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Copper ferrocyanide loaded track etched membrane: an effective cesium adsorbent

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Abstract For the first time, the use of a membrane based copper ferrocyanide loaded sorbent for removal of Cs^+ from neutral aqueous solution is reported in this work. The results indicated high Cs^+ exchange capacity (1.75 mmol/g), large distribution coefficient, as well as fast absorption of the cation in the membrane. The membrane, inspite of presence of other metal ion, exclusively absorbed ^{137}Cs from a simulated nuclear waste solution, though the absorption rate is affected due to their presence. This composite membrane showed promising properties for Cs^+ removal from nuclear waste solution.

Keywords Cs · Ferrocyanide · Track etched membrane · Adsorbent · Nuclear waste

Introduction

Cesium (Cs) is produced with considerable yield in the fission of U, Pu, and is of major environmental concern due to its radiotoxicity (^{137}Cs). The yearly yield of ^{137}Cs alone is reported to be $\sim$27 MCi [1]. Final disposal of the wastes, generated in the nuclear industry require pretreatment to remove certain radionuclides. ^{137}Cs is one of the major sources of radioactivity and heat in nuclear wastes. Its removal greatly simplifies the subsequent processes of waste handling and storage. Handling of the large volume is the major challenge in decontamination of nuclear waste. Solvent extraction (using crown ethers, cobalt dicarbollide), resin based ion exchange or precipitation method [2, 3] have been used for the removal of ^{137}Cs from aqueous waste solution. These methods have associated drawbacks, like, requirement of large amount of undesirable solvents and macrocyclic carriers, insufficient selectivity and generation of voluminous secondary nuclear waste [4]. Use of inorganic ion exchangers can circumvent some of these problems.

Transition metal ferrocyanides of Fe, Ni, Cu, Zn, Co are known to be excellent adsorber of Cs^+. The adsorption property increases with the ferrocyanides series: $Fe < Cu < Zn < Ni < Co$ [4–8]. Though ion exchange mechanism has been proposed for Cs absorption in these compounds, but it is reported that the mechanism is dependent on both the composition and the physical properties of the ferrocyanide solids. It can be a relatively fast ion exchange method or a slower change in chemical structure. In most of the cases, intermediate rates and mixed mechanisms are often observed [5].

Practical application of the ferrocyanides for removal of cesium demands chemical and physical stability as well as complete separation of solids from the solution [5]. Since most of these metal ferrocyanides are available as fine powders, it is difficult to use them for radionuclide separation from aqueous solution by filtration process. Also, low permeability limits their use in column based separation methods [4]. In order to avoid these associated difficulties, several attempts [9–20] have been made to immobilize these compounds on suitable solid supports, like, silica granules [9], chelating organic ion exchangers [4], polyurethane foam [10, 11], cartridge water filter [12], polymer chain grafted fibers [13], nanoscale magnetite substrate [14], mesoporous silica [15], latex particles [16], biopolymer foams [17] etc. Clarke and Wai [4] have

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reported 98 % removal of cesium from a simulated acid waste solution by immobilizing copper ferrocyanide (KCFCN) on a chelating resin (Chelex - 20). Rao et al. [10] has applied KCFCN-polyurethane foam for Cs removal from low level radioactive waste. The overall volume reduction factors in this process are reported to be ~4,000. Use of such matrices involves filtration of large volume liquid radioactive wastes and generation of voluminous secondary waste. In another attempt [21], Chen et al. have reported use of nanoparticle film of copper ferrocyanide for electrochemical separation of cesium from waste water. Recently, ion exchange membranes have been used as selective sorbent for preconcentration of different metal ions from larger volume of solution [22–24]. In this context, immobilization of metal ferrocyanides on some suitable polymeric membrane, like polycarbonate track etched membrane can be a promising alternative for preconcentration of radioactive cesium from aqueous solution.

