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ScienceDirect

Applied Radiation and Isotopes 65 (2007) 482–487

Applied Radiation and Isotopes

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Preparations of PAN-based adsorbers for separation of cesium and cobalt from radioactive wastes

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Received 25 June 2006; received in revised form 12 December 2006; accepted 12 December 2006

Abstract

Ion-exchange adsorbers are widely used for radioisotope separation, as well as for the removal of hazardous fission products from aqueous waste prior to discharge to the environment. Inorganic exchangers are of particular interest because of their resistance to radiolytic damage and selectivity for specific fission products. Composite inorganic–organic adsorbers represent a group of inorganic ion exchangers modified by using binding organic material, polyacrylonitrile, for preparation of larger size particles with higher granular strength. At the same time, kinetics of ion exchange and sorption capacity of such composite adsorbers are not influenced by the binding polymer. The contents of active component in composite adsorber were varied over a very broad range of 5–95% of the dry weight of the composite adsorber, and tested for separation and concentration of various stimulated wastes. Three different inorganic sorbents, granular hexacyanoferrate-based ion exchanger, were developed for the removal of Cs and Co ions from waste solutions containing different complexing agents as detergents. Radiation and thermal stability studies show that these adsorbents can be used for medium-active waste treatment.

Keywords: Hexacyanoferrates; Polyacrylonitrile binder; Radioisotope separation; Sorption properties

1. Introduction

The operation of nuclear power plants, reprocessing plants, research facilities and the use of radioisotopes in industry and diagnostic medicine produce a wide variety of radioactive wastes (IAEA, 1984; Navratil, 1985; Kubota, 1989; Schultz, 1983). The waste streams from nuclear facilities include low, intermediate and highly radioactive wastes and may also include α-emitting radioisotopes. In addition to radioisotopes, these waste streams could contain various toxic and hazardous materials such as heavy metals, organic material from decontamination procedure, etc. Many of these wastes have to be treated in order to reduce the radioisotopes concentration to levels acceptable for discharge to the environment. One of the most conventional processes used for the treatment process is ion exchange.

Over the past four decades, many different ferrocyanides have been prepared, and their structure and ion exchange properties have been investigated. In most of the ion exchange and adsorption studies, single transition metal complexes of hexacyanoferrate (CNF) (II) have been prepared, whereas less attention has been paid to double transition metal complexes (Janardanan et al., 1988; Pekarek and Vesely, 1972; De and Sen, 1978; Hooper and Phillips, 1984; Loewenschuss, 1982; Lehto and Harjula, 1987; Arino and Kramer, 1973). The advantages of these ion exchangers are their stability in acidic to moderately alkaline medium, and their radiation and temperature stability. Other ferrocyanides of Cu, Cu and Co, Zn, Fe and Ti have also been found satisfactory in the isolation of Cs ions from acidic wastes, arising in the nuclear fuel reprocessing (Pekarek and Vesely, 1972; Prout et al., 1965).

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doi:10.1016/j.apradiso.2006.12.003

The selective isolation of ^{137}Cs and ^{60}Co from radioactive waste solutions and determination of radionuclides in the environment have attracted great interest in recent years owing to the application of these radioisotopes, as a radiation source, in medicine and in industry (IAEA, 1993; Harjula and Lehto, 1993). ^{137}Cs is the major radioactive component in most waste solutions from nuclear power plant mainly owing to the relatively long half-life of ^{137}Cs (30y) and its high yield from fission. Therefore, separation of ^{137}Cs from waste solutions is essential prior to the discharge of the residual solutions to the environment (Pekarek and Vesely, 1972; Loewenschuss, 1982; Prout et al., 1965; Hendrickson and Kiel, 1975).

CNFs are being used as precipitation agents for the removal of Cs from nuclear waste solutions (Mimura et al., 1997a–c). Precipitation with CNF is rather effective compared with most other precipitation agents, but gives a colloidal sludge that is very difficult to remove from solution. Utilizing CNF in granular form as packed-bed columns instead of precipitation agent considerably increases the efficiency of the separation. The main limiting factor in the use of CNF in a column has been their poor mechanical properties; the grains disintegrate and clog the bed (Tusa et al., 1993; Lehto et al., 1993).

