Int. J. Environ. Sci. Technol. (2014) 11:1073–1080
DOI 10.1007/s13762-013-0478-7

ORIGINAL PAPER

Evaluation, characterization and analytical application of a new composite material for removing metal ions from wastewater

**R. Yavari · S. J. Ahmadi · F. Farkhondehru ·
V. Gholipoor · L. Kamel**

Received: 22 July 2013 / Revised: 27 October 2013 / Accepted: 9 December 2013 / Published online: 8 January 2014

Abstract A new organic/inorganic composite based on polyacrylonitrile and stannic molybdophosphate (PAN–SMP) as an adsorbent was synthesized under various conditions. The physicochemical properties of this material were specified by elemental analysis, scanning electron microscopy, infrared spectroscopy and thermogravimetry studies. The synthesized material was found to be stable in demineralized water, in dilute acids, under gamma radiation up to the total radiated of 100 kGy doses and in high temperature up to 500 °C. Ion exchange capacity of the synthesized composite and its distribution coefficient (K_d) for several metal ions were determined. The results showed that PAN–SMP has a great affinity toward some metal ions such as T^{l+}, Sr^{2+}, Ba^{2+}, UO_2^{2+} and La^{4+}. Based on the determined K_d values, two binary quantitative separations of metal ions (Cr^{6+} from Cu^{2+} and Pb^{2+} from Cu^{2+}) have been achieved on columns of this ion exchanger. The ability of PAN–SMP to decontaminate low-level liquid waste was also investigated.

Keywords Composite · Ion exchange · Stannic molybdophosphate · Polyacrylonitrile · Decontamination

Introduction

The operation of a large number of nuclear power plants, and charged particle accelerators, as well as the wide use of radionuclides in medicine, science and engineering, has caused the proliferation of various types of nuclear waste, which is often stored in underground stainless steel tanks. Due to the leak of some of these tanks for a long time, toxic and hazardous radionuclides can be released into the surrounding soil and groundwater (Danilin and Drozhzhin 2003). Also, the contaminants may be infiltrated into the environment as a the results of nuclear weapon tests, nuclear accidents such as Chernobyl nuclear power plant disaster in 1986, unauthorized release or puffs and the possible influx of certain toxic industrial effluents (Al Hamarneh et al. 2003). Therefore, separation and removal of these hazardous and toxic metal ions may always be considered to be worthwhile. In this regard, using highly selective sorbents such as inorganic ion exchanger or their composites, which is the main goal of the mandate of green chemistry for reducing the use of toxic and carcinogenic solvents, is the most common method.

Compared with the new adsorbents, a composite of organic/inorganic ion exchanger is considered as a particular material that can improve the mechanical properties of the organic polymers due to the intrinsic properties of these exchangers such as their excellent high selectivity with respect to certain element or group of elements, good kinetics of sorption, high chemical stability and stability at elevated temperature (Yavari et al. 2008; Inamuddin et al. 2007). Therefore, with the synthesis of new composite, the feature of the pristine organic and inorganic components in the synthesized materials is completed and improved. In other words, the composite materials give the opportunity to use two different compounds with complementary

R. Yavari · S. J. Ahmadi (✉)
Nuclear Science and Technology Research Institute, NFCS,
P.O. Box 11365/8486, Tehran, Iran
e-mail: sjahmadi@yahoo.com

F. Farkhondehru · V. Gholipoor · L. Kamel
Faculty of Chemistry, Tarbiat Moallem University,
Mofatteh Ave. No.49, 15614 Tehran, Iran

properties in a single material and to take advantage of the best properties of each component. Some recent examples are the composite preparation from organic binder polymers such as polyacrylamide, polyacrylonitrile (PAN), polyaniline, nylon-6,6, polyvinyl alcohol with inorganic ion exchanger such as zeolite, heteropolyacids, oxides (Inamuddin et al. 2007; Varshney et al. 2001; Khanchi et al. 2007; Ali Khan and Inamuddin 2006; Abd El-Latif and El-Kady 2008; Ali et al. 2005; Moon et al. 2005; Todd et al. 2002; Akyil and Eral 2005).