In our earlier work [25], synthesis of copper ferrocyanide (KCFCN) nano-crystals in the pores of track etched membrane (by two compartment permeation method) has been described. It has been observed that the conical shaped pores of the membrane are uniformly filled with the nanosized (~40 nm) KCFCN crystals. Among all the metal ferrocyanides, the copper analogous has been chosen as it is reported in literature [5] that the composition of copper ferrocyanide product does not vary with change in mole ratios of the reactants. KCFCN is also reported to offer better mechanical characteristics and more radiation stability as compared to others [5]. Highest sorption capacities have been reported in literature for copper and zinc ferrocyanides [5]. In our earlier work [25], the KCFCN loaded track etched membrane has been found to be a promising separation matrix for Cs^+ over Na^+.

The aim of the present work is to systematically study the KCFCN loaded track etched membrane (KCFCNm) as sorbent for removal of Cs^+ from neutral aqueous solution. The membrane has been characterized for Cs^+ exchange kinetics and ion exchange capacity. The Cs^+ exchange kinetics has been measured from the self-diffusion study of Cs^+ in the KCFCNm. The efficiency of the membrane for ^{137}Cs removal from different volume of solution have also been studied. The composite membrane has been used to remove Cs^+ from a simulated nuclear waste (SNW) solution. The chemical and radionuclide composition of the SNW has been found out by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and gamma spectrometry. The uptake kinetics and the decontamination from other radionuclides have also been studied. The possibility of using the membrane as effective sorbent for Cs^+ removal from large volume of solution has been discussed.

Experimental

Reagents and chemicals

The metal salts CsCl, $CuSO_4$ and $K_4[Fe(CN)_6]$ have been procured from Sisco Research Lab., Mumbai, India. Deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q USA) has been used in the present study. The 0.1 M salt solutions have been prepared by dissolving a known amount of the respective salt in 250 mL deionized water. Radiotracer ^{137}Cs used in the present study has been obtained from Board of Radiation and Isotope Technology, Mumbai, India. Whatmann grade Nuclepore Track Etched Membrane (0.2 µm pore size and 10 µm thickness) has been used for the present set of experiments.

Synthesis and characterization

The KCFCN crystals have been grown in the pores of the polycarbonate track-etched membrane by two compartment permeation method using 0.01 M $CuSO_4$ and 0.01 M $K_4[Fe(CN)_6]$. The details of the synthesis procedure are given in ref. 25. Briefly, the membrane has been exposed to $CuSO_4$ solution from one side and $K_4[Fe(CN)_6]$ solution from other side in two compartments permeation cell without stirring for 4 days under ambient conditions. The solution in each compartment has been interchanged on alternate days to ensure uniform growth of the crystals within the pores. The loaded membrane has been taken out and annealed at 40 °C for 2 h. The process of loading and annealing has been repeated twice for growth of the crystal. The synthesized KCFCN crystals have been characterized by XRD, SAXS and TEM methods [25].

Measurement of ion exchange capacity, SDC and uptake kinetics of Cs^+

The ion (Cs^+) exchange capacity and the self diffusion coefficient of Cs^+ in this membrane have been measured by standard radiotracer method as described elsewhere [27]. In brief, for measurement of self diffusion kinetics, a 1 cm × 2 cm KCFCNm sample (equilibrated with Cs) has been placed in 30 ml of ^{137}Cs (carrier free) tagged 0.1 N CsCl solution. The solution has been stirred vigorously (~300 rpm) to avoid film controlled diffusion. The sample has been taken out at regular time intervals, washed thoroughly with deionised water and counted for gamma ray in a fixed geometry using a well type NaI(Tl) detector. The 662 keV peak of ^{137}Cs have been monitored. The membrane sample has again been placed in the equilibrating solution after counting. The process has been continued till equilibrium is attained. The actual residence time of the membrane in equilibrating solution has been used as the time of cation absorption.

