁻) was kept in contact with 0.01M solution of Na₂EDTA. Chloride ion was completely substituted with EDTA²⁻ substitution of Cl⁻ was confirmed by Mohrs method. In the modified resin contains two nitrogen of amine group and two oxygen of carboxylic acid group offering chelating sites to metal ion and behave as cation exchange unit. The chelating property of modified resin was studied by a batch process. The structure of chelate has been shown in Fig. 2.

![Proposed structure of Pb(II) exchanged modified resin](image)

Fig. 2: Proposed structure of Pb(II) exchanged modified resin

Further, EDX of Amberlite-IR400(Cl⁻) functionalized resin and Pb (II) metal loaded functionalized resin (Fig. 3 to Fig. 5) respectively were recorded. Absence of Cl⁻ ion in the functionalized resin indicates that Cl⁻ ion has been removed by EDTA²⁻. Images of EDX also confirmed uptake of Pb(II) on modified resin.

![EDX of amberlite-IR400 (Cl⁻)](image)

Fig. 3: EDX of amberlite-IR400 (Cl⁻)
Fig. 4: EDX of functionalized resin

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>68.62</td>
<td>74.29</td>
</tr>
<tr>
<td>N K</td>
<td>1.80</td>
<td>1.67</td>
</tr>
<tr>
<td>O K</td>
<td>29.58</td>
<td>24.04</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 5: Pb(II) ion loaded modified resin

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>66.46</td>
<td>72.92</td>
</tr>
<tr>
<td>N K</td>
<td>3.64</td>
<td>3.43</td>
</tr>
<tr>
<td>O K</td>
<td>28.62</td>
<td>23.57</td>
</tr>
<tr>
<td>Pb M</td>
<td>1.29</td>
<td>0.08</td>
</tr>
<tr>
<td>Totals</td>
<td>100.00</td>
<td>-</td>
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</table>
TGA of Amberlite IR-400(Cl) functionalized resin and metal loaded exhibits mainly two regions of weight loss. The first weight loss in the temperature range 30-200°C could be attributed to the loss of moisture/hydrated water. Second weight loss in the temperature range of 200-450°C is corresponding to the organic moiety after 500°C nature of graph became straight (Fig. 6 to Fig. 8).

Fig. 6 : Thermogram of amberlite IR-400(Cl)

Fig. 7 : Thermogram of functionalized amberlite-IR400(Cl) with EDTA

Fig. 8 : Thermogram of Pb (II) ion loaded modified resin
The FTIR spectra of Amberlite-IR400 functionalized resin and metal loaded functionalized resin were recorded in the region 400-4000cm\(^{-1}\) (Fig. 9 to Fig. 11). FTIR absorption frequencies among Amberlite resin and functionalized resin are not very prominent. But in functionalized resin peak ~1610cm\(^{-1}\) indicated the presence carboxylate ion in the functionalized resin. It is confirmed the association of Na\(_2\)EDTA with amberlite IR-400(CI). Absorption peak ~1610cm\(^{-1}\) also observed in the metal loaded functionalized resin. Metal ion possesses positive character when it attached with coordinating sites of functionalized resin with draw the electron density towards itself. So energy of bonds are changed consequently small peaks get merged which appeared as intense bands in the FTIR spectra.

Fig. 9 : IR spectra of Amberlite-IR400(CI)

Fig. 10 : IR spectra of functionalized resin

Fig. 11 : IR spectra of Pb(II) ions loaded functionalized resin
Cation exchange properties of modified resin

Plot of fractional attainment of equilibrium $U(t)$ vs. time($t$) indicates that maximum equilibrium time for modified resin is 5 hour (Fig. 12). Initially rate of adsorption is faster due to availability of a large number of chelating sites. A maximum removal of Pb(II) is observed at 6 hour. Subsequently with decrease in number of chelation sites rate of metal uptake decreases. It is observed that with increase in metal ion concentration, $K_d$ values increase. Above a particular concentration $K_d$ values are constant which could be explained to be due to the fact that at lower concentrations almost all the ions are exchanged due to availability of exchangeable sites, which are not available at higher concentrations. A plot of $K_d$ values vs. metal ion concentration (Fig. 13) shows optimum concentration for metal ions. It is observed around neutral pH percentage uptake of the metals ions is more. When pH is lowered consequently percentage uptake of metal ions is also decreased. It is because of (a) the lack of sorption at low pH could be attributed to high concentration of hydrogen ions competing with the metal ions for sorption/exchange sites and (b) functionalized resin is having two carboxylic groups when $H^+$ ions are added due to common ions effect deprotonation of $H^+$ ions from carboxylic groups of resin is hindered. Therefore adsorption of metal ions also decreased with decreased the pH. At higher pH, metal get precipitated as a corresponding metal hydroxide therefore sorption of metal ions is hindered (Fig. 14).

Elution of metal ions

The elution behavior of metal ions have been carried out using different electrolytes such as $\text{HNO}_3$, citric acid and $\text{HClO}_4$ of 0.02 and 0.2 M concentration and results are presented in Table 2. The % metal eluted in all cases is in the range 81-94%. Good elution is observed due to presence of single metal ion and non-interference of elements (Table 3). Typical elution curves for Pb(II) ions with different electrolytes has been presented in Fig. 15. Higher concentration of eluent and acids in general are better eluents. It is also observed that metal ion with high $K_d$ values in the electrolytes are less eluted and vice versa.
Fig. 14: Plot of % uptake of Pb(II) ion Vs different pH

Fig. 15: Single elution curves for Pb(II) ion in different electrolytes: (a) 0.02M NH₄NO₃, (b) 0.2M NH₄NO₃, (c) 0.02 M HNO₃, (d) 0.2 M HNO₃, (e) 0.02 M HClO₄, (f) 0.2 M HClO₄, (g) 0.02M CH₃COOH and (h) 0.2M CH₃COOH citric acid using modified resin
Table 3: Percentage elution of metal ions in different electrolyte media using modified resin

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02 M</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>92</td>
</tr>
<tr>
<td>HNO₃</td>
<td>89</td>
</tr>
<tr>
<td>HClO₄</td>
<td>94</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>81</td>
</tr>
</tbody>
</table>

In case of electrolytes, NH₄NO₃, HNO₃ and HClO₄ eluent volume is 20ml for 0.02M and 0.2M concentrations. In case of electrolyte, CH₃COOH eluent volume is 40ml and 30ml for 0.02M and 0.2M respectively. Maximum deviation in % elution of metal ions = ±2.

**CONCLUSION**

In the present work, a new and novel cationic ion exchange has been prepared by using an inexpensive and easily available chemicals amberlite-IR 400(Cl) with di-sodium salt of ethylenediamine tetraacetic acid. The practical applicability of functionalized resin was evaluated for removal of toxic metal ion Pb(II). Elution properties of resin in various electrolytic media/concentrations also has been evaluated. The studies reveal the promising use of modified resin as a cationic exchanger for removal of Pb(II) metal ion from the industrial effluents.

**ACKNOWLEDGEMENT**

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**REFERENCES**


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