Among the inorganic ion exchangers, polyoxometalates based on tetravalent metals such as tin (IV), titanium (IV) and zirconium (IV) have been objects of considerable research in recent decades for the removal of radionuclides from nuclear waste solution. These materials are known to possess the better properties such as ion exchange capacity and selectivity in comparison with the normal salts of multivalent metals. The selectivity may be enhanced by varying the composition of materials (Yavari et al. 2009; Maragheh et al. 1999). One of the well-known polyoxometalates is stannic molybdophosphate (SMP) (Gupta et al. 2000). This material has a strong affinity toward some radionuclides such as cesium, strontium and cerium, which can be used for the removal of these toxic and hazardous metals from wastewater. However, like other inorganic ion exchangers, it has some disadvantageous properties in its usage in column operations such as poor mechanical strength, irregular shape of the sorbent grains, slow adsorption kinetics and rather high density (Abe et al. 1991). All these defects can be improved by intercalation of these materials into the organic binder polymers and the formation of new composite. On the other hand, PAN was proposed as a universal binding polymer for different inorganic ion exchangers (Ali et al. 2005). This binder has proven to be an adsorbent that none of the radionuclides were released even when the PAN was decomposed to be disposed underground safely after cementation or vitrification (Moon et al. 2005).

Therefore, the aim of the present study is to prepare and synthesize the organic/inorganic composite, SMP–PAN, and to investigate its characteristics, ion exchange properties and analytical applications for the removal of some hazardous and toxic metal ions from the wastewater channels.

Materials and methods

Chemicals

All the chemicals and reagents used in this study were of analytical grade obtained from E. Merck or Fluka. The radioactive tracers used in ion exchange experiments (^{140}La, ^{153}Sm and ^{147}Nd) were prepared by neutron irradiation of natural radioisotopes of elements and were supplied by the Nuclear Science Research School of NSTRI, AEOI, Tehran, Iran.

Apparatus

Powder X-ray diffraction analysis was obtained using a Jeol GDX-8030 instrument with Ni-filtered Cu-Kα radiation. Thermogravimetry was carried out with a Dupont model 951 at a heating rate of 10 °C/min. Infrared spectra were recorded with a Perkin Elmer IR-843 spectrometer utilizing KBr disks. To determine the quantitative amount of metal ions, inductively coupled plasma (ICP, Perkin Elmer model 5500) and atomic absorption spectrometer (AAS, Varian model 20) were employed. Electron micrographs were recorded with a Philips XL-30 scanning electron microscope (SEM). A gamma spectrometer model Ortec EG&G, HPGe, high-resolution, coaxial, GMX detector with 4,096 channels was used during determination of radionuclide distribution coefficients.

Synthesis of stannic molybdophosphate

Stannic molybdophosphate was prepared using the method followed by Khanchi et al. (2007), by gradual addition of molybdophosphoric acid solution (0.05 M) to stannic chloride solution (0.05 M in 0.3 M HCl) with the volume ratio of 2:1, respectively. This solution was stirred for 1 h at room temperature (25 ± 1 °C). While the reaction mixture was thoroughly stirred by a magnetic stirrer, the pH of system was adjusted to 0.62 for the completion of green precipitation. The formed gel was refluxed in mother liquor at 85–90 °C for 24 h. The synthesized material was then left to settle down overnight, centrifuged at 10,000 rpm for 3 min and washed with deionized water five times. The washed material was air-dried in an oven at 50 °C for 18 h. Finally, to obtain the samples in H^+ form, they were soaked in 0.1 M nitric acid, washed again by demineralized water to remove the excess acid and again dried at 50 °C.

Preparation of the beads

The composite of SMP with PAN was prepared via mixing the SMP powders in DMSO that contained 4 % (w/w) sodium dodecyl sulfate surfactant. In another vessel, PAN was mixed with DMSO to form a viscous solution. Then, the contents of the two vessels were mixed and stirred for 18 h to form a homogenous solution. The obtained composite solution was fed into the dual nozzle and sprayed into water that contained surfactant to form the spherical beads of composite.

Various samples of composite were prepared by varying the ratio of PAN and SMP solutions. The maximum hardness and complete sphericity were detected when the proportion of PAN–SMP ratio was 1:0.8. Therefore, it was selected for further studies.

Characterization

To determine the ratio of inorganic ion exchanger to organic moiety, carbon, hydrogen and nitrogen contents of the material were determined by CHNOS analyzer. The weight percent composition of the selected composite beads was as follows: C, 36.68; N, 13.18; and H, 3.96, which resulted in SMP/PAN = 0.86:1. The composite contained approximately 46.2 % SMP and 53.8 % PAN.

X-ray powder diffraction method using nickel-filtered Cu-Kα radiation at 298 K was used for X-ray studies of samples in H^+ form. The study was conducted between 4 and 75° 2θ values with a step size of 0.05. XRD spectrum of PAN–SMP is given in Fig. 3.

Chemical stability of PAN–SMP was assessed in three mineral acids (HCl, HNO_3 and H_2SO_4) and one strong base (NaOH). For this purpose, 200 mg (dry mass) of PAN–SMP composite was taken in 25 mL of aforementioned solvents and kept for 24 h at room temperature with occasional shaking. The total amount of Sn, Mo and P in the supernatant was determined by ICP emission spectrometry and titration method.