For measurement of ion exchange capacity using radiotracer method, 0.1 N CsCl solution (30 ml) containing carrier free ^{137}Cs activity has been prepared. Filter paper standard has been prepared by drying 100 µL of the radiolabelled CsCl solution on Whatman-41 filter paper (1 cm × 2 cm). A 1 cm × 2 cm KCFCNm sample (equilibrated with Cs) has been equilibrated (for 5 h) in the radiotracer tagged CsCl solution. The membrane sample and filter paper standard have been counted in a well type NaI(Tl) detector in a fixed counting geometry. The Cs^+ exchange capacity of the membrane sample has been obtained from the ratio of the γ-activity of ^{137}Cs in the samples and the filter paper standards as given below:

$$\text{Ion-exchange capacity} = \frac{\mathrm{Cs}^*_{\,(\mathrm{mem})}}{\mathrm{Cs}^*_{\,(\mathrm{std})}} \times \mathrm{Cs}_{(\mathrm{sol})}. \tag{1}$$

where $\mathrm{Cs}^*_{(\mathrm{mem})}$ and $\mathrm{Cs}^*_{(\mathrm{std})}$ are ^{137}Cs γ-radioactivity (counts/min) in sample and standard, respectively. $\mathrm{Cs}_{(\mathrm{sol})}$ is moles of Cs^+ in the equilibrating solution.

In order to study the Cs^+ removal efficacy, standard activity (^{137}Cs) has been added to a measured volume of deionised water. A 1 cm × 2 cm KCFCNm piece has been placed in the solution, which has been continuously stirred to avoid film controlled diffusion. The ^{137}Cs activity in the solution has been monitored by aliquoting a fixed volume of solution at regular time interval and counting in NaI(Tl) counter. In the case of solution with very low amount of added radioactivity (<1,000 Bq), the membrane sample has been counted at regular time interval. The measurements have been repeated 5 times for 15 ml solutions and twice for 1,000 ml solution.

Treatment of simulated nuclear waste

In the present work, highly alkaline nuclear waste solution composition has been chosen. The composition of the simulated waste solution was same as that of a waste cycle evaporated condensate of reprocessing plant origin. It is reported in literature [5] that the metal ferrocyanides are chemically stable over a pH range 1–12 and they are decomposed beyond this pH range due to the following chemical reaction [5].

$$\begin{aligned} &\mathrm{Cs_2CoFe(CN)_6} + 6\mathrm{NaOH} \rightarrow 2\mathrm{CsOH} + \mathrm{Co(OH)_2} \\ &\quad + \mathrm{Fe(OH)_2} + 6\mathrm{NaCN} \\ &3\mathrm{Fe(CN)_6^{4-}} + 4\mathrm{H^+} + \mathrm{NO_3^-} \rightarrow 3\mathrm{Fe(CN)_6^{3-}} \\ &\quad + \mathrm{NO} + 2\mathrm{H_2O} \end{aligned}$$

Clarke and Wai [4] have observed that all of the immobilized KCFCN is decomposed from the chelating resin in 4 M LiOH solution. The Cs removal efficiency by KCFCN is known to be best in the pH range of 7–10 [5]. Thus, in the present work, the SNW solution has been neutralized with HNO_3 to pH 6–7. 400 ml of the waste solution has been treated by a 2 cm × 2 cm KCFCNm. The time dependence of removal of ^{137}Cs by the membrane has been monitored by aliquoting 5 ml solution after regular time interval and counting in HPGe detector. The absolute activity at different gamma ray energies of the waste solution has been determined by counting 5 ml of the initial solution in a HPGe detector. The efficiency of the detector at different energy has been obtained by counting a standard 5 ml ^{152}Eu source at the same source to detector distance. The composition of the SNW has been determined by atomic emission spectroscopy using Jobin–Yvon Ultima high resolution ICP-AES having practical resolution of 0.005 nm and has a continuous coverage of spectral range 200–800 nm.