In this work, an inorganic–organic adsorber consisting of an inorganic ion exchanger-modified polyacrylonitrile (PAN) binding matrix is prepared. This type of ion exchanger refers to a composite group of inorganic ion exchangers, which are modified by some binding material for the preparation of larger size particles with higher granular strength (Šebesta, 1992). PAN, an inexpensive raw material used in the textile industry, has been shown to effectively immobilize ion exchange materials into useful forms, such as spherical beads. PAN beads are highly porous and can accommodate very high loadings of ion exchange material (5–95%) into the PAN matrix. These highly porous PAN beads exhibit a number of advantages over other granular sorbents. These advantages include significantly improved kinetics and sorbent capacity owing to the increased availability of the sorbent material, easy modification of physico-chemical properties (hydrophilicity, porosity, mechanical strength) and simplified production. In the present work, Ni, K–Ni and K–Cu–Ni CNF were synthesized, the effects of EDTA and oxalate complexing agents on exchange of simulated waste containing Cs and Co were examined and the corresponding distribution coefficients were measured.

2. Experimental

All the reagents and chemicals used were of analytical grade and were obtained from Merck or Aldrich. ^{137}Cs and ^{60}Co radioisotopes were supplied by Nuclear Research Centre, Atomic Energy Organization of Iran. The pH measurements were taken with a Schott pH-meter, model CG841; the infrared spectra were recorded using a Perkin-Elmer spectrophotometer; thermogravemetric analyses were conducted with a DuPont model 951 thermobalance; X-ray diffraction studies were conducted with a Philips model PW3710; and elemental analyses were performed with a Perkin-Elmer model 5500 inductively coupled plasma spectrophotometer and an Ortec γ-ray spectrometer were used for radioactivity measurement.

2.1. Preparation of potassium nickel hexacyanoferrate (II)

A non-stoichiometric KNiCNF was prepared by slowly adding 0.5 M $K_4[Fe(CN)_6]$ to 0.5 M $Ni(NO_3)_2$ at a Ni/Fe molar ratio of 1.33. The composition of the product was determined to be $K_{0.87}Ni_{0.57}[NiFe(CN)_6]\cdot nH_2O$ (Šebesta, 1992). The product was ground and sieved to 50–100 mesh. The theoretical ion exchange capacity was calculated to be 5.92 meq./g (2.58 meq. K and 3.34 meq. Ni).

2.2. Preparation of potassium copper nickel hexacyanoferrate (II)

KNiCNF was prepared as above and heated on a boiling water bath for 2 h, and was then allowed to stand for 48 h at room temperature. The compound produced was then washed thoroughly with distilled water and dried in hot air oven at 70 °C, and finally grinded. A 20 g sample of the material was then treated with 150 mL of 10% Cu nitrate solution in 0.1 M HNO_3 at room temperature and the slurry was shaken for 30 min. The resultant material KCuNiCNF was washed with deionized water until pH value of effluent was 5. It was then dried at 110 °C. The product was ground and sieved to give particle sizes of 50–100 mesh.

2.3. Composite sorbents consisting of inorganic ion exchangers and PAN binding matrix

Modified PAN has been used as a universal binding polymer for many inorganic ion exchangers (Šebesta, 1992; Harjula and Lehto, 1993). The initial components for preparing the inorganic ion exchanger can be mixed directly with the solution of the binding polymer. The active component of the composite ion exchanger is then formed during the coagulation of the binding polymer.

2.4. Chemical stability of PAN-based composite sorbents

A PAN-binding polymer is stable in all common aqueous electrolytes, except in concentrated solutions of $ZrCl_2$, LiBr, $CaCl_2$ and NaSCN, which are known to dissolve polyacrylonitrile. This polymer also dissolves in strong mineral acids such as 8 M HNO_3, 5 M H_3PO_4 and 5 M H_2SO_4.The chemical stability of the PAN binder is excellent in neutral to weakly acidic solutions. In alkaline solutions at $pH > 13$, chemical stability of PAN is inversely affected by its hydrolysis, which increases with increasing pH and temperature. The PAN polymer subsequently hydrolyses to gel, becomes hydrophilic and finally dissolves. The hydrolysis itself does not deteriorate the sorption properties of composite sorbents; it only affects their mechanical stability. The produced sorbents are stored hydrated without drying; the hydrated beads contain 60% (w/w) of water. The contents of active component in composite exchangers can be varied over a very broad range, depending on the application foreseen.

