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Ion exchange resins applied in the removal of uranium from contaminated effluents

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1. Introduction

Advances in studies and technological development have provided increased use of radioisotopes in various activities that include nuclear technology in industry, research, medicine and agriculture (JESUS, 2013). In addition to the benefits produced by the use of nuclear energy, there is an important issue to be studied, which is radioactive waste. With the increasing advancement of nuclear applications, there is a greater production of these environmental liabilities. Radioactive waste has peculiar characteristics and must be controlled and treated, following specific standards and treatment (HIROMOTO et al., 1999).

Ion exchange is an analytical or process technique for separating compounds. It is based on the differences in affinities between the components of a mobile phase and a stationary phase (ABRÃO, 2014). The main objective of this work is to remove uranium from aqueous solutions using the ion exchange technique. In addition, evaluate the removal efficiency of anionic resins Dowex 1-X8 and IRA 910 and evaluate the experimental parameters applicable to the proposed ion exchange operation such as: resin type, pH, flow rate and conditioning.

2. Methodology

2.1 Dowex 1-X8 resin

To carry out the ion exchange experiments, effluent samples provided by the Institute for Energy and Nuclear Research (IPEN) were used. These effluents were obtained in the nuclear fuel production cycle after the fluoridation step to obtain UF_4 (uranium tetrachloride) and UF_6 (uranium hexafluoride).

The first ion exchange runs in this work were performed using Dowex 1-X8 resin. The anionic resin was chosen since the experimental strategy was based on the retention of the main uranium anions dissolved in the effluent. A 2 cm internal diameter and 20 cm high glass column was used. The column was packed with 30 ml of resin immersed in distilled water.

Initially, the resin was washed to eliminate impurities and degradation products. Washing was performed with 4M hydrochloric acid, 2M sodium hydroxide and ethanol solutions. In bach, the resin was conditioned with 0.1 M HCl to return to the Cl^- form, after this procedure successive washings with distilled water were carried out in order to adjust the pH to 7.

Table I shows the experimental conditions of the ion exchange runs carried out with Dowex 1-X8 resin, the experiments were named as Experiment 1 and Experiment 2.

Table I - Experimental conditions of ion exchange procedures with Dowex 1-X8 resin.

Parameters	Experiment 1	Experiment 2
pH	7	7
Resin volume (mL)	30	30
Flow rate (mL min^{-1})	4,5	5,5
Sample volume (L)	0,05	1
U concentration (mg L^{-1})	163	163
Temperature (°C)	21	21

The effluent samples were percolated down the column and collected in centrifuge tubes. After being collected in 50 mL aliquots, the samples were analyzed by Optical Emission Spectrometry with Argon Plasma Source, ICP-OES, at the Center for Chemistry and Environment (CEQMA) at IPEN.

2.2 IRA 910 resin

A 2 cm internal diameter and 20 cm high glass column was used. The column was packed with 30 ml of resin. At this stage, the resin was washed to eliminate impurities and degradation products. Washing was performed with 4 M hydrochloric acid, 2 M sodium hydroxide and ethanol solutions, following the procedure performed with the Dowex 1-X8. Subsequently, in bach, successive washings were done with distilled water until the resin pH was stabilized at 7.

The experiments were called Experiment 3, 4, 5 and 6. The parameters were the same, changing only the pH value of each resin. The pH values were adjusted in bach by slowly adding drops of HCl or NaOH solutions and determined in a pHmeter, Model 420A, Orion Analyzer, calibrated with certified buffer solutions pH 7 and pH 4. Table II presents the experimental conditions of each procedure. The 1L effluent samples were percolated down the column and collected in centrifuge tubes. After being collected in 50 mL aliquots, the samples were analyzed by ICP-OES, at the Center for Chemistry and Environment (CEQMA) at IPEN.

Table II - Experimental conditions of ion exchange procedures with IRA 910 resin.

	Experiments			
Parameters	**3**	**4**	**5**	**6**
pH	3	5	7	8
Resin (g)	30	30	30	30
Flow rate (mL.min^{-1})	4,5	4,5	4,5	4,5
Sample volume (L)	1	1	1	1
U concentration (mg L^{-1})	163	163	163	163

3. Results and Discussion

3.1 Dowex 1-X8 resin

As shown in Table III, the uranium ions are retained right at the beginning of the passage of the solution through the column, thus obtaining the separation of the uranyl ions from the effluent solution. The U recovery was 99.97% in Experiment 1 and 99.93% in Experiment 2 (Table IV), reaching the initially expected result.

