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Removal of *n*-Tributyl Phosphate from Synthetic Intermediate Level Waste

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ABSTRACT

Experiments were carried out on the removal of *n*-tributyl phosphate (TBP) from the synthetic effluents of intermediate level waste (ILW). The candidate materials selected for this study were XAD-4 resin, Tulsion-A-72 MP resin, activated charcoal, and polyurethane foam. These materials were characterized for their distribution coefficients of TBP in a TBP–ethanol–water medium. XAD resin and PU foam showed better removal of TBP. To understand the mechanism of removal of TBP by the candidate materials, such physical properties as specific surface area, pore size distribution, and zeta potentials were determined. The zeta potential of the TBP in an ethanol–water medium was measured. The pore size distribution compared to the specific surface area and surface charges of the samples played an important role in the removal of TBP. XAD-4 resin was used in column studies for the removal of TBP from synthetic ILW. About 13,500 bed volumes of ILW could be passed before a 0.1% breakthrough capacity was attained.

INTRODUCTION

A considerable amount of liquid waste is generated in the reprocessing of spent nuclear fuel by the PUREX process. The liquid waste is classified according to the radiation level at the surface into high, intermediate, and low level wastes (HLW, ILW, and LLW, respectively). While the treatment for HLW and LLW is fairly well established (involving vitrification and solidification into concrete or organic matrices, respectively), the treatment for ILW (1) has become increasingly more interesting as a research topic.

It is common practice for all ILW solutions to be combined, concentrated in an evaporator, neutralized, and cemented. Mixing the sodium carbonate waste of the organic phase with nitric acid wash solutions results in a salt loading as high as 4 M sodium nitrate in the ILW. Recent considerations for reducing shielding costs and the considerable amount of space needed in the final repository suggest the possibility of partitioning ILW. In order to reduce the volume of ILW, chemical precipitation or sorption methods are primarily considered for partitioning ILW.

n-Tributyl phosphate (TBP) (2) associated with an inert hydrocarbon is the principal solvent used in the reprocessing of irradiated fuel from a nuclear reactor. TBP, which is slightly soluble in water, is present in ILW (3). Alkaline wastes, which contain uranium, TBP, etc., are generated at uranium treatment plants. Recovery of uranium from these wastes by using anion-exchange resins has been reported (4). The presence of organics such as TBP cause organic fouling (5) to ion exchangers, and thereby reduce their performance. It is also reported that organics present in the waste may reduce the decontamination factors (6) during the chemical treatment process. Even in the case of direct disposal of ILW in cement matrices, the removal of organics helps in the reduction of microbial effects (7) on the waste matrix. The literature describes the use of various materials such as XAD resin (8), polyurethane foam (9), and activated charcoal for the removal of organics. XAD-4 resin was used in the removal of TBP and its degradation products from aqueous nitric acid solutions in the PUREX extraction process (10).

This paper describes the evaluation of such adsorbents as XAD-4 resin, activated charcoal, polyurethane foam (PU foam), and Tulsion-A-72 MP resin with respect to their degree of extraction of TBP; the study of the candidate materials for their specific surface area, pore size distribution, and zeta potential to understand the mechanism of removal of TBP by them; and the removal of TBP from synthetic ILW by using XAD-4 resin.

EXPERIMENTAL

Materials

All the chemicals were of reagent grade unless otherwise indicated. *N*-Tributyl phosphate (BDH Chemicals Ltd, England) was purified in accordance with the standard procedure (2). XAD-4 resin is a commercial resins supplied by M/S Amberllite. The typical sample of activated charcoal was prepared at our department, the Centralized Waste Management Facility. We used commercially available polyurethane foam Tulsion-A-72 MP resin as anionic resins supplied by Thermax, India.

