

Technical note

# Uranium recovery from industrial effluent by ion exchange—column experiments

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## Abstract

The recovery of uranium from nuclear industrial effluent has been studied using laboratory column and polymeric ion exchange resin. The industrial effluent, at pH around 10, contains uranium (40 mg/L), ammonium (80 g/L) and carbonate (170 g/L) and cannot be discharged without previous treatment. Uranium is in the form of uranyl quadrivalent complex anions  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ . The resin IRA 910 U was employed for its specific application for uranium extraction. Adsorption was carried out at flow rate of 1.0, 2.0, and 5.0 mL/min, which corresponds to a retention time of 10, 5.0 and 2.5 min, respectively. The use of ion the exchange technique makes the recovery of more than 98% of the uranium possible. Elution was carried out with ammonium carbonate solutions and also with the diluted effluent. The eluate contained uranium ranging from 2.4 to 2.7 g/L. The solution eluate might be recycled back into the process with the advantage of saving this valuable metal.

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## 1. Introduction

The nuclear fuel cycle consists of a great number of different mineral-chemical processes. Some of them produce liquid effluents with significant concentrations of uranium. For example, the precipitation process produces the uranyl ammonium tricarbonat (TCAU), a yellow solid. This yellow cake feeds the fluidized bed furnace and is converted into  $\text{UO}_2$ . The exhaust gases from the furnace, which contain uranium, ammonium and carbon dioxide, are reabsorbed in towers by the contact with water stream generating an alkaline uranium rich effluent ([www.inb.gov.br](http://www.inb.gov.br)). In the alkaline medium of the industrial effluent, uranium is capable of forming anionic species mainly as uranyl carbonate complexes,  $[\text{UO}_2(\text{CO}_3)_2]^{2-}$  and  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  (Song et al., 1999).

The strong base anion exchanger is the most suitable resin for uranium when it is mainly present as uranyl carbonate complexes. Anion exchange resins have been successfully employed to recover uranium in mining industry, especially from leach liquor (Merritt, 1971; Kumin, 1972). The recovery of uranium from industrial effluents by using resins was also studied (Huntley, 2001; Seneda et al., 2001; Nascimento et al., 2004). Seneda et al. (2001) assessed the uranium uptake from an industrial ammonium fluoride solution. An effective separation and recovery of uranium fluoride was achieved by determining the suitable pH and the flow rate of uranium solution in the resin column. Nascimento et al. (2004) studied the uranium recovery from acid mine drainage in concentration of 10 mg/L. The authors achieved a uranium resin loading of 28 g/L with an overall recuperation of 94%.

In a previous study, Ladeira and Morais (2005) used ion exchange resins for uranium recovery from synthetic solutions. The authors studied the influence of

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carbonate, fluoride and ammonium on the uranium uptake and concluded that the uranium concentration in solution relative to other ions was the main factor which interfered in the separation process. The results showed that the elevated concentration of carbonate and fluoride completely inhibited the adsorption of uranium and that ammonium had no deleterious effect on the adsorption process. Although the selectivity of the resin for  $[\text{UO}_2\text{CO}_3]_3^{4-}$  is much higher than for  $\text{CO}_3^{2-}$  and  $\text{F}^-$ , if these ions are present in a great content, the resin sites are completely filled by them. Therefore, the extent to which uranium adsorbed in the resin was influenced by its concentration in solution relative to other ions, by pH and also by the relative affinity of the resin for the anionic species.

In the present study, strong base ion exchange resin has been used to recuperate the uranium from a nuclear industrial effluent. This industrial effluent contained uranium around 40 g/L and could not be discharged without previous treatment. This study was motivated by the necessity of finding a viable environmental solution to the problem of storing the industrial effluent. An alternative for this problem would be the recovery of uranium and its recirculation into the industrial process.

## 2. Experimental details

### 2.1. Resin

A commercial strong base resin, type II, Rohm and Haas IRA 910 U, consisting of a polystyrenic matrix, specially developed for the extraction of uranium and with a capacity of 1.0 equiv/L was selected for this study.