Ion exchange capacity (IEC)

The ion exchange capacity, which is the amount of the hydrogen ion released by passing the neutral salt solution through the composite loaded into a column, was determined by the standard process. The composite ion exchange material (1.0 g dry mass) in the H^+ form was placed in a glass column (1 cm inner diameter and 40 cm length) with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained sticking on the particles. Then, 100 mL of 1 mol L^{-1} KCl solution was used to elute the H^+ ions with the flow rate of 0.5 mL min^{-1}. The collected effluent was titrated against a standard solution of sodium hydroxide, using pH meter as an indicator to obtain and calculate the released hydrogen ions. The residue ion exchanger was regenerated by soaking in 300 mL of 0.1 mol L^{-1} HNO_3 and rinsing with demineralized water to neutralize it. This procedure was repeated thrice, and the standard deviations were also calculated.

Distribution studies

Distribution coefficients (K_d) for some transition metals, heavy metals, rare earth metals and radionuclides were determined in aqueous solution by batch operation (Yavari et al. 2008). In 20 mL of 1.2×10^{-4} mol L^{-1} metal ion solutions, 0.2 g of composite material in H^+ form was kept at 25 ± 1 °C for 5 h, with intermittent shaking to reach equilibrium. The solution was then filtered, and metal ions were determined using ICP emission spectroscopy, atomic absorption spectrometry and gamma spectrometer techniques (Winge et al. 1985). Blank solutions were prepared without composite material, having the same concentration of metal ions. This solution was treated in the same way as mentioned above.

Distribution coefficient values were calculated by the following equation:

$$K_{\mathrm{d}} = (C_{\mathrm{i}} - C_{\mathrm{f}})/C_{\mathrm{f}} \times V/m$$

where C_{i} and C_{f} are the initial and final amounts of metal ion in the solution phase, respectively, V is the volume of initial solution in milliliters and m is the weight of composite material in grams. Standard deviation for K_{d} values was checked by three determinations and was <8 %.

Metal ion separations

Binary metal ions were separated quantitatively on the column of composite ion exchanger. One gram (dry mass) of this adsorbent in H^+ form was placed in the glass column of the inner diameter 8 mm with a glass wool support at the bottom. The column was washed thoroughly with demineralized water, and the mixture of 0.2 mL of each ion (0.005 M) in 10 mL demineralized water was then loaded by passing the mixture through the column at a slow rate of 0.2 mL min^{-1}. The column was washed with demineralized water because the remaining non-exchanged metal ions should be removed. The metal ions adsorbed on the exchanger were then eluted with 0.1 M HCl, and the flow rate of the effluent was maintained at 0.2 mL min^{-1} until the metal ions were completely eluted out of the column. The effluents were collected in 5 mL fractions and determined by ICP method. The metal ion solutions were either concentrated or diluted as much as required to ensure accessing to the further detection.

Low-level liquid waste (LLLW) treatment

Nuclear waste was treated with SMP and PAN–SMP ion exchangers. For this purpose, 0.5 g (dry mass) of these ion exchangers was separately added to 25 mL of LLLW and shaken for 3 h. The mixtures were then filtered, and metal ions before and after decontamination were determined by gamma spectrometry.

Results and discussion

In the present study, incorporation of inorganic matrices and SMP into PAN by changing the mixing volume ratio of reagents was performed to develop new hybrids of

Table 1 Ion exchange capacity of SMP and PAN–SMP

Sample	I.E.C (meq g^{-1} dry)	Standard deviation
SMP	1.10	0.07
PAN–SMP	0.42	0.05

PAN–SMP. Among the samples, sample having a PAN–SMP ratio of 1:0.8 possessed good yield and reproducible behavior as well as chemical and thermal stability.

The most important characteristics of the composite (PAN–SMP) were their granulometric property and suitable density for applying them in an aqueous medium. Also, the composite can be regenerated and used several times. The obtained ion exchange capacity (IEC) of the selected SMP and related composite at room temperature was 1.10 and 0.42 meq g^{-1}, respectively (Table 1). The lower IEC of PAN–SMP can be due to the fact that the hybrid material contained approximately 46.2 % of the active component and PAN was serving as a supporting moiety.

