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Synthesis and Ion-Exchange Properties of Inorganic Ion Exchanger Zirconium Phosphate

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Abstract: Zirconium phosphate (ZrP) is synthesized and characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis (TGA) as well as pH titration experiments. A distribution coefficient (K_d) at different trace elements for pH value of 4 and at different pH was calculated experimentally. Also the K_d of strontium at different shaking times was calculated. Stability of inorganic ion exchanger at different pH was investigated too. The results show that ZrP is almost stability in acid medium, especially with the lower molarity. Also titration shows a that it has high ability of displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution. In pH value of 4, ZrP is an useful inorganic ion exchanger and shows a high affinity for some elements such as Cs and Sr. The degree of ionization of ZrP depends on acid strength of solution. So when the pH drops, the capacity and K_d values fall off. In conclusion ZrP ion exchanger was found to have very good ion exchange capacity and high distribution coefficient for some elements. Also ZrP is a good inorganic ion exchanger for separation of strontium from other elements.

Key words: Inorganic ion exchanger, zirconium phosphate (ZrP), distribution coefficient, separation

INTRODUCTION

Ion exchange materials have found extensive application in analytical and industrial chemistry in view of their elegant characteristics such as insoluble matrix, stoichiometric exchange, good selectivity, specificity and applicability to column operations (Jayswal and Chudasama, 2007). In this project the development of highly selective inorganic ion exchangers for the removal of radionuclide from nuclear waste solutions has been studied (Möller *et al.*, 2001; Harjula *et al.*, 1999; Dyer *et al.*, 2000a, b). One of the major drivers for these investigations has been the fact that such ion-exchangers generally display superior selectivity for given aqueous metal cations over that of the more traditional organic-based ion-exchange resins, even in the presence of high concentrations of competing cations Na, K, H₃O (Christopher *et al.*, 2005).

In the last decade, ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants and removal of the formulation chemicals from the coolant (Velmurugan *et al.*, 1991). Zirconium-based ion exchangers have received attention because of their excellent ion-exchange behaviors and some important chemical applications in the field of ion exchange, ion-

exchange membrane and solid-state electrochemistry (Weqar and Shakeel, 2007). Up to now ZrP has been extensively studied as an intercalation substrate for material synthesis (Bhambhani and Kumar, 2006; Huang *et al.*, 2004; Jagannadham *et al.*, 2006; Wang *et al.*, 2005) also it was mentioned that as a family of inorganic cation exchangers, zeolite or zeolite-based sorbents have been studied extensively for selective removal of heavy metals (Lv *et al.*, 2004; Wingenfelder *et al.*, 2005a, b). In this paper, the preparation and characterization of ion-exchanger Zirconium Phosphate is presented and ion exchange properties and analytical application are discussed.

MATERIALS AND METHODS

Materials and instrument: All the chemicals were prepared of analytical grade (E. Merck or Aldrich). Thermogravimetry was carried out with a Rheometric scientific 1500 at the heating rate of 10°C min⁻¹. IR spectra were recorded with a Bruker vector 22 spectrometer using KBr disks. Powder diffraction analyses were done using a Jeol GDX-8030 instrument with Ni-filtered Cu-K α radiation. Electron micrographs were recorded with a Philips XL-30 Scanning Electron Microscope (SEM). A Varian liberty 150 XL Inductively Coupled Plasma (ICP)

and a Varian model 20 Atomic Adsorption Spectrometer (AAS) used for analysis of metal ions. A digital pH-meter Schott CG 841 was used for the pH measurements.

Synthesis of ZrP: In the process of synthesis ZrP, at first zirconil was dissolved in the 2 M HCL solution, then it was added slowly to the 3.5 M phosphoric acid. This solution has been shaking for 24 h until the precipitates was formed totally and then the precipitated were filtered, washed with distilled water and dried at 40°C (over night) in oven.

Ion-exchange capacity: About 0.5 g of exchanger in the H⁺ form was shaken for 2 h at 22±1°C in a polyethylene bottle containing 40 mL of 0.5 M KCl solution. The filtered solution was titrated by 0.005M NaOH solution. The pH of the solution was recorded after each addition of 1.0 mL of the titrant till the pH became constant. From the pH values before and after the exchange process, the milliequivalents of OH⁻ ion consumed were determined. The ion exchange capacity was calculated as reported by Velmurugan *et al.* (1991).

