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Preparation of poly (4-vinylpyridine-DVB) based anion exchangers and its applications on the separation of $^{99}TcO_4^-$ ions from reprocessing waste solution

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ABSTRACT

Three strong-base anion exchange resins were prepared by quaternization of poly(4-vinylpyridine-DVB) with different alkyl ($-CH_3$, $-C_2H_5$, and $-n-C_4H_9$) halides. The base polymer in granular form was also synthesized in the laboratory. All three synthesized anion exchangers and a conventional strong-base anion exchanger were tested for separation of TcO_4^- ions from acidic and alkaline test solutions, each containing 1.0 M NO_3^- ions and ^{99m}Tc radiotracer. These resins were also evaluated for batch uptake of $^{99}TcO_4^-$ ions from actual reprocessing waste solution. Both batch results showed that the resin with *n*-butyl group on the pyridine nitrogen has higher affinity for $^{99}TcO_4^-$ ions. Further, removal of $^{99}TcO_4^-$ ions from actual reprocessing waste solution was examined using column of poly(4-vinylpyridine-DVB) resin containing *n*-butyl group on the pyridine nitrogen. Almost complete removal of $^{99}TcO_4^-$ ions was obtained for 150 bed volumes of waste treated, indicating excellent column performance of the resin. Elution of $^{99}TcO_4^-$ ions was carried out using 6 M HNO_3 solution, whereby a broad elution profile is obtained. These results indicate the usefulness of this novel resin in the treatment of effluent generated at the back end of nuclear fuel cycle.

Keywords: Separation; Pertechnetate; Radioactive waste; Anion exchange resin; Vinylpyridine; Removal

1. Introduction

^{99}Tc is one of the radioelements produced with very high yield in thermal neutron induced fission of ^{235}U. The radioisotope enters the fuel reprocessing cycle predominantly as pertechnetate $^{99}TcO_4^-$ ion during dissolution of spent fuel in concentrated nitric acid. The $^{99}TcO_4^-$ ions are highly soluble in water and because of its high mobility, traces of the radioelement is often encountered in effluents generated from reprocessing plants. Further, radiochemical characteristics of the element ($t_{1/2} = 2 \times 10^5$ y, $\beta_{max} = 290$ KeV) coupled with high ability to migrate into the environment makes it a potential candidate for long term hazard to the environment [1,2].

Many efforts have been made over the last two decades on selective separation of $^{99}TcO_4$from various types of aqueous medium viz., acidic, alkaline and neutral as well as actual alkaline intermediate level waste solution [3–14]. Although the concentration of ^{99}Tc in such waste is very low, few ppm only, the presence of molar level of competing nitrates makes its separation very difficult. Among conventional resins, the Dowex 1, a strong base anion exchanger based on poly styrene-divinyl benzene (DVB) matrix with quaternary ammonium ion as functional group was first reported as an effective resin for separation of $^{99}TcO_4^-$ ions [3].

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However, throughput is very low owing to lower selectivity in presence of high NO_3 ions [4]. Recent development of a strong-base anion exchange resin containing methylated quaternary pyridinium cation on poly (4-vinylpyridine-DVB) backbone showed remarkably improved performance for removal of the radioelement [5–9]. It is also reported that the resin is promising for separation of the anion from high nitrate containing acidic, neutral and alkaline waste solution [5,7]. Better performance of this resin is attributed to the more hydrophobic nature of the pyridinium amine cation.

It is therefore of interest to prepare strong-base anion exchange resins based on poly (4-vinylpyridine-DVB) matrix quaternized with alkyl halides for selective separation of $^{99}TcO_4^-$ ions from the nuclear waste effluents generated in reprocessing plants in India. Further, efforts were also made to enhance the selectivity for $^{99}TcO_4^-$ ions by incorporating more hydrophobic alkyl groups on pyridine nitrogen. This paper reports the preparation of three anion exchange resins by quaternization of poly (4-vinylpyridine-DVB) with different alkyl halides such as $-CH_3$, $-C_2H_5$, and $-n-C_4H_9$ and evaluation of their performance for removal of $^{99m}TcO_4^-$ ions from acidic and alkaline test solutions containing 1.0 M NO_3^- ions. The performance of these resins for removal of $^{99}TcO_4^-$ ions from actual radioactive waste solution, including loading and elution behavior of ^{99}Tc from n-C_4H_9 group containing poly(4-vinylpyridine-DVB) resin column is also discussed.

