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Synthesis, characterization and some adsorption properties of TMMA chelating resin

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Abstract

In order to separate U(VI) ions and lanthanide ions from acidic media, *N*,*N*,*N*′,*N*′-tetramethylmalonamide, (TMMA), chelating resin was synthesized by chemically bonding the functional group to the main chain of chloromethylstyrene–divinylbenzene copolymer. Characterization of the resin in terms of IR, solid-NMR, porosity and elemental analysis suggested that TMMA was uniformly linked to the polymer particles following the expected synthetic scheme and that the introduction ratio was ca. 75%. The uptake behavior of Ce(III) ions and of U(VI) ions from different acidic media were investigated using the batch technique. The kinetic and equilibrium studies showed that the obtained resin is promising for the proposed separation.

Keywords: Chelating resins; Diamide; Adsorption; ^{13}C solid NMR; U(VI); Ce(III)

1. Introduction

CMP (dihexyl-*N*,*N*-diethylcarbamoylmethyl-phosphonate) and CMPO (*n*-octyl(phenyl)-*N*,*N*-isobutylcarbamoylmethylphosphine oxide) have been known to be useful extractants for the removal of actinide (An) and lanthanide (Ln) species from acidic radioactive wastes. Therefore, the authors have developed chelating resins, which contain CMP or CMPO as a functional group, for the separation of actinide ions and rare earth ions from nitric acid media [1–3]. In these resins, CMP and CMPO are chemically bonded to the main chain of the resin and work as a functional group. Both CMP and CMPO are well-known bidentate extractants for actinide ions in liquid–liquid extraction systems and the two resins have also shown relatively efficient adsorptions of actinide ions. This is in fact due to the high affinity of the phosphoryl groups towards actinide ions. The disadvantages encountered were mainly due to the difficulty in eluting adsorbed ions, the need of the addition of basic compounds like $Ca(OH)_2$ for neutralizing the H_3PO_4 generated during incineration, the increase in the amount of the second wastes and their high cost. Therefore, the application of some other extractants as functional groups in chelating resins may be preferable. The utilization of substituted monoamides and diamides for the extraction of actinides and other metals has recently received interest. Several workers proposed amides as alternative extractants to TBP used in the PUREX processing of spent nuclear fuels. The important advantages of amides are: acceptable resistance to hydrolysis and radiolysis, complete burnability and low cost [4]. Different amides have been reported in the literature to be good extractants for actinide and/or lanthanide elements [5–10]. The decrease in the number of carbon atoms of the functional groups makes them hydrophilic, which leads to an improvement of adsorption. Therefore, a diamide resin with *N*,*N*,*N*′,*N*′-tetramethylmalonamide (TMMA) functional group, TMMA resin, was examined in this study.

2. Experimental

2.1. Synthesis of TMMA resin

According to the synthetic scheme shown in Fig. 1, the polymer particles were synthesized by the

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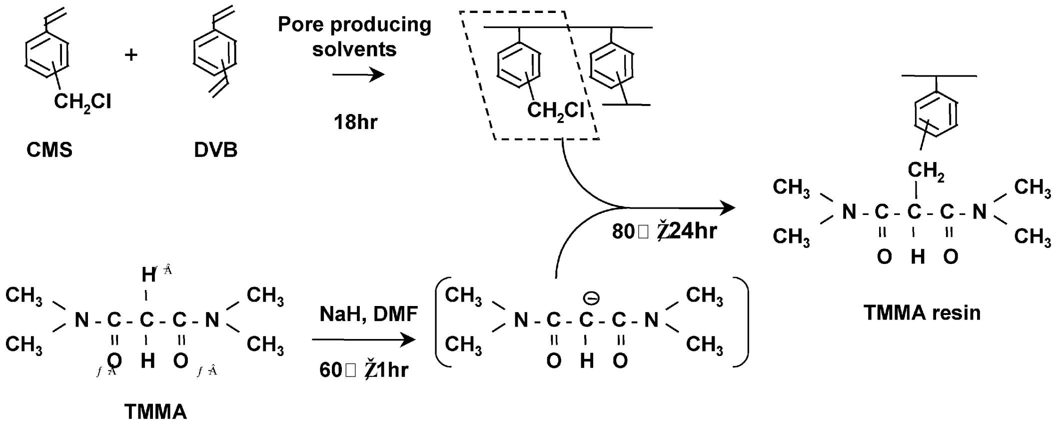

Fig. 1. Synthetic scheme of TMMA resin.

conventional suspension polymerization of chloromethylstyrene (CMS) and divinylbenzene (DVB) in the presence of pore producing solvents. The crosslinkage ratio was 10%. The CMS–DVB copolymer particles obtained were fully washed with distilled water and acetone. Particles were sieved into two main fractions of 210–300 and 300–500 μm, vacuum-dried and used for the next reaction, TMMA introduction, in which the chlorine atom of CMS is substituted by TMMA.