2.5. Batch distribution coefficient (k_d)

The batch distribution coefficient (K_d) is an experimental measure of the ability of the solid-phase ion exchange material to remove an ion from solution under a set of conditions at equilibrium. To ensure accurate comparison among the K_d values of various exchangers, the experimental conditions such as liquid volume-to-solid mass ratio, temperature, solution composition, and material pretreatment have to be identical for all experiments. Distribution coefficient (K_d) values were calculated by

$$K_d = \frac{(A_i - A_f)}{A_f}\frac{V}{m},$$

where A is the initial radioactivity of the solution before contracting sorbent, A_f is the final radioactivity of the solution after contacting sorbent, V is the volume of solution (mL) and m is the mass of sorbent material (g).

The K_d values of Cs^+ and Co^{2+} as a function of HNO_3 concentration were determined by shaking 0.01 g samples of the exchanger with 10 mL of HNO_3 solutions containing 7.5×10^{-5} M Cs^+ and Co^{2+} ions as nitrates and 50 μL of ^{137}Cs and ^{60}Co tracers. After 3 h shaking at 25 °C, the solid was filtered off and the ion concentration in the aqueous phase was determined by measuring the γ-activities of ^{137}Cs and ^{60}Co. In addition, the effect of EDTA and oxalate complexing agents on exchange of ^{137}Cs and ^{60}Co in sorbents prepared was studied by measuring the corresponding K_d's in the simulated solutions with a pH ranging from 6 to 12. The dose of added complexing agents was 1 and 10 g/L.

2.6. Chemical composition

The elemental analysis of the material was accomplished by decomposing 0.05 g of CNF in 1 mL of conc. H_2SO_4 with heating, and the resulting solution was evaporated to dryness. The residue was taken up in 10 mL of 0.1 M H_2SO_4 and diluted to 50 mL with deionized water. An aliquot was then used for measuring the amount of K, Cu, Ni and Fe, by ICP-AES.

2.7. Solubility

The solubility of the exchanger was determined at room temperature by equilibrating 0.1 g of the sieved material in various solutions overnight. The supernatant was analyzed by ICP spectrophotometer.

2.8. γ irradiation

γ Irradiation of the freshly prepared materials was carried out by a ^{60}Co source at a dose rate of 0.741 Gy/s for a total dose of 100 kGy.

3. Results and discussions

The chemical composition of KCuNiCNF is summarized in Table 1. The values of the molar ratio were calculated taking CNF equal to two. The water content of the product was calculated by weight difference before and after drying. The ICP analysis indicated that the composition of synthesized KCuNiCNF was $K_{2.3}Cu_{0.65}Ni_{1.7}[Fe(CN)_6]_2 \cdot 13H_2O$. Similarly, the compositions of NiCNF and KNiCNF were $Ni_{1.7}Fe(CN)_6 \cdot nH_2O$ and $K_{0.87}Ni_{0.57}[NiFe(CN)_6] \cdot nH_2O$, respectively.

Fig. 1 shows the effect of equilibration time on the percentage of adsorption of Cs and Co. The rate of adsorption increases with the increase in shaking time, and equilibrium is reached after 2 h in both cases. This is the same trend as shown by other inorganic ion exchangers studied, i.e. KCFC-PAN (Nilchi et al., 2006).

Fig. 2 shows the effect of Cs and Co adsorption as a function of pH values of solution. As shown, there is no significant change in the adsorption of Cs with the increase in pH values.

The effects of drying temperature of samples on ion-exchange capacity for Cs and Co were also studied. The exchange capacity increases with the increase in drying temperature, and reaches a maximum of 2.85 and 2.15 mmol/g for Cs and Co, respectively, when KCNF-PAN is dried at 110 °C. By drying at higher temperatures, the water molecules travel to the surface of the solid more

Table 1
Chemical composition of KCNF

Amount	K	Cu	Ni	Fe	$[Fe(CN)_6]^{4-}$	H_2O
mmol/g	2.50	0.70	1.80	2.25	2.15	13.80
mg/g	100	47	114	126	476	264

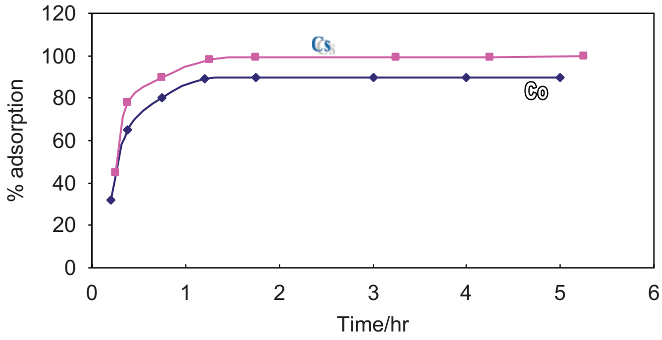

Fig. 1. Cs and Co adsorption on KCNF-PAN.

