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Studies on the Adsorption of Uranium and Fission Product Elements from Nitric Acid Medium by Novel Silica-Based Polyvinylpyridine Anion Exchange Resin

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To develop a new ion exchange process for the separation of uranium from fission products we have synthesized a novel silica-based macro-reticular polyvinylpyridine anion exchange resin. This resin has been used for the adsorption studies of uranium and some of the fission products from nitric acid medium. The distribution coefficient values for the adsorption of uranium in both tetravalent and hexavalent oxidation states were measured with the new resin and these values have been compared with the literature values for conventional anion exchange resin with quaternary ammonium as functional group. The newly synthesized silica-based macro-reticular polyvinyl pyridine anion exchange resin has the particles diameter of 50 μm, which results in fast adsorption kinetics, low swelling and pressure drop as compared to a conventional polymer based anion exchange. The distribution coefficient values for tetravalent uranium are considerably higher as compared to most of the fission products. The results indicate that complete separation of U(IV) from most fission products can be achieved.

KEYWORDS : ion exchange, uranium, silica-based polyvinylpyridine anion exchange resin, adsorption, separation

I. Introduction

Although solvent extraction has been used in the nuclear industry for number of processes like purification of uranium, nuclear fuel reprocessing etc, there are some of the problems like use of large amount of organic solvent, loss of extractants due to its solubility in aqueous phase and evaporation losses of diluents. This also results in generation of great amount of liquid organic waste and utilization of large-scale extraction equipment for the process. As compared to solvent extraction, ion exchange process has following advantages i) organic solvent free process, which means generation of less liquid organic waste, ii) compact equipment, iii) excellent phase separation between solid resin and treated solution. Although the ion exchange resins have been used since long time in nuclear industry for wide range of applications like separation of actinides and lanthanides, purification and concentration of plutonium, removal of toxic elements from waste solutions [1, 2]. However, the ion exchange technology has not been applied for industrial use as a main reprocessing process due to slow adsorption and elution kinetics, instability of organic resin in nitric acid medium.

Anion exchange resins are generally polymer-based matrix. In these resins quaternary ammonium groups are anchored to styrene-divinylbenzene copolymer through $-CH_2-$ group. This type of resin can react exothermally with nitric acid under certain conditions and more susceptible to radiolytic degradation. A new type of macroretcular anion exchange resin containing polyvinyl pyridine was reported by Marsh [3]. In polyvinyl pyridine the functional group is in the aromatic ring and due to this it is reported to have higher chemical and radiolytic stability in nitric acid medium as compared to conventional anion exchange resin [4].

In the present work to combine the properties of macroreticular resin along with small particle size we have synthesised the novel silica-based macro-reticular polyvinyl pyridine anion exchange resin (SiPyR). In this resin, polyvinylpyridine / divinylbenzene copolymer is immobilized in silica particles with a diameter of 50 μm and pore size of 600 nm. We have carried out the systematic adsorption studies of U(IV) and U(VI) and typical fission products (FP) elements.

II. Experimental

1. Synthesis of silica-based polyvinylpyridine anion exchange resin (SiPyR)

Silica particles with the diameter of 40-50 μm, mean pore size of 600 nm and pore fraction of 0.69 were used as a support for the polymer. The silica particles were taken in rotary evaporator flask. The flask was evacuated by using vacuum pump, a mixture of monomers (85 wt % vinyl pyridine and 15 wt % m/p divinylbenzene), initiators (α, α-azobisisobutyronitrile and 1,1'-azobiscyclohexane-1-carbonitrile) and diluents (acetophenone and diethyl phthalate) was sucked into the flask. The flask was rotated so that pores of silica will soaked the mixture completely. Afterwards the flask was filled with nitrogen gas. The flask was heated in silicone oil slowly and temperature was raised to 363 K and this was maintained for 20 hours for complete polymerization. The silica grafted anion exchange resin was washed with water and acetone several times. This silica embedded tertiary polyvinyl pyridine polymer was reacted with dimethylsulphate to convert it to

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quaternary ammonium salt. The content of polymer embedded in silica was measured by thermo gravimetric analysis (TGA) and found to be 27 wt %.