The differences in surface morphology of PAN and PAN–SMP were revealed by the observation of their scanning electron microscopic (SEM) graphs, as given in Fig. 1. The graphs “a” and “b” in Fig. 1 show the cross sections of the composite absorber PAN–SMP and PAN-binding polymer grains, respectively. These graphs exhibit that the composite particles were not homogeneous. A crust of PAN with many holes allowed to probe the inner active sites and to be available for the ion exchange process. According to our observations, the kinetic of sorption on these new absorbers was expected to be very fast because the finely divided particles of the active component were embedded into the macropores of the binding matrix (Gupta et al. 2000). Comparison of these figures demonstrates the deposition of the active component inside the macrospores. Detailed analyses of these photographs show that the particles of PAN–SMP were completely spherical and their particle size is about 500 nm, which is suitable for chromatographic applications (Fig. 1c,d).

Figure 2 shows the Fourier transform infrared spectra (FTIR) of SMP (a) and PAN–SMP (b). For FTIR spectroscopy studies, the samples were washed thrice with ethanol and then dried at 50 °C for 12 h. As shown in Fig. 2b, the intense bands at about 2,250 cm^{-1} can be ascribed to stretching vibration of CN bond. Meanwhile, the presence of the band at 1460 cm^{-1} is due to the CH bending of methylene groups in PAN (Todd et al. 2002), which confirms the presence of the organic moiety in the intercalation compound spectra. Further interesting information about their structure in both graphs is related to an asymmetric absorption broad band found in the 3,500–3,000 cm^{-1} region with the maximum 3,400 cm^{-1}, which is a characteristic of the presence of water molecules and OH groups. Also, sharp peak in the region of 1,500–1,750 cm^{-1} with maximum 1,680 cm^{-1} may be assigned to interstitial water molecule and OH groups. Less-intense bands in the region of 400–1,000 cm^{-1} may be ascribed to the metal–oxygen bonds. The bands in the

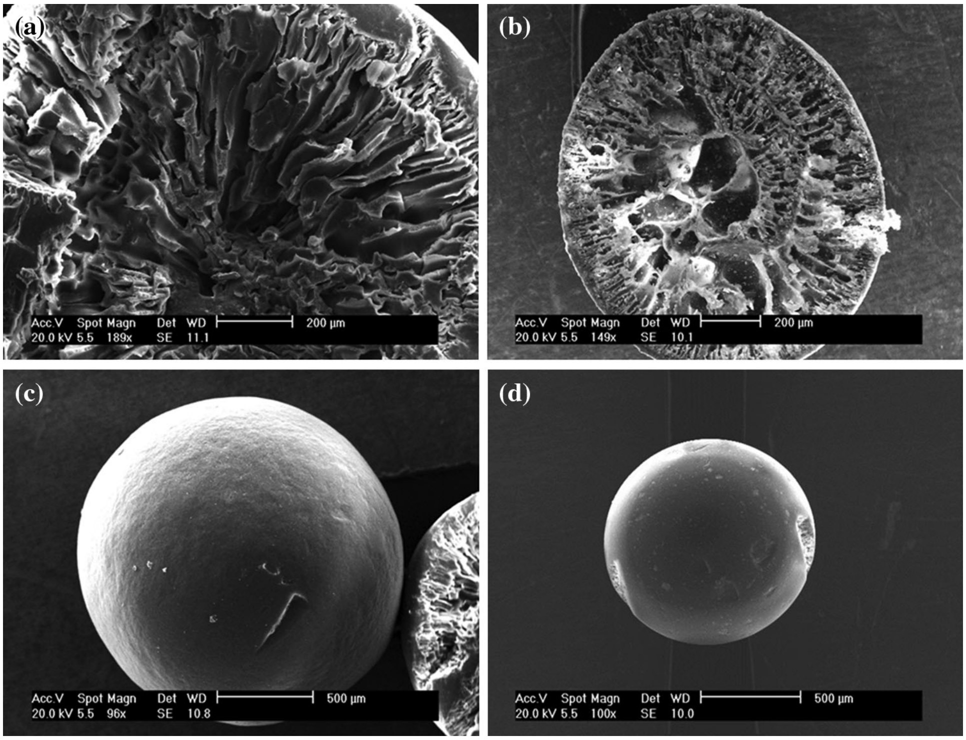

Fig. 1 Scanning electron photographs of PAN (**a** and **c**) and PAN–SMP (**b** and **d**)