### 2.2. Sample

The industrial effluent was supplied by INB (Brazilian Nuclear Industry). The solution was heated until boil during 6 h to decrease the carbonate concentration, before been used in column experiments. According to our previous work (Ladeira and Morais, 2005), prior to the ion exchange contact, the carbonate has to be removed from the effluent up to <5 g/L by evaporation. Chemical analyses of the sample effluent before and after carbonate removal are shown in Table 1.

### 2.3. Adsorption and elution experiments

Trials were carried out in a glass column which operated with the industrial effluent after carbonate removal, at a flow rate of 1, 2 and 5 mL/min, at pH 9.7 and room temperature. Ten milliliter of resin Rohm and Haas IRA 910 U, previously treated with NaCl, was packed into a glass column. The operation was performed by down-

Table 1

Chemical characterization of the industrial effluent before and after carbonate removal

Analyses	Original Industrial effluent	Industrial effluent—after carbonate removal
U	43 mg/L	63 mg/L
$\text{CO}_3^{2-}$	170.9 g/L	4.0 g/L
$\text{F}^-$	0.35 g/L	0.5 g/L
$\text{NH}_3$	78.4 g/L	9.0 g/L
Fe	2 mg/L	3 mg/L
Na	<0.1 mg/L	<0.1 mg/L
pH	10.1	9.7

stream flow using a peristaltic pump. The adsorbed uranium was eluted with ammonium carbonate solution 0.5, 1.0, 2.0 and 3.0 mol/L. The original industrial effluent was diluted and used as eluant also. Dilution was necessary to avoid uranium precipitation into resin. The carbonate concentration in this diluted industrial effluent was 1.3 and 2.3 mol/L.

### 2.4. Uranium content determination

Uranium was determined by both neutron activation and energy-dispersive X-ray spectrometry techniques. The neutron activation analyses consist of exposing a chemical element to a neutron flux producing a new radioactive nuclide. At our laboratory the irradiation is performed in the Triga Marki IPR-R1 reactor. The radioactive nuclide measurement was carried out after two days of cooling based on  $^{239}\text{Np}$  nuclide with a detection limit of 1  $\mu\text{g/mL}$ . The energy-dispersive X-ray spectrometry (Kevex system) has a radioactive source of americium ( $^{241}\text{Am}$ ) for the X-ray generation. The X-ray spectrum formed is due to the K layer excitement, which produces simpler spectra compared to those obtained by the L layer. The detection limit of this technique depends on the atomic number of the element and the counting time.

## 3. Results and discussion

The adsorption performance of the resin for service in column was evaluated by means of adsorption or loading curves as shown in Fig. 1. These curves describe the breakthrough profiles for uranium at different flow rates in which the uranium concentration of the column effluent (mg/L) is plotted against cumulative bed volumes. Bed volume refers to the volume of solution equivalent to the resin volume in place. All curves present a sharp profile which indicates the high affinity of this resin with the metal. Generally, the steepness of the curve is an important characteristic and reflects the efficiency of the resin (Merritt, 1971). Although the profiles seem similar, the BV which corresponds to the

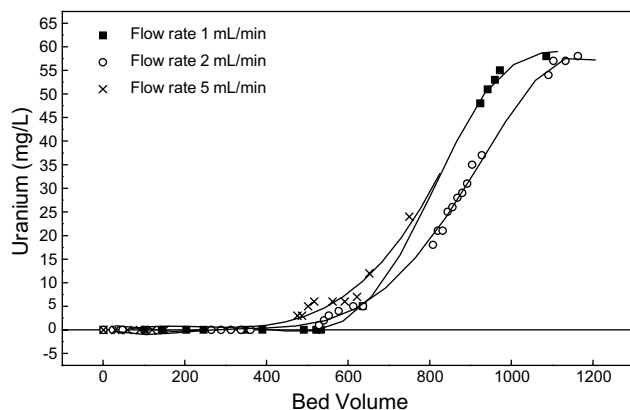


Fig. 1. Breakthrough profiles for different flow rates.

breakthrough point is slightly different. The breakthrough point is usually defined as the volume fed until the effluent reaches a uranium concentration equal to 2% of that in the feeding solution (Merritt, 1971). In this study it was set at 4 mg/L of uranium according to the industry quality criteria. As shown on Fig. 1, the breakthrough point was reached at approximately 600 bed volume (BV) for flow rate of 1 and 2 mL/min. For the flow rate of 5 mL/min the breakthrough point was reached at about 500 BV. Therefore, the recommended operation flow rate should be 2 mL/min which corresponds to the retention time of 5 min. The calculated resin capacity was 40 g of uranium/L for a flow rate of 2 mL/min.

