Ion exchange method for the detection of trace amounts of Mn$^{2+}$ using nano cerium zirconium phosphate cation exchanger

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ABSTRACT

Manganese (Mn) is an essential element present in all living organisms and is naturally present in rocks, soil, water, and food. The electron transfer property of cerium ions and the presence of phosphate ions of the newly synthesized exchanger were made use of in the detection of trace amounts of Mn$^{2+}$ in aqueous solutions. Characterization of the exchanger was done by ICP-AES method and structural studies were carried out using TGA, XRD and FTIR. Distribution studies showed that the selectivity of the exchanger towards various metal ions was in the order Pb$^{2+}$ > Cu$^{2+}$ > Zn$^{2+}$ > Mn$^{2+}$ > Cd$^{2+}$ > Y$^{3+}$ > Bi$^{3+}$ > Co$^{2+}$ > Ni$^{2+}$ > Ca$^{2+}$ > Al$^{3+}$ > Th$^{4+}$ > Hg$^{2+}$. Based on this, binary separation of Pb$^{2+}$ and Cu$^{2+}$ from Hg$^{2+}$ and Th$^{4+}$ were carried out on a column of the exchanger. Detection of Mn$^{2+}$ in the presence of other ions like Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Th$^{4+}$, Hg$^{2+}$ etc. using the ion exchanger were also carried out.

Keywords: ion exchanger; cerium zirconium phosphate; distribution coefficient; catalytic activity; binary separation

INTRODUCTION

Inorganic ion exchangers are distinguished by their greater thermal stability at elevated temperatures, high chemical stability, resistance to high radiation fields, and their selectivity to certain ions which are the properties the organic resins tend to lack. Some of the inorganic ion exchangers have proved to have greater selectivity for trace radio nuclides compared to organic ion exchangers, and can be used over a wide pH range. Amongst the synthetic inorganic ion exchangers, tetravalent metal acid (TMA) salts are gaining importance due to their excellent thermal stability and chemical resistivity. TMA salts being synthesized by sol–gel routes, materials with varying water content, composition, ion exchange capacity and crystallinity can be obtained by varying the parameters such as stoichiometry and concentration of the reagents used, temperature at which they are mixed, rate of addition, mode of mixing, and pH.

New mixed materials of this class with cation substitution are of interest since they show improved ion exchange properties and selectivity for particular metal ions in comparison to their single salt counter parts, because cation substitution alters the properties, composition and dimensions of the structure. It has been reported that the affinity of antimony silicate towards cesium can be improved by doping with Ti$^{IV}$, Nb$^V$, Mo$^{VI}$ or W$^{VI}$ in different mole ratios and it was found that cesium selectivity in acid increased with a ternary Sb-Si-W system. Preparation and characterization of sodium iron titanate ion exchanger and its application in heavy metal removal from waste waters has also been reported.

Zirconium based ion exchangers have received attention because of their excellent ion exchange behavior, stability and some important chemical applications in the field of ion exchange, ion exchange membrane, and solid–state electrochemistry. Synthesis of a mixed material
of this class, zirconium titanium phosphate (ZTP)\textsuperscript{11} (tetravalent bimetallic acid salt –TBMA salt) by the sol-gel technique has been reported recently and various properties studied.

Manganese is the twelfth most abundant element in the earth’s crust and is an essential element for humans, animals, and plants, required for growth, development, and maintenance of health. It is naturally present in food, with the highest concentrations typically found in nuts, cereals, legumes, fruits, vegetables, grains, and tea. It is also present at low levels in drinking water. Daily intakes range from 2-9 mg/day for adults and approximately 3-5 % is absorbed from the gastrointestinal tract. It is an antioxidant that protects cells from damage due to free radicals\textsuperscript{12}. In the present work an environmentally friendly method for the detection of trace amounts of Mn\textsuperscript{2+} is suggested by using cerium zirconium phosphate, a novel inorganic cation exchanger. Ion exchange properties of the newly synthesized material were also studied.

**EXPERIMENTAL**

Zirconium oxy chloride (Loba Chemie, India), Ceric sulphate (E.Merck) and sodium dihydrogen phosphate(E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

**Apparatus and instruments:** A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements and an electric thermostat oven was used for heating the samples at various temperatures. UV-Visible Spectrophotometer model JASCO V660 was used for spectrophotometric measurements. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies, Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used. Chemical composition was determined by ICP-AES method using ICP-AE Spectrometer Thermo Electron IRIS Intrepid II.