2. Experimental

2.1. Preparation of resins

Initially, beads of poly(4-vinylpyridine-DVB) were prepared by suspension polymerization technique from freshly distilled 4-vinylpyridine (distilled under reduced pressure) and DVB in the molar ratio 3:1 and 0.1% benzoyl peroxide. Aqueous solution containing 0.5% carboxy methyl cellulose (Na-salt) and 3% NaCl was used as suspension medium in the ratio of organic to aqueous of 1:8 vol vol^{-1}. The polymerization was carried out under N_2 atmosphere at 55°C for 5 h followed by another 3 h at 90°C. After polymerization, the product was washed with water and methanol, filtered, air-dried, sieved to 0.3–0.85 mm size. This polymer was then used for preparation of resins, which involves soaking the polymer (10 g) in methanol (100 ml) for about 2 d, addition of alkyl halide and heating the mixture at 50°C for 8 h on two consecutive days. Alkyl halide to pyridine nitrogen ratio of 2:1 was used for alkylation reaction. The product resin was washed in methanol, converted to chloride form by passing NaCl (2.0 M), washed with distilled water, air dried, sieved to 0.3–0.85 mm size.

2.2. Determination of uptake of $^{99}TcO_4^-$ ions

Batch equilibration tests, using 0.1 g of resin and 10 ml of solution, were carried out to measure the uptake of $^{99}TcO_4^-$ ions. Two test solutions (i) 1.0 M $NaNO_3$ + 0.1 M HNO_3 and (ii) 1.0 M $NaNO_3$ + 0.1 M NaOH, each spiked with $^{99m}TcO_4^-$ tracer, were used in this study. After 2 h of equilibration, the solid–liquid mixture was separated by filtration and the concentration of $^{99m}TcO_4^-$ in solution was determined by measuring the activity of ^{99m}Tc (E_γ = 140 KeV) using NaI/Tl scintillation detector. From the measured counts, the uptake of $^{99}TcO_4^-$ ions was calculated and expressed as % removal. Similar batch tests were also carried out using actual reprocessing waste solution of composition shown in Table 1. Details of origin and composition of the waste solution is given elsewhere [12]. After 24 h of equilibration, the solution was separated by filtration using whatman 42 paper and the filtrate was used for analysis of ^{99}Tc. The ^{99}Tc present in waste was separated as a white precipitate of tetraphenylarsonium pertechnetet and tetraphenylarsonium perchlorate (carrier), then the precipitate was collected by filtration using microfiltration system, dried under IR lamp and counted using GM counter [15].

2.3. Column tests

About 1.5 g of nC4H9-PVP resin was loaded in a glass column provided with sintered disc support for the resin. The volume of the bed obtained was 5 ml. The column was conditioned by passing of about 50 ml 0.1 M NaOH solution, and then waste solution was passed through the column from top to bottom at the flow rate of 5 bed volumes per hour. The effluent was collected periodically and analyzed for ^{99}Tc activity. The column run was terminated after passing of about 300 bed volumes of waste.

The loading was followed by rinsing the column using 5 bed volumes of 0.1 M NaOH solution. Thereafter, elution of ^{99}Tc was carried out using 6 M HNO_3 solution at the flow rate of 3 bed volumes per hour. Eluates were collected in 10 ml fractions and monitored by measuring gross β activity.