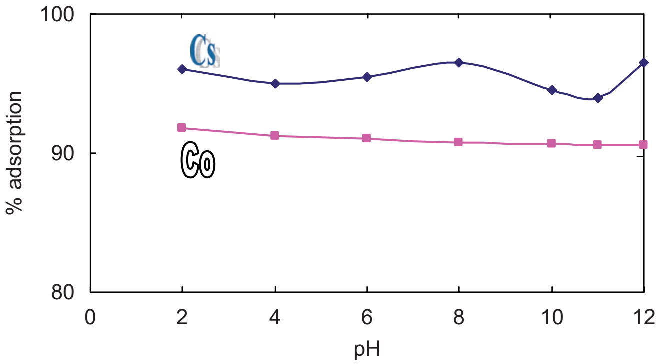

Fig. 2. Cs and Co adsorption at various pH values.

Table 2
Surface characterization of KCNF-PAN dried at various temperatures

Drying temperature (°C)	Surface area (m^2/g)	Median pore diameter (Å)	Intrusion volume (cm^3/g)	Capillary (%)
60	79	54	0.2152	7
80	93	66	0.3345	14
110	108	87	0.4952	24

quickly, and pores are created that cause an increase in the surface area, pore size and percentage capillary. These materials also show better surface properties compared with those dried at lower temperatures, shown in Table 2.

The KCNF-PAN exchangers with Cs capacity of 2.85 mmol/g of exchanger are dark brown in color, while with Co they are brown. The color of both exchangers remains unaltered after they were subjected to γ-ray irradiation and they could be easily sieved to different mesh sizes. These ion exchangers were found to be stable in water, dilute mineral acids and alkaline solutions, but decomposed in concentrated HCl and HNO_3.

The IR spectrum of KCNF-PAN ion exchanger, dried at 110 °C, before and after irradiation is recorded in Fig. 3. There is no significant change observed, as a result of irradiation up to 100 kGy. The first peak at 3450 cm^{-1} is owing to the interstitial water and hydroxyl group. The sharp and strong absorption peak at 2095 cm^{-1} corresponds to cyanide stretching region, and the peak at 1620 cm^{-1} is owing to the deformation vibration of the free water molecules. The bands in the 350–500 cm^{-1} region are due to the M-C stretching. However, the IR spectrum of the sample heated to 500 °C is typical of oxide spectra. Furthermore, the sample is completely decomposed and no cyanide band, water molecule or OH group is observed in the 500 °C heated sample. These samples are simply a mixture of oxides.

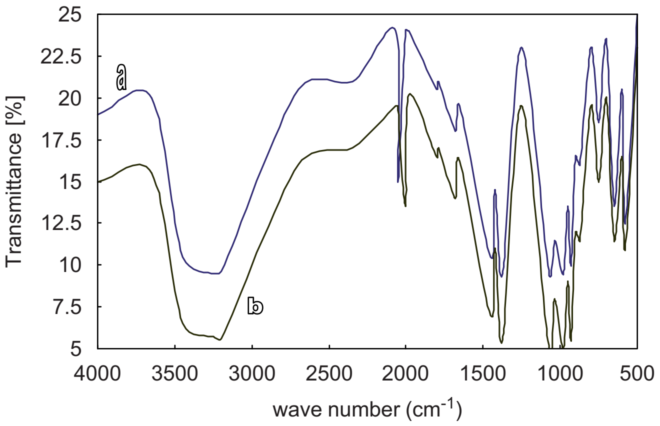

Fig. 3. IR spectrum of (a) unirradiated and (b) irradiated samples of KCNF-PAN.

Table 3
Comparison of $K_{d,}$ values of Cs and Co ions for various inorganic ion exchangers in 3 M HNO_3

Inorganic ion exchanger	$K_{d,\mathrm{Co}}$ (cm^3/g) in 3 M HNO_3	$K_{d,\mathrm{Cs}}$ (cm^3/g) in 3 M HNO_3
NiFC	5.1×10^2	7.2×10^4
NiFC-PAN	5.9×10^2	8.0×10^4
KniFC	6.4×10^2	8.5×10^4
KNiFC-PAN	6.8×10^2	8.9×10^4
KcuNiFC	7.4×10^2	9.5×10^4
KCuNiFC-PAN	7.8×10^2	9.9×10^4

V/m 100 (10 mL, mesh size = 50–100; $[Co^{2+}] = [Cs^+] = 7.5 \times 10^{-5}$ M); 25 °C, 48 h.

