METAL PHOSPHATE (M = Zr, Ce) COMPOSITE MATERIALS FOR THE SEPARATION, CONCENTRATION AND DETECTION OF TRACE Pb(II) IN WATER.

DAVID A. PACHECO TANAKA, MARGOT A. LLOSA TANCO, HIROMICHI HAYASHI YUKIKO TAKAHASHI AND TOSHISHIGE M. SUZUKI

National Institute of Advanced Industrial Science and Technology.
Research Center for Compact Chemical Process.
4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551, Japan.

Abstract Zr(IV) and Ce(IV) phosphates were incorporated into organic supports and applied to the selective adsorption of Pb(II). α -Zirconium phosphate (ZrP) was loaded into porous Amberlite XAD-7 and used for the column enrichment of Pb(II) (10ppb) from aqueous solution. The recovery efficiency was dependent on the pH and the feeding rate of the sample solution. A Pb(II) selective membrane filter was fabricated by blending Ce(IV) phosphate (CeP) with cellulose fiber. Enrichment of Pb(II) was achieved by filtration of the aqueous sample through the membrane and was visually detected by immersing the membrane in a 3% solution of Na₂S. A dark spot was observed at Pb(II) concentrations as low as 5 ppb.

INTRODUCTION

Lead poisoning has been a significant public health problem for centuries since lead is a cumulative poison. In humans, toxic effects occur to the central nervous system, long-term neurobehavioral and cognitive deficits occur even with mildly elevated blood lead levels. Drinking water is a significant exposure source of lead for both children and the fetuses of pregnant women. The allowance of Pb concentration recommended by WHO is less than 0.01 ppm for environmental and drinking water¹. For quantification of such low concentration, it is necessary to utilize either very sensitive instrumental techniques or preconcentration methods in order to achieve detection limits within the range of the available equipment. Solid phase adsorption process provides several advantages over other alternatives due to the high concentration efficiency and easy in phase separation. On the other hand, simple, cheap on-site detection methods of trace Pb(II) are of great interest.

Pb(II) forms sparingly soluble products with phosphates. Thus, phosphoric acid², rock phosphate³ and hydroxiapatite⁴ have been used for the treatment of Pb(II). Ce(IV) and Zr(IV) phosphates have been extensively studied as inorganic ion exchangers for alkaline and alkaline metal ions, however the exchange behavior with soft metals like

Pb(II) have been less investigated.

In this study, we have incorporated α -zirconium phosphate (ZrP) into the pores of a solid substrate in order to overcome the handling difficulty of the fine powder. This porous polymer beads loaded with ZrP was used for enrichment of Pb(II) prior to instrumental analysis. Taking advantage of the fibrous nature of Cerium (IV) phosphate (CeP), we have prepared a composite CeP-cellulose membrane for the naked-eye detection of trace amounts of Pb(II). Passing a buffered sample solution through the membrane and immersing the membrane in Na₂S solution, we successfully detected up to 5ppb of Pb(II).

EXPERIMENTAL

Preparation of the α -zirconium phosphate loaded macroporous resin (ZrP-resin)

To a solution containing 10g of zirconyloxychloride (ZrOCl₂·8H₂O) in 100 mL of methanol was added 20 g of dried Amberlite XAD-7 (macroporous cross-linked polyacryl ester, surface area 450 m² g⁻¹) beads and the mixture was stood at room temperature for 1 h, then the methanol was evaporated, 40 g of 85% phosphoric acid was added and stood at room temperature for overnight. The mixture was transferred to a Teflon container of handy autoclave and heated at 150 °C in an oven for 10 h. Fine precipitates generated were removed from the resin beads by repeated decantation and finally 1 M NH₄NO₃ solution was added to remove excess phosphoric acid. After washing with water and acetone, the resin beads were dried under reduced pressure.

Percentage extraction of metal ions by the ZrP-resin

To a 0.5 g portion of ZrP-resin beads, 32 mL of water, 3 mL of buffer solution and 5 mL of 0.02 M metal ion solution were added. Then the system was shaken for 5 days at 25 °C. The resin beads were filtered off, and the filtrate was diluted to 50 mL. The metal ion concentration in the solution was determined by ICP-AES. The % extraction was calculated by the difference in metal ion concentration between the initial and the final solution.