Estimation of Distribution Coefficients

Sample solutions were prepared by adding 1 mL TBP to 100 mL demineralized water containing 10% ethanol by volume. About 0.25 g of the above materials were equilibrated with a 100-mL sample solution. The initial and final TBP contents in the solution were measured using a gas chromatograph made by Shimadzu. The degree of extraction (E) and the distribution coefficients (D) were calculated using the following equations:

$$E = (\text{TBP}_{\text{initial}} - \text{TBP}_{\text{final}})/\text{TBP}_{\text{initial}}$$

$$D = \frac{E \times (\text{volume of solution})}{(100 - E) \times (\text{weight of foam})}$$

Characterization of the Materials

All the candidate materials were characterized for their size, specific surface area, pore size distribution, and zeta potential. The size of the particles was determined by using either a microscope or a Mavern particle size analyzer. The specific surface area and pore size distribution of XAD resin and activated charcoal were analyzed by the nitrogen adsorption technique using a Quantasorb Jr instrument. To determine the pore size of PU foam and Tulsion-A-72 MP resin, the specimens were viewed under a scanning electron microscope and an optical microscope, respectively. The zeta potential measurements were carried out using a Mavern Zeta Sizer 3.

RESULTS AND DISCUSSION

The density and the size of the candidate materials used in the TBP distribution studies are given in Table 1. The distribution coefficients (D)

TABLE 1
Physical Properties of the Candidate Materials

	XAD resin	PU foam	Activated charcoal	Tulsion-A-72 MP
Size (in meters)	$0.3–1.2 \times 10^{-3}$	5×10^{-3}	$<53 \times 10^{-6}$	$0.3–1.2 \times 10^{-3}$
Density (kg/m^3)	1200	23.8	451.9	670–720
Distribution coefficient (L/kg)	1592	1086	971	423
Surface area (m^2/mg)	0.820	7.0×10^{-4}	1.6	2.0×10^{-4}
Pore size	54 Å	1–4 μm	38 Å, 115 Å	17 μm
Zeta potential (mV)	1.20	−8.06	−10.96	7.89

obtained for these materials are also given in Table 1. It was observed that the D of TBP on XAD resin was higher than that of activated charcoal, PU foam, and Tulsion-A-72 MP resin.

In order to understand the mechanism of removal of TBP by the candidate materials, their pore size distribution and specific surface area were determined. The specific surface area of the samples is given in Table 1. The surface area of the activated carbon was larger than that of the other materials. The specific surface areas of PU foam and Tulsion-A-72 MP were quite low.

The average pore size of the candidate materials is given in Table 1. XAD resins are isoporous in nature. The average pore size of them is 54 Å, which is in agreement with the reported value (8). The activated carbons showed pores sizes of 38 and 115 Å. The pore size distributions of PU foam and Tulsion-A-72 MP resin are given in Figs. 1 and 2. From Fig. 1 it is evident that PU foam has a honeycomb-like network. The outer pores of PU foam were 0.5 mm in size, but the inner pores were in the micrometer range. The pore sizes of Tulsion-A-72 MP resin were also in the micrometer range. Figure 2 shows the pores of Tulsion-A-72 MP resin and the channels connecting the pores.

The zeta potential (Z) of TBP in an ethanol–water medium was 3.93 mV. The Z values of the candidate materials are given in Table 1. The activated carbon and PU foam showed negative Z values whereas Tulsion-A-72 MP showed a positive value.

Even though activated carbon has a larger surface area and a favorable surface charge, the removal of TBP was less compared to that of XAD resin. The higher distribution coefficients obtained with XAD resins were attributed to their pore size distribution. The minimal D values obtained