Total capacity of the resin was measured to be 4.5 meq/g-resin and quaternary rate was almost 100%. This indicates that tertiary polyvinyl pyridine was completely converted to quaternary ammonium salt. **Fig.1** shows the structure and the photos of the synthesized resin and the commercial Dowex 1 resin.

2. Adsorption experiment

The metal ions used for distribution coefficients measurement were U(IV), U(VI), Nd(III), Sr(II), Zr(IV), Cs(I), Mo(VI), Re(VII), Ru(III), Rh(III), and Pd(II). The U(VI) solution for the adsorption studies was prepared by dissolving uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$] in nitric acid solution of appropriate concentration. Similarly the solutions of other metal ions were prepared by dissolving their nitrate salts of analytical grade in nitric acid solution of required concentration. U(IV) was generated by electrochemical reduction of U(VI) using flow type electrolysis cell (Hokuto Denko co. HX-201) 5).

The distribution coefficient values were measured by batch experiment method. Before carrying out adsorption of metal ions the resin was conditioned with nitric acid solution of concentration varying from 0.1 to 9 mol/dm^3. About 1 g of resin in NO_3^- form and 20 cm^3 of metal ion solution were taken in a glass flask and shaken mechanically at temperature of 298 K in water bath till the equilibration is achieved. The solution was separated by filtration. The concentrations of elements were measured before and after the adsorption experiment by ICP spectroscopy (Seiko Instruments Inc. SPS 5000). The resin was washed with dilute nitric acid and distilled water and finally dried at 333 K for 10 hours. The distribution coefficients (K_d) were calculated by using the following relation;

$$K_d = \frac{C_0 - C_S}{C_S} \times \frac{V_S}{W_R} \qquad (1)$$

where C_0 and C_S denote metal ion concentration in aqueous solution before and after adsorption. W_R and Vs indicate weight of dry resin and volume of aqueous phase, respectively.

III. Results and Discussion

The results of the measured distribution coefficients of U(VI), U(IV) and some of the FP elements in various nitric acid concentrations are presented in **Fig.2** to **Fig.5**. The concentration of nitric acid was in the range 0.1 to 9 mol/dm^3. The anion exchange reaction between metal complexes and the anion exchange resin in NO_3^- form is considered as follows:

$$\nu_A (R^+ \cdot NO_3^-) + A^{-\nu A} = (\nu_A R^+ \cdot A^{-\nu A}) + \nu_A NO_3^- \qquad (2)$$

where R^+, A, ν_A denote the fixed ionic group, the anionic complexes and the charge of the anion, respectively.

From **Fig.2** it is found that the distribution coefficient values for U(IV) and U(VI) increased with the increase in concentration of nitric acid. Similar results were also obtained for the adsorption of U(IV) andU(VI) with the commercial anion exchange resin, Dowex 1 as shown in **Fig.3**. With the increase in HNO_3 concentration, the formation of stable anionic nitrato-complex also increases which in turn enhance the adsorption of metals 6, 7). In both the resins the maximum K_d values for the adsorption of U(VI) is less than 20, while maximum K_d of U(IV) is higher than 10^3. The possible anionic nitrato-complexes are $UO_2(NO_3)_3^-$, $UO_2(NO_3)_4^{2-}$ for U(VI) and $U(NO_3)_5^-$, $U(NO_3)_6^{2-}$ for U(IV). Since U(IV) has much stronger complex formation ability with nitrate ion in comparing with U(VI), it was presumed that U(IV) is adsorbed onto anion exchanger as the form of $U(NO_3)_6^{2-}$, while the predominant adsorption species of U(VI) is $UO_2(NO_3)_3^-$ 8). On the other hand, high adsorbability shown by U(IV) is