**Synthesis of the exchanger:** zirconium oxy chloride solution (1M), ceric sulphate in sulphuric acid solution(1M) and sodium dihydrogen phosphate solution(1M) were prepared. Sodium dihydrogen phosphate solution was added to mixtures of zirconium oxy chloride solution and ceric sulphate solution with constant stirring in different volume ratios so that final volume was 750ml. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1. pH was adjusted with 1M NaOH/1M HNO\textsubscript{3}. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H\textsuperscript{+} form by treating with 1M nitric acid for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60-100 mesh.

**Ion exchange capacity (IEC):** The ion exchange capacity of the material was determined by column method. 1g of the exchanger in H\textsuperscript{+} form was taken in a glass column of 1.1 cm diameter. The H\textsuperscript{+} ions were eluted by percolating 250 ml of 1M sodium chloride solution. The effluent was collected and titrated against standard sodium hydroxide solution. The exchange capacity in meq/g, IEC was calculated using the formula,

\[
IEC = \frac{av}{w}
\]

where ‘a’ is the molarity, ‘v’ is the volume of alkali used during titration and ‘w’ is the weight of the exchanger taken\textsuperscript{14}.

**Chemical resistivity:** The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 mL of different solvents, kept for 24 hrs and changes in colour, nature and weight of the sample were noted.

**Effect of temperature on IEC:** The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for three hours in an air oven and Na\textsuperscript{+} ion exchange capacity in meq g\textsuperscript{-1} was determined by the column method after cooling them to room temperature.

**pH titrations:** Topp and Pepper method\textsuperscript{13} was used for pH titrations using NaOH–NaCl, KOH-KCl, systems. 0.5g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. After equilibrium, the pH of the solutions was measured and plotted against the milli equivalents of OH\textsuperscript{-} added.

**Distribution coefficient(Kd):** Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 mL of the metal ion solutions for 24 hrs at room temperature.
Distribution coefficient is defined as the ratio of the concentration of the metal ion in the ion exchanger and in the solution. The metal ion concentrations before and after sorption were determined spectrophotometrically/complexometric titration against standard EDTA solution. In the complexometric method, the $K_d$ values were calculated using the formula,

$$K_d = \frac{(I-F) \times V}{W}$$

where ‘I’ is the initial volume of EDTA used, ‘F’ the final volume of EDTA used, ‘V’ is the volume of the metal ion solution (mL) and ‘W’ is the weight of the exchanger.

### Determination of concentration of $\text{Mn}^{2+}$ in solution:

$\text{Mn}^{2+}$ concentration is determined spectrophotometrically using potassium periodate. In hot acid solution, periodate oxidizes it quantitatively to permanganic acid. A calibration curve is plotted with absorbances at 545 nm against concentration of standard $\text{MnSO}_4$ solutions. Concentration of $\text{Mn}^{2+}$ before and after equilibration with the exchanger is determined by measuring the absorbances. For studies on variation of $K_d$ with pH of solutions, 0.005M $\text{MnSO}_4$ solutions were equilibrated with the exchanger at different pH (which is adjusted using $\text{HNO}_3$). Initial and final concentrations were noted and $K_d$ determined.

### Binary separation of metal ions:

Separations of some metal ions of analytical utility were achieved on the column of cerium zirconium phosphate. The column on which the separations were to be carried out was filled uniformly with the exchanger. First of all distilled water was added to pack the granules so that no air bubbles get stuck. Then the mixture of the metal ion solutions was slowly poured. The process was repeated for maximum sorption. The exchanged metal ions were eluted using suitable eluent.

### RESULTS AND DISCUSSION

The exchanger, CZP4 obtained as yellow transparent amorphous solid having maximum ion exchange capacity 1.5 meq/g was selected for detailed study (Table 1). It was found to be stable in water, acetic acid, one molar nitric acid and sulphuric acid.

#### Table 1. Synthesis and properties of various samples of exchanger using IM solutions each.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volume ratio</th>
<th>pH</th>
<th>Appearance</th>
<th>Capacity for Na⁺ (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZP 1</td>
<td>1:1:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.60</td>
</tr>
<tr>
<td>CZP 2</td>
<td>1:2:1</td>
<td>1</td>
<td>Yellow</td>
<td>0.95</td>
</tr>
<tr>
<td>CZP 3</td>
<td>1:1:2</td>
<td>1</td>
<td>Yellow</td>
<td>0.58</td>
</tr>
<tr>
<td>CZP 4</td>
<td>2:1:1</td>
<td>1</td>
<td>Yellow</td>
<td>1.50</td>
</tr>
<tr>
<td>CZP 5</td>
<td>2:1:2</td>
<td>1</td>
<td>Yellow</td>
<td>1.20</td>
</tr>
<tr>
<td>CZP 6</td>
<td>1:2:2</td>
<td>1</td>
<td>Yellow</td>
<td>0.69</td>
</tr>
</tbody>
</table>

