Studies on the adsorption behavior of trace amounts of $^{90}Sr^{2+}$, $^{140}La^{3+}$, $^{60}Co^{2+}$, Ni^{2+} and Zr^{4+} cations on synthesized inorganic ion exchangers

A. Nilchi [a,*], M.R. Hadjmohammadi [b], S. Rasouli Garmarodi [b], R. Saberi [c]

[a] Nuclear Science and Technology Research Institute, Nuclear Science Research School, J. I. H. Research Laboratories, P.O.Box 11365/8486, Tehran, Iran
[b] Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
[c] Environment and Energy Faculty, Science and Research Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

Three inorganic ion exchangers namely potassium zinc hexacyanoferrate(II) (PZF), magnesium oxide–polyacrylonitrile composite (MgO–PAN) and ammonium molybdophosphate (AMP) were synthesized. The physicochemical properties of these ion exchangers were determined using different techniques including inductively coupled plasma (ICP), CHNSO elemental analysis, infrared spectroscopy (IR), X-ray diffraction (XRD), thermogravimetric (TGA) and pH – titration curve analysis. The solubility of the synthesized ion exchangers in different acidic and alkaline media, their thermal stability and the effect of gamma irradiation were investigated. It was observed that the exchange capacity of the ion exchangers depend upon the pH value of the solution used. Furthermore, the adsorption of $^{90}Sr^{2+}$, $^{140}La^{3+}$, $^{60}Co^{2+}$ and the distribution coefficient of these ion exchangers for Ni^{2+} and Zr^{4+} were studied. The effect of parameters such as pH and contact time on the adsorption was also investigated and the optimum conditions for separation of these ions were determined.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

A rapid development in nuclear energy, hydrometallurgy and recovery of materials from industrial wastes has enforced attempts to synthesize highly selective ion exchange materials [1–4]. The ability of ion exchangers to remove trace ions from solution and the concentration which may be achieved on elution with suitable solutions have been used in the treatment of wastes and in processes for recovery of metals from very dilute solutions. Ion exchangers have been used extensively in treating rinse water wastes in plating industry for example, where valuable metals are recovered at costs comparable to or less than conventional chemical treatment, with appreciable saving in space for treatment plant. Also, a large number of ion exchangers such as zeolites, sodium titanates, titanosilicates, hexacyanoferrates, acidic salts of multivalent metal, salt of heteropolyacids and hydrous oxides have been investigated for removal of fission products (^{137}Cs, ^{90}Sr) and activation corrosion products such as ^{60}Co, ^{63}Ni, ^{65}Zn, ^{51}Cr, ^{54}Mn, ^{59}Fe and ^{95}Zr from nuclear waste [5–16]. The major attraction in the use of inorganic ion exchangers in such applications compared with synthetic organic ones is their high thermal and radiation stabilities and compatibility with matrices used for their immobilization. In this work,

the synthesis, characterization, ion exchange potential and analytical application of three inorganic ion exchangers for efficient separation of $^{90}Sr^{2+}$, $^{140}La^{3+}$, $^{60}Co^{2+}$, Ni^{2+} and Zr^{4+} cations present in nuclear wastes are examined.

2. Experimental

2.1. Reagents and apparatus

All the reagents and chemical used were of Analytical grade and were obtained from Merck. ^{60}Co, ^{140}La and ^{90}Sr radionuclides were supplied by Nuclear Science Research School of Iran.

The infrared spectra were recorded using a Brucker-Vector 22 spectrophotometer; X-ray powder diffractometry was carried out using an 1800 PW Philips diffractometer with CuKα beam in order to determine the structure of the adsorbers. The finely powdered sample of the adsorbers was packed in a flat aluminium sample holder, where the X-ray source was a rotating anode operating at 40 kV and 30 mA with a copper target. Data were collected between 5° and 70° in 2θ; CHN analysis was performed using an Elementar-Vario ELIII, CHNSO elemental analyzer, thermogravimetric analysis were carried out using a DuPont model 951; the amount of Ni^{2+} and Zr^{4+} were measured by a PerkinElmer inductively coupled plasma (ICP) spectrometer model 5500; the concentration of Na^+ and Mg^{2+} ions was determined by a PerkinElmer atomic adsorption spectrometer (AAS) model 843; the radioactivity was counted using an

* Corresponding author. Tel.: +98 2188020273; fax: +98 2188021412.
E-mail addresses: anilchi@aeoi.org.ir, anooshn@hotmail.com (A. Nilchi).

ultra low level liquid scintillation spectrometer Quantuluse^{TM} 1220 (PerkinElmer, Wallac)/a high purity germanium detector gamma spectrometer Ortec model GMX-15185-5 and finally the pH measurement were made with a Schott pH-meter model CG841.

2.2. Preparation of inorganic ion exchangers

2.2.1. Potassium zinc hexacyanoferrateII (PZF)

This material was prepared by drop-wise mixing of 1 M potassium hexacyanoferrate(II) and zinc sulphate (volume ratio 1:4) under continuous stirring at 25 °C for 2 days. After pulverizing, the precipitate was washed thoroughly with deionised water, dried again at 70 °C for 7 days and sieved; the 50–100 mesh fractions were used.

