



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

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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 $^{90}\text{Sr}^{2+}$, $^{140}\text{La}^{3+}$, $^{60}\text{Co}^{2+}$ 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.

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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 $^{90}\text{Sr}^{2+}$, $^{140}\text{La}^{3+}$, $^{60}\text{Co}^{2+}$, 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 Bruker-Vector 22 spectrophotometer; X-ray powder diffractometry was carried out using an 1800 PW Philips diffractometer with $\text{CuK}\alpha$ 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 was 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

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ultra low level liquid scintillation spectrometer QuantulusTM 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 hexacyanoferrate(II) (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 HNO₃. 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 H₂SO₄ solution. The resulting solution was diluted with deionized water and the amount of Mg²⁺ 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 ⁶⁰Co 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 Ni²⁺ and Zr⁴⁺ 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 ⁹⁰Sr²⁺, ¹⁴⁰La³⁺, ⁶⁰Co²⁺, Ni²⁺ and Zr⁴⁺ 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 CH₂ vibration. IR spectrum of PZF shows adsorption peak at 450–600 cm⁻¹ region which are due to the Fe–C stretching. The

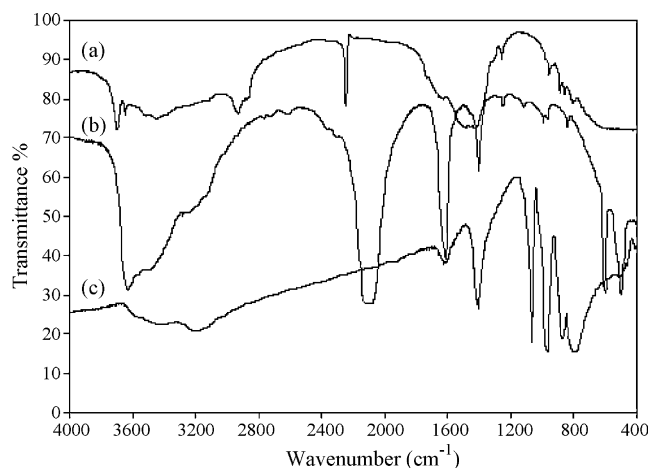


Fig. 1. IR spectrum of (a) MgO-PAN (b) PZF (c) AMP.

peak near 1300 cm^{-1} could be due to sulphate anions adsorbed. The adsorption peaks in IR spectrum of AMP in the range of $740\text{--}970\text{ cm}^{-1}$ and $250\text{--}400\text{ cm}^{-1}$ have been assigned to MoO_4^- , while at $950\text{--}1100$ and $400\text{--}600\text{ cm}^{-1}$ to PO_4^{3-} , and finally at $3000\text{--}3400$ and $1400\text{--}1500\text{ cm}^{-1}$ to NH_4^+ .

The result of IR and chemical composition studies of MgO-PAN confirms the incorporation of MgO to polymer matrices.

The X-ray powder diffraction patterns of the three synthetic compounds are presented in Fig. 2. Potassium zinc hexacyanoferrate(II) ($\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$) and ammonium molybdophosphate ($(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$) were identified when compared with the XRD data corresponding to synthetic samples with standard data for PZF and AMP [17]. The X-ray powder diffraction pattern of the composite exhibited the presence of sharp peaks with d -values 5.24, 4.79, 2.38, 2.29 and 1.57 \AA at angles (2θ) 17.1° , 18.8° , 37.8° , 50.1° and 58.2° , respectively, suggesting a crystalline nature for the synthesized material.

Thermogravimetric curves of ion exchangers are recorded in Fig. 3. Thermogram of PZF shows that the weight loss of the ion exchanger up to 150°C is due to the removal of free external water molecules. A further loss in weight up to 410°C could be due to the removal of internal water molecules and cyanogen. Beyond 410°C , the weight of the exchanger becomes constant up to 600°C . A loss in weight between 600 and 800°C could be due to removal of C as CO_2 and formation of zinc and iron oxides. Assuming that only the external water molecules are lost at 150°C , the $\sim 18.2\text{ wt.}\%$ loss of PZF represented by TGA must be due to the loss of $n\text{H}_2\text{O}$. Thus, the

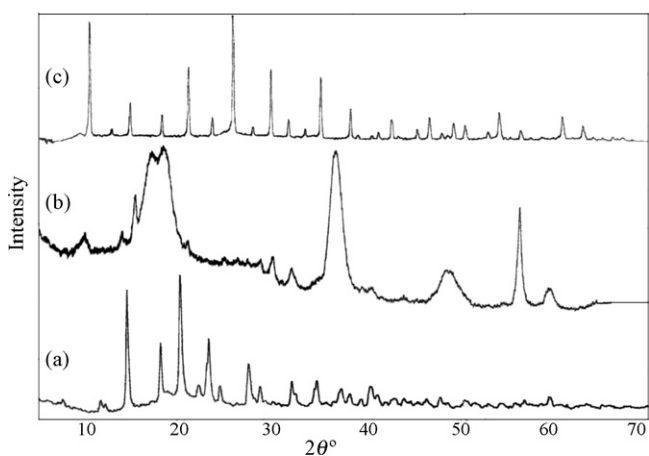


Fig. 2. Powder X-ray diffraction patterns of synthetic (a) PZF (b) MgO-PAN (c) AMP.