Enrichment of trace Pb(II) using ZrP- resin

An aqueous solution (4 L) of fixed pH containing 10 ppb of Pb(II) was continuously passed through the column packed with 2 g of ZrP-resin (5.5 mL, ϕ 1.0 x 7.0 cm) at a constant flow rate. After the whole solution was supplied to the column, the adsorbed metal ions were eluted with 30 mL of 2 M nitric acid solution. The eluate was collected into a volumetric flask (50 mL) and finally diluted to the mark with water and the concentration of Pb(II) was determined by ICP-AES, the percentage recovery was calculated by the ratio of the metal ion recovered and that in the feed

solution.

Fabrication of CeP membrane filter (CeP-membrane)

The fibrous CeP crystals were prepared by the modified method described in the literature.⁵ Addition of 0.05 M $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$, 1 M H_2SO_4 solution (200 mL) into 6 M H_3PO_4 solution (200 mL) at a rate of 3 mL min^{-1} under stirring at 95°C gave a pale yellow precipitate. Upon stop stirring, the mixture was heated at 95°C and then maintained for another 7 h. Fibrous crystals formed were isolated by filtration. The CeP fiber (1.1 g) was mixed with the suspension of cellulose fiber (4.3 g in 200 mL of water) which was made of filter paper (Advantec-Toyo Co., No.5A) broken into pulp. The pulp slurry was gently homogenized by mechanical stirring and the slurry was spread over the filter paper (No.2, $\phi 15\text{cm}$) placed on a Buchner funnel, filtered by suction, washed with water and then dried

Detection of Pb(II)

A square piece of CeP-membrane (ca. $1.5 \text{ cm} \times 1.5 \text{ cm}$) was sandwiched between a separable filter holder as shown in Fig. 4a, an aqueous solution containing Pb(II) adjusted at pH 3.5 with 0.01 M monochloro acetate buffer was passed through the CeP membrane filter (effective filtering area: 0.25 cm^2) at a constant feed speed (typically 3.5 mL min^{-1}), the solution was supplied to the reservoir by the peristaltic pump to maintain constant filtration rate. Pb was detected as dark brown spot of PbS by treating the membrane filter with 3% aqueous Na_2S solution.

RESULTS AND DISCUSSION

Preparation and characterization of the ZrP-resin

By impregnation of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ into Amberlite XAD-7 beads followed by heating the resin beads with 85% phosphoric acid, crystals of α -zirconium phosphate was deposited on the interior surface of porous resin beads. The Zr : P ratio in the ZrP-resin was determined to be 1 : 2 by degradation of the sample and analysis by ICP-AES. This agrees well with the stoichiometry of $\text{Zr}(\text{HPO}_4)_2$. The X-ray diffraction patterns of the ZrP-resin is shown in Fig 1.

Percentage extraction of metal ions by the ZrP-resin

Figure 2 shows the percentage extraction of some metals as a function of pH. It can be notice that not only hard metal, but also rather soft metal ions are retained in the resin. Almost quantitative extraction of Pb(II), Cu(II) and Fe(III) was attained above pH 2.5. ZrP forms a layer-structured crystal, where three phosphate oxygen bonds to zirconium atoms and the remaining proton-bearing oxygen points into the interlayer space.⁶ The acidic protons of the phosphate terminal in ZrP can be exchanged with

various cations, which can accommodate between the layers. The diffraction pattern of ZrP changed upon capture of Pb(II) (Fig 1), however, the original diffraction peaks were restored reversibly when Pb(II) is released from the resin. The irregular diffraction pattern indicates that the uniform layer structure of ZrP may be partially expand to accommodate Pb(II) giving a differently expanded phases⁷. The adsorbed Pb(II) can be released from the ZrP resin with 1M of nitric acid and the resin can be used repeatedly.

Fig 1. X-Ray diffraction patterns of a) α -ZrP loaded into a porous resin and b) the same resin after saturation with Pb(II)

Fig 2. Percentage extraction of metal ions by $\text{Zr}(\text{HPO}_4)_2$ loaded resin as a function of pH. Resin, 0.5 g ; initial concentration of ions, $1 \times 10^{-3} \text{M}$; shaking time, 100 h at 25 °C.