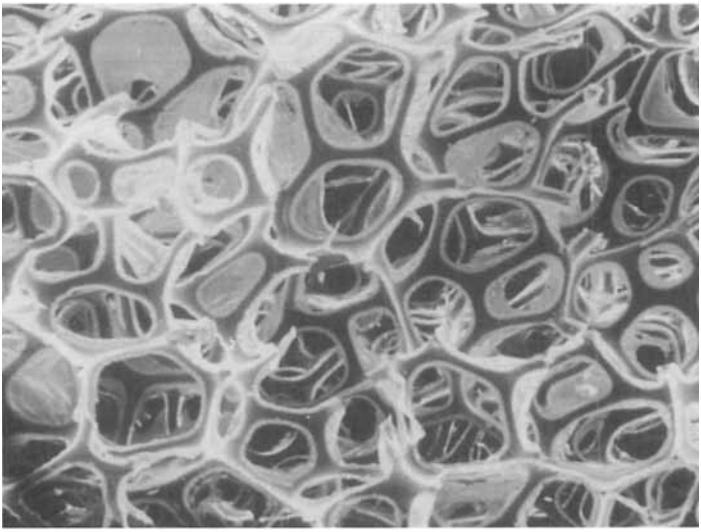

FIG. 1 Microscopic view of PU foam.

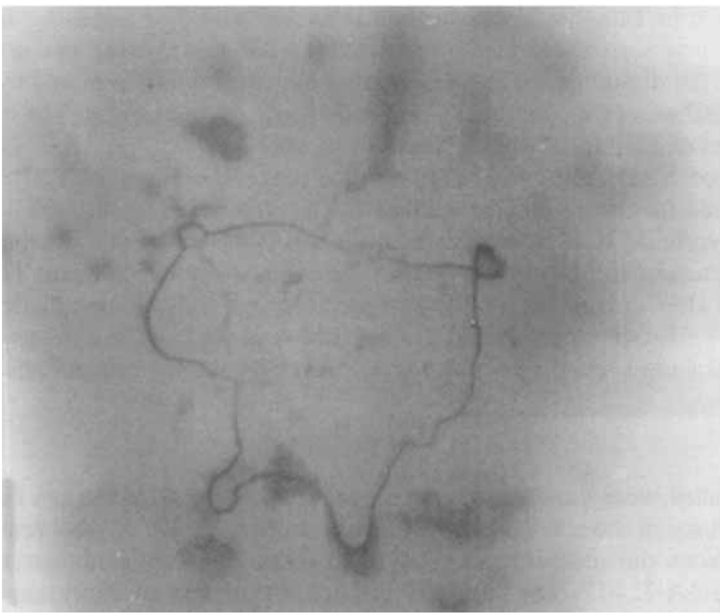

FIG. 2 Microscopic view of Tulsion-A-72 MP.

TABLE 2
Composition of Intermediate Level Waste

Chemical	Quantity (kg/m^3)
Sodium nitrate	340
Sodium carbonate	159
Sodium sulfate	5
Sodium chloride	5
Sodium phosphate	17.8

for Tulsion-A-72 MP resin were attributed to their lower specific surface area, large pore size, and unfavorable surface charges. In the case of PU foam, although the specific surface area was low and the pores were larger in size, higher distribution coefficients were observed, which was attributed to a different kind of mechanism, viz., an ether-like solvent extraction mechanism as described in the literature (9).

To prepare a synthetic ILW solution, the required chemicals were dissolved in demineralized water. The chemical composition of the solution is given in Table 2. It was further saturated with TBP, and the aqueous layer was separated after centrifugation. After preparing the synthetic ILW, the dissolved TBP was extracted by using chloroform and the soluble TBP was estimated by a gas chromatographic technique. The concentration of TBP in ILW was found to be 80 mg/L.

Since XAD resin was found to give higher D values of TBP, it was selected for use in column studies for the removal of soluble TBP from the synthetic ILW solution. About 1 mL XAD resin was washed with acetone and slurried into a column having a diameter of 1 cm. The synthetic ILW containing TBP was passed through the column at a flow rate of 5–8 $mL \cdot cm^{-2} \cdot min^{-1}$. The concentration of TBP in the eluate was less than 0.1 mg/L even after passing 13,500 bed volumes of synthetic ILW.

CONCLUSION

Studies were conducted to compare the candidate materials for their efficiency in the removal of TBP from synthetic ILW. XAD-4 resins and PU foams showed better removal of TBP than did activated charcoal and Tulsion-A-72 MP. The pore size distribution played an important role in the removal of TBP. Soluble TBP from ILW could be removed using XAD-4 resin. These studies can be applied in the removal of TBP from the alkaline effluents created in uranium treatment plants.

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