USING THE SOFTWARE OriginPro® 9.1.0 AS A TOOL FOR OPTIMIZATION OF THE PROCESS OF REMOVING URANIUM CONTAMINATED WATER SOUR - PHASES AND LOADING ELUTION

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Abstract: The decontamination of uranium contaminated acidic waters consists of selective removal of uranium by ion exchange using strong base anion resin. This is a process that can dramatically reduce ionic contaminants from the effluent concentration levels established by regulatory agencies. This document aims to describe the optimization of Ion Exchange (IT) process using OriginPro ® 9.1.0 software in phases of loading and elution, adopted for the removal of uranium from waters originating from acid mine drainage (AMD) from Basin Nestor Figueiredo (BNF) of Ore Treatment Unit (UTM), located in Caldas, Minas Gerais.

Keywords: Software OriginPro ® 9.1.0, optimization, removal of uranium contaminated water and ion exchange.

1. INTRODUCTION

DC 4401 (Decanter 4401), is returned to the pit of the mine by pumps and the supernatant is released into the medium currently in BNF collected water is pumped to the mine pit, adding to the existing volume there, an average flow 130 m^3 / h, and then goes directly to the treatment area AA 440 with hydrated lime, raising the pH 3.5 to 11.0, for precipitation of contaminants, yielding a precipitate, called Duca (Calcium diuranate) containing about 3 g_ (U_3 O_8) / kg_sólido. The precipitate, separated in the decanter thickener environment.

It is estimated that annually are deposited in the pit of the mine about 20 tons of U3O8 resulting from the treatment of acidic waters with hydrated lime. The contribution of BNF this amount is 55 to 60% of U3O8 generated in the treatment with lime.

Decontamination of uranium by Ion Exchange (IT) process allows the final treatment of solid waste BNF is virtually free of uranium and can be arranged with less radiological impact. Additionally you can take advantage of the extracted uranium, thereby aiding the economic sustainability of the decontamination unit and generating interest for the good of society, given the principle of justification set out in Standard CNEN-NN-3.01: 2011.

This study aims to optimize the Ion Exchange Unit (ICU) using Sotfware OriginPro ® 9.1.0 through mathematical simulation of the behavior of the ion-exchange column in the retention of uranium, helping to identify the process parameters.

2. MATERIALS AND METHODS

For this study, the industrial plant Ion Exchange UTM de Caldas was used, of which the main structures, equipment, supplies and reagents used in a simplified way were:

- Acidic water contaminated arising from BNF;
- Multimedia Filters: Responsible for the removal of micro-organisms and suspended solids from water arising from the BNF;
- Three Column Ion Exchange upflow 5 m^3 containing anion resin (bed volume - V/L- 5 m^3);
- Solution of NaCl 1.5 mol / L sulfuric acid medium in 0.05 mol / L;
- Other equipment: hydraulic pumps, reagent reservoir, reservoir of acidic water from BNF, clean water reservoir, reservoir eluate, valves, lines connecting the pipes to test treatment plant effluents, among others.

In this study the resin Ambersep ® Cl 920U, manufactured by Rohm and Haas Company (now Dow Chemical), which has a minimum theoretical capacity of 1.0 eq / L and capable of exchanging chloride resin bound by uranyl sulfate was used ([UO_2 (SO_4) _x] ^ ((2-2x))) present in the water.

Process steps of UTI include:

i. Loading - Water flow through the columns of the BNF extraction and loading the resin with uranium - Continuous Step;
ii. Elution - Removal of uranium from the resin using a solution of acidified sodium chloride - Step by batch;
iii. Dry - Dry the resin with clean water to remove the residual chloride solution - Step by batch, and;
iv. Precipitation and thickening of DUS - Precipitation and thickening of uranium concentrate with sodium hydroxide (soda) - Step by batch;

This study does not address the optimization phases of washing, precipitation and thickening of DUS and therefore more detailed information of these steps are not presented.

The ICU system operates with three columns of 5 m^3 each. Two columns in series (Column 1 - loading; Column 2 - Polishing) and third column (Column 3 - stand-by) outside ready for regime change operation.