Enrichment of trace Pb(II) by the ZrP loaded resin

Enrichment of Pb(II) (10 ppb) spiked in water was examined by passing the aqueous solution through the column packed with ZrP-resin. The metal ion retained was released from the resin as the concentrated form using 2M nitric acid. The percentage of recovery was determined by the ratio of Pb(II) in the eluate and that in the feed solution and listed in Table 1. The recovery percentage depends on the pH and the rate of the feeding solution. The recovery efficiency is much favorable at pH 3.7 than that performed at pH 5.1. When the flow rate was controlled under 5 mL min⁻¹ at pH 5.1, Pb(II) was quantitatively recovered in a 80 times concentrated form. However, at flow rate higher than 10 mL min⁻¹ the decrease in recovery inevitably occurs due to small leaking of Pb(II) from the column. Whereas, quantitative recovery of Pb(II) was attained up to the rate of 19.2 mL 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 mL min⁻¹. The column was used repeatedly at least 10 times adsorption regeneration cycles without any apparent loss of the performance.

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

pH	Flow rate/ mL min ⁻¹	Foreign ion ^a	% Recovered
5.1	4.8	-	100.7±3.2
5.1	8.9	-	98.7±3.0
5.1	5.8	Fe(III), Ca(II)	101.3±2.9
5.1	9.0	Fe(III), Ca(II)	82.0±2.7
3.7	12.6	Fe(III), Ca(II)	99.9±1.0
3.7	19.2	Fe(III), Ca(II)	100.2±1.1

^a1 ppm each of Fe(III) and Ca(II) was added. Resin: 2.0 g (5.5 cm³), Pb(II) feed: 10 ppb

Fabrication and characterization of the membrane filter

The crystal morphology of CeP depends on the phosphoric acid and cerium ratio and the reaction time. Fibrous crystalline material was obtained when the molar ratio of H₃PO₄/Ce is higher than 100 and heating for 6 h at 95°C (Fig. 3). The atomic ratio of P and Ce determined by ICP-AES in the product was 1.8. Therefore, Ce(HPO₄)₂ must be the mayor species present in the crystal. The crystal structure of CeP is similar to ZrP, forming layered structures with the proton in the interlayer capable of forming complexes with metals.

Fig 3. Fibrous crystals of Cerium phosphate observed by SEM

Detection of trace amount of Pb(II) by the membrane filter

The CeP membrane filter was cut into small pieces and sandwiched between the separable filter as shown in Fig.4a. A 100 mL pH 3.5 buffered sample solution containing 5 ppb of Pb(II) was continuously filtered through the membrane at constant flow rate of $3.5 \text{ mL}\cdot\text{min}^{-1}$. After filtration, the membrane was washed with water and then immersed into a 3% Na_2S solution. The Pb(II) adsorbed in the membrane was converted into PbS producing a black spot. As it is shown in Fig. 4b, 5 ppb level of Pb(II) in 100 mL of the original sample could be detected by naked-eye observation. The features of this method are the remarkably low detection limit, simplicity, low cost and possible use as on site monitoring of Pb(II).

a)

b)

Fig. 4. a) Apparatus for the enrichment of Pb(II). The CeP membrane was placed between the separable filter holder and the solution was supplied by the peristaltic pump.

b) Black spot was developed by treatment of the CeP membrane with 3% aqueous Na_2S solution after filtration of 100 mL of 5ppb Pb(II) (pH 3.5, feeding rate: $3.5 \text{ mL}\cdot\text{min}^{-1}$).

REFERENCES

- 1) Guidelines for drinking water quality, 2nd ed. Vol 1, World Health Organization, (1993).
- 2) J. Yang, E.E. Mosby, S.W. Casteel, R.W. Blanchar, Environ. Sci. Technol. **35**, p. 3553 (2001).
- 3) M. Prasad, S. Saxena, S.S. Amritphale, N. Chandra, Ind. Eng. Chem., **39**, p. 3034 (2000).
- 4) E. Mavropoulos, A.M. Rossi, A.M. Costa, C.A. Perez, J.C. Moreira, M. Saldanha, Environ. Sci. Technol. **36**, p. 1625 (2002).
- 5) G. Alberti, M. A. Massucci, E. Torracca, J. Chromatog., **30**, p. 579 (1967).
- 6) A. Clearfield, Chem. Rev., **88**, p. 125 (1988); K. Ohtsuka, Chem. Mater., **9**, p. 2039 (1997); U. Constantino, M. Nocchetti, R. Vivan, J. Am. Chem. Soc., **124**, p. 8428 (2002).
- 7) G. Alberti, Acc. Chem. Res., **11**, p. 163 (1978).