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The Effect of Degree of Impregnation in Amberlite Resins with Organophosphorous Extractants for Y(III), La(III), Ce(III), Th(IV) and U(VI) Ions

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Abstract: Background: The sorption of Y(III), La(III), Ce(III), U(VI) and Th(IV) ions with solvent impregnated resins using diphenylphosphate (DPP), and diphenylphosphinic acid (DPPA) as extractant and Amberlite XAD 16 and Amberlite XAD 2000 as a polymeric support has been studied. The impregnated resins containing various amounts of extractants (10/90, 20/80, 50/50, 60/40) have been prepared by a dry method. The effects of pH, types of extractant, extractant content, surface area of polymeric support and contact time have been investigated by batch method.

Results: The impregnation for DPP on XAD-16 and XAD-2000 was 111 and 46% at 60/40 extractant/resin mass ratio, respectively. The impregnation of DPPA at all ratios on both resins was found constant and lower than DPP. The sorption percentage of studied metal ions was within 90-99% for DPP and DPPA on both resins after 20/80 extractant/resin mass ratio.

Conclusions: The sorption of DPP on Amberlite XAD 16 and XAD 2000 resins is rather more than DPPA. It could be seen that 20/80 extractant/resin mass ratio is generally adequate for single metal analysis where 60/40 could be suitable for multi-metal analysis.

Keywords: Amberlite XAD resins, impregnation, diphenyl phosphate, diphenylphosphinic acid, sorption

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INTRODUCTION

Solvent extraction has been widely used as a basic technique for the separation of metal ions from aqueous solutions (1, 2). However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to get successful separation (3).

Solvent impregnated resins (SIRs) are relatively new types of ion selective exchangers based on the solvent extraction (4). A SIR has some potential advantages over solvent extraction applied to hydrometallurgical processes due to its high selectivity, high concentration ratio, and ease of preparation as well as handling (1).

Solvent impregnated resins, first proposed by Warshawsky (4), are obtained by the simple immobilization of a common extracting agent into or onto an insoluble, non-functionalized polymer support (5). Generally, these supports are macroporous organic polymers with a high surface area and good mechanical stability. Of these support, the Amberlite XAD resins are among the most suitable (6).

SIRs have been prepared with different extracting agents, including phosphinic acids (7), phosphoric acids (8), thiophosphoric acids (9), hydroxyoximes (10), amines (11), aliquat 336 (12), and Cyanex 923 (13). Although organophosphorous extractant impregnated resins (14–22) were extensively used in the extraction of several metals, there is little work on rare earth metals and actinides.

Jerabek et al. found that the mechanism of impregnation was not affected from the types of preparation methods (23). By impregnating resin, the pore size of resins up to 10 nm is filled by extractant, after this point surface adsorptions become dominant (5). However, Rovira et al. found that impregnation of resin with extractants is independant of particle size (24). By Mendoza et al. it is found that the sorption efficiency increased by the increase in concentration of extractant (7).

In this work, SIR were prepared by the immobilization of the reagents of diphenyl phosphate (DPP) and diphenyl phosphinic acid (DPPA) onto Amberlite XAD-16 and XAD-2000 (styrene-divinyl-benzene copolymers) polymeric supports for the removal of Y(III), La(III), Ce(III), U(VI), and Th(IV) ions from aqueous solution. Using FTIR spectroscopy, the proposed SIRs were characterized and also the interaction between SIR and metal was investigated. Firstly, the optimum pH for each metal ion for each extractant was determined. Then, the types of extractant, extractant content, the surface area of polymeric support and contact time have been studied for the determination of the effect of impregnation degree on the removal of the each investigated ions from aqueous solution.

EXPERIMENTAL

Apparatus

FTIR spectra of metal sorbed, DPP-DPPA impregnated and free Amberlite XAD 2000 resin were recorded with a Perkin Elmer Spectrum BXII FT-IR

Spectrometer using KBr discs in the range 4000–400 cm^{-1} with 2 cm^{-1} resolution and 50 scans.