At the loading stage for gathering information about the dynamics of the operation, input consumption, frequency and duration of cycles, etc.. scheme was adopted for collecting samples equalized throughout the day in three daily shifts. The withdrawal of the sample at the sampling points was performed to ensure, insofar as possible, the representativeness of the sample. Aliquots of 500 ml were taken per sampling point, and, in Ion Exchange Columns, these were sampled at the entrance of the first column, the same column in the output (load) and the outlet of the second column (Polish), generating a total 9 samples a day.

Sampling in the elution step included collecting samples of the eluent and its inputs, eluate and washings. Thus it was possible to measure the cost of inputs and the uranium recovery system. The sampling frequency of the eluted solution varied, since it depended on the operating conditions. Sampling was performed every 1 m^3 of eluent solution or washing system, passing by the system. The final operation is determined by the uranium content in the washing system (approximately 24 m^3 total) water.

The samples were sent to the laboratory UTM, and the concentrations of certain uranium. The samples were analyzed spectrophotometrically in the ultraviolet / visible using Arsenazo III as a complexing agent, or via ICP-OES varying the method according to the level found.

After generating the data, we used the OriginPro ® 9.1.0 software for data organization, plotting and mathematical models of the retention behavior of uranium by ion exchangers.

3. RESULTS AND DISCUSSION

The operating process parameters cited in the text were obtained from the operating system test. Acid filtered water was pumped into the set of ion exchange columns. The columns operated in fixed bed mode, with upward flow operation and the effluent of the system, ie, acid low in uranium, water went to the Effluent Treatment Station (AA 440) for decontamination of other metals dissolved.

The average rate of percolation of the system was 26 VL / h (Bed volume per hour). As the volume of strong base anion resin per column, equal to 5 m^3 average system flow rate was 130 m^3 / h. The residence time was considered to be 2.3 minutes.

Due to the characteristics of chemical equilibrium of uranium between the resin and the water may be leaking uranium from the main column during loading, such leakage occurs due to the approach to saturation of the column (breakthrough). To avoid loss of material, and impaired quality of the system uses a second column with the same dimensions and characteristics, in series with the load. During operation this polishing system is always active. It is established as a safety margin of the system when changing the output stream of the polishing column reaches the concentration of 2 mg_U / L (breakthrough adopted).

For the process can take place continuously, was considered a carousel system between three columns, according to the scheme shown below in Table 1.

Table 1 - Carousel of operation of the ion exchange columns.

Regime	Loading	Polish	Elution
A	Column 1	Column 2	Column 3
B	Column 2	Column 3	Column 1
C	Column 3	Column 1	Column 2

Considering the scheme of Table 1 carousel operation is conducted as follows:

- begins charging the column 1, column 2 acting as a polishing system and column 3 on stand-by.
- The loading cycle is considered complete when the output stream from column 2 to reach a concentration of 2 mg_U / L.
- The column 1 is disconnected from the system for performing elution.
- Column 2, which was operating in polish, shall enter into charging cycle and column 3, which was in standby, enter the polishing cycle.
- Start of the new regime.
- Perform the elution column 1, then the operation is completed, this column goes into stand-by.

The flow of the eluting solution operated as a fixed bed in a downward direction. Elution of uranium is made by passing NaCl solution 1.5 mol / l in sulfuric acid medium than 0.05 mol / L, at a percolation rate of 2 VL / h over the resin by noting the time applying the solution in 60 minutes. The eluate followed for the eluate reservoir for subsequent precipitation

3.1. Mathematical modeling of the concentrations of uranium in Rafinate and evaluate

3.1.1. Supply of Data Columns

Figure 1 shows the behavior of the uranium concentration of BNF water during the tests. Tool for smoothing adjacent average of 20 points available in OriginPro ® software and through this smoothing, it can be seen that the content of food is not very far from a linear behavior was used. The average of the results obtained for this concentration was 7.76 mg_U / L. This value represents the expected speaker output load when this finding is fully saturated result.