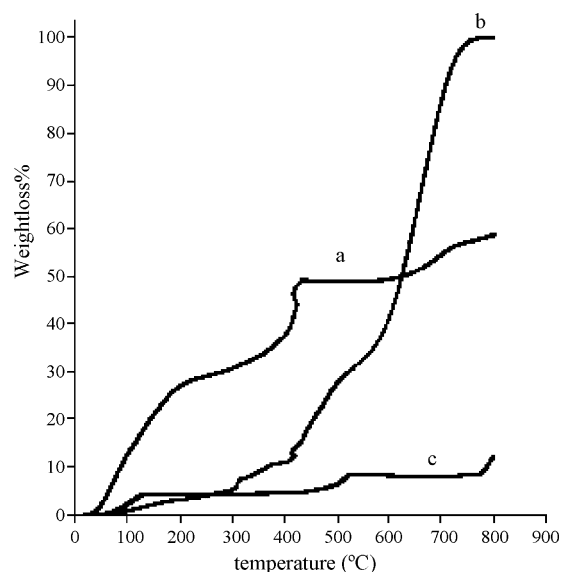


Fig. 3. Thermogravimetric curve of (a) PZF (b) MgO-PAN (c) AMP.

value of (n) can be calculated using Alberti's equation [18]:

$$18n = \frac{x(M + 18n)}{100}$$

where x is the percent weight loss of the exchanger and M is the molecular weight of the material without water molecules. The value of n is calculated to be 8.67.

Thermogram of composite shows that the weight loss of up to 140°C is due to the removal of external water molecules. At higher temperatures, complete decomposition of the organic part of the material takes place.

In thermogravimetric analysis curve of AMP, initial weight loss of $\sim 2.9\%$ of the exchanger, at up to 130°C , is due to the loss of external water molecules present. Weight loss observed between 130 and 400°C is due to the removal of internal water molecules and further weight loss between 400 and 600°C could be due to the removal of ammonia gas. The calculation gives the number of external water molecules present per molecule of AMP to be 3.1.

Determination of the stability of the ion exchangers toward various solvents showed that potassium zinc hexacyanoferrate(II) is stable in water, dilute mineral acids, ethanol, methanol, acetone and ether but it is soluble in concentrated mineral acids and 4 M NaOH solution. MgO-PAN composite is stable in water, dilute acidic and alkaline solutions and ethanol. However, in concentrated HNO_3 and $12\text{ M H}_2\text{SO}_4$, it decomposes. AMP is stable in water, dilute mineral acids, but it completely decomposes in dilute alkaline solutions such as 0.1 M NaOH .

Investigation of infrared spectra and X-ray diffractograms of ion exchange materials prior to and after irradiation showed that there is no significant difference. Therefore, these ion exchangers were resistant to gamma irradiation of up to 150 kGy .

The pH-titration curves of PZF and AMP given in Fig. 4 show only one sharp plateau and thus indicating that these ion exchangers behave as a monofunctional acid type exchangers. Also, it can be easily inferred from the curves that the exchangers are not appreciably hydrolyzed in acidic media. However, MgO-PAN showed the amphoteric nature (Fig. 4).

The capacity-pH curves of ion exchangers are shown in Fig. 5. The results showed that the sodium exchange capacity of the three samples increase when the pH increases. This is due to the fact that lower competition between H^+ and sodium ion at high pH exist.

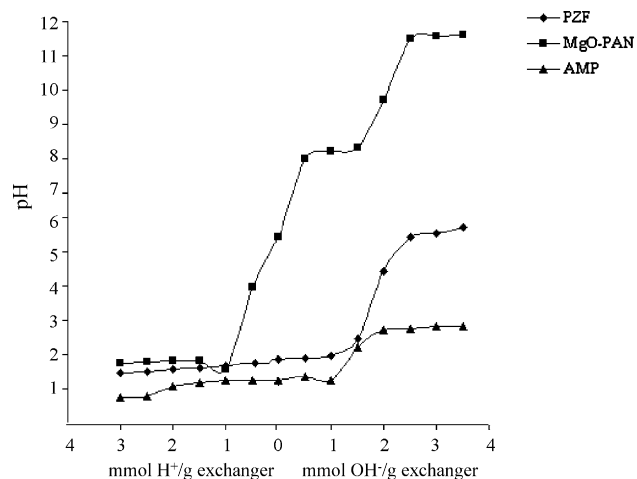


Fig. 4. pH-titration curves of PZF, MgO-PAN and AMP.