The surface of the resins was observed with an emission scanning electronic microscope before and after impregnation of extractants and after the sorption of metals on resins. The samples were coated with a thin gold layer (two times, 40 mA, 60 s; approx. 30 nm) by a sputter coater unit (BALZER SCD 050 Sputter Coater, BAL-TEC) and surface topography was analyzed with a JEOL JSM 6300F Scanning Electron Microscope(SEM) operated at an acceleration voltage of 5 kV.

A Shimadzu 1601 model uv-vis spectrophotometer was used in the determination of metals. An Inolab WTW model pH-meter and a Heidolp MR 3001 magnetic shaker were used in the sorption experiments.

Chemicals and Reagents

Diphenyl phosphate (DPP) (Aldrich) and diphenyl phosphinic acid (DPPA) (Fluka) were used as extractants and no further purification was done before use. All organic solvents and chemicals were used as analytical reagent grade.

Stock standard solutions (1 mg mL^{-1}) of Y(III), La(III), Ce(III), and Th(IV) from nitrate salts and U(VI) from acetate salt were prepared. Their working and standard solutions were freshly prepared using deionized water. pH of metal ion solutions were adjusted using diluted HNO_3 and NaOH solutions.

The resins of Amberlite XAD-16 (styrene-divinyl benzene copolymer, surface area: 800 m^2g^{-1}, pore diameter: 10 nm and bead size: 20–60 mesh) and Amberlite XAD-2000 (styrene-divinyl benzene copolymer, surface area: 580 m^2 g^{-1}, pore diameter: 4.2 nm and bead size: 20–60 mesh) were supplied from Sigma-Aldrich. The resins were washed with 50% ethanol-water solution containing 4 mol L^{-1} HCl, deionized water and ethanol, respectively, filtered and then dried at 50°C in oven before use.

Impregnation of the Resin

Solvent impregnated resins were prepared at four different impregnation ratios (extractant: resin; w/w %); 10:90, 20:80; 50:50; and 60:40. The resins have been prepared by a wet impregnation method. 20 mL of extractant solution (DPP in acetonitrile, DPPA in acetone-ethanol (1:1)) was mixed with dry Amberlite XAD resin. Then, the mixture was stirred for 24 h at 250 rpm and room temperature. After 24 h, the SIR beads were filtered, washed with deionized water and dried overnight at 50°C in oven.

The extractant content in the impregnated resin was determined by measuring the mass ratio between before and after impregnation.

Batch Sorption Method

100 mg of SIR was shaken with 10 mL of the metal ion solution (10 mg L^{-1}) at studied pH for different periods of time at 300 rpm and room temperature. After shaking, both phases were separated by standing for 2 min and then the concentrations of metal ions were determined spectrophotometrically using Arsenazo-III reagent (25, 26). In this method, calibration solutions and sample solutions containing 2.0 mL of standard/sample solution + 0.2 mL of Arsenazo III (0.1%(w/v) solution + 1 mL of pH 2 (KCl/HCl) solution were diluted to 5.0 mL with 0.01 mol L^{-1} HCl and measured at 653 nm for Y(III), La(III), Ce(III), and U(VI). For Th(IV) at 667 nm, instead of adding pH 2 solution, the solution was completed by 2.0 mol L^{-1} HCl. The working calibration range was 0.6 to 3.0 mg mL^{-1} for each one except Th(IV) (0.6–7.0 mg mL^{-1}).

RESULTS AND DISCUSSION

Extractant Impregnation Capacities of Amberlite XAD Resin

Table 1 shows the effect of the amount of extractant used in the impregnation of DPP and DPPA on Amberlite XAD resins. It can be seen that the sorption of DPP on both XAD resins is rather more than DPPA. Sorption percentages increases with increasing extractant-resin mass ratio for DPP in both resins; however, this kind of relation can not be seen for DPPA.

The impregnation of extractants on resins mostly depends on pore filling and surface adsorption. The sorption of DPP on XAD 16 resin is higher than XAD 2000. This could be explained by the pore diameter of XAD 16 and higher surface area than XAD 2000. The sorption of DPPA on XAD 2000 is higher than XAD 16 because DPPA has smaller molecular size than DPP. XAD 16 and XAD 2000 are and hydrophobic resins. So the impregnation degree of these extractants could be explained by the difference in the polarity of the phosphoryl group.