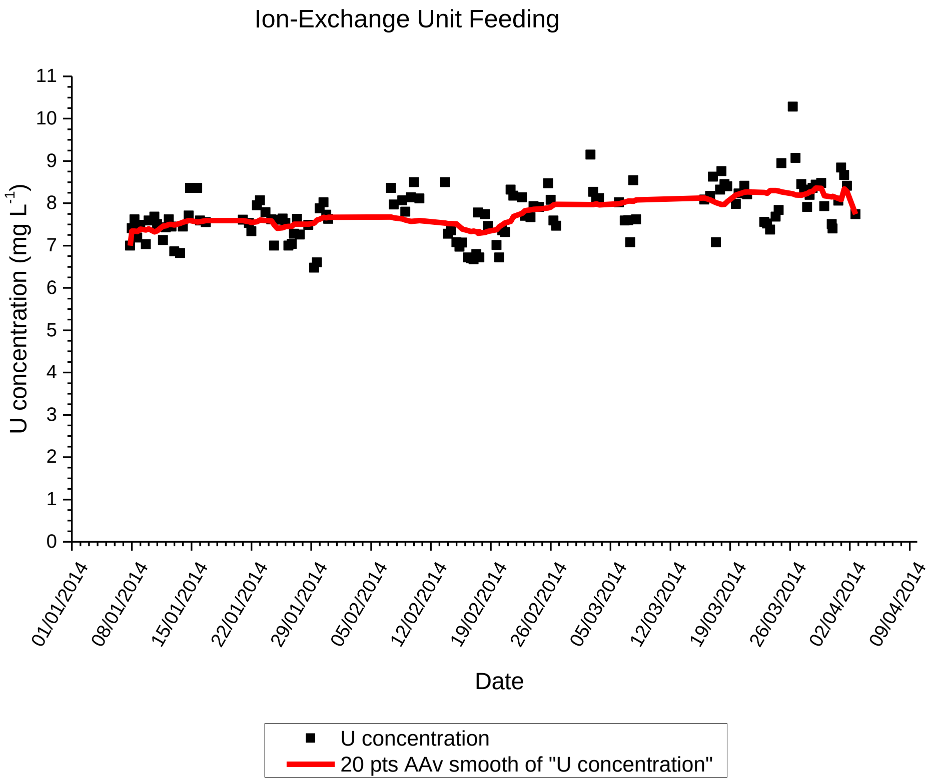

Figure 1 - Concentration of uranium from water BNF during the Test Unit Ion Exchange

3.1.2. Loading of columns

During the test period of 5 complete cycles of loading of the columns were obtained, whereas a loading cycle comprises the operations of polishing and loading. Figure 2 below shows the results of overlapping speaker output during cycling. From these results it was possible to estimate what will be the future of his columns during loading cycles and behavior, based on the parameters obtained, estimating the volume to the point of breakthrough is reached.

The data used for the model are based on leachate volume rather than time, because during loading there were no shutdowns due to intermittency of supply effluent (condition in which no effluent to be treated) or stops for maintenance.

