SHORT NOTE

Removal of Solubilized Solvent
Extractants from Aqueous
Waste Streams

James D. NAVRATIL
Rockwell International, Rocky Flats Plant*

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The loss of solvent extractant by solubility in the various streams of a solvent extraction plant is of prime importance in determining the economic viability of the plant. In addition, the losses may cause problems in subsequent processing or waste treatment steps of the raffinate and even cause pollution problems. The usual method to avoid the loss of extractant is to wash the aqueous waste stream with the diluent used in the extraction process. However, this requires additional solvent extraction contactor equipment.

This note deals with using non-ionic, macroporous resins in column equipment to sorb dissolved extractants from aqueous waste solutions. The method was primarily developed to remove tributyl phosphate (TBP) from nitric acid raffinate streams of a modified Purex process, because of the interference of TBP in a subsequent anion exchange step (1). Because dibutyl phosphate (DBP) is also present in nitric acid waste streams and the sodium carbonate scrub streams, removal of this extractant was studied. Preliminary results of removing the bidentate organophosphorous extractant, dihexyl-N,N-diethylcarbamoylmethylene phosphonate (DHDECMP), are also given. Initial data from these studies were presented elsewhere (2).

Three non-ionic, macroporous resins (co-polymer of divinyl benzene-polystyrene) were tested in laboratory-scale columns for the removal of solubilized solvent extractants from aqueous waste. The resins, Rohm and Haas Amberlite XAD-2, XAD-4 and XAD-7, 20 to 50 mesh, were loaded into 0.6 cm diameter columns to a bed height of 11 cm. The resins were washed with 80 ml each of methanol, water, and the respective aqueous medium prior to each experiment.

The waste solutions were prepared as 0.2 ml, TBP/1, 5 M HNO₃; 1 ml, DBP/1, 5 M HNO₃; 1 ml, DBP/1, 1 M Na₂CO₃, and 0.4 ml, DHDECMP/1, 7 M HNO₃. All chemicals were reagent grade and the Baker TBP was further purified by sodium carbonate washing prior to use. A description of the impure DHDECMP used is given elsewhere (2).

The waste solutions were passed through the columns of resins at a constant flow rate using a tubing pump. Fractions of the column effluents were collected and analyzed. After the solution was passed, the resin was washed with several column volumes of water. Then methanol was passed to elute the sorbed extractant. Fractions of the eluate were also collected and analyzed.

The concentration of solubilized extractants in the aqueous solutions was determined by extracting the sample with carbon tetrachloride (CCl₄). The C-H adsorption (3.4 microns) of the CCl₄ extract was determined by infrared spectroscopy and compared to standard samples to determine the concentration of extractant. For methanol samples, the methanol was evaporated and the residual extractant dissolved in CCl₄, and treated as described above.

To determine the extractant breakthrough capacity, the ratio of concentration of the extractant in the effluent to the extractant concentration in the feed was plotted against volume of solution fed to the columns. The elution values were obtained by plotting percent extractant eluted vs. volumes of methanol passed.

* P.O. Box 464, Golden, Colorado 80401, USA.
† Current address: IAEA, Vienna International Center, P.O. Box 200, A-1400, Vienna, AUSTRIA.
The breakthrough and elution results are shown in Table 1, and are in all cases at least an average of two runs. The TBP and DBP capacity is greatest with Amberlite XAD-4 resin, and with the slower flow rate used. The elution of extractant is faster with the smaller crosslinked resin (XAD-2), but the extractants are still eluted easily from XAD-4.

Several tests were made recovering TBP from a 5 M HNO₃ solution containing 0.03 g, U/l with XAD-4. No difference was observed in the TBP capacity of the resin between feeds with and without uranium. Most of the uranium appeared to follow the effluent in these tests.

Confirmatory runs were also made of all the solutions containing TBP and DBP using 28 ml of XAD-4 in 1.8 cm diameter columns. The effluent contained <0.01 ml, TBP/1 and <0.02 ml, DBP/1 before approaching breakthrough, and the 20% breakthrough capacity agreed with data in Table 1.

Preliminary runs were also made in removing DHDECMP from 7 M HNO₃. At 20% breakthrough, the breakthrough capacity was approximately 0.01 ml/ml with XAD-2, and 90% DHDECMP could be eluted with 2 ml, methanol. The lower DHDECMP breakthrough capacity, compared to TBP, is probably due to the impure DHDECMP used.

This work on a laboratory scale has shown that several extractants can be effectively removed from aqueous waste solutions with non-ionic, macroporous resins. The best resin for pilot-plant testing appears to be Amberlite XAD-4. The resin should also be capable of removing diluents such as dodecane from waste solutions.

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