Table 1. Sorption of extractants by Amberlite XAD resins

Extractant/ resin ratio (%)	Sorption capacity (mg/g of resin)			
	DPP		DPPA	
	XAD 16	XAD 2000	XAD 16	XAD 2000
10	33	6	13	22
20	89	29	17	25
50	106	33	17	26
60	111	46	16	26

Maximum sorption was found as 111 mg/g XAD 16 for DPP at high extractant content where the sorption of DPPA changes in the range of 13–26% for both resins.

FTIR studies and SEM Results

The FTIR spectra of XAD 2000, DPP and DPPA impregnated XAD 16 and 2000 have been recorded (Figs. 1 and 2). The spectrum associated with the polymeric matrix of styrene/divinyl benzene exhibits two strong bands at 3019 and 2925 cm^{-1} attributed to the stretching modes of the aromatic and aliphatic C-H groups. In addition, the three absorption bands between 1603 and 1446 cm^{-1} are due to ring vibration of benzene rings, which also contain bending bands at 895, 830, 794, and 707 cm^{-1} ascribed to out of plane ring C-H bending vibrations. The IR absorption frequencies assignments for DPP and DPPA impregnated XAD 2000 show small modifications on the characteristic normal modes compared with the spectrum of the pure Amberlite XAD 2000.

The IR absorption frequencies assignments for DPP and DPPA molecules on DPP-XAD 2000 and DPPA-XAD 2000 show some modifications of the characteristic normal modes of these extractants compared with the spectrum of the free reagent.

There can be seen two peaks between 1191 and 1100 cm^{-1} assigned to P═O stretching for both DPP and DPPA impregnated XAD 2000 resins. The main difference is observed in the P-Ph and P-O-aryl frequencies. A

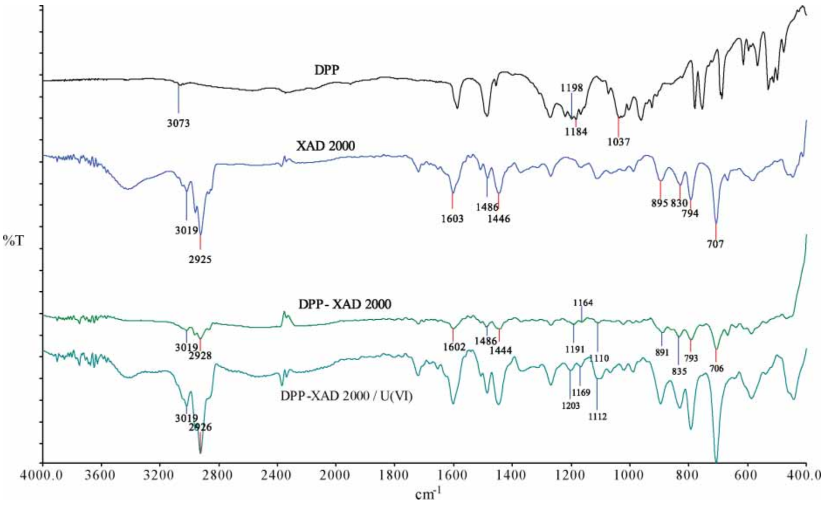

Figure 1. FTIR spectra of DPP, XAD 2000, DPP-XAD 2000, and DPP-XAD 2000/U(VI).

