Article

**Loading of Crystalline $\alpha$-zirconium Phosphate onto Porous Materials: ----Preparation and Application to the Concentration of Trace Ions----**

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(Manuscript submitted January 24, 2003; accepted March 12, 2003)

Abstract

Crystalline $\alpha$-ZrP was loaded onto the interior surface of porous materials including polymer resin, silica gel and alumina tube, in which $\alpha$-ZrP is distributed uniformly in the pore. This modification method can be applicable to the various size and shape of the porous matrix for the desired applications. The $\alpha$-ZrP loaded polymer resin revealed high affinity toward the adsorption of soft metals including Pb(II) and Cd(II). Due to the remarkable selectivity, fast kinetics and chemical stability the present resin was effectively applied to the pre-concentration of trace amount of Pb(II).

1 Introduction

$\alpha$-Zirconium phosphate ($\alpha$-ZrP) forms structurally well defined layered crystal and it has been extensively studied as the selective ion exchanger and catalysis.[1] However, use of such inorganic materials often accompanies with an operational difficulty in separation and reaction processes since they are obtained as very fine powder. Loading of such fine particles onto porous substrates of desired size and shape can overcome such drawback and opens wide applications of them.[2]

We recently noticed that $\alpha$-ZrP can retain metal ions including those belong to soft metals. Compared to hard metal ions like alkaline and alkaline earth metals, ion exchange properties of the $\alpha$-ZrP for soft heavy metal elements have been less investigated.[3] In this study we have attempted to incorporate $\alpha$-ZrP into the pores of porous materials in order to improve the handling difficulty of the finely powdered $\alpha$-ZrP. We also have applied the obtained composite material to the metal ion adsorbent. This paper deals with the preparation and characterization of $\alpha$-ZrP loaded polymer resin and its application to the enrichment of Pb(II) prior to instrumental analysis.

2 Experimental

2.1 Loading of $\alpha$-zirconium phosphate onto porous materials

To a solution containing 10 g of zirconyloxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) in 100 cm$^3$ of methanol was added 20 g of dried Amberlite XAD-7 beads. After stood for 1 h, methanol was evaporated off in order to incorporate zirconium salt into the pores of XAD-7 resin.[2] To the dried resin residue, 40 g of 85% phosphoric acid was added and then the mixture was heated at 150 °C for 10 h. Fine precipitates generated were removed by
decantation and after washing with water and acetone, the resin was dried. A similar synthetic procedure was applied to other substrates including silica gel and porous alumina tube. X-ray diffraction, EDX analysis and porosity measurements were carried out to characterize the obtained resin.

2.2 Enrichment of trace Pb(II)

An aqueous solution (4000 cm$^3$) of fixed pH containing 10 ppb of Pb(II) was continuously passed through the column packed with 2 g of α-ZrP resin (5.5 cm$^3$, φ 1.0 x 7.0 cm) at a constant flow rate. The adsorbed metal ions were eluted with 30 cm$^3$ of 2 M (M = mol dm$^{-3}$) nitric acid solution and the percentage recovery was calculated by the ratio of the metal ion recovered and that in the feed solution.

3 Results and Discussion

3.1 Preparation and characterization of the α-ZrP resin

By impregnation of ZrOCl$_2$·8H$_2$O into porous substrate followed by heating with 85% phosphoric acid, crystals of α-ZrP was deposited on the interior surface of pores. The Zr : P ratio in the XAD-7 resin was determined as 1 : 2 by degradation followed by chemical analysis. The X-ray diffraction pattern of the α-ZrP resin coincides with that of the authentic α-Zr(H$_2$PO$_4$)$_2$·2H$_2$O crystals, which shows a typical periodical peaks. Fig. 1 shows the cross section SEM image of the resin bead sample and porous alumina tube along with the EDX peaks of Zr and phosphorus. Obviously the α-ZrP particles are almost uniformly dispersed from outer surface to inner part of the substrates.

Pore distribution profile of α-ZrP loaded resin beads indicated that the pores of large diameter in the substrate disappeared and pore size became narrower upon modification with α-ZrP. Although the specific surface area and pore volume decreased about 45-50%, highly porous nature of the support polymer is still maintained upon loading of α-ZrP. The pore size allows the access of any hydrated metal ions into the interior surface of the polymer resin.

![Fig. 1](image_url) The cross section SEM images of the resin bead sample (a) and porous alumina tube (b) along with the EDX peaks of Zirconium (black line) and phosphorus (white line).
3.2 Adsorption characteristics of α-ZrP loaded resin

The acidic protons of the phosphate terminal in α-ZrP can be exchanged with various cations, which can accommodate between the layers.[1] The adsorption selectivity of the α-ZrP was evaluated by the % extraction of metal ions. Figures 2 shows the percentage extraction of (a) Pb(II), Cu(II), Cd(II), Zn(II), Ca(II) and (b) Fe(III), Fe(II), Al(III), K⁺ as a function of pH. The observed extraction of metal ions can be attributed to the ion exchange with loaded α-ZrP, since the polymer resin itself did not retain these metal ions. It is noteworthy, not only hard metal ions but rather soft heavy metal ions can be retained on the resin. In fact, almost quantitative adsorption of Pb(II) and Cu(II) was attained above pH 2.5. Similarly, Zn(II) and Cd(II) can be retained on the α-ZrP resin above pH 4.0. According to the % extraction vs. pH correlation, Pb(II) can be retained most firmly on the α-ZrP resin among the metal ions examined. No significant interference to the % extraction of Pb(II) was observed in the presence of Na⁺, Ca(II) and Fe(III) up to 100-folds excess of Pb(II) (20 ppm) at pH 5.3.