Table III - Initial and final uranium concentrations in Experiments 1 and 2.

Total U concentration	**Experiment 1**	**Experiment 2**
Start	163 mg L^{-1}	163 mg L^{-1}
End	0,053 mg L^{-1}	0,122 mg L^{-1}

The two experiments were carried out under the same conditions, differing only in flow. Where 1 took place at a flow rate of 4.5 mL min-1 and 2 at 5.5 mL min-1. From the results obtained, it is possible to observe that even changing the flow rate, the Dowex 1-X8 resin removed more than 90% of the ions from the solution.

Despite having obtained a high removal percentage (Table IV), the values are not sufficient to meet CONAMA Resolution 357/2005. It is believed that the initial pH of the solution (pH 7) facilitated the presence of free H+ in the resin, thus interfering with the interaction and, consequently, with the retention in its entirety of the anionic uranium complexes with the OH- ions present in the resin.

Table IV – Percentage of removal of experiments performed.

Experiment	**Removal (%)**
1	99,97

2	99,92

The results of these experiments, for having shown almost total retention of anionic uranium complexes, contributed to the understanding of what happens in the ion exchange run using the effluent solution, these initial experiments contributed to the development of the next items.

3.2 IRA 910 resin

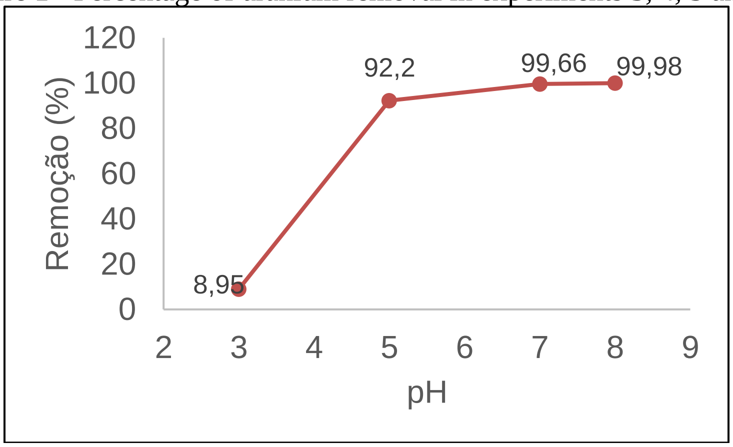
In the initial tests with the IRA 910 resin, experiments 3, 4, 5 and 6 aimed to evaluate the behavior of uranium removal by varying the pH of the resin, in bach, between 3 and 8. Table V shows that in pHs higher (7 and 8) obtained a final uranium concentration of 0.55 and 0.02 mg L-1, respectively. Experiment 6 reached 99.98% efficiency and with this, reached the value established by CONAMA Resolution 357/2005.

Table V - Experiments performed at four different pH values

	Experiments			
	3	**4**	**5**	**6**
Total U concentration (mg L^{-1})	**pH 3**	**pH 5**	**pH 7**	**pH 8**
Start	163	163	163	163
End	148,40	12,70	0,55	0,02

Figure 1 shows that at pH 3 almost all uranium (IV) ions passed straight through the column without significant retention. This is because at low pH values there is a greater formation of cationic uranium complexes present in the solution. It is observed that, at pH 5, the retention of ions in the column increases and reaches the value of 99.98% retention at pH 8.

Figure 1 - Percentage of uranium removal in experiments 3, 4, 5 and 6.



4. Conclusions

The results indicate that the ion exchange technique can be applied for the removal of uranium from aqueous solutions. Using Dowex 1-X8 resin, a removal of 99.97% of uranium and a solution with 0.05 mg L^{-1} was obtained. At pH 8, the IRA 910 resin achieved 99.98% efficiency for removing uranyl ions (UO_2^{2+}).

Even if still on bench scale, the entire cycle of this process can be easily reproduced for higher scales, such as a pilot assembly. Furthermore, ion exchange resins are an easy-to-purchase solution on the market. For the application in the treatment of radioactive liquid effluents, this condition is a great advantage as it greatly reduces the cost of the process as a whole.

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