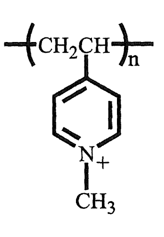
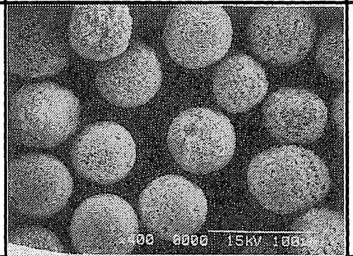
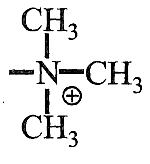
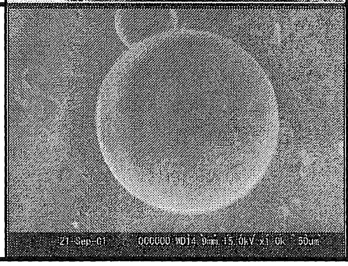
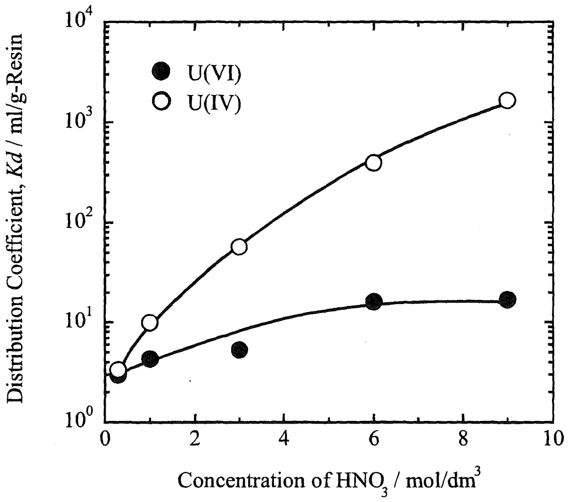
Ion Exchanger	Functional Group	SEM Photograph	Total Capacity (meq/g-Resin)	Quaternary Ratio (%)
SiPyR			4.5	100
Dowex 1	 $-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3$		3.5	94

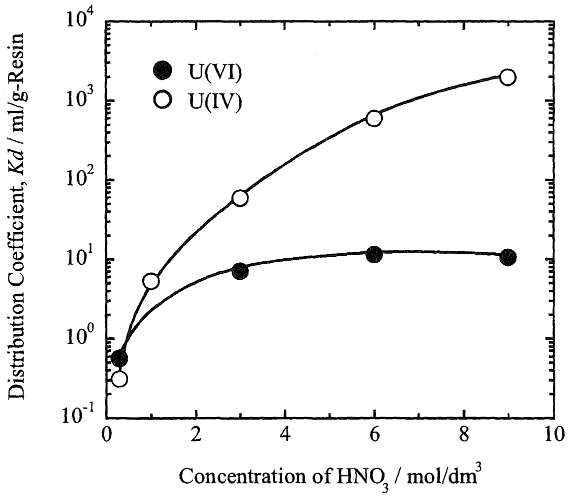
Fig.1 Structure and Properties of SiPyR and Dowex 1

considered to be partly due to the larger charge density (ratio of charge to size) of U(IV) nitrato-complexes than those of U(VI).



Conc. of U(IV, VI) : 10 mmol/dm^3, Temp. : 298 K

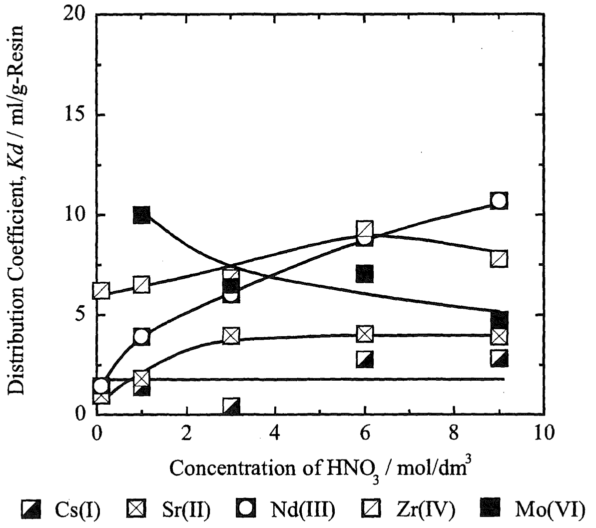
Fig.2 Effects of nitric acid concentration on distribution coefficient of U(IV) and U(VI) for SiPyR