![Figure 2](image)

Fig. 2 Percentage extraction of metal ions by α-ZrP loaded resin as a function of pH. Resin, 0.5 g; [M]=2 mM

The adsorbed metal ions were released by treatment of the resin beads with 1 M nitric acid and the resin can be used repeatedly. Practically no leaking of zirconium or phosphorus was observed during the adsorption and desorption cycles. The maximum amount of Pb(II) retained on one gram of the α-ZrP resin (29 wt.% load) was around 200 mg (1 mmol g⁻¹). The periodical X-ray diffraction pattern of α-ZrP resin changed more complicated peaks upon capture of Pb(II), but the original diffraction peaks were restored reversibly when the ion is released from the adsorbent. Thus the uniform layer structure of α-ZrP may be partially expand to accommodate Pb(II) giving a differently expanded phases.[4]

3.3 Adsorption rate

The kinetic study for the adsorption of Pb(II) by the α-ZrP resin was carried out at several pH conditions. The apparent rate is fast in the range pH 3-4, but retarded at acidic region and at pH higher than 4.5 as well. This phenomenon is likely to relate to the acid dissociation of phosphate moiety which varies the surface charge of interlayer into more negative. The negatively charged surface can enhance the attraction of positively charged cations. However, at higher pH region, the chemical species of Pb(II) may change to hydroxyl complexes[5] due to hydrolysis leading to decrease the positive charge of Pb(II) species.
3.4 Pre-concentration of trace Pb(II)

Enrichment of trace metal ions prior to instrumental analysis is important to the precise monitoring of water quality in environments. Among the separation and concentration procedures of trace metal ions, adsorption process provides several advantages over other alternatives due to high concentration efficiency and ease in phase separation. Pre-concentration of Pb(II) (10 ppb) was examined by passing the aqueous solution through the column of α-ZrP resin and then the retained ion was recovered from the resin as the concentrated form. The percentage of recovery was listed in Table 1 along with the flow rate, pH of the solution and foreign ions added. As expected by batch kinetic experiments, recovery efficiency at pH 3.7 is much favorable than that performed at pH 5.1 with respect of the flow rate of feed. When the flow rate was controlled under 5 cm$^3$ min$^{-1}$ at pH 5.1, Pb(II) was quantitatively recovered in a 80 times concentrated form. However, at the flow rate higher than 10 cm$^3$ min$^{-1}$ the decrease of recovery inevitably resulted due to small leaking of Pb(II). Whereas, quantitative recovery of Pb(II) was attained up to the rate of 19.2 cm$^3$ min$^{-1}$ at pH 3.7 where the fast adsorption takes place. Moreover, interference from Na$^+$, Ca(II) and Fe(III) was not significant when they were present in concentrations of about 100 times to that of Pb(II) at the rate of 19.2 cm$^3$ min$^{-1}$. The column was used repeatedly at least ten times adsorption regeneration cycles without any apparent loss of the performance.

Table 1  Enrichment of trace amount of Pb(II) by the α-ZrP resin column.

<table>
<thead>
<tr>
<th>Entry No.</th>
<th>pH</th>
<th>Flow rate/ cm$^3$ min$^{-1}$</th>
<th>Foreign ion$^b$</th>
<th>% Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.1</td>
<td>4.8</td>
<td>-</td>
<td>100.7±3.2</td>
</tr>
<tr>
<td>2</td>
<td>5.1</td>
<td>8.9</td>
<td>-</td>
<td>98.7±3.0</td>
</tr>
<tr>
<td>3</td>
<td>5.1</td>
<td>5.8</td>
<td>Fe(III), Ca(II)</td>
<td>101.3±2.9</td>
</tr>
<tr>
<td>4</td>
<td>5.1</td>
<td>9.0</td>
<td>Fe(III), Ca(II)</td>
<td>82.0±2.7</td>
</tr>
<tr>
<td>5</td>
<td>3.7</td>
<td>12.6</td>
<td>Fe(III), Ca(II)</td>
<td>99.9±1.0</td>
</tr>
<tr>
<td>6</td>
<td>3.7</td>
<td>19.2</td>
<td>Fe(III), Ca(II)</td>
<td>100.2±1.1</td>
</tr>
</tbody>
</table>

$^a$ Average of three experiments. $^b$1 ppm each of Fe(III) and Ca(II) was added.

Resin: 2.0 g (5.5 cm$^3$), Pb(II) feed: 10 ppb, pH= 5.08, The solution pH was adjusted with sodium acetate buffer or sodium chloroacetate buffer (1x10$^{-3}$ M).

References