TMMA supplied by Tokyo Chemical Industry was used without further purification. The *N*,*N*-dimethylformamide (DMF), used as a solvent during the introduction of CMP into the polymer beads [1], was successfully used for TMMA introduction. Using a separation funnel, TMMA was added dropwise to DMF suspended with NaH at room temperature. The mixed solution was heated at 60°C for 1 h and cooled to room temperature. The vacuum-dried copolymer was immersed in DMF and put into the reaction flask. The reactants were heated at 80°C for 24 h with continuous stirring. The end of the reaction was determined using IR spectrophotometry. The synthesized TMMA chelating resin was fully washed with methanol and distilled water. The introduction of TMMA to the copolymer particles was conducted under argon atmosphere.

2.2. Characterization of TMMA resin

The TMMA chelating resin synthesized was characterized by elemental analysis, IR spectrophotometry using a FT/IR-410 spectrophotometer supplied by JASCO. ^{13}C solid-state nuclear magnetic resonance (NMR) using a JNM-EX270 FT NMR system supplied by JEOL, in addition to porosity analysis using the mercury porosimeter Micromeritics Pore Sizer 9320 supplied by Shimadzu.

2.3. Adsorption properties

Adsorption properties were examined by the batch method. Two solution media of 0.05 M HNO_3 + 3 M $NaNO_3$ and 3 M HNO_3 were used for the batch tests. The solid/liquid ratios adapted were 1 g-wet/100 cm^3, in the case of U(VI), and 2 g-wet/100 cm^3, in the case of Ce(III). In kinetic study, the initial concentration of U(VI) was 1000 mg/dm^3. While, in the case of Ce(III) the initial concentration used was 200 mg/dm^3. For adsorption rates, each sample solution was contacted with the resin at 25°C and small amounts of solutions were sampled at appropriate intervals. For the distribution coefficient study, the initial concentration of U(VI) was 100 mg/dm^3 while in the case of Ce(III) the initial concentration was 60 mg/dm^3. These solutions were mixed with resin for 1 week at 25°C. The concentrations of U or Ce ions in the solution samples were measured by ICP-AES.

3. Results and discussion

In total, three TMMA resins were synthesized; TMMA1, TMMA2 and TMMA3. They are identical from the chemical point of view but differ in pore size and/or particle diameter. The particle size of TMMA1 ranges from 210 to 300 μm, while TMMA2 and TMMA3 particle size ranges from 300 to 500 μm. The pore diameter will be discussed later.

3.1. Characterization of TMMA resin

The characterization results given below are for TMMA2 unless otherwise stated. The elemental analyses and the IR spectrum of the resin have shown that TMMA functional groups had successfully substituted for the chlorine atoms of the CMS–DVB copolymer. Table 1 shows the elemental analysis results. The mass balance, based on the Cl atom concentration, shows that 94% of the Cl atoms were substituted. On the other hand, the mass balance, based on the N atom concentration, proved that 75% of TMMA functional groups substituted Cl atoms in the polymer, which is higher than the case of the CMP resin, 61% [1]. This might be attributed to the fact that TMMA is less bulky than CMP. The reminder 19% of Cl atoms is believed to be substituted by other impurities such as those shown in Fig. 2. The IR spectrum obtained for the TMMA resin is shown in Fig. 3a. The strong band appearing at 1637 cm^{-1} is believed to be due to the C=O bond of amides. There is no clear band around 1700 cm^{-1}, maybe it is overlapped by the strong C=O band at 1637 cm^{-1}, which assures that the carboxylic impurities in the TMMA resin are limited. When the TMMA functional group was hydrolyzed a small carboxylic band at 1700 cm^{-1} was observed as can be seen in Fig. 3b. This phenomenon takes place if the humidity was not completely removed during the introduction of the TMMA functional group into the polymer beads.

Table 1
Elemental analysis of TMMA chelating resin

	C	H	N	O	Cl
Experiment	70.9	8.1	7.50	12.2	0.7
Calculated	71.7	8.1	9.4	10.8	0

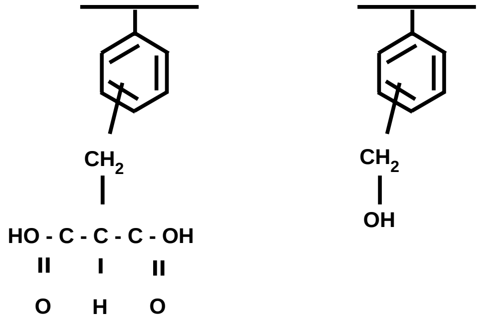

Fig. 2. Impurities expected during TMMA resin synthesis.