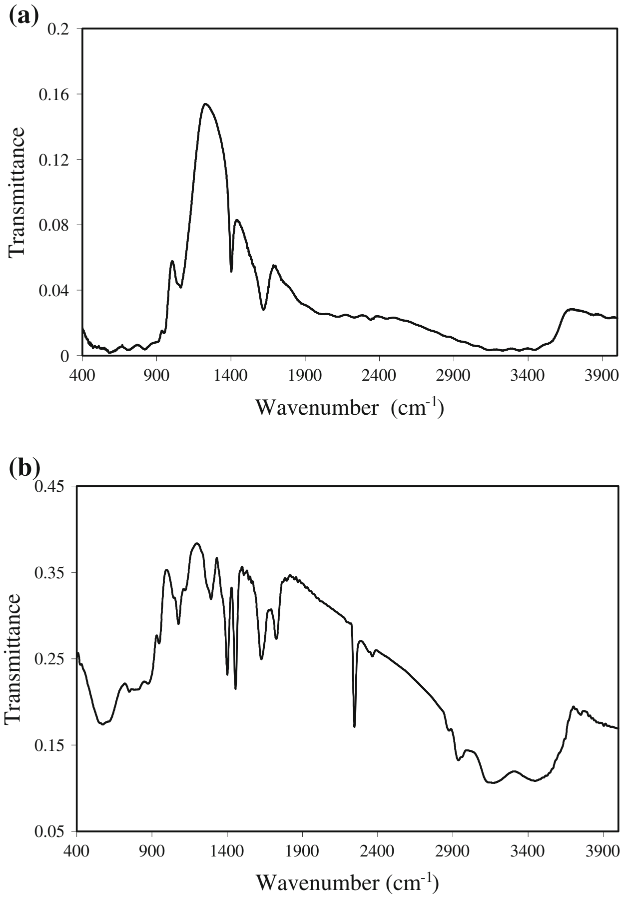

Fig. 2 FTIR spectra of SMP (**a**) and SMP–PAN (**b**)

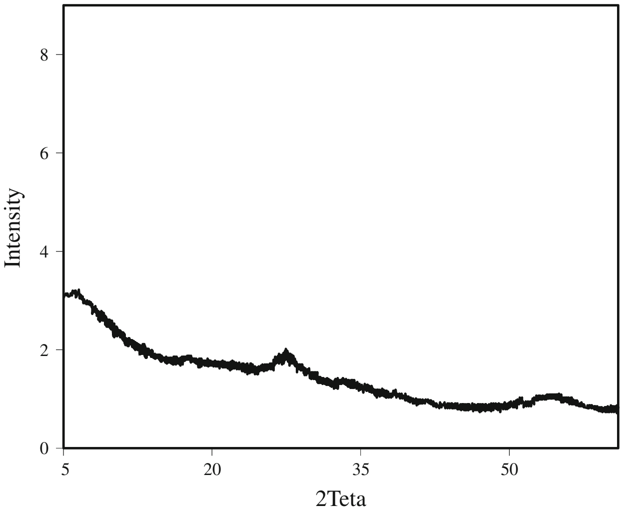

Fig. 3 XRD spectrum of SMP–PAN

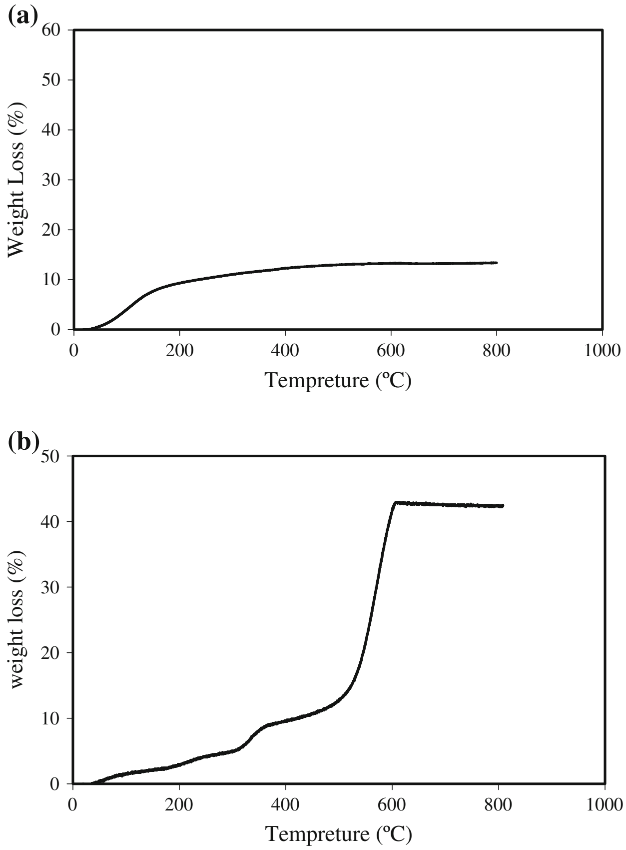

Fig. 4 TGA plots of SMP (**a**) and SMP–PAN (**b**)

1,000–1,100 cm^{-1} region are attributed to the symmetric and antisymmetric nature of P–O bands in the highly symmetric phosphate groups (Maragheh et al. 1999).