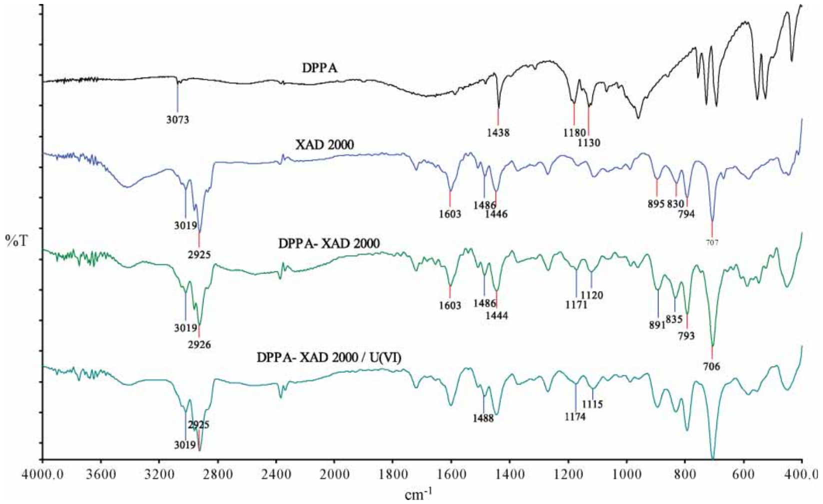

Figure 2. FTIR spectra of DPPA, XAD 2000, DPPA-XAD 2000, and DPPA-XAD 2000/U(VI).

peak can be seen at 1191cm^{-1} to P-O-aryl for DPP-XAD 2000 resin however, DPPA-XAD 2000 has a peak at 1486 cm^{-1} attributed to P-Ph stretching.

The FTIR spectra of DPP and DPPA-XAD 2000/U(VI) complexes have also been recorded (Figs. 1 and 2). It is seen that the characteristic frequency of P═O stretching bands of DPP and DPPA have been shifted in the interval of 1–12cm^{-1} for U(VI).

SEM analysis has been applied to three samples of XAD 2000 and XAD 16 before and after impregnation, but only the photos of the surface of XAD 2000 at 300 µm are shown in Fig. 3 because of the similarities of the images. According to SEM images of the samples, it can be claimed that the size of the regular shaped spheres increased by impregnation of DPPA and also after U(VI) sorption the size of the spheres increased much more.

Optimum pH for the Sorption of Investigated Ions

The pH is an important parameter for quantitative sorption of metal ions on extractant impregnated Amberlite XAD resins. The effect of pH on sorption of five different metal ions was investigated in the pH range of 1–6 for 50/50 extractant/sorbent ratio on each resin. pH is generally not affected by the structure of the extractant and resin. Optimum pH values for the quantitative sorption of Ce(III), Y(III), La(III), U(VI), and Th(IV) ions were found similar for DPP and DPPA (Fig. 4). Metal ions were quantitatively sorbed at pH's 4.5; 4; 6; 5 and 4.5; respectively. All other experiments were carried out at optimum pH for all metal ions.

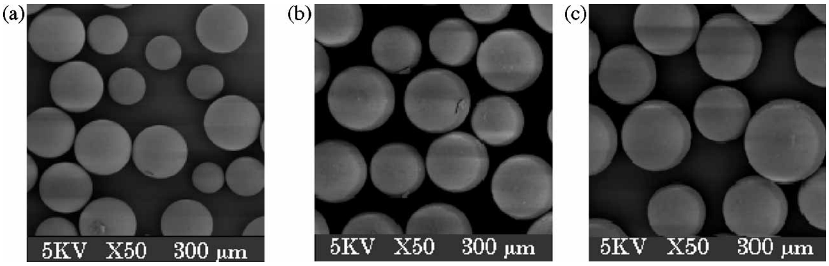

Figure 3. SEM photographs of the surface of XAD 2000 before and after impregenation at 300 µm (a) Before impregnation, (b) After impregnation with 60 w/w% of DPPA, (c) After extraction of U(VI).

In the impregnation process, DPP and DPPA as organophosphorous extractants could be impregnated as mostly dimeric form but also as monomeric form depending on the solvent used. So in this work, as given in literature, the extraction of metal ions could be as in the following reaction (1, 27):

$$M^{n+} + mH_2R_2 \leftrightarrow M(HR_2)_n(HR_2)_{m-n} + nH^+$$

Effect of Stripping Condition on Recovery

Under higher acidic medium, loaded lanthanide and actinide ions could be easily released from adsorbent into the desorption medium. So, the stripping of studied ions was studied by using various concentrations and volumes of HCl and HNO_3 solution. The results revealed that 10 mL of 1 mol L^{-1} HCl solution was sufficient for quantitative elution of the adsorbed ions. The reusability of impregnated resin was over 12–15 sorption-regeneration cycles.