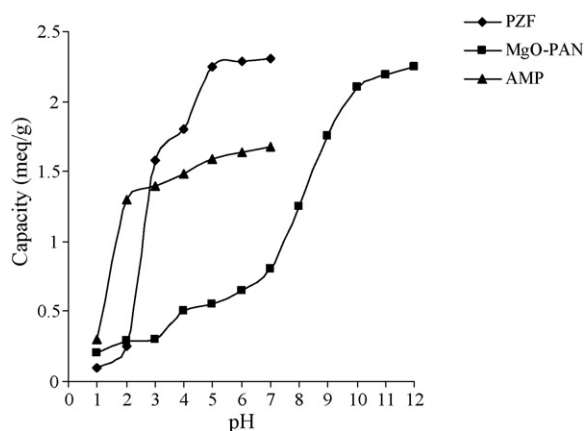


Fig. 5. The capacity-pH curves of ion exchangers.

The change in distribution coefficient of Ni^{2+} and Zr^{4+} as a function of contact time are given in Figs. 6–8. The adsorption yield increases with contact time. The time required in order to reach equilibrium were found to be 180, 300 and 60 minutes for AMP, PZF and MgO-PAN, respectively.

Figs. 9–11 show the effect of pH on distribution coefficient (K_d) of $^{90}\text{Sr}^{2+}$, $^{140}\text{La}^{3+}$, $^{60}\text{Co}^{2+}$, Ni^{2+} and Zr^{4+} on the synthesized ion exchangers. The adsorption of the cations in potassium zinc hex-

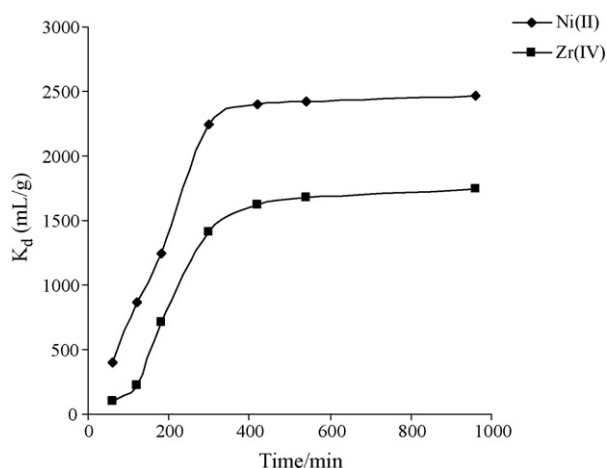


Fig. 6. The effect of contact time on K_d of Ni^{2+} and Zr^{4+} on PZF.

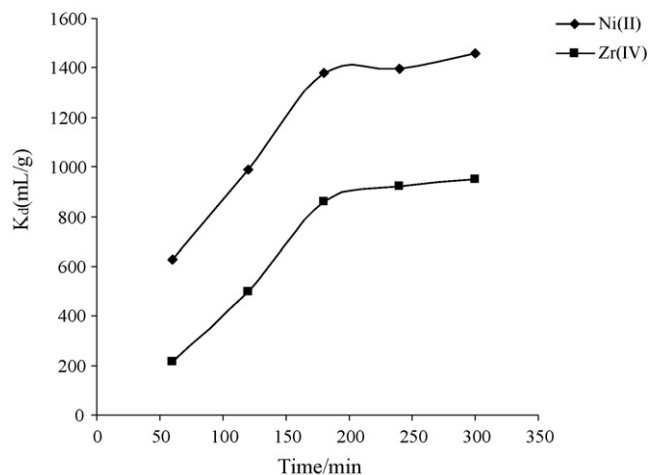


Fig. 7. The effect of contact time on K_d of Ni^{2+} and Zr^{4+} on AMP.

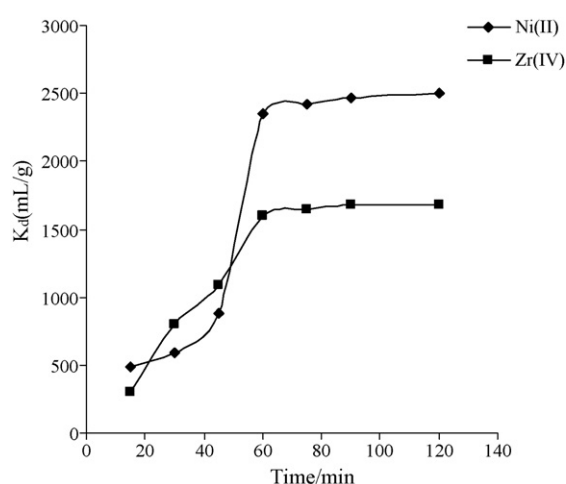


Fig. 8. The effect of contact time on K_d of Ni^{2+} and Zr^{4+} on MgO-PAN.