Results and discussions

Characterization

It is reported in the literature [26] that potassium copper ferrocyanide may also precipitate along with copper ferrocyanide. In the present work, as indicated by XRD, SAXS and EDXRF analysis, presence of a mixture of nano-sized (~40 nm) potassium copper ferrocyanide and $Cu_2[Fe(CN)_6]$ crystals have been considered [25]. Thus a mixed potassium copper ferrocyanide composition, represented as KCFCN has been assumed and in this work. A representative TEM figure of the KCFCNm is shown in Fig. 1. This rod like structures indicate uniform distribution

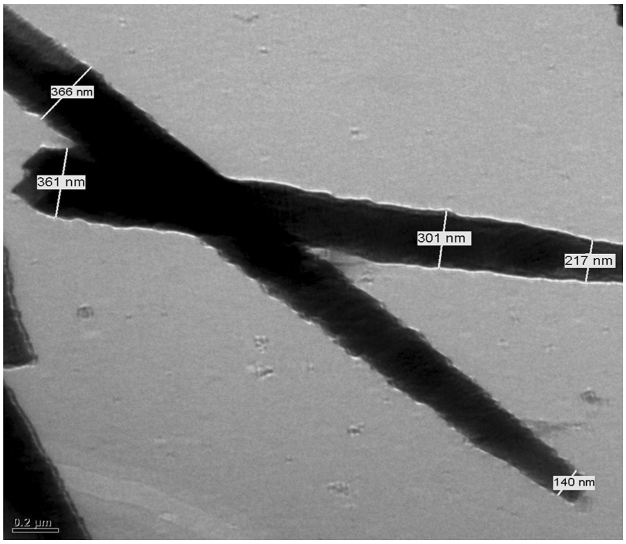

Fig. 1 TEM image of KCFCNm

of nanosized KCFCN crystals within the conical shaped pores of the track etched membrane [25].

Self diffusion and ion exchange capacity

Self-diffusion is diffusion of a species in a medium or between two media having no concentration gradient. In such a case, the diffusion constant, called the self-diffusion coefficient (SDC), gives the true mobility of any species in the matrix [27]. It is reported that the composition and particle size of the ferrocyanide solids may influence the rates cesium sorption [5, 6] due to the differences in the removal mechanisms. In general, the Cs^+ sorption is rapid for $K^+/Na^+/H^+$ containing ferrocyanides as compared to $M_2Fe(CN)_6$ [5]. Due to the presence of K^+ in the synthesized ferrocyanides, a faster rate of Cs^+ diffusion in KCFCNm is expected. The self diffusion profile of Cs^+ in KCFCNm, as shown in Fig. 2, supports this. The figure indicates that, within 100 min, 85 % exchange of the cations into the membrane take place. Sheha [14] have reported 80 % sorption of Cs onto Zn ferrocyanide magnetic nanocomposites within 2 h. Rao et al. [11], using copper ferrocyanide loaded composite ion exchange resin, have also reported 85 % Cs removal in 200 min.

In the present work, the value of SDC for Cs^+ (D) ion in this membrane at room temperature has been obtained from a fit of the experimental data (Fig. 2) with the equation obtained from the analytical solution of Fick's second law given below [27].

$$n(t_k) = n * \left[1 - \left(\frac{8}{\pi^2}\right)\left\{\exp\left(-D\pi^2 t_k/L^2\right) + \frac{1}{9}\exp\left(-9D\pi^2 t_k/L^2\right) + \ldots\right\}\right] \quad (2)$$

where n^* is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$), $n(t_k)$ is the amount of radiotracer at any time t_k in the membrane and L is the thickness of the membrane (10 μm) in swollen condition. n^* and D have been taken as free parameters and only first three terms in the Eq. 1 have been used for fitting. The D has been found to be 6.15×10^{-8} cm²/sec. The value is about an order of magnitude less than that of conventional ion exchange membranes (Nafion-117) [27].