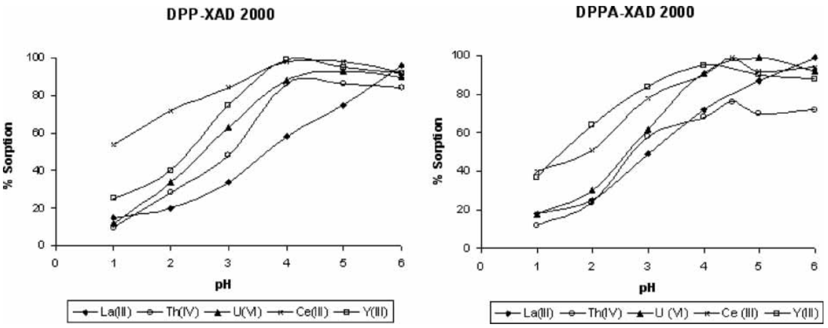

Figure 4. Effect of pH on sorption of metal ions on extractant impregnated XAD 2000.

Sorption Behavior of Metal Ions

In this study the sorption of Y(III), La(III), Ce(III), U(VI), and Th(IV) ions on Amberlite XAD resins loaded with DPP and DPPA at different mass ratios were investigated. The studied rare earth ions were sorbed by free XAD resins at very much low degree. However, studied actinide ions were moderately sorbed. The sorption time for each metal ion for two types of resins having two different extractants was found completed up to 20 min.

Figure 5 shows the effect of extractant-resin mass ratio on the sorption of Y(III) ion. Sorption percentage of Y(III) ion changes generally in the range of 83–99% for both resins impregnated with DPP and DPPA for all studied extractant-resin mass ratios except 10/90 impregnated DPP-XAD 16 with a sorption of 36%. It can be seen that 10 min is usually adequate for the sorption to reach equilibrium at different extractant/resin ratio. The minimum sorption time as 1 min was seen at 50/50 and 60/40 impregnated DPP-XAD 2000 with a sorption of 99%.

The sorption results for La(III) were given Fig. 6 Sorption of La(III) by XAD resins having extractant-resin mass ratio between 20/80 and 60/40 was highest, only slightly less in DPPA-XAD 16 resin. The loaded metal ion was lower at XAD resins having 10/90 impregnated extractant-resin mass ratio, especially in DPP-XAD 2000. The sorption equilibrium was reached within 15 min for almost all loaded XAD resins. The shortest sorption time as 3 min was obtained in DPP-XAD 2000.

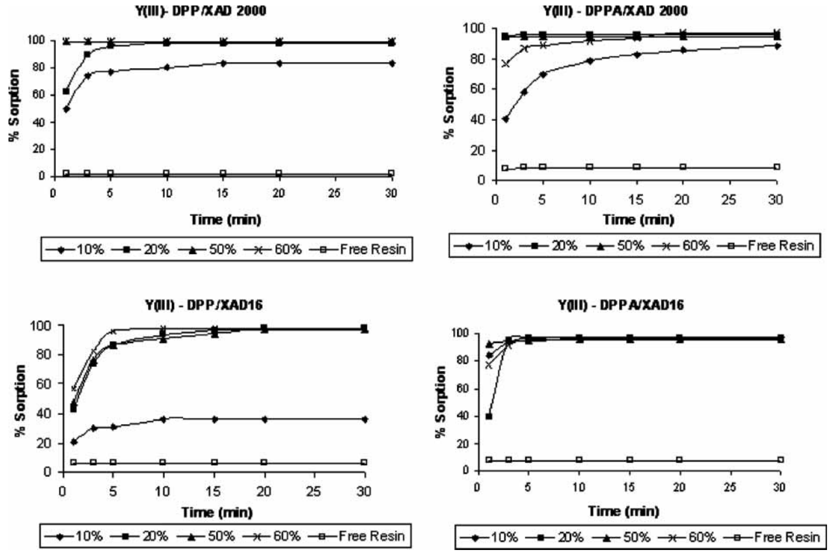

Figure 5. Sorption behaviour of Y(III) with extractants at different mass ratio on Amberlite resins.