Saturation volume is the volume fed until the uranium concentrations in the feeding and column effluent solutions are equal. These points are shown in Fig. 1, except for flow rate 5 mL/min, and are 1104 BV and 1163 BV, for flow rate 1 and 2 mL/min, respectively. The ratio of the breakthrough volume to the saturation volume reflects the efficiency of the resin. A 0.5 or larger ratio to the breakthrough to saturation volume is considered satisfactory for uranium operations (Merritt, 1971). The ratios determined in this study are 0.55 and 0.51 for flow rate 1 and 2 mL/min, respectively.

Elution was carried out with concentrated carbonate solutions that offered the advantage of recycling the eluate to the industrial circuit. Carbonate has an adverse effect on adsorption and, therefore, is an effective eluting agent. The use of diluted industrial effluent as eluant was also assessed. The industrial effluent, which contains 170 g/L of carbonate, was diluted to prevent uranium precipitation into the resin. Fig. 2 shows the elution curves with laboratory carbonate solutions as well as diluted industrial effluent for a retention time of 10 min. Fast reaction is desired for elution process, with the least possible volume of eluate. Observing the plots one can see that carbonate elution is best accomplished with concentration of 3 mol/L of  $\text{CO}_3^{2-}$  which provided the sharpest elution curve. It was able to extract 99% of

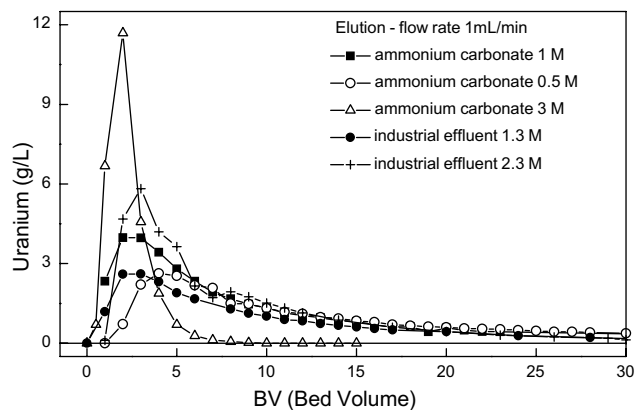


Fig. 2. Elution curves for different  $(\text{NH}_4)_2\text{CO}_3$  concentrations, including diluted industrial effluent. Eluant flow rate of 1 mL/min.

the uranium by using around 8 BV of solution. The average uranium concentration in this eluate was 2.7 g/L. On the other hand, the diluted effluent in a concentration of 2.3 mol/L was the second most efficient agent. In this case it was used 41 BV of carbonate solution and the uranium concentration on the eluate was 2.4 g/L, which gives 98% of overall elution.

The other eluants were not so efficient, presenting a slower elution rate with a long “tailing-off” period required before elution is completed. The results also showed that the increase in carbonate concentration from 0.5 mol/L to 3 mol/L effectively improved the elution at a fixed retention time. The performance of the carbonate solution containing 0.5 mol/L is similar to the diluted industrial effluent 1.3 mol/L. Although the latter has higher carbonate concentration, its poor performance compared to more the diluted one may be explained by the presence of other ions that interferes on the elution process.

#### 4. Conclusion

The resin was efficient for uranium removal from nuclear industrial effluent. The uranium loading capacity was greater than 40 g/L. Although carbonate concentration 3 mol/L was the best eluant, the diluted industrial effluent also presented a good efficiency. The obtained eluate contains from 2.4 to 2.7 g/L of U depending on the eluant used (laboratory carbonate solution or diluted industrial effluent). Both of these eluants are technically suitable for recirculation to the industrial process. The final effluent presented uranium content <4 mg/L according to the industry specification.

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