Table 1
Composition of ^{106}Ru and ^{99}Tc bearing effluent

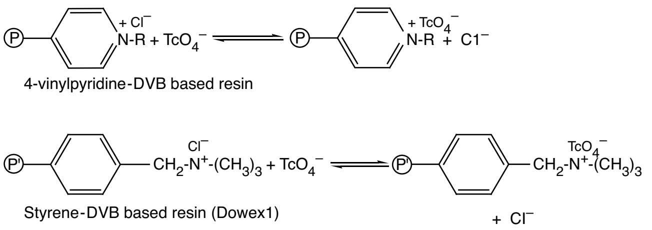
Constituent	Concentration
pH	12.8
TDS, g l^{-1}	140
Gross β, mCi l^{-1}	0.06
^{137}Cs, mCi l^{-1}	4.0×10^{-5}
^{106}Ru, mCi l^{-1}	5.2×10^{-3}
^{99}Tc, mCi l^{-1}	5.1×10^{-2}

3. Results and discussion

Suspension polymerization of 4-vinylpyridine cross-linked with 25% DVB initiated by benzoyl peroxide was used to prepare the poly(4-vinylpyridine-DVB) (Fig. 1). The final product was obtained in the form of cream colored irregular granules. Though not exactly spherical, the granules were in the 0.3–0.85 mm size range, suitable for column application.

The nucleophilic addition reaction of the polymer to alkyl halides (also shown in Fig. 1) was used for preparation of the anion exchange resins [16]. The alkyl halides, viz., CH_3-I, C_2H_5-Br and n-C_4H_9-I were used for preparation of the three anion exchange resins (Fig. 1). Detailed characteristics of the resins have been discussed earlier [17].

Results of batch equilibration tests on removal of $^{99}TcO_4^-$ ions from alkaline radioactive waste solution are shown in Table 2. The uptake of $^{99}TcO_4^-$ ions by the strong-base anion exchange resin can be represented as follows:



It can be seen that all the synthesized anion exchangers have much higher affinity for $^{99}TcO_4^-$ ions than the conventional anion exchange resin (Dowex 1). Furthermore, the affinity of the synthesized *N*-alkylated resins for $^{99}TcO_4^-$ was found to increase in the order PVP-CH_3 < PVP-C_2H_5 < PVP-n-C_4H_9.

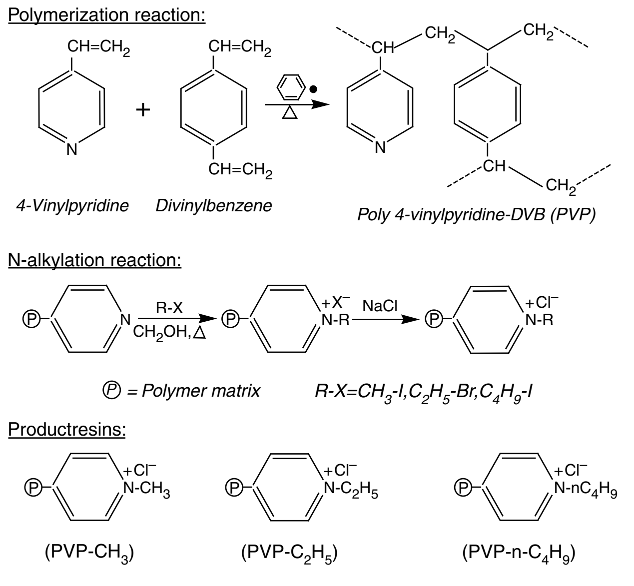


Fig. 1. Synthesis of poly(4-vinyl pyridine-DVB) and *N*-alkylated anion exchange resins.