2.2.2. Hydrous magnesium oxide–polyacrylonitrile composite (MgO–PAN)

A three neck flask was used for composite beads preparation reactor. The weighed amount of magnesium oxide powder was mixed with the solvent dimethylsulfoxide (DMSO) and a few drops of Tween-80 surfactant and stirred at 50 °C for 1 h to form homogeneous solution. Then, polyacrylonitrile powder was added to this solution with continuous stirring at 50 °C for 5 h to obtain homogeneous solution of the composite dope. The dissolved air in the dope was removed by vacuum pump, and the air-free composite dope was fed into the dual nozzle to obtain the spherical composite beads. The beads were filtered and washed with deionized water and dried at 50 °C in an oven for 24 h.

2.2.3. Ammonium molybdophosphate (AMP)

This was prepared by mixing 0.1 M ammonium molybdate, 500 mL of 0.1 M ammonium nitrate and 500 mL of 0.25 M phosphoric acid and the final solution was made to 6–7 M in terms of HNO$_3$. The yellow precipitate was filtered and washed with deionized water and dried at 50 °C in an oven for 24 h.

2.3. Chemical composition of MgO–PAN

The elemental analysis of composite was accomplished by decomposing 0.25 g of MgO–PAN in 25 mL of 2 M H$_2$SO$_4$ solution. The resulting solution was diluted with deionized water and the amount of Mg^{2+} was measured by AAS. In order to determine carbon, hydrogen and nitrogen contents of the composite, a sample of dried adsorbent was analyzed by CHNSO elemental analyzer. The weight percent composition of the material was as follows: Mg, 26.4; C, 36.1; H, 4.6; N, 15.4.

2.4. Thermal, radiation and chemical stability

Thermogravimetric study was carried out by heating the samples up to 800 °C at a constant rate of 10 °C min^{-1} in the Argon atmosphere.

The gamma irradiation of the freshly prepared samples was carried out, using ^{60}Co as a source, at a dose rate of 0.38 Gy s^{-1}, for a total dose of 150 kGy.

Chemical stabilities were determined by placing 0.1 g of the exchangers with 25 mL of different solvents for a period of 2 days followed by the determination of the percentage of materials that have been dissolved.

2.5. Ion exchange capacity

0.1 g of the cation-exchangers in the H$^+$ form were placed in each of 50 mL conical flasks, followed by the addition of equimolar solutions of (NaCl + NaOH/HCl) in different volume ratios, the final volume being 10 mL to maintain the ionic strength constant. The

pH of solution was recorded after equilibrium which was attained in a thermostated shaker at 25 °C for 48 h, and was then plotted against the milliequivalents of H$^+$ or OH$^-$ ions added. The supernatant solutions were also analyzed for sodium ions by AAS, and Na$^+$ ion exchange capacity in different pH values was determined. The value of capacity (q) can be calculated using the following equation:

$$q(\text{meq/g}) = (C_i - C_f) \times \frac{V}{M}$$

where C_i is the initial metal ion concentration in the solution, C_f is the metal ion concentration in solution after equilibrium with the adsorber, V is the volume of solution (mL), and M is the weight of the ion exchanger in contact with solution (g).

2.6. Effect of contact time on batch distribution coefficient (K_d)

Distribution coefficient measurement has generally been accepted as a convenient method for expressing the sorption of various ions from liquid solutions. The distribution coefficient values were calculated using one of the formulas given below:

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V}{M} \quad \text{or} \quad K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{M}$$

where C_i is the initial metal ion concentration in the solution, C_f is the metal ion concentration in solution after equilibrium with the adsorber, A_i is the initial activity of solution, A_f is the activity of solution after equilibrium with the adsorber, V is the volume of solution (mL), and M is the weight of the ion exchanger in contact with solution (g).

The distribution coefficient of Ni^{2+} and Zr^{4+} on the adsorbers was studied as a function of contact time. 20 mL of 10^{-4} M solutions of cations were shaken with 0.1 g of the exchangers at pH of 7 and 25 °C at different time intervals. The supernatant solutions were filtered and concentration of each metal ion or activity of solution determined.

2.7. The effect of pH on batch distribution coefficient (K_d)

The pH of the aqueous solution is an important controlling parameter in the adsorption process. In order to investigate the effect of pH on distribution coefficient of cations, 10^{-4} M solutions of ^{90}Sr^{2+}, ^{140}La^{3+}, ^{60}Co^{2+}, Ni^{2+} and Zr^{4+} cations at different pH values were prepared. 20 mL of these solutions were added to 0.1 g of the exchangers at 25 °C and then by setting the contact time required (as established in previous section) the equilibrium is reached. The supernatant solutions were then filtered and the concentration of each metal ions or activity of solutions was determined.

3. Results and discussions

In this study, potassium zinc hexacyanoferrate(II) (PZF), magnesium oxide–polyacrylonitrile composite (MgO–PAN) and ammonium molybdophosphate (AMP) were prepared. The infrared spectra of these ion exchangers are recorded in Fig. 1. In the IR spectra of ion exchangers, the broad band in the region of 3200–3650 cm^{-1} is due to interstitial water and hydroxyl groups and the peak at 1620 cm^{-1} is due to the deformation vibration of the free water molecules. The IR spectrum of MgO–PAN (1a) and PZF (1b) composite revealed the adsorption peak at 2250 and 2100 cm^{-1}, respectively, that correspond to cyanide stretching vibration. In the IR spectrum of MgO–PAN composite, the peak at 1200 cm^{-1} corresponds to M–O–H bending mode which shows the presence of Mg–O–H. The band in the 1465 cm^{-1} is due to CH$_2$ vibration. IR spectrum of PZF shows adsorption peak at 450–600 cm^{-1} region which are due to the Fe–C stretching. The