Table 4
The effect of concentration of HNO_3 on the $K_{d,}$ values of Cs and Co ions for KCuNiFC-PAN ion exchanger

Conc. HNO_3 (M)	$K_{d,\mathrm{Co}}$ (cm^3/g)	$K_{d,\mathrm{Cs}}$ (cm^3/g)
0.001	150	5.1×10^5
0.01	120	4.3×10^5
0.1	100	2.5×10^5
1	80	1.7×10^5

X-ray powder diffractometry showed the exchangers to have crystalline structure. Furthermore, the X-ray diffractograms of ion-exchange complexes before and after irradiation show that there is no significant change in the crystalline nature of the materials owing to the irradiation, up to 100 KGy studied.

The K_d values of Cs and Co for various CNF- and PAN-based adsorbents in presence of 3 M HNO_3 are summarized in Table 3. The CNF and PAN-based adsorbents show high K_d values and, as a result, are effective for the removal of Cs (and to lesser extent Co) from highly acidic solutions, $[H^+] \leqslant 3$ M. The effect of different concentrations of HNO_3 on the K_d of Cs and Co radioisotopes was also studied, and this is shown in Table 4. A slight decreasing effect in the case of Cs^+ and to some extent, Co^{2+}, at higher concentration of HNO_3 can be seen. In nitric acid solutions of 0.001 M and higher concentrations, the order of the K_d value for metals was $Cs^+ \gg Co^{2+}$, which correlates well with the order of the size of their hydrated cations (Cs^+, 3.3 Å; Co^{2+}, 2.95 Å). This is in line with other research workers (Mimura et al., 1997a–c) who reported that insoluble NiCNF has high resistance to acids and high ion-exchange selectivity toward Cs^+, and also suggested that in the presence of HNO_3 above 0.1 M, the order of K_d value for different metals closely followed the increasing order of the size of their corresponding hydrated cations.

The effects of EDTA and oxalate-complexing agent on adsorption of ^{137}Cs and ^{60}Co have been shown in Fig. 4(a) and (b), respectively. In both cases, EDTA had a strong decreasing effect on the K_d values of ^{137}Cs and ^{60}Co above pH 10 at a dose of 10 g/L. Oxalate did not have any detectable effect at any pH value covered in this experiment. At a lower dose of 1 g/L, no decrease was observed in the K_d for any of the reagents studied.

Differential thermal (DTA) and thermogravimetric curves of ion exchanger, dried at 110 °C, before and after γ-ray irradiation are shown in Fig. 5. The DTA curve shows an endothermic effect, with a peak at 300 °C corresponding to the removal of water molecules. The next endothermic peak at 550 °C shows the decomposition of CNF into oxides. The exothermic effect at 530 °C exhibits a reaction that causes the removal of structural inhomogeneities associated with the appearance of non-stoichiometric phases. The thermogravimetric analysis shows that the loss in mass takes place in different steps at different temperatures, which correspond to the endothermic and exothermic peaks in the DTA curve. Furthermore, there is no significant difference between the thermal behavior of the initial and irradiated samples. The first stage (up to 110 °C) corresponds to the removal of adsorbed moisture; the second stage (110–300 °C) to where dehydration takes place and about 10 mmol of water per gram of the exchanger is lost. The third stage, between 300 and 550 °C shows the formation of Cu, Ni and Fe oxides. And, finally, the small increase in mass, between 550 and 680 °C could be due to oxidation of the residue.

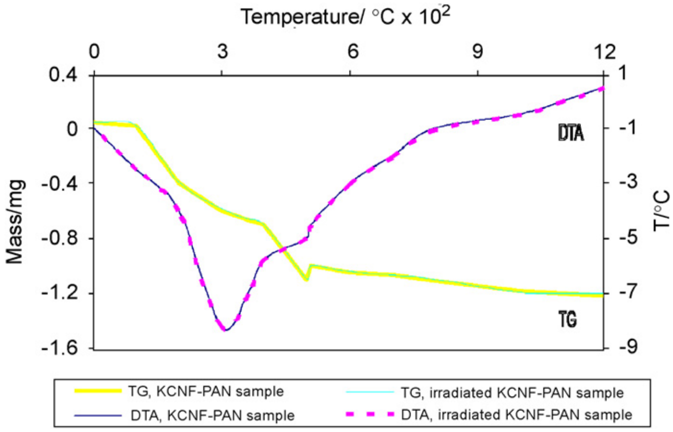

Fig. 5. Thermograms of KCNF-PAN.