The X-ray diffraction pattern for the synthesized SMP and PAN–SMP given in Fig. 3 shows weak intensities, thereby suggesting that our materials are amorphous in nature.

Figure 4 shows the thermograms of the synthesized SMP (a) and PAN–SMP (b). The TG curves show the presence of water of hydration, which is lost slowly up to 130 °C (Ali et al. 2005). At higher temperatures (130–500 °C), gradual weight loss may be due to the condensation of phosphate groups to pyrophosphate groups (Moon et al. 2005). Further weight loss between 500 and 620 °C may be due to complete decomposition of the organic part of the material.

The chemical stability results of the materials in different selected solutions are summarized in Table 2. As can be seen, the composite of ion exchanger is quite stable in water and fairly stable in mineral acids even in high concentration, while it is less stable in basic solutions. This chemical stability may be due to the presence of binding polymer, which can prevent the dissolution of heteropolyacid salt or leaching of any constituent elements into the solution (Yavari et al. 2009).

In order to evaluate the capability of this cation exchange material in the separation of metal ions, the distribution coefficients of 22 metal ions were investigated using batch technique. The obtained values for K_d given in Table 3 show that T^{l+}, Cu^{2+}, Cs^{+}, Sr^{2+}, UO_2^{2+}, La^{3+} and

Table 2 Chemical stability of PAN–SMP in different solvents

Solution	Sn released (mg/25 ml)	Mo released (mg/25 ml)	P released (mg/25 ml)
D.M.W	0.00	0.00	0.00
HCl (concentrated)	70.36	13.07	1.23
HCl 4 M	68.72	12.47	0.84
HCl 2 M	6.97	4.20	0.12
HCl 1 M	2.32	1.48	0.02
HCl 0.1 M	0.00	0.00	0.00
HNO_3 (concentrated)	1.03	2.32	0.24
HNO_3 4 M	0.44	1.74	0.03
HNO_3 2 M	0.00	1.06	0.00
HNO_3 1 M	0.00	0.81	0.00
HNO_3 0.1 M	0.00	0.00	0.00
H_2SO_4 (concentrated)	0.27	6.05	0.00
NaOH 0.1 M	Dispersed	Dispersed	12.00
$NaNO_3$ 2 M	0.00	0.04	0.00

Table 3 Distribution coefficients of cations on SMP and PAN–SMP

Metal ion	K_d (mL g^{-1})		
	SMP	PAN–SMP	pH
K^+	88	308	4.32
Rb^+	2173	3009	4.08
Cs^+	1956	2100	4.41
Cu^{2+}	1440	3750	2.60
Co^{2+}	942	1135	2.50
Ni^{2+}	950	1160	2.44
Pb^{2+}	15	33	3.32
Tl^+	T.A.	T.A.	2.26
Zn^{2+}	706	933	2.65
Cr^{6+}	N.A.	14	2.78
Mo^{6+}	N.A.	N.A.	3.12
Cd^{2+}	>600	>600	2.44
Sr^{2+}	1696	21712	5.00
Sb^{3+}	43	2658	1.72
Zr^{4+}	3530	4322	3.73
UO_2^{2+}	242	13246	3.05
Ba^{2+}	492	33932	4.06
Th^{4+}	2946	3121	2.78
W^{6+}	N.A.	94	4.61
Nd-147	–	1220	1.67
Sm-153	–	3351	1.43
La-140	–	10111	1.54