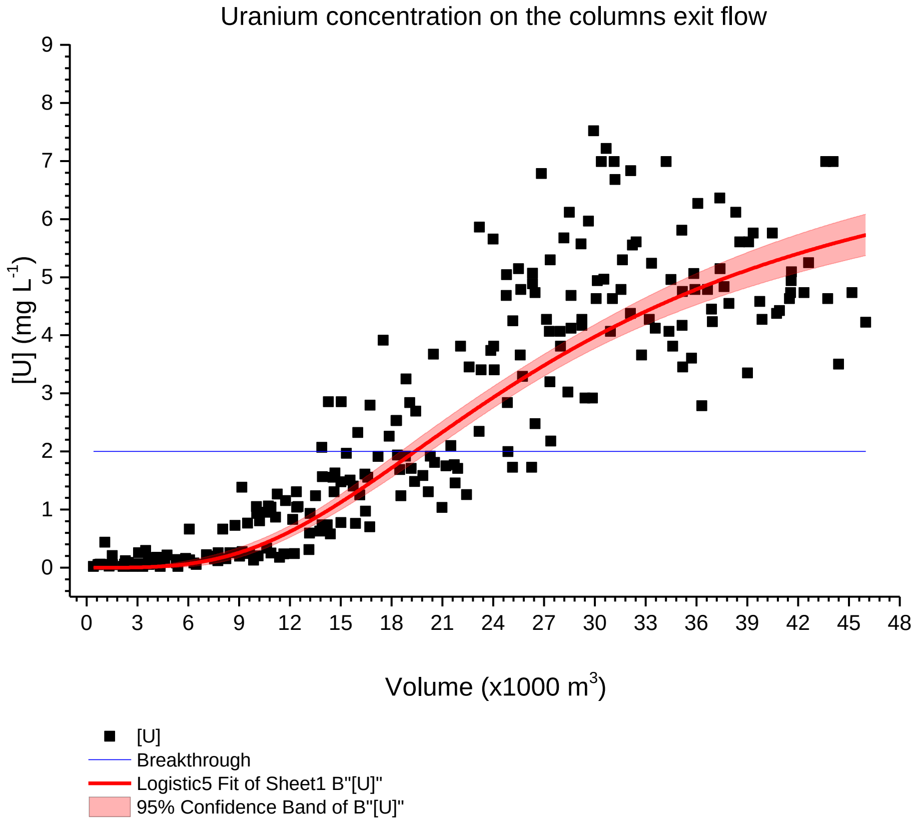

Figure 2 - Concentration of uranium in the speaker output during the 5 charging cycles.

The uranium concentration in the column volumes exiting the model follows a sigmoidal (S-shaped). This model can be explained due to:

i. Concentration changes in the input column. Initially the column is fed with the effluent of lower concentration (polishing) and after regime change is fed with the effluent of higher concentration (loading);
ii. Variation of uranium retention efficiency due to the chemical equilibrium during charging (the higher the loading uranium retained in the lower retention efficiency of the column);

From the models of sigmoidal functions by available software was selected one that had better fit to the data. This adjustment was observed for the highest value of R^2 found among all models. Due to changes in methodology on the analysis of uranium (ICP OES and spectrophotometry) used was decided to consider a statistical weight function for calculating the fit of the model.

Table 2 below shows the data obtained from the model calculated using the software. The [U_3 O_8] _min and [U_3 O_8] _max were defined constants from the expected to the column ([U_3 O_8] results _min is the smallest value that should come out of the column and [U_3 O_8] _max represents the value when the column is saturated). The R^2 value indicates a good fit of the forward model to the experimental data.

Table 2 - Data sigmoidal model for the loading of columns.

Model	**Logistic**
Equation	$[U_3O_8] = [U_3O_8]_{min} + \frac{([U_3O_8]_{max} - [U_3O_8]_{min})}{\left(1+\left(\frac{x_0}{V}\right)^h\right)^s}$
R^2_{red}	0,299
R^2_{ajust}	0,875
$[U_3O_8]_{min}$	0,00
$[U_3O_8]_{max}$	7,76
x_0	20.427
h	2,09
s	1,81

From this model it can be assumed that the volume of effluent necessary for the breakthrough point is reached. It is estimated that this volume is 19,300 m^3. Considering an average flow of 130 m^3 / h, and uninterrupted operation, this volume would be reached after approximately 6 days. After this time the output concentration of the loading column is estimated at 5 mg_U / L value still below the saturation concentration of the column.

This term ensures that there is sufficient time to perform the steps of elution and possible maintenance to be performed on adjacent systems

3.2. Process efficiency

The from the proposed model it is possible to evaluate the efficiency of retention of uranium in each work cycle. Is adopted as the basis of uranium expected to feed out of loading and departure of polishing. The area between the uranium corresponds to the expected functions retained by the system.

Figure 3 shows the area of intersection of the functions.