Conc. of U(IV, VI) : 10 mmol/dm^3, Temp. : 298 K

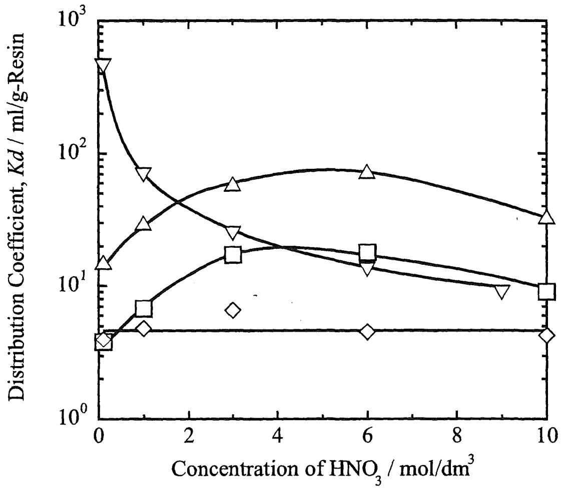
Fig.3 Effects of nitric acid concentration on distribution coefficient of U(IV) and U(VI) for Dowex 1

Fig.4 shows that the distribution coefficients of some of the fission products like Cs (I), Sr (II), Nd(III), Zr (IV) and Mo(VI). The K_d values for Cs (I) and Sr(II) are less than 5 because of their inability to form stable nitrato-complexes. The K_d values for Nd(III) varied from 2 at lower HNO_3 concentration to around 10 at higher HNO_3 concentration, and this could be due to the weak ability of Nd(III) to form anionic complex with nitrate ion. The K_d values of Mo(VI) decreases from 10 at 1 mol/dm^3 HNO_3 to around 4 at 9 mol/dm^3 HNO_3, and this may be due to formation of anionic hydroxyl complexes like $HMoO_4^-$ and MoO_4^{2-} at lower acidity and the formation of H_2MoO_4 at higher acidity. The K_d values of Zr(IV) is in the range of 6 to 9 and shows almost no dependence on HNO_3 concentration. It is reported that Zr(IV) weakly adsorbed on anion exchangers like Dowex-1 and Dowex-2 [9, 10] in nitric acid medium. However the adsorption mechanism of Zr is not completely understood.



Conc. of Metals : 10 mmol/dm^3, Temp. : 298 K

Fig.4 Effects of nitric acid concentration on distribution coefficient of Cs(I), Sr(II), Nd(III), Zr(IV) and Mo(VI) for SiPyR



Conc. of Metals : 10 mmol/dm^3, Temp. : 298 K

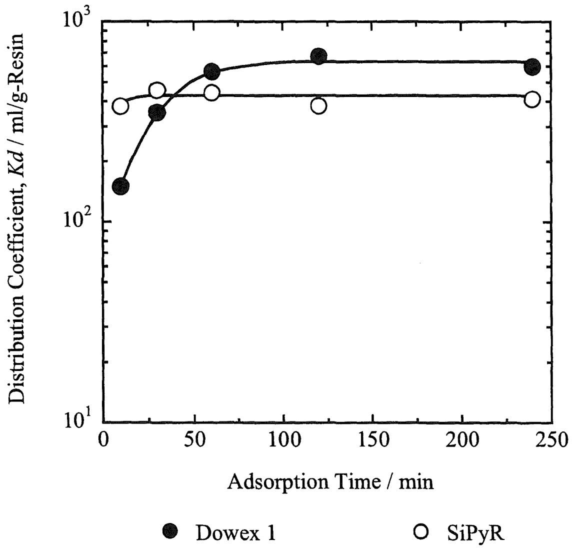
Fig.5 Effects of nitric acid concentration on distribution coefficient of Re(VII), Ru(III), Rh(III) and Pd(II) for SiPyR