Although the affinity of an anion to the resin is governed by many factors, including ion-water interaction, degree of hydration of the resin and the effect of the anion on the water structure, the relative solvation ability of the coions in aqueous phase plays a major role in deciding the affinity sequence [7,18]. Among the ions, solvation needs for TcO_4^- is weaker (because of bigger size) and therefore it is pushed into the phase of poorer solvation (resin phase) to yield a minimization of free energy of the system as a whole. In other words, hydrophilic anions like OH^-/NO_3^- form strong hydrogen bonds with water and reduce the free water availability for other anions. This results in a more favorable ion pairing between Na^+/NO_3^- or Na^+/OH^- than Na^+/TcO_4^-. These two factors increase retention of NO_3^- by external aqueous phase and push the bulkier TcO_4^- to the resin phase. In resin phase, the exchange of highly hydrated anion (OH^-/NO_3^-) with the poorly hydrated anion (TcO_4^-) is energetically favorable because of the release of large number of water molecules and formation of stronger ion pairs. This is experimentally proved by Ashley et al. by conducting batch tests as a function of OH-ion concentration and it was found that the Kd for TcO_4^- increases with the increase of OH- concentration [5]. At higher OH- concentration, the solvation for TcO_4^- is further reduced, leading to higher uptake. The same logic holds good in explaining the observed sequence of TcO_4^- uptake among the synthesized resins, which are different only with respect to the size of the alkyl group attached to pyridine nitrogen. With increase of alkyl chain length, hydrophobicity of pyridine nitrogen also increases, making the site weaker for solvation and hence TcO_4^- ion uptake.

The observed sequence of TcO_4^- uptake by the synthesized can also be explained by hard-soft acid base theory [19,20]. The alkyl group attached to pyridine nitrogen imparts an inductive effect (+I effect) on the nitrogen, making the +ve charge more diffuse (soft acid). The magnitude of +I effect increases with the increase in length of the alkyl group and is expected to be maximum when n-butyl group is attached on nitrogen. The TcO_4^-, the softest base among the anions present in waste, forms a stronger complex with the acids (soft–soft interaction) whose charge is diffused to a greater extent. This explains stability of the ion pairs and hence uptake of TcO_4^- increase as PVP-CH_3 < PVP-C_2H_5 < PVP-n-C_4H_9.

In the case of acidic test solution, it is seen that even the base polymer has high affinity for $^{99}TcO_4^-$ ions (Table 2). This is attributed to the fact that the pyridine nitrogen of the polymer is protonated in acidic medium and functions as an anion exchanger. In this case also,

Table 2
Removal of $^{99}TcO_4^-$ ions from acidic and alkaline waste by anion exchange resins

Resin	% Removal of $^{99}TcO_4^-$ ions from		
	Alkaline soln.[a] (0.1 M NaOH)	Acidic soln.[a] (0.1 M HNO_3)	Actual reprocessing waste solution
PVP	13.3	81.2	NT
PVP-CH_3	78.3	78.1	78
PVP-C_2H_5	84.7	82.9	80
PVP-n-C_4H_9	88.5	85.9	88
Dowex 1	74.6	71.1	70

[a] Batch size: 0.1 g resin + 10 ml solution containing 1.0 M $NaNO_3$ + $^{99m}TcO_4^-$ tracer, NT: not tested.

the PVP-*n*-C_4H_9 resin shows superior performance amongst the anion exchangers tested.

Results of batch uptake of $^{99}TcO_4^-$ ions from alkaline low level reprocessing waste solution showed similar performance as that obtained using alkaline test solution (Table 2). It can therefore be concluded that uptake of $^{99}TcO_4^-$ ions by the resins remained same even in the presence of higher concentrations of competing NO_3^- ions in actual waste. In this case also, the resin containing *n*-butyl group on pyridine nitrogen (PVP-*n*-C_4H_9) is superior for removal of $^{99}TcO_4^-$ ions. In view of this encouraging result, the resin was used in further studies, as described below.