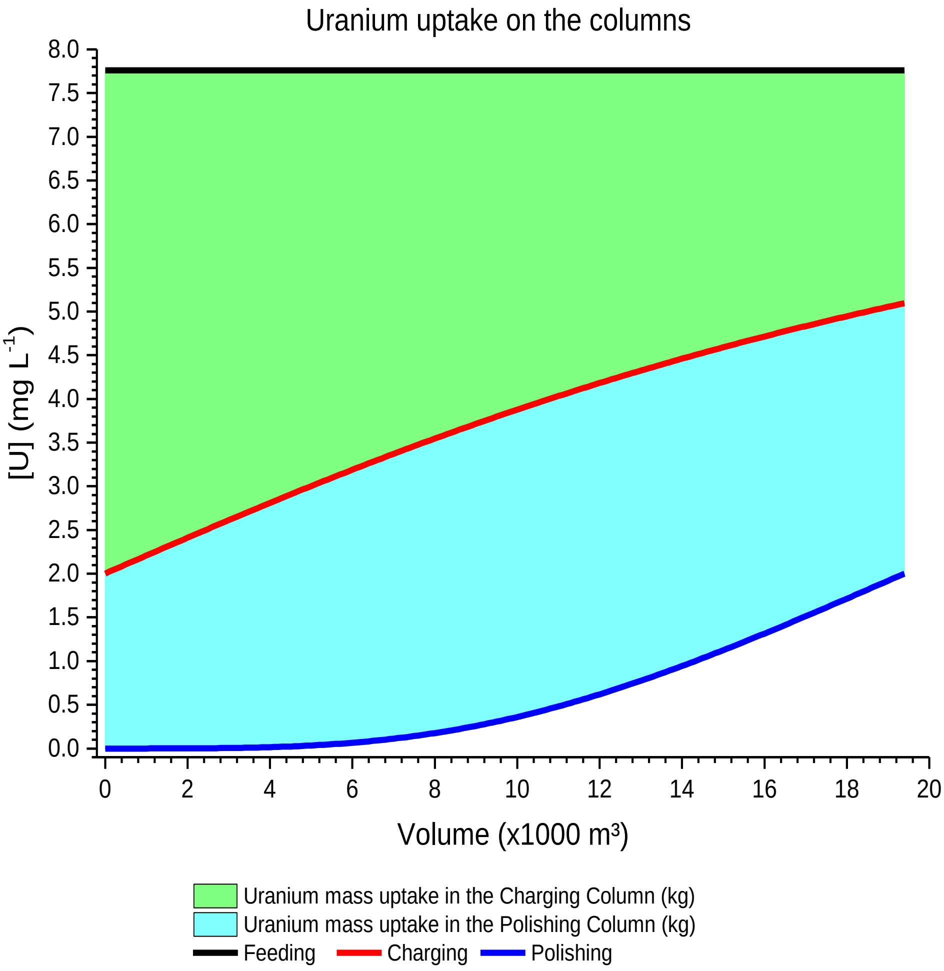

Figure 3 - Model of retention efficiency of uranium in the system.

To calculate the masses parameters of interest relating to compute the area under the power curve (150.54 kg) and the area under the curve of polishing (11.24 kg). The difference between these two areas is the mass of retained (139.29 kg) in the system for a uranium scheme.

The ratio of the mass in the system (power) and the mass of retained uranium corresponds to the retention efficiency of the system, ie the ICU operates at 92.5% efficiency.

3.3 Elution of the columns

During the test period of six complete cycles of elution the column was obtained. Figure 4 below shows the results of overlapping samples of eluate. From these results it is possible to estimate what the future behavior of the columns during their cycles of elution.

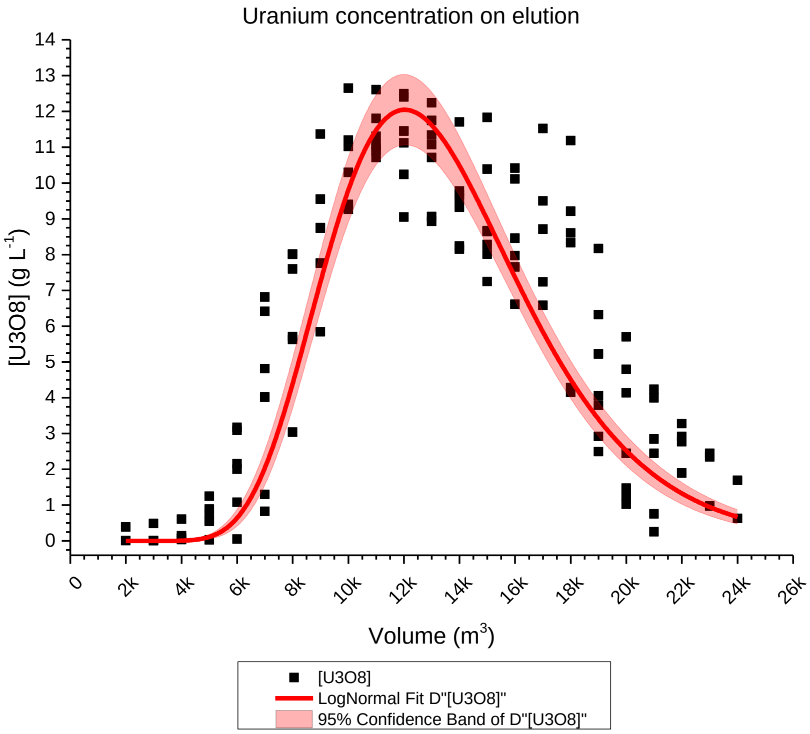

Figure 4 – Concentration of uranium in the speaker output during the 6 cycles of elution.