Fig. 4 shows the ^{13}C MAS NMR spectrum of TMMA at room temperature. A strong band was observed at 37.0 ppm, which was assigned to CH$_2$, while the smaller band at 48.3 ppm, which slightly overlaps the band at 37.0 ppm, was assigned to CH. Three different overlapping bands were observed at 128.1, 137.4 and 144.6 ppm, respectively. These bands were assigned to the aromatic ring. The last band observed at 170.2 ppm was assigned to the C=O amide bond. From the results of the elemental analysis, IR spectrum and ^{13}C MAS NMR spectrum mentioned above, it could be concluded that the synthesis of the TMMA chelating resin was carried out successfully according to the synthesis scheme shown in Fig. 1.

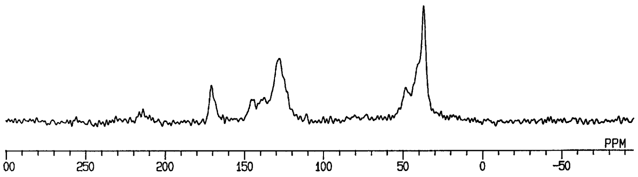

Fig. 4. ^{13}C MAS NMR spectrum of TMMA resin.

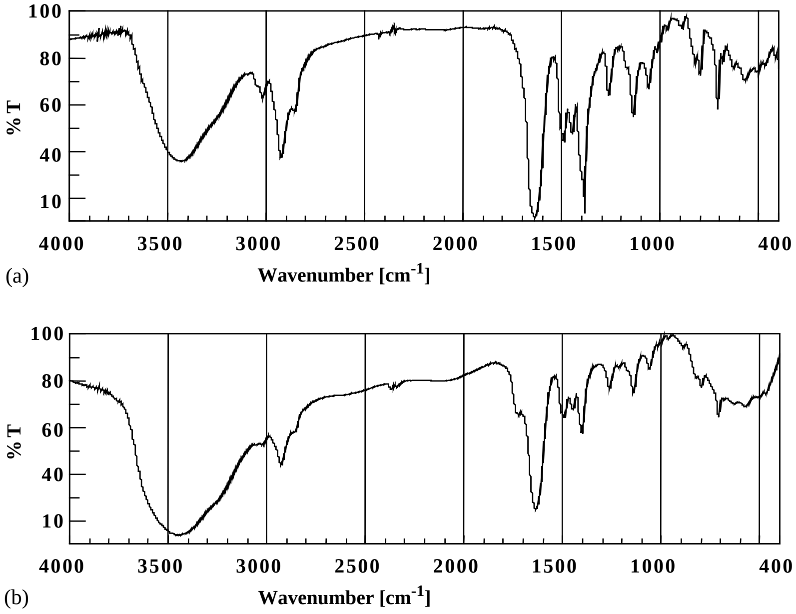

Fig. 3. IR spectra (a) for TMMA resin; (b) for hydrolyzed TMMA resin.

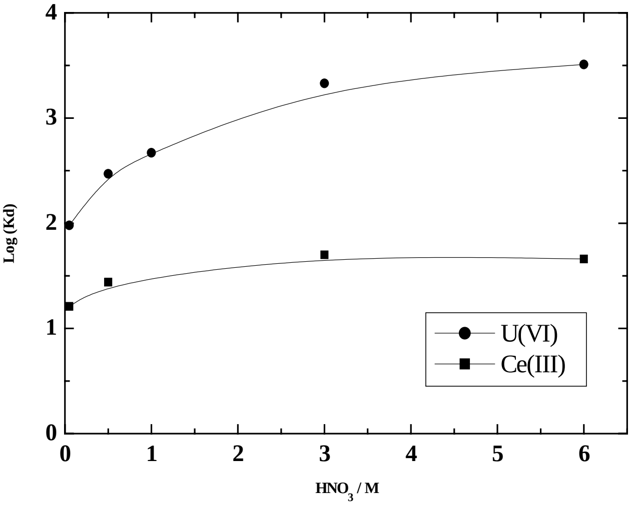

Fig. 5. Effect of nitric acid concentration on the distribution coefficient, K_d.