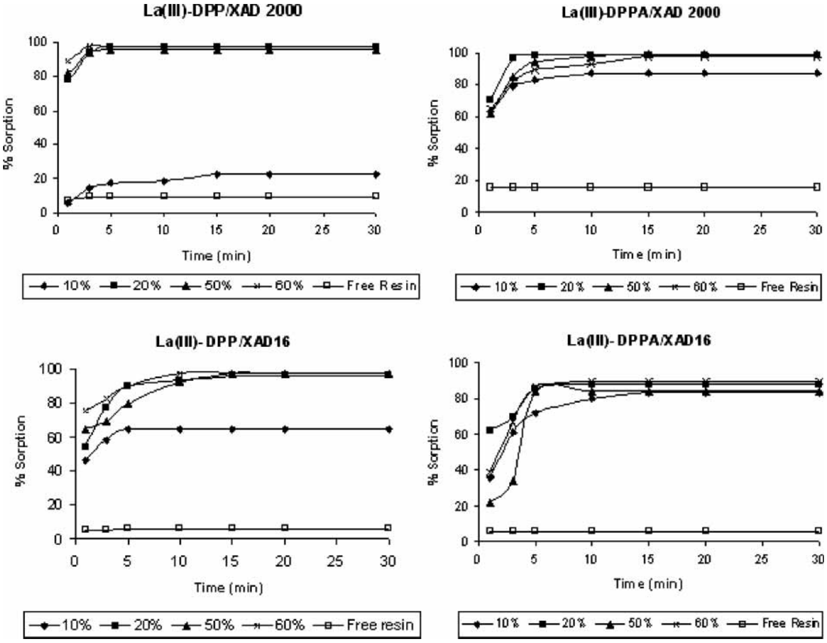

Figure 6. Sorption behaviour of La(III) with extractants at different mass ratio on Amberlite resins.

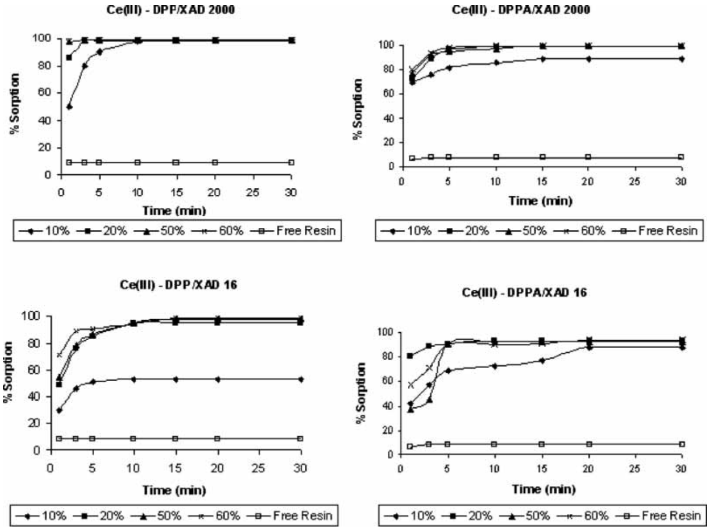

Figure 7. Sorption behaviour of Ce(III) with extractants at different mass ratio on Amberlite resins.

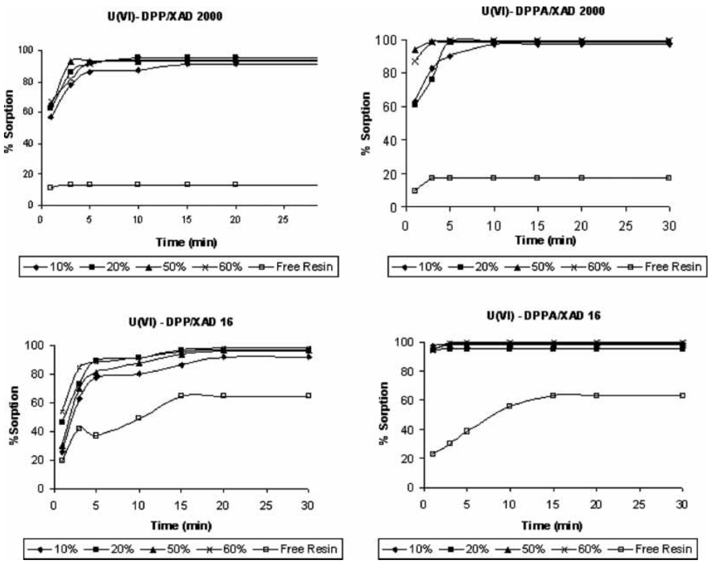

Figure 8. Sorption behaviour of U(VI) with extractants at different mass ratio on Amberlite resins.