Distribution coefficients (K_d): In the batch sorption experiments 0.1 g of the powdered sorbent was shaken with 19.5 mL of the specific pH acidity solution and 0.5 mL of 0.005 molar of metal ion solution for 24 h in polyethylene bottles. After filtering this solution the concentration of the element after equilibration was measured by ICP and AAS technique. Distribution coefficients (K_d) of the different trace elements were calculated according to the equation:

$$K_d = [(X_1 - X_2) / X_2] [V / M] \text{ mL g}^{-1}$$

where, X₁ is the initial amount of the metal ion in the solution phase, X₂ is the final amount of the metal ion in the solution phase, V is the volume of the metal ion solution (mL) and M is the weight of the ion exchanger. K_d was determined for different elements. Also K_d with this experimental method was determined in different times of shaking for strontium.

Chemical stability: The chemical resistivity of ZrP in various media (acids and bases) has been assessed. The powdered sorbent was contacted with acid and base solutions for 24 h at ambient temperature. After filtering, the liquid phase of this solution was analyzed with ICP.

Separation of elements at pH = 4: In the batch sorption experiments 0.2 g of the powdered sorbents were shaken with 19 mL of pH = 4 solution and 0.5 cc mL solution of

0.005 M from any two elements for 5 h in polyethylene bottles. After filtering this solution, the concentration of trace element was determined using ICP.

RESULTS AND DISCUSSION

Characterization: The material has been characterized by spectral analysis (FT-IR), thermal analysis (TGA) and X-ray diffraction. The SEM micrographs of the granular ZrP are shown in Fig. 1. As can be seen the materials have irregular particle shapes and enormous range of particle size.

As suggested by XRD studies (Fig. 2), the ZrP particles are amorphous in nature as elucidated elsewhere (Clearfield and Stynes, 1964; Trobajo *et al.*, 2000; Zhao *et al.*, 2005).

In addition, the thermo gravimetric curve in Fig. 3 indicated that about 10% of the total weight of ZrP was lost as the temperature increased from 20-120°C due to the evaporation of the external water existing in the particles and the weight loss of 5% is from 120-550°C, due to condensation of exchangeable hydroxyl groups take place which is the usual behavior of inorganic ion exchangers. The IR spectra (Fig. 4) indicates the presence of external