Column performance of PVP-*n*-C_4H_9 resin for the separation of $^{99}TcO_4^-$ ions from reprocessing waste solution is shown in Fig. 2. The effluent samples generated during initial stages of column run contained a negligible amount of ^{99}Tc ($<1 \times 10^{-4}$ mCi l^{-1}) activity and this trend was found to continue till breakthrough point, during which about 150 bed volumes of waste was treated. Complete removal of ^{99}Tc from 150 bed volumes of waste indicated the excellent performance of the resin. After breakthrough point, the concentration of ^{99}Tc is found to increase slowly, as indicated by the slow rise of the breakthrough curve. The sample collected before run termination, that is, after about 300 bed volumes of waste treatment showed that only about 55% breakthrough is reached. The column run could not be continued further due to limitation of waste volume. From the measured ^{99}Tc activity in accumulated effluent and in feed solution, the loading of ^{99}Tc on bed was calculated and found to be about 60 μCi. The breakthrough capacity for ^{99}Tc, calculated from ^{99}Tc concentration (5.1×10^{-2} mCi l^{-1}) in solution and the volume of waste treated (750 ml) upto breakthrough point, was found to be 1.5 mg g^{-1} (0.45 mg ml^{-1}) of the resin. This value is significantly lower than that of the total strong base ion exchange capacity of the resin, possibly due to low ^{99}Tc concentration in waste.

The elution profile of $^{99}TcO_4^-$ ions from PVP-*n*-C_4H_9 resin column is shown in Fig. 3. It can be seen that a maximum of about 5% activity was eluted in a fraction, leading to a broad elution profile. Complete elution was achieved after passing about 36 bed volumes of eluate. This broad elution profile is attributed to the very high affinity of $^{99}TcO_4^-$ ion for the exchanger. This result also indicates that higher concentration of HNO_3 may lead to effective elution of the anion in a small volume. However, the use of higher concentration of HNO_3 is of concern in practical application mainly with respect to the management of the eluate. It will be interesting to examine other options like use of reducing and complexing agents for effective elution of the radioelement [9]. Two factors such as further management of the ^{99}Tc rich

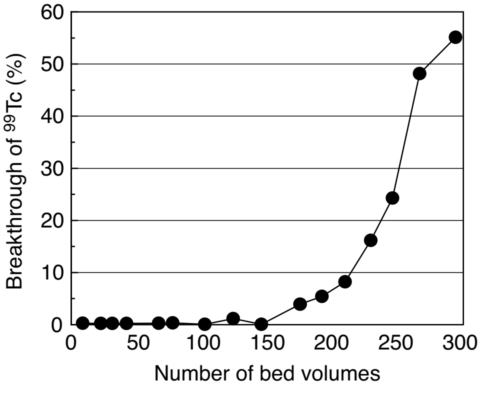


Fig. 2. Removal of $^{99}TcO_4^-$ ion from alkaline reprocessing waste using nC_4H_9-PVP resin column; volume of the bed: 5 ml, flow rate: 5 bed volumes h^{-1}.

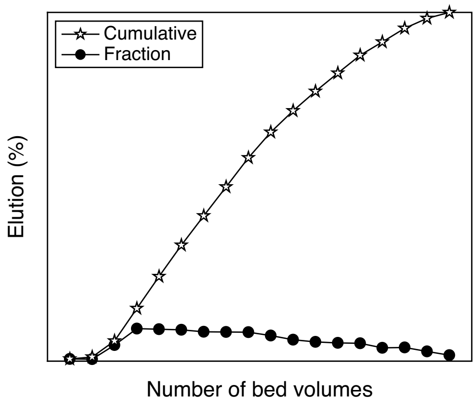


Fig. 3. Elution of $^{99}TcO_4^-$ ion from nC_4H_9-PVP resin column using 6 M HNO_3.

solution (eluate) and reusability of the resin are being addressed to ascertain the overall utility of the highly selective anion exchanger.

4. Conclusions

Three strong-base anion exchangers were prepared by reaction of poly(4-vinylpyridine-DVB) with different alkyl halides. Uptake of $^{99}TcO_4^-$ ions from actual reprocessing waste solution by synthesized anion exchangers was found to be superior to conventional strong base anion exchange resins. Among the synthesized resins, affinity for $^{99}TcO_4^-$ ions was found to increase with increase in length of alkyl group ($\text{-CH}_3 < \text{-C}_2\text{H}_5 < \text{-}n\text{-C}_4\text{H}_9$). The anion exchanger containing *n*-butyl group on pyridine nitrogen showed excellent column performance for removal of the $^{99}TcO_4^-$ ions from reprocessing waste.

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