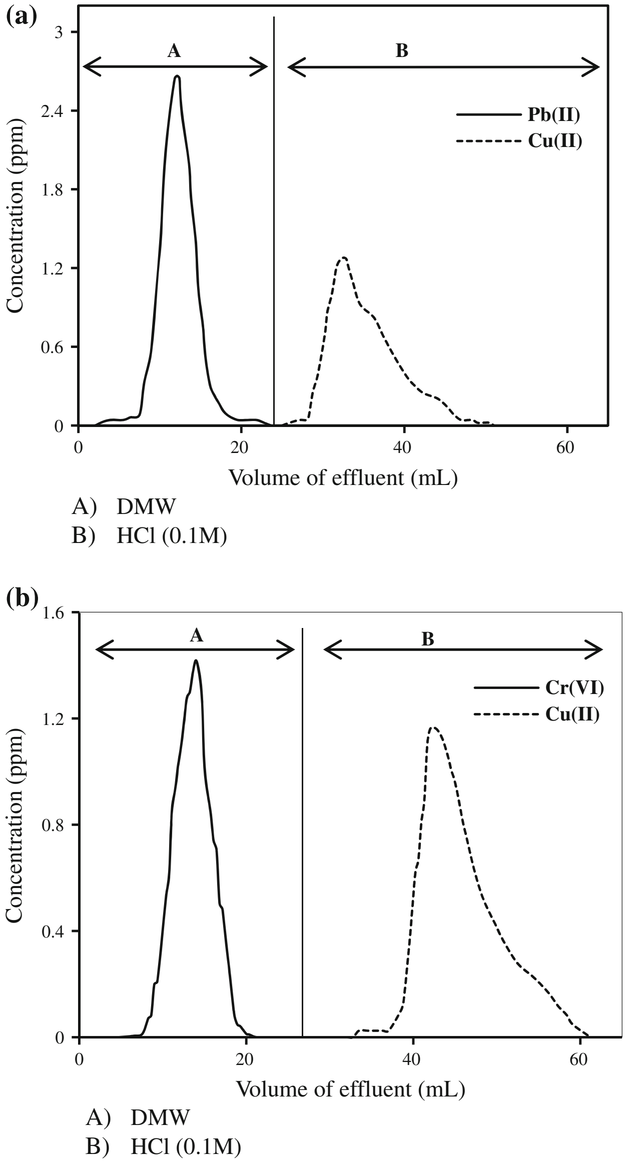

Fig. 5 Elution curve for separation of Cr^{6+}–Cu^{2+} (**a**) and Pb^{2+}–Cu^{2+} (**b**)

Ba^{2+} are more strongly adsorbed than other metal ions. Therefore, PAN–SMP can be used for the selective removal of these metal ions from aqueous solution especially from the radioactive wastewater, which has some of these metal ions such as ^{137}Cs, ^{90}Sr and $^{235,238}UO_2^{2+}$. Considering the difference in the K_d values, the separation capacity of the material has been demonstrated by achieving some important binary separations such as Cr(VI)–Cu (II) and Pb(II) from Cu (II). Figure 5 shows the salient features of the mentioned separations. The separations are quite sharp, and recovery is quantitative and reproducible.

The radiation stability of SMP and PAN–SMP materials was evaluated by investigation of change in their ion exchange capacities, IR adsorption spectra, thermograms and the amount of Sn, Mo and P, which were released in the solution after being exposed to gamma radiation up to the total dose of 50 and 100 kGy (Table 4). The results obtained from these experiments reveal that IR spectra and

Table 4 Ion exchange capacity and amount of Sn, Mo and P released after irradiation

Ion exchanger	Sn (mg/ 20 ml)	Mo (mg/ 20 mL)	P (mg/ 20 mL)	I.E.C (meq g^{-1})
SMP (50 kGy)	<0.10	4.70	0.20	0.94
SMP (100 kGy)	<0.10	5.01	0.20	0.82
PAN–SMP (50 kGy)	<0.10	0.45	0.08	0.40
PAN–SMP (100 kGy)	<0.10	0.45	0.10	0.38

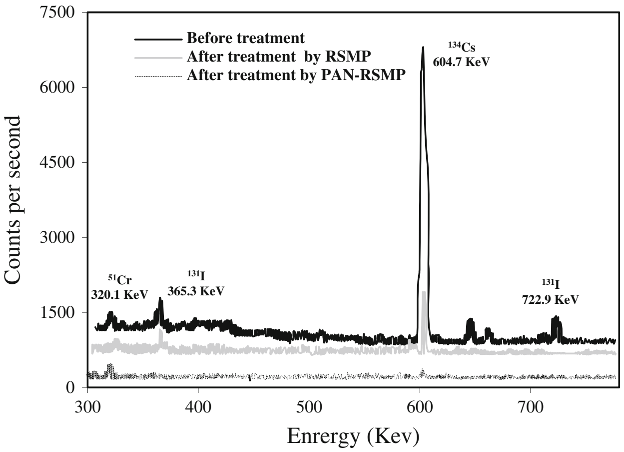

Fig. 6 Section of the gamma spectra of low-level liquid waste solution before and after treatment with RSMP and PAN–RSMP

the thermograms of PAN–SMP and SMP are relatively stable toward these radiations. Also, a negligible amount of the metal ions released and insignificant change in ion exchange capacities of composite and ion exchange confirm that these materials are stable against radiation. These results are summarized in Table 4.

It is well known that cesium, which is created mainly from fission products, is one of the major radioactive contaminants in low-level liquid waste (LLLW) solutions. Therefore, separation of cesium or other hazardous and toxic radionuclides from these solutions would substantially reduce their activity. Even in some cases, they could be treated as normal liquid waste discharge to the environment. For this purpose, LLLW was obtained from the storage tank of the nuclear research center of AEOI. It was then treated with SMP and PAN–SMP. The gamma spectra of LLLW before and after decontamination with SMP and PAN–SMP are shown in Fig. 6. As shown in this figure, the removal of all the radionuclides, especially cesium, in waste solution is complete, while using RSMP, the removal of radionuclides is incomplete. According to the results, the composite ion exchanger is applicable for the treatment of LLLW and a complete decontamination of radioactive elements from these solutions.