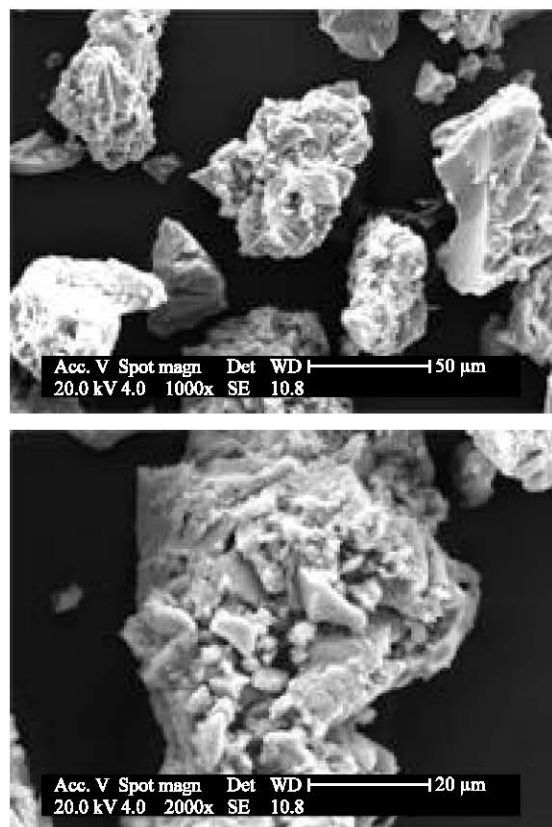


Fig. 1: SEM of ZrP

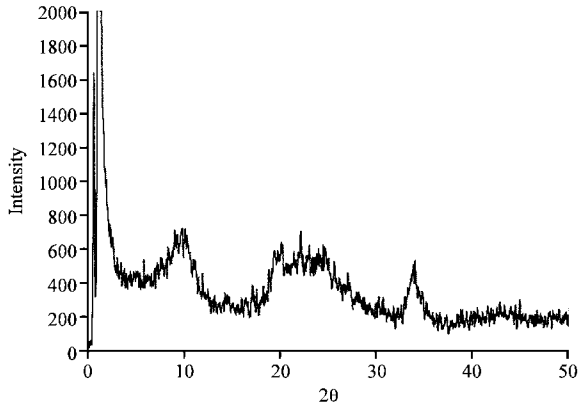


Fig. 2: XRD spectrum of ZrP

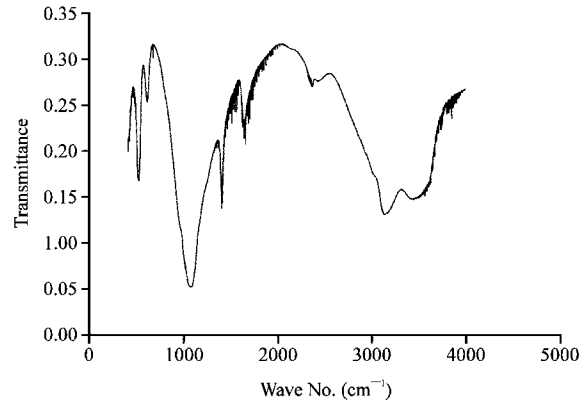


Fig. 4: IR Spectrum of ZrP

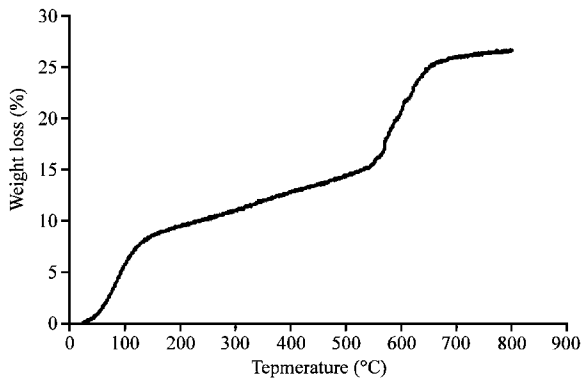


Fig. 3: TGA curve of ZrP

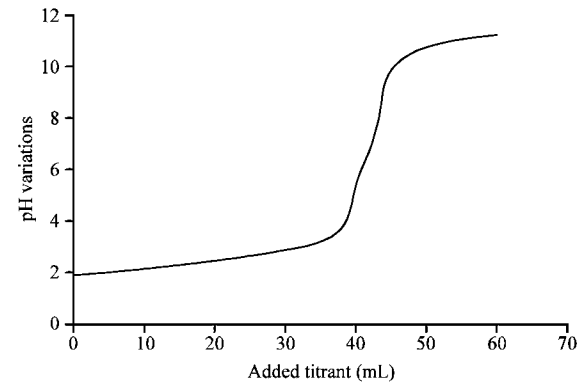


Fig. 5: pH-titration curve of ZrP

Table 1: Chemical stability of ZrP in different solvents

	Zr released (ppm)	P released (ppm)
1M HNO ₃	1	5.5
2M HNO ₃	1	4.9
8M HNO ₃	22.4	4.2
1M HCl	1	5.6
2M HCl	1	5.6
8M HCl	28	10.8
0.1M NaOH	1	508.0

water in addition to the strongly hydrogen-bonded OH by the sharp peaks at 3500 and 1650 cm⁻¹ (Varshney *et al.*, 1998; Kim *et al.*, 1997; Yang *et al.*, 1993). Symmetrical stretching vibration of (PO₄)³⁻ appears at 1050-1080 cm⁻¹ (Bakmutova *et al.*, 2003; Varshney *et al.*, 1998) and the peak at 600-610 cm⁻¹ represents the Zr-O stretching vibration (Varshney *et al.*, 1998; Xu *et al.*, 2005).

Chemical stability: Table 1 shows that ZrP is almost stable in acid medium, especially with the lower molarity. It is not stable in basic media.

Ion exchange capacity: From the pH values before and after the exchange process, the milliequivalents of OH⁻ ion consumed were determined. That it shows

capacity of exchanger. As it is shown in Fig. 5: $(pH_2 - pH_1) / (v_2 - v_1) = (10 - 3) / (40 - 30) = 0.7$. It shows a good ion exchange capacity or it has high ability of displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution.

Distribution coefficients (K_d) of different elements at pH value = 4: As can be seen in Fig. 6, ZrP is an useful inorganic ion exchanger in pH range 4, showing a high affinity for some elements such as Cs and Sr. It was observed that for some of elements such as Cd, Co, Ni, Hf and Zr, K_d values is low due to slower replacement of those elements in pH value 4.

Distribution coefficients (K_d) of different trace elements at different values of pH: As can be seen in Fig. 7, the presence of different values of pH in solutions of some ions affects the K_d value of ions. The degree of ionization of ZrP depends on acid strength of solution. So, when the pH drops, the capacity and K_d values fall off. Because of it in pH values 4-7, high affinity and corresponding