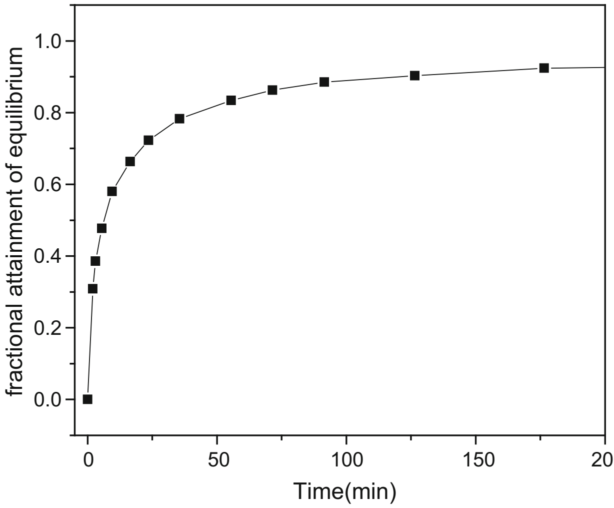

Fig. 2 Self diffusion profile of Cs^+ in KCFCNm

Table 1 shows a comparison of the Cs^+ exchange capacity (mmol of Cs/g) of KCFCNm along with that of other literature reported transition metal ferrocyanide loaded composite sorbents. In the present work, the ion exchange capacity of the KCFCNm (total adsorbent weight was 0.0044 g) has been found out to be 1.75 mmol/g. Thus a 1 cm × 2 cm KCFCNm piece can absorb ~15 mCi (specific activity 22 Ci/g) of ^{137}Cs activity. This indicates that only a very small membrane area is required to treat a very large amount of activity. The data given in Table 1 indicates that this composite membrane has higher ion exchange capacity than most of the other literature reported composite ferrocyanide sorbents. The higher values of Cs^+ exchange capacity as observed by Sheha [14] and Vincent et al. [17] have been obtained using potassium-zinc ferrocyanide and potassium-nickel ferrocyanide respectively.

Removal of ^{137}Cs

The percentage ^{137}Cs absorption by a 1 cm × 2 cm KCFCNm piece from different volume of water and the corresponding distribution coefficients (K_d) are given in Table 2. The distribution coefficients have been obtained as

Table 1 Comparison of the different adsorption parameters of KCFCNm with other literature reported ferrocyanide sorbents

Reference	Log K_d	Ion (Cs^+) exchange capacity (mmol/g)
Present work	5.6	1.75
4	4	1.3
11[a]	4.4	–
14[b]	3.75	14.7
15[c]	6.15	0.13
16[d]	5.6	0.03
17[e]	–	1.8
18	4	–
19	3	–
20	4.8	–

[a] At 0.1 mM

[b] K-Zn- ferrocyanide for sample RZ2

[c] pH = 6.3, for river water

[d] At <25 g/L $NaNO_3$

[e] Ni–K ferrocyanide

Table 2 Dilution effect on the activity removal efficacy of a 1 cm × 2 cm KCFCNm piece with logarithm of the corresponding distribution coefficients (K_d)

^{137}Cs Activity (Bq)	Solution volume (mL)	Contact time (h)	Percentage of ^{137}Cs activity removal	Log K_d
3.8×10^5	15	8	98	5.2 ± 0.4 %
8,000	15	8	99	5.4 ± 3 %
8,000	1,000	20	81	5.9 ± 6 %
800	1,000	20	73	5.8 ± 11 %

$$K_d = \frac{\text{activity of } ^{137}\text{Cs sorbed per g of adsorbent}}{\text{activity of residual } ^{137}\text{Cs in solution per mL}}$$

It is seen from the table that the membrane can efficiently remove 99 % of the ^{137}Cs activity (even up to 3.8×10^5 Bq activity) from 15 ml water in 8 h. From larger volume of solution, the percentage removal of activity reduces even with higher (~20 h) equilibration time. It is also to be noted that the membrane is able to remove ^{137}Cs even from a very dilute solution (800 Bq/L). A comparison of the log(K_d) of KCFCNm, obtained in the present work, with that of other literature reported transition metal ferrocyanide loaded composite sorbents have been given in Table 1. In the present work, on an average, the value of log(K_d) has been found to be ~5.6, which is much higher than most of the other literature reported values. Avramenko et al. have also reported a log(K_d) value of 5.6 for mixed potassium-copper ferrocyanide. Our earlier results [25] have shown negligible uptake of Na^+ in KCFCNm, i.e., the K_d of Na^+ in the membrane is very low. Thus the selectivity of Cs^+ with respect to Na^+ is very high in the composite membrane (KCFCNm).