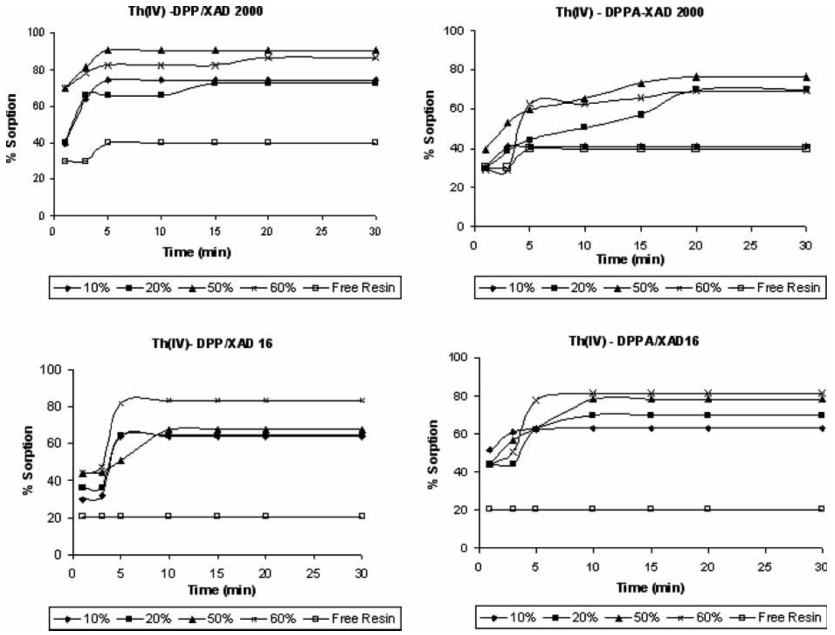

Figure 9. Sorption behaviour of Th(IV) with extractants at different mass ratio on Amberlite resins.

The sorption of Ce(III) ion was similar and extremely high for all extractant-resin mass ratios of DPP-XAD 2000 and for 20/80, 50/50, 60/40 impregnated DPP-XAD 16, DPPA-XAD 16 and DPPA-XAD 2000 while the results were quite low for 10/90 impregnated DPP-XAD 16 (Fig. 7). Equilibrium of the sorption was reached within 20 min for all resins except DPP-XAD 2000 which has the shortest sorption time as 3 min.

As can be seen from Fig. 8 optimum time for the sorption of U(VI) ion was very short for DPPA-XAD 16 and DPPA-XAD 2000 (5 min), but rather long especially for DPP-XAD 16 (20 min) and DPP-XAD 2000 (10 min).

All sorption results were found between 92–99% for two different Amberlite XAD resin loaded with DPP and DPPA at different mass ratios.

The results obtained for the sorption of Th(IV) ion were shown in Fig. 9. The sorption capacities for Th(IV) ion were fairly less than the other studied metal ions (31–90%). The time required for sorption equilibrium is constant and achieved within 10 min for DPPA-XAD 16; however, it is very high for DPPA-XAD 2000 (20 min). The equilibrium time changes between 5–20 min for Amberlite XAD resins loaded with DPP. DPPA and DPP impregnated Amberlite XAD 16 was more efficient for the sorption of Th(IV) than XAD 2000.

CONCLUSIONS

The sorption of Y(III), La(III), Ce(III), U(VI), and Th(IV) ions with various amounts of DPP and DPPA on Amberlite XAD 16 and XAD 2000 resins has been studied with respect to time. It was suggested that the extractants are filled on the pore of resins and the surface of particles. The quantitative sorption of metal ions with DPP and DPPA was obtained at pH values within the range of 4–6. It was found that the sorption of each studied metal ion for two types of resins having DPP or DPPA is fast. At lowest extractant mass ratio, it was concluded that the sorption degree is low and the sorption time is slow.

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