**C. CerO₂, Z.ZrOCl₂, P. NaH₂PO₄**

Elemental analysis by ICP-AES revealed a cerium, zirconium, phosphorous ratio of 1:2:2.5. Thermo gravimetric analysis (Figure1) indicated about 30% weight loss up to about 120°C due to the evaporation of external water molecules. The number of water molecules was determined on the basis of Alberti-Torraca formula. From these, the proposed formula is $\text{CeO}_2\cdot2\text{ZrO}_2\cdot1.25\text{P}_2\text{O}_5\cdot14\text{H}_2\text{O}$. Decomposition of the material was shown to take place at about 350°C and 360°C.

FTIR spectra of CZP (Figure 2) showed a broad band in the region ~3433 cm⁻¹ which is attributed to symmetric and asymmetric $\nu$-OH stretching, while the band at ~1632 cm⁻¹ is attributed to H-O-H bending. A band in the region ~1051 cm⁻¹ is attributed to P=O stretching and a band at ~1384 cm⁻¹ is attributed to the presence of $\delta$ (POH). This indicates the presence of structural hydroxyl protons in CZP, which is more evident from the obtained IEC values. Bands at ~604 cm⁻¹ and ~521 cm⁻¹ may be due to the presence of Zr-O and Ce-O bonds.

XRD analysis(Figure 3) showed amorphous nature of the exchanger and the average diameter of particle was found to be 20.4 nm which is in the nano range. The particle size was calculated from the full width at half-maximum of the peak using Debye Scherrer equation,

$$D = \frac{0.9\lambda}{\beta_d\cdot\cos\theta_{max}}$$

where D is the average crystal size in nm, $\lambda$ is the characteristic wavelength of X-ray used, $\theta$ is the diffraction angle and $\beta_d$ is the angular width in radians at an intensity equal to half of the maximum peak intensity.
pH titration curve showed monofunctional nature of the exchanger (Figure 4). The exchange capacity obtained from the curve is in agreement with that obtained by the column method.
The distribution studies of metal ions (Table 2) showed that the exchanger has very high affinity towards Pb\(^{2+}\) ion in comparison to other metal ions studied. The selectivity was found to be in the order Pb(II) > Cu(II) > Zn(II) > Mn(II) > Cd(II) > Y(III) > Bi(III) > Co(II) > Ni(II) > Ca(II) > Al(III) > Th(IV) > Hg(II).

Table 2 K\(_d\) values of various metal ions in water

<table>
<thead>
<tr>
<th>Ions</th>
<th>Taken as</th>
<th>K(_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>Nitrate</td>
<td>1228.0</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>Sulphate</td>
<td>192.6</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>Sulphate</td>
<td>170.5</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>Chloride</td>
<td>95.6</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>Chloride</td>
<td>NE</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>Chloride</td>
<td>78.1</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>Chloride</td>
<td>144.5</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>Chloride</td>
<td>106.7</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>Sulphate</td>
<td>683.0</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>Sulphate</td>
<td>74.5</td>
</tr>
<tr>
<td>Bi(^{3+})</td>
<td>Nitrate</td>
<td>115.8</td>
</tr>
<tr>
<td>Y(^{3+})</td>
<td>Nitrate</td>
<td>126.0</td>
</tr>
<tr>
<td>Th(^{4+})</td>
<td>Nitrate</td>
<td>NE</td>
</tr>
</tbody>
</table>

**NE:** negligible exchange

Its high selectivity for lead ions enabled it to act as an efficient ion exchanger for the separation of Pb\(^{2+}\) and Cu\(^{2+}\) from Hg\(^{2+}\) and Th\(^{4+}\). For this, effect of electrolytes (HNO\(_3\) and NH\(_4\)NO\(_3\)) concentrations on K\(_d\) values were studied and some binary separations were carried out using the exchanger.