Conclusion

According to the results obtained from this study, PAN–SMP shows a great adsorbability on various metal ions such as Tl^{+}, Cu^{2+}, Cs^{+}, Sr^{2+}, UO_2^{2+}, La^{3+} and Ba^{2+}, irradiation resistance, thermal and chemical stability. Besides, this material can be easily regenerated to be reused along with very suitable morphology and good mechanical resistance for column operations. Therefore, this newly synthesized hybrid material can be applicable in chromatographic separations and treatment of aqueous nuclear wastes.

Acknowledgments The authors are thankful to the Nuclear Spectroscopy and Instrumental Analysis Section of Nuclear Fuel Cycle School, NSTRI, Tehran, for their help and for some laboratory facilities.

References

Abd El-Latif MM, El-Kady MF (2008) Developing and characterization of a new zirconium vanadate ion exchanger and its novel organic–inorganic hybrid. J Appl Sci Res 4:1–13

Abe M, Kataoka T, Suzuki T (1991) New developments in ion exchange. Elsevier, Kodansha, Tokyo

Akyil S, Eral M (2005) Preparation of composite adsorbents and their characteristics. J Radio Nucl Chem 266:89–93

Al Hamarneh I, Wreikat A, Toukan K (2003) Radioactivity concentrations of ^{40}K, ^{134}Cs, ^{137}Cs, ^{90}Sr, ^{241}Am, ^{238}Pu and $^{239+240}$Pu radionuclides in jordanian soil samples. J Environ Radioact 67:53–67

Ali Khan A, Inamuddin (2006) Preparation, physico-chemical characterization, analytical applications and electrical conductivity measurement studies of an ‘organic–inorganic’ composite cation-exchanger: polyaniline Sn(IV) phosphate. React Funct Polym 66:1649–1663

Ali IM, El-Zahhar AA, Zakaria ES (2005) Thermal and sorption behavior of polyacrylonitrile supported hydrous titanium dioxide. J Radio Nucl Chem 3:637–644

Danilin LD, Drozhzhin VS (2003) Inorganic sorbents based on modified microspheres for treatment of liquid radioactive waste. Radiochemistry 49:319–322

Gupta AP, Verma GL, Ikram S (2000) Studies on a new heteropoly-acid-based inorganic ion exchanger; zirconium(IV) selenomolybdate. React Funct Polym 43:33–41

Inamuddin, Khan SA, Siddiqui WA, Ali Khan A (2007) Synthesis, characterization and ion-exchange properties of a new and novel ‘organic–inorganic’ hybrid cation-exchanger: nylon-6, 6, Zr(IV) phosphate. Talanta 71:841–847

Khanchi AR, Yavari R, Pourazarsa SK (2007) Preparation and evaluation of composite ion exchanger for the removal of cesium and strontium radioisotopes. J Radio Nucl Chem 273:141–145

Maragheh MG, Husain SW, Khanchi AR (1999) Selective sorption of radioactive cesium and strontium on stannic molybdophosphate ion exchanger. Appl Radiat Isot 50:459–465

Moon JK, Lee EH, Han Lee BC, Kim HT (2005) Multi-component ion exchange kinetics with PAN-KCoFC composite ion exchanger. Korean J Chem Eng 22:127–132

Todd TA, Mann NR, Tranter TJ, Sebesta F, John J, Motl A (2002) Cesium sorption from concentrated acidic tank wastes using ammonium molybdophosphate polyacrylonitrile composite sorbents. J Radio Nucl Chem 254:47–52

Varshney KG, Tayal N, Khan AA, Niwas R (2001) Synthesis, characterization and analytical applications of lead (II) selective polyacrylonitrile thorium (IV) phosphate: a novel fibrous ion exchanger. Colloids Surf A 181:123–129

Winge RK, Fassel VA, Peterson VJ, Floyed MA (1985) Inductively coupled plasma atomic emission spectroscopy. Elsevier Science, Amsterdam

Yavari R, Ahmadi SJ, Huang YD, Bagheri G (2008) Synthesis, ion exchange properties, and applications of amorphous cerium(III) tungstosilicate. Sep Sci Technol 15:3920–3935

Yavari R, Ahmadi SJ, Huang YD, Khanchi AR, Bagheri G, He JM (2009) Synthesis, characterization and analytical application of a new inorganic cation exchanger: titanium(IV) molybdophosphate. Talanta 77:1179–1184