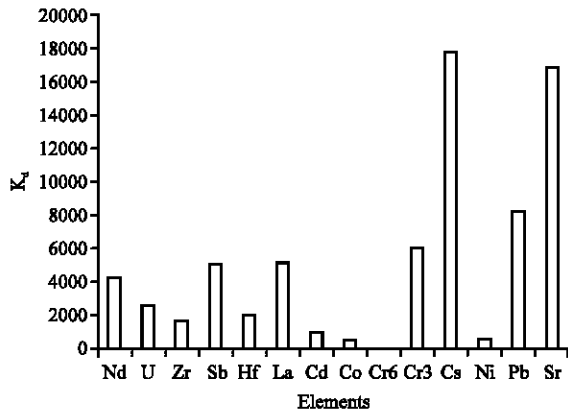


Fig. 6: K_d diagram of metal ions on ZrP at pH= 4

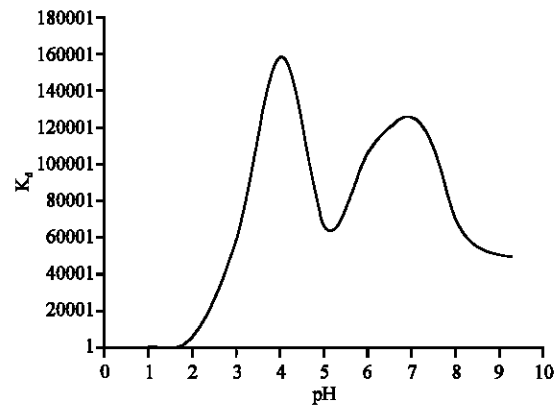


Fig. 8: K_d of strontium in different values of pH

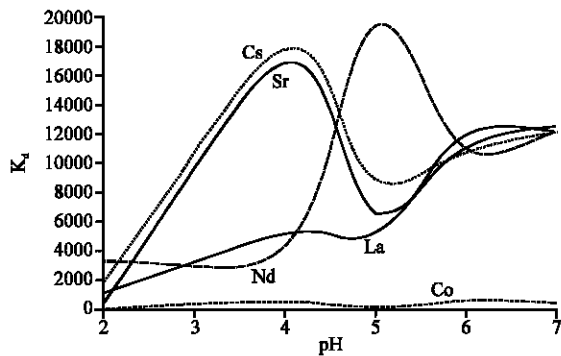


Fig. 7: K_d Curves of metal ions on ZrP in different pH

Table 2: K_d values of strontium on ZrP at different shaking times

1 h	2 h	4 h	6 h	10 h	24 h
2573	6250	6673	7715	16833	16833

to it, was seen in elements such as Cs, Sr, Nd and La. Sorption behavior of element Co with respect to other elements show a good selectivity for it from the other elements.

Distribution coefficients (K_d) of strontium with different shaking times: It can be seen in Table 2 that K_d is the highest since 10 h shaking. From this time sorption behavior was become constant. It was saturated. In this environment temperature and with this value of pH, it has no more acceptance capacity for Sr.

Distribution coefficients (K_d) of strontium in different values of pH: As can be seen in Fig. 8, different values of K_d , in different values of pH, show ionization degree of inorganic ion exchanger. In low values of pH the acid was becomes nonionic and thus K_d falls off. Also in

Table 3: Separation of elements at pH= 4

M^{n+}	Separation	M^{n+}
Co-Sr	Co (7.35*, 34%**)	Sr (11*, 5%**)
Ni-Sr	Ni (5.3, 43%)	Sr (11, 7%)
Cr-Sr	Cr (2.5, 0%)	Sr (11, 2%)
Zr-Sr	Zr (16, 67%)	Sr (11, 1.7%)
Sb-Sr	Sb (3, 17%)	Sr (11, 8%)
Nd-Sr	Nd (15, 5%)	Sr (11, 10%)
Sr-Cs	Sr (11, 4%)	Cs (12, 1%)
Co-Cs	Co (7.35, 38%)	Cs (12, 2%)
Ni-Cs	Ni (5.3, 16%)	Cs (12, 3%)
Co-Nd	Co (7.35, 47%)	Nd (15, 0)

*Added (ppm), **Found (%)

pH values 3 and 7, it was seen peaks that show strength sorption behavior of Sr.

Separation of trace elements in pH = 4: Study of coefficient distribution of some elements in pH value of 4, 3 has been shown in Fig. 6 that a good separations may be done by using ZrP inorganic ion exchanger. Based on this study, binary separations have been carried out for ten sets of elements. As it can be seen in Table 3, a good separation is performed for Co-Nd, Ni-Sr, Co-Sr, Co-Cs and Zr-Sr.

CONCLUSION

ZrP ion exchanger was found to have very good ion exchange capacity and high distribution coefficient for some elements. The chemical stability of this product is stable for acidity values of pH. At brief in total experiments that we have done it was clear that ZrP is a good inorganic ion exchanger for separation of strontium from other elements. It should be mentioned that this separation is for using strontium in making a radiopharmaceutical.

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