**Detection of Mn\(^{2+}\) ions:**

Under mild reductive atmosphere, cerium can exist in the solid solution as Ce\(^{4+}\) and Ce\(^{4+}\) while zirconium exists as Zr\(^{4+}\) only. The acid-strength of the Ce\(^{4+}\) (radius 0.97 Å) site is expected to be higher than that of the Ce\(^{3+}\) (radius 1.14 Å) site because of the higher charge/radius ratio of the former. The zirconium ion (Zr\(^{4+}\)) radius is 0.84Å smaller than that of the Ce\(^{4+}\) ion and it is likely to exhibit acidic nature in solid solution\(^1\). Zr(IV) substitution increases the oxygen storage capacity of cerium ion and hence the exchanger oxidizes Mn\(^{2+}\) strongly than Al\(^{3+}\), Sb\(^{3+}\) or Bi\(^{3+}\) substituted cerium phosphates. Phosphate ions also favor oxidation of Mn\(^{2+}\) ions.

In manganese(II) salt solutions, Ce\(^{4+}\) and phosphate ions in the exchanger oxidizes the diffused Mn\(^{2+}\) to higher oxidation states and hence the color of the exchanger changes from yellow to intense purple (almost black). So it can be used as a very good solid reagent for the detection of Mn\(^{2+}\) in solutions. Since the rate of diffusion and oxidation increases with temperature, the presence of even 1ppm of manganese ion in solution can be easily detected by heating the solution with a very small granule of the exchanger and observing the color of the exchanger. It was observed that rate of change of color increased with increase of concentration, temperature and decrease of pH up to 2 (Figure 5). No diffusion or colour change was observed below pH 0.2 which is due to solubility of cerium ions in highly acidic solutions.

![Figure 4: pH titration curve of CZP](image)

Figure 4: pH titration curve of CZP

![Figure 5: Variation of K\(_d\) of Mn\(^{2+}\) ions with pH of solution](image)

Figure 5: Variation of K\(_d\) of Mn\(^{2+}\) ions with pH of solution

With this exchanger, we could detect the presence of Mn\(^{2+}\) concentrations even less than 1ppm, though it takes more than one day for the color change. But in presence of other salts having redox potentials higher than that of Mn\(^{2+}\), minimum concentration that could be detected is 10ppm. Also, above this concentration, they were not found to interfere much in the exchange or oxidation of Mn\(^{2+}\) ions as revealed by the K\(_d\) values (Table 3).

Table 3: K\(_d\) and color change of Mn\(^{2+}\) in presence of other cations

<table>
<thead>
<tr>
<th>Metal ions in solution (10ppm each)</th>
<th>K(_d) of Mn ions after equilibration for 24 hrs. at pH 2</th>
<th>Colour change of the exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+}) &amp; Mn(^{2+})</td>
<td>211</td>
<td>Light purple</td>
</tr>
<tr>
<td>Zn(^{2+}) &amp; Mn(^{2+})</td>
<td>215</td>
<td>Light purple</td>
</tr>
<tr>
<td>Cu(^{2+}) &amp; Mn(^{2+})</td>
<td>213</td>
<td>Light purple</td>
</tr>
<tr>
<td>Th(^{4+}) &amp; Mn(^{2+})</td>
<td>220</td>
<td>Light purple</td>
</tr>
<tr>
<td>Hg(^{2+}) &amp; Mn(^{2+})</td>
<td>218</td>
<td>Light purple</td>
</tr>
</tbody>
</table>
The exchanger after use can be regenerated with hydrogen peroxide (redox potential 0.682) to regain its colour and can be used repeatedly. UV-Visible spectrum of the manganese exchanged CZP corresponds to that of MnO₂ (Figure 6) which shows that manganese in the +2 state is oxidized to the +4 oxidation state.

The XRD of manganese exchanged CZP is shown in Figure 7. The particle size calculated from the full width at half-maximum of the peak using Debye Scherrer equation was found to be 38nm.

The electron exchange property of the exchanger (Ce³⁺/Ce⁴⁺ redox potential = 1.61) can also be observed when it is in contact with an iodide (redox potential = 0.5355) solution. There is an immediate release of iodine into the aqueous solution.

Figure 6: (a) UV-Vis spectrum of Manganese exchanged CZP, (b) UV-Vis. Spectrum of MnO₂

Figure 7: XRD of manganese exchanged CZP
CONCLUSIONS
The exchanger, Cerium zirconium phosphate can be used as an environment friendly reusable solid reagent with a very low detection limit for the analysis of Mn$^{2+}$ in solutions over a wide pH range (0.2 – 7). It exhibits the characteristics of a promising inorganic cation exchanger for the removal of lead also. The presence of protons contained in structural hydroxyl groups indicates good potential for application in solid acid catalysis. Studies have to be continued to explore the potential of this material in various fields because of its ion exchange property, electron exchange property and nano size.

REFERENCES