acyanoferrate(II) and ammonium molybdophosphate increases, as the pH increase. This is due to the fact that at lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the adsorbent. The distribution coefficient results showed that with the increase of pH of the media, the amount of adsorption of cations on the surface of magnesium oxide composite increases, and this is due to amphoteric nature of the ion exchanger. Magnesium

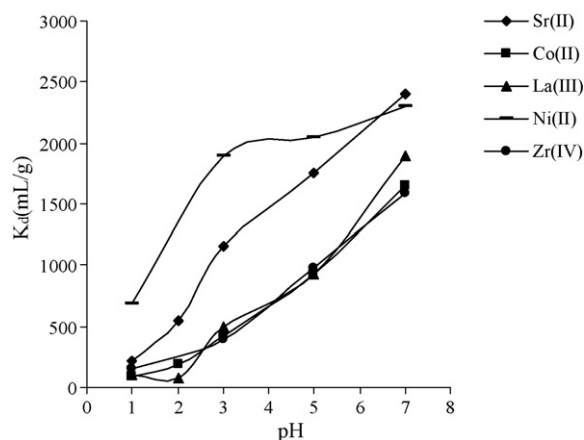


Fig. 9. K_d of cations on PZF at different pH.

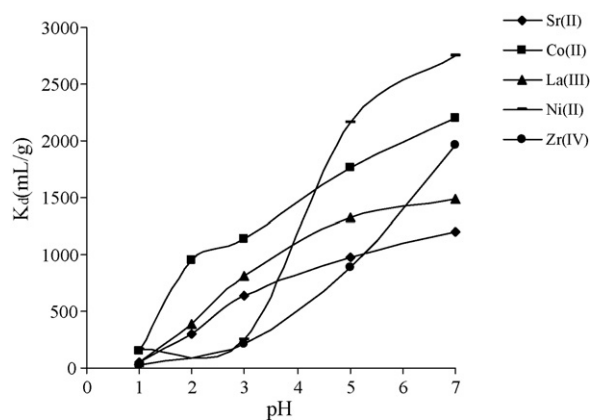


Fig. 10. K_d of cations on MgO-PAN at different pH.

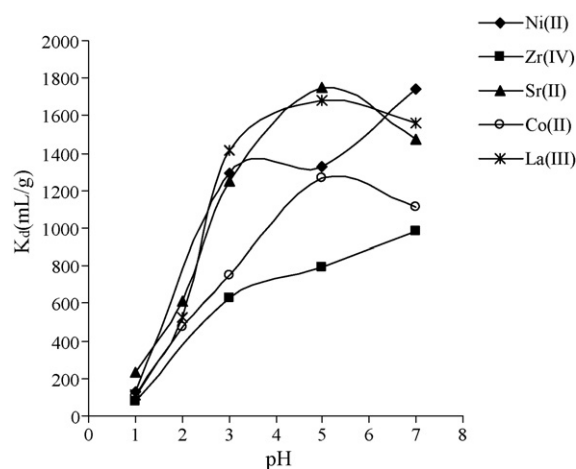


Fig. 11. K_d of cations on AMP at different pH.

oxide has an isoelectric point at pH 12, which means that below pH 12, the surface is positively charged whereas above pH 12 it is negatively charged [19]. At lower pH values where little adsorption occurs; there is an isoelectric repulsion between cations and positively charged surface of the oxide. As the pH increases, the surface becomes less and less positively charged, and thus the repulsion between cations and the oxide surface will decrease.

4. Conclusion

These studies showed that the ion exchangers have crystalline structure and were thermally stable, resistant to gamma irradiation of up to 150 kGy and also chemically stable in acidic solutions. The

adsorption properties showed that the adsorption of the cations is directly depended upon the contact time and pH of the media used, and as these controlling parameters increase, the adsorption of cations for the ion exchangers, increase. The distribution coefficient results of AMP and MgO-PAN showed great affinity towards Ni^{2+} , Zr^{4+} , $^{90}\text{Sr}^{2+}$, $^{140}\text{La}^{3+}$ and $^{60}\text{Co}^{2+}$ cations; however binary separation of these ions in pH range of 1–7 was not possible. Ni^{2+} is highly adsorbed on potassium zinc hexacyanoferrate(II) and hence its quantitative separation from Zr^{4+} , $^{140}\text{La}^{3+}$ and $^{60}\text{Co}^{2+}$ in pH range of 1–5 was successfully achieved.

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