Preconcentration from simulated nuclear waste

The elemental composition of the SNW has been obtained from AES and gamma spectrometry. The concentrations of different metal ions, obtained from ICP-AES, are shown in Table 3. It is seen from the table that major element in the solution is Na. The radioactive isotopes which are present in the solution at a concentration more than the detection limit of gamma spectrometry are ^{137}Cs, ^{125}Sb and ^{106}Ru with corresponding activity concentration of 1.05×10^4, 3.34×10^4 and 2.11×10^4 Bq/L respectively.

The gamma spectra of the SNW solution, initial and after 3 h membrane preconcentration are shown in Fig. 3a. For comparison purpose, both the spectra have been normalized to the same counting time. Peaks seen at energies other than that of ^{137}Cs, ^{125}Sb and ^{106}Ru, are due to the background. For better clarity, the zoomed view of the spectra in the energy range 615–675 keV are shown in Fig. 3b. After 3 h preconcentration, reduction in the count rate of ^{137}Cs (662 keV) alone is obvious from this figure, indicating selective uptake of ^{137}Cs in the membrane. Figure 3c shows the spectra of the membrane after 3 h of preconcentration which shows the peak of ^{137}Cs only, confirming the high degree of selectivity of the membrane. Table 4 shows the count rate of different radionuclides in the SNW at different time of equilibration with KCFCNm. It can be seen from the table that there is continuous decrease in the ^{137}Cs cps with increasing preconcentration time. There is a 42 % decrease (from 0.253 to 0.146 cps) in the count rate at 662 keV after 3 h preconcentration. The absorption rate of the ^{137}Cs decreases with increasing time and after 9 h equilibration, the count rate becomes 0.13 cps. During the experiment, no significant change in the count rates of ^{125}Sb and ^{106}Ru have been observed. Though the self diffusion profile of Cs^+ in the membrane shows a faster rate of absorption, the actual ^{137}Cs uptake rate from SNW is much slower. Lehto [28] reported that the Cs absorption rates by ferrocyanides are much slower for concentrated (high alkali metal) solutions than for dilute solutions. It is also reported in the literature that the presence of large amount of Na in the solution interferes with the Cs ion exchange process with transition metal ferrocyanide. Han et al. [29] have reported that K_d of Cs^+ decreases drastically when Na^+ ion concentrations in the solution are greater than 2,000 mg/L. As seen in Table 3, the SNW contains high amount of Na (19,700 mg/L), which might have affected the uptake kinetics.

Thus the results of the present work shows that the KCFCNm can be used as an efficient adsorbent for removal

Table 3 Elemental composition and corresponding concentration of SNW as obtained from ICP-AES

Metal ion	Na	Ca	Zn	Cr	Al	Mg	Fe	Cu	Ni	Cd	Co	B	Pb
C_M (mg/L)	19,700	8	7	5	3	1.1	0.6	0.4	0.4	<0.0.1	<0.0.1	<0.0.1	<0.0.1