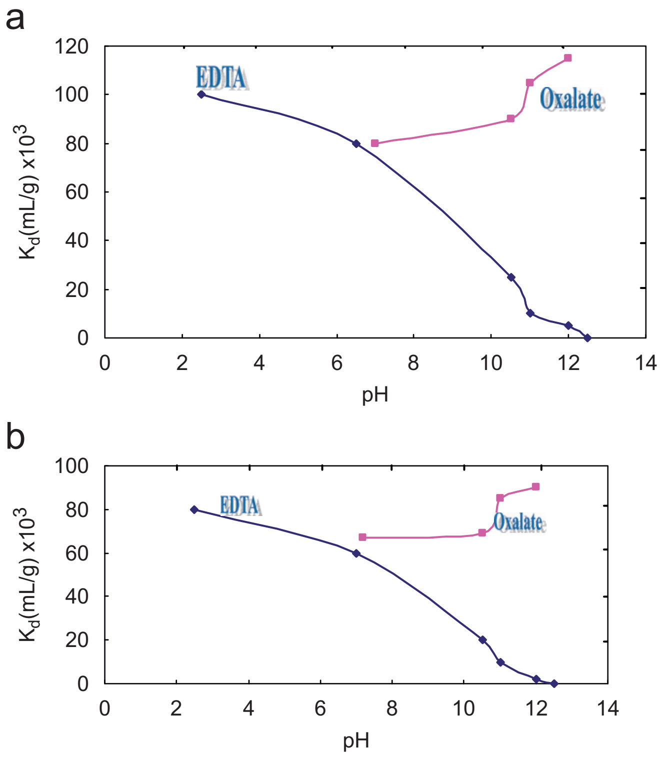

Fig. 4. (a) Distribution coefficient K_d of ^{137}Cs and ^{60}Coas a function of pH for KCNF-PAN ion exchanger in simulated waste dosed with 10 g/L of complexing agents and (b) distribution coefficient K_d of ^{60}Co as a function of pH for KCNF-PAN ion exchanger in simulated waste dosed with 10 g/L of complexing agents.

4. Conclusion

Three different inorganic sorbents, granular CNF-based ion exchanger, Ni CNF, K–Ni CNF and KCuNi CNF were synthesized. The composition of the exchangers were determined to be $Ni_{1.7}Fe(CN)_6 \cdot nH_2O$, $K_{0.87}Ni_{0.57}[NiFe(CN)_6] \cdot nH_2O$ and $K_{2.3}Cu_{0.65}Ni_{1.7}[Fe(CN)_6]_2 \cdot 13H_2O$, respectively, the addition of polyacrylonitrile. The CNF- and their PAN-based composites were chemically and thermally stable, and in strong acidic solutions $[H^+] \leqslant 5$ M did not disintegrate. X-ray powder diffractometry showed that the ion exchangers and their PAN-based composites have similar crystalline cubic structure, and almost identical XRD curves.

The results obtained for the three adsorbers showed that they withstand γ-ray irradiation of up to 100 kGy. The physical properties, IR spectra and X-ray diffractogram of the exchanger remain unaltered upon irradiation. The higher drying temperature of the adsorbers gave better surface properties, which was due to an increase in the surface area, pore size and percentage of capillary. The adsorption of Cs and Co aqueous solutions of stimulant prepared was investigated. The adsorption of Co was much lower than Cs and neither was affected by an increase in the pH value.

EDTA had a strong decreasing effect on the K_d values of ^{137}Cs and ^{60}Co above pH 10 at a dose of 10 g/L. Oxalate did not have any detectable effect on any pH value covered in these studies. Murrhy et al. (2004) reported that the uptake of Cs on organic-based adsorbers is only affected at higher acidities. Our results also show that the amount of Cs and Co adsorbed is decreasing with the increase in nitric acid concentration. This could be attributed to the availability of larger sorbent sites for relatively smaller number of Cs and Co ions at higher dilutions. These results also favorably compare to the previous reported results of Todd et al. (2002).

Finally, the rate of adsorption of Cs and Co for these PAN-based adsorbers increase with the increase in shaking time and quickly reaches equilibrium, which is similar to that with other ion exchangers.

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