Table 3 below shows the data obtained from the model calculated using the OriginPro ® 9.1.0 software. The parameter [U_3 O_8] _i defined constant (0.00) expected from the concentration of U3O8 to the water used to prepare the eluting solution and washing results. The R^2 value indicates a good fit of the forward model to the experimental data.

A log-normal model was chosen due to the theoretical best fit to the experimental data parameters. It is considered that the change between the operation of washing and slow elution contribute significantly to the response has such behavior .

Table 3 - Data log-normal for the elution of the column model.

Model	Log-normal
Equation	$[U_3O_8] = [U_3O_8]_i + \frac{A}{V\sigma\sqrt{(2\pi)}} e^{\frac{-\left[ln\left(\frac{V}{\mu}\right)\right]^2}{2\sigma^2}}$
$□^2_{red}$	0,769
R^2_{ajust}	0,870
$[U_3O_8]_i$	0,00
□	13065
□	0,287
A	108810

From this model it is possible to calculate what the expected load of uranium to the columns. Using the following equation (1) calculates the mass of U3O8 eluted from the columns.

$$m_{U_3O_8 retained} = \int_{V_i}^{V_f} \left([U_3O_8]_i + \frac{A}{V\sigma\sqrt{(2\pi)}} e^{\frac{-\left[ln\left(\frac{V}{\mu}\right)\right]^2}{2\sigma^2}} \right) dV \quad (1)$$

Whereas Vi and Vf = 1 L = 24,000 L obtains the result of the load uranium equal to 107 kg_ (U_3 O_8) / column. Figure 5 below shows the relationship between the elution volume, mass and concentration of the eluate eluted U3O8.

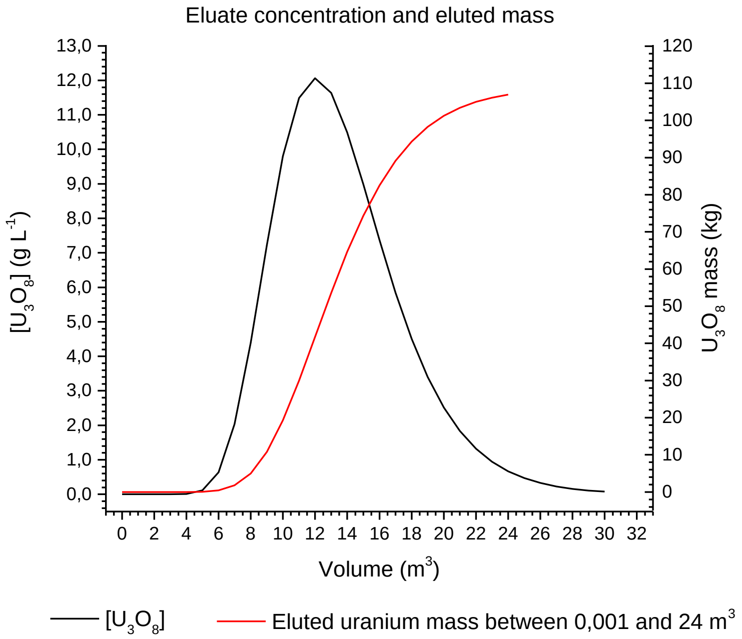

Figura 5 – Graph of the relationship between concentration of the eluate eluted mass and elution volume.

For the operational capacity retention recalculates this value is a function of the column volume. The result shows that the columns operate with a capacity of 21.4 g_ (U_3 O_8) / L_resina, ie 76% of its expected capacity.

4. CONCLUSION

The study enabled the creation of a mathematical model by, for simulating the operation of the Ion Exchange Columns concerned OriginPro ® 9.1.0 software, with uranium concentrations in the leachate both loading and in Polish.

From the model, and set the point breakthrought Columns can calculate the parameters of volume saturation of the columns, period of operation of the plant and efficiency of ICU, which in this case amounted to 92.5%.

The created model can be used on other occasions, to simulate different conditions, just to give input parameters of the equation, allowing to predict the behavior of the ICU, establish and optimize the parameters of uranium concentration in the eluate, inputs used, cycle time, among others, which satisfies the goal proposed by the study.

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