Errors on all the data points are less than 2 %

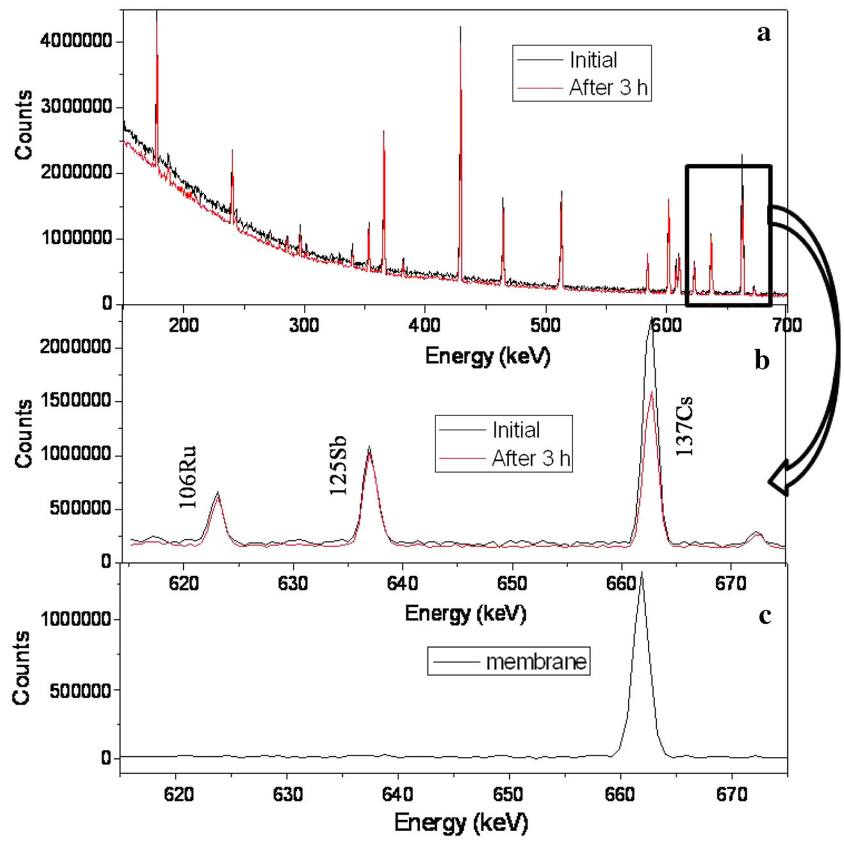

Fig. 3 Comparison of the gamma spectra (obtained using HPGe detector) radioactive waste solution, initial and after 3 h membrane preconcentration **a** full energy range **b** zoomed view of (**a**) in the energy range of 615–675 keV. **c** Gamma spectra of KCFCNm after 3 h preconcentration

Table 4 Count rates of different nuclides as observed in the 5 ml radioactive waste solution acquired using a HPGe detector

Energy (keV)	Nuclide	Background Cps	Solution (5 ml) Cps			
			Initial	After 3 h	After 6 h	After 9 h
176.3	^{125}Sb	–	0.2564	0.2522	0.2557	0.2538
352	^{238}U	0.0731	–	–	–	–
364.5	^{131}I	0.2443	–	–	–	–
427.9	^{125}Sb	–	0.4899	0.4724	0.4704	0.4723
463.4	^{125}Sb	–	0.1743	0.1700	0.1711	0.1753
511.9	^{106}Ru*	0.0574	0.2371	0.2327	0.2318	0.2368
600.6	^{125}Sb	–	0.2114	0.2074	0.2074	0.2079
621.9	**^{106}Ru**	–	**0.0790**	**0.0709**	**0.0706**	**0.0757**
635.9	^{125}Sb	–	0.1376	0.1380	0.1351	0.1340
661.6	**^{137}Cs**	**0.0562**	**0.3092**	**0.2023**	**0.1568**	**0.1345**
1,173.2	^{60}Co	0.0994	–	–	–	–
1,293.7	^{41}Ar	0.5087	–	–	–	–
1,332.5	^{60}Co	0.1042	–	–	–	–

The data for ^{137}Cs and ^{106}Ru has been indicated in bold to highlight that the membrane exclusively adsorbs Cs and not any other metal ions present in the solution

* Contribution from background annihilation peak also is there

of radio cesium from the SNW, even in presence of large amount of Na. The advantage of this method lies in the fact that large volume of waste solutions or environmental solutions can be treated using this membrane based adsorbent and the generated low volume secondary waste is very easy to store in terms of disposal.

Conclusion

The present work, for the first time, describes the use of a membrane based transition metal ferrocyanide loaded composite adsorbent for Cs^+ removal. KCFCNm absorbs ^{137}Cs efficiently with high selectivity as shown by the equilibration uptake measurement from a SNW. The kinetics of Cs^+ absorption in this membrane is fast in absence of other metal ion but slows down in presence of high Na^+ concentration. For ^{137}Cs removal from radioactive solutions, this method is a promising alternative to commonly used precipitation method or immobilization of copper ferrocyanide in other suitable solid supports.

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