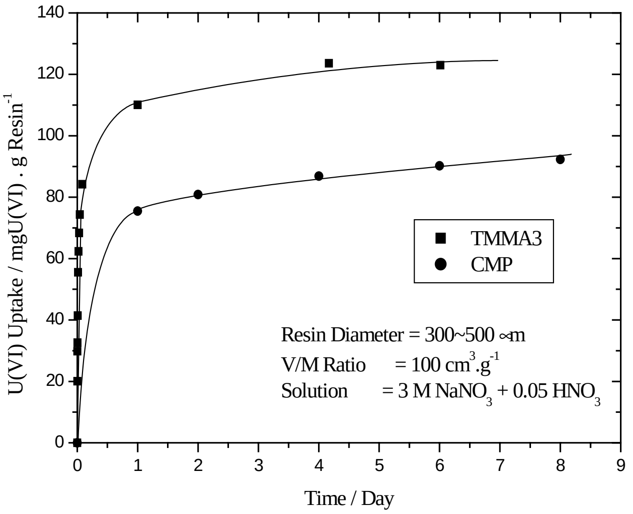

Fig. 6. Rate of uptake of U(VI) by TMMA and CMP resins.

The particle diameter and the pore structure of the TMMA resins have a direct effect on the adsorption properties, especially the uptake rate. To be able to compare such adsorption properties with those of the CMP resin, it was essential to measure the pore diameter of these resins and choose the resin with particle diameter and pore diameter equivalent to that of CMP resin, 17 nm [1]. The Mercury porosity measurement has shown that the average pore diameters of TMMA1, TMMA2 and TMMA3 are 19, 490 and 17 nm, respectively. Consequently, the adsorption properties of TMMA3 were measured and compared with those of CMP.

3.2. Adsorption properties

The distribution coefficient, K_d, of U(VI) and Ce(III) at different HNO_3 concentrations and the rate of uptake of U(VI) and Ce(III) by TMMA and CMP resins are shown below. The effect of HNO_3 acid concentration on the K_d of U(VI) and Ce(III) at equilibrium is of great interest. If the value of K_d at very low acid concentration was found to be decreasing with HNO_3 concentration before it starts to increase at higher concentrations, the resin would be slightly hydrolyzed. As can be noticed from Fig. 5, the K_d value is always increasing with the increase in HNO_3 concentration. This supports the previously mentioned findings, based on the IR spectrum, that TMMA chelating resin contamination with carboxylic groups is limited. It is also clear that the K_d of U(VI) is greater than that of Ce(III). This was expected as the diamides are highly selective for U(VI) ions as compared to the lanthanide ions.

The uptake rate of U(VI) and Ce(III) by TMMA and CMP resins from 3 M $NaNO_3$ + 0.05 M HNO_3 solution are shown in Figs. 6 and 7, respectively. It is clear that the uptake of U(VI) is much higher than that of Ce(III) which proves that TMMA resin is highly selective towards U(VI). Comparing the adsorption properties of TMMA with those of the CMP resin, TMMA had shown a higher rate of adsorption and adsorption capacity for U(VI) and Ce(III). These advantages of TMMA resins compared with CMP resin are due to the structure of the diamide group, which is less bulky when compared with CMP. This enables higher introduction ratio into the base polymer, 75%, compared with only 61% in the case of CMP. This means that the number of active sites per resin mass or volume increased in the case of TMMA resins.

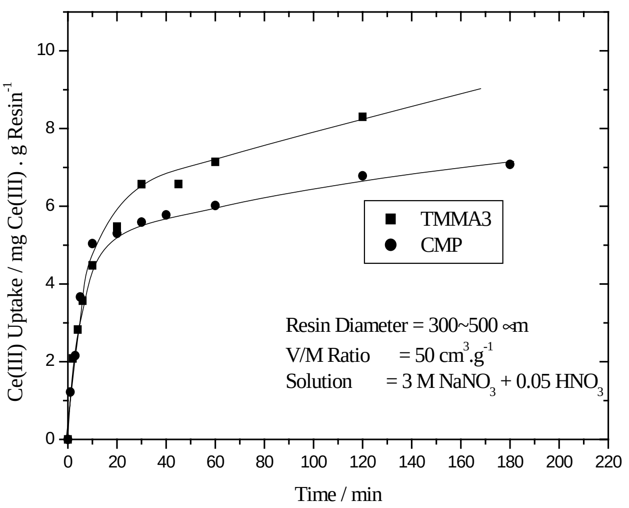

Fig. 7. Rate of uptake of Ce(III) by TMMA and CMP resins.

4. Conclusions

The aspects of TMMA resins synthesis were explained and the resin characterizations were investigated. It was shown that the introduction of the functional group was easier in TMMA resins than in CMP resin. The adsorption properties of TMMA resin were studied and compared with that of CMP. It was shown that the TMMA resins have a higher adsorption performance than the CMP resin for U(VI) and Ce(III).

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