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A purification process for the tetrauranium fluoride effluent

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1. Introduction

The Nuclear Fuel Center (CECON) at IPEN (Nuclear and Energy Research Institute from Brazil) is scaling up (by a factor of 6) the production of nuclear fuel elements based on uranium silicide, to assure the supply for the new Brazilian Multipurpose Reactor (RMB) [1], [2]. In this sense, high quantities of radioactive waste are expected to be generated, increasing the amount of waste accumulated at the plant and sent to the radioactive waste management of IPEN.

In this context, the management of liquid residues produced in the nuclear fuel fabrication process pose significant challenges that necessitate effective management strategies. Most of these residues (radioactive or not) are already properly chemically treated at CECON, and some are reused at the production process. However, a part of the residues still does not have an established procedure for its reuse, so they remain accumulated at the facility, or they are sent as waste to the Radioactive Waste Management Department at IPEN, in accordance with safeguards, safety and security regulations.

Uranium tetrafluoride (UF_4) is compound that plays a crucial role in nuclear fuel technology as an intermediate product for producing metallic uranium, which is integral for U_3Si_2 production processes [3]. At CECON, UF_4 is precipitated from the ox reduction between UO_2F_2 solution and stannous chloride in the presence of HF. After this step, UF_4 must be washed with water to remove the excess of tin and fluorine from the precipitate. As a result, this aqueous solution becomes contaminated and must be purified before discharge to conventional sewage system. The main objective of this work is to develop a route to treat this effluent in order to be discharged as regular sewage. After chemical steps, Covalent Organic Framework (COF) membranes were used to adsorb the remaining uranium in the nuclear fuel production waste solution in such a way that the effluent was considered de-contaminated.

The management of these liquid residues is important for ensuring environmental protection, operational safety, and regulatory compliance within the nuclear industry.

2. Methodology

The effluent was generated as a byproduct of the UF_4 produced during the routine fabrication of the Nuclear Fuel Elements at CECON.
The treatment process of the liquid effluent starts by adding Na_2CO_3 to the contaminated aqueous solution (from UF_4 washing), in order to hydrolyze and precipitate tin as $Sn(OH)_4$. After filtration, the pH of the solution is lowered back up to -2.0 with HCl, in order to be able to precipitate the CaF_2 with the following reaction with CaO.
The remaining solution still has some uranium contamination and its removal using membranes based on molecular sieves is the main subject of this work. The Covalent Organic Framework (COF) membranes were fabricated using a procedure described elsewhere [4]. Membrane filtration experiments with aqueous uranium solutions were conducted in a 10 mL Amicon filtration cell. The driving force for permeation in the experiments was provided by compressed nitrogen gas.
pH was measured by a benchtop meter. Sn and U concentrations were determined by Induced Coupled Plasma Optical Emission Spectrometry (ICP-OES, Spectro Spectroblue). Fluorine was determined by specific electrode in solution.

3. Results and Discussion

The initial solution had the following characteristics described in table I.

Table I: Initial characteristics of the aqueous effluent generated at the UF_4 washing step process.

U^{+6} concentration ($mg \cdot L^{-1}$)	**Other contaminants**	**pH**
120	Sn^{4+} 50$g \cdot L^{-1}$, F^- 47$g \cdot L^{-1}$, Cl^- 30 $mg \cdot L^{-1}$	2,43

The chemical procedure employed (as described in methodology section), was successful in removing the most of $Sn^{4+}$and F^-, that were deleterious for the membrane use. Most of uranium was also co-precipitated from the solution in this step, what is beneficial, since the solid form is a much-reduced volume and stable form to storage contaminated waste.
The remaining solution had pH of 10 and U^{6+} concentration of 8.3 $mg \cdot L^{-1}$, what is still high according to the Brazilian standards for 20% ^{235}U enriched uranium discharge [5], calculated as 0.2155 $mg \cdot L^{-1}$.
In this sense, tests were performed using the COF membranes, in a pressurized stirring cell (fig. 1).

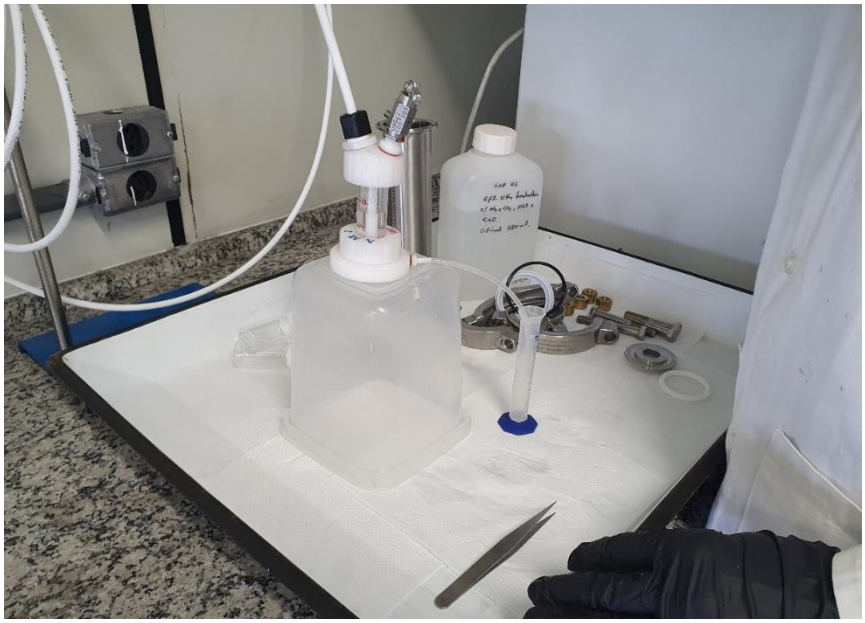

Figure 1: Pressurized stirred cell used to flow the aqueous solution thru the Covalent Organic Framework membranes.

Several tests were performed, and the results are summarized in table II. The permeation batch # concerns the sequence which the filtrate was taken (1^{st+}, 2^{nd} or 3^{rd}) to assess any possible saturation of the membrane.

Table II: Uranium concentration after the tests performed with the Covalent Organic Framework membranes.

Sample name	Membrane used	Permeation batch #	$[U^{+}]$ content ($mg \cdot L^{-1}$)
DS-2B	Plain enamine-linked COF	2	0.14 ± 0.05
DS-2C	Plain enamine-linked COF	3	0.13 ± 0.03
DS-4A	Sulfonated enamine-linked COF	1	< 0.01
DS-4B	Sulfonated enamine-linked COF	2	0.14 ± 0.02
DS-4C	Sulfonated enamine-linked COF	3	0.18 ± 0.04
DS-5A	Sulfonated and ammoniated-linked COF	1	< 0.01
DS-5B	Sulfonated and ammoniated-linked COF	2	< 0.01
DS-5C	Sulfonated and ammoniated-linked COF	3	< 0.01

4. Conclusions

The utilization of the molecular sieves membranes has demonstrated to be effective in reducing the uranium content from contaminated aqueous solutions, however, in many cases the final uranium concentration was too close to the detection limit of the ICP-OES equipment. In this sense new test should be employed using ICP-MS, that would extend the detection limit and produce more accurate results.

This innovative approach not only demonstrates significant potential in mitigating environmental hazards but also offers a promising avenue for enhancing the sustainability of waste management practices in nuclear fuel production. By leveraging membrane technology, the process showcases a greener and more cost-effective solution for uranium remediation, paving the way for a more efficient and environmentally conscious approach to addressing radioactive contamination challenges.

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