Distribution coefficients of precious group metals like Re(VII), Ru(III), Rh(III) and Pd(II) are given in **Fig.5**. The K_d values of Re(VII) are very high at lower HNO_3 concentration and decrease dramatically with increasing HNO_3 concentration. This may be due to the formation of anionic hydroxyl complexes like ReO_4^- at lower acidity and the formation of neutral complex like $HReO_4$ at higher acidity, which is difficult to adsorb. Pd(II) showed fairly strong adsorption in a broad HNO_3 concentration range of 0.1-10 mol/dm^3 with K_d values of about 15 to 80. The adsorption behavior of Pd(II) was reported to have a strong dependence on the structure of functional group in anion exchangers [11, 12]. From the results shown in **Fig.5**, it is considered that Pd(II) was adsorbed as anionic nitrato-complexes such as $Pd(NO_3)_4^{2-}$. However at low HNO_3 concentration the Pd(II) adsorption may result from complex formation with the anion exchanger through the coordination bond with nitrogen atom as follows:

$$RN^+\cdot NO_3^- + Pd^{2+} + 2NO_3^- = RN^+{:}Pd(NO_3)_3^- \qquad (3)$$

Ru(III) also showed weak adsorption at a broad HNO_3 concentration range with a maximum K_d near 20 at 3-6 mol/dm^3 HNO_3. The Ru(III) adsorbs on anion exchanger probably as nitrosylruthenium nitrato complexes like $RuNO(NO_3)_5^{2-}$ [13] in which charge to size ratio is very less. Rh(III) showed very weak adsorption with *Kd* values less than 5.

Fig.6 presents the kinetic behavior of SiPyR by comparing with a conventional polymer resin of Dowex 1 with respect to the adsorption of U(IV). It is found that in newly synthesised SiPyR the adsorption equilibrium is reached in less than 30 minutes, while for Dowex 1 resin with about same particle size (50-60 μm) it takes more than 75 minutes. It was reported that the adsorption of Pu(IV) onto the polymeric matrix REILLEX™HPQ resin containing polyvinylpyridine reached the equilibrium more than 100 minutes [3]. Fast adsorption kinetics shown by the novel SiPyR is due to the small particle size of porous silica support and the polymer resin is retained inside the macro-pore of about 600 nm which shortens the diffusion range of the adsorption ions. Furthermore, as the new resin is embedded in the rigid silica, which can suppress the swelling of polymer resin, it showed very lower pressure drop as compared to conventional polymeric resins with almost same particle size.



Feed : [U(IV)] = 10mmol/dm^3, [HNO_3] = 6mol/dm^3, Temp. : 298 K

Fig.6 Time evolution of U(IV) adsorption from nitric acid solution for Dowex 1 and SiPyR

IV . Conclusion

A novel SiPyR has been synthesized and characterized. The adsorption behavior of uranium and some typical fission product elements by this new resin were investigated experimentally. Compared to U(VI), U(IV) shows significantly stronger adsorption and the maximum distribution coefficient is more than 10^3 which is about 100 times higher than that of U(VI) . This may be due to the stronger complex formation ability of U(IV) with nitrate ion and the larger charge density of the U(IV) nitrato-complexes. Most fission products such as Cs(I), Sr(II), Nd(III), Zr(IV), Mo(VI), Rh(III) showed only weak adsorption on the new resin with distribution coefficients less than 10. A few precious metals like Pd(II), Ru(III) and Re(VII) showed fairly strong adsorption. Compared to conventional polymeric matrix resins, the novel polyvinylpyridine resin presents a faster adsorption kinetics and lower pressure drop. The adsorption studies indicate that U(IV) can be separated from FP in nitric acid medium by using new SiPyR. Since SiPyR resin shows very high K_d values for U(IV) in nitric acid medium, it is expected that this resin will also show strong adsorption for Pu(IV). It is under consideration to use this resin for the recovery and purification of Pu(IV) in a new process of nuclear fuel reprocessing.

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