RESIDUE-FREE NUCLEAR FUEL PRODUCTION AT IPEN, BRAZIL

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Abstract

The Nuclear Fuel Center (CECON) at IPEN (Instituto de Pesquisas Energeticas e Nucleares), Brazil, will scale up the production of nuclear fuel elements based on uranium silicide in the coming years to ensure a future supply for the planned Brazilian Multipurpose Reactor (RMB). This expansion is expected to generate significant amounts of liquid radioactive waste (LRW) containing low enriched uranium (LEU). However, a portion of this LRW currently lacks a defined procedure for reutilization, resulting in their accumulation at the facility or their transfer as waste to the Institute's Radioactive Waste Management Department, in compliance with safeguards, safety, and security regulations. The increasing volumes of LRW present a significant challenge due to the difficulties associated with long-term storage of radioactive material in liquid matrix, which requires stringent containment measures to prevent leaks and contamination. In this study, LRW from the UF_4 production process were treated with biochar (BC) and covalent organic framework membrane (COF) to reduce uranium concentrations. The results indicate that uranium levels could be lowered to below 0.22 $mg \cdot L^{-1}$, which meets the Brazilian standard for discharge as regular sewage.

Keywords: *Uranium, UF_4, Liquid Radioactive Waste (LRW), Biochar, Covalent organic framework (COF)*

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 ensure a sufficient supply for the future Brazilian Multipurpose Reactor (RMB) [1, 2]. Consequently, a significant increase in liquid radioactive waste (LRW) generation is anticipated, leading to greater accumulation of LRW at the CECON plant and at IPEN's Radioactive Waste Management facility (CERER). In this scenario, the management of LRW produced in the nuclear fuel fabrication process poses significant challenges that call for effective management strategies.

Among the various uranium forms involved in the nuclear fuel element production process, uranium tetrafluoride (UF_4) plays a crucial role as an intermediate compound in producing metallic uranium, which is integral for uranium silicide (U_3Si_2) production processes [3, 4]. At CECON, UF_4 is precipitated from the ox-reduction between uranyl fluoride UO_2F_2 solution and stannous chloride in the presence of hydrofluoric acid (HF). Subsequently, UF_4 undergoes a washing process with water to remove the excess of tin and fluorine from the precipitate. As a result, the remaining effluent is classified as LRW because it contains uranium in concentrations that surpasses the permissible thresholds established by the Brazilian National Nuclear Energy Commission (CNEN), [5].

The generated LRW undergo appropriate chemical treatment at CECON to remove fluoride and stannous ions, ensuring compliance with the Brazilian environmental standards [6]. Although a large portion of the uranium contained in the liquid waste is removed during these initial pre-treatment operations, its levels in the treated waste still exceed the limits established by CNEN regulations [5]. In this context, it is essential to develop a method to treat the waste in order to reduce its uranium concentration to levels suitable for discharge as regular sewage. The limit in liquid effluents containing low enriched uranium (LEU, up to 20% of ^{235}U), as defined by CNEN, is 0.22 mg U/liter of solution [5].

Biochar (BC), a type of charcoal produced from organic materials through pyrolysis, can be successfully employed for this purpose due to its adsorption capacity, attributed to its extensive surface area and porosity, facilitating the adsorption of heavy metal ions from solutions [7, 8]. Moreover, biochar typically exhibits chemical stability and offers a cost-effective solution, since it can be produced from inexpensive, renewable biomass feedstocks.

Recent studies have demonstrated the effectiveness of biochar in the uranium removal from aqueous solutions. Liao et al. [9] reported that pig manure-derived biochar, treated with $KMnO_4$ and H_2O_2, achieved maximum adsorption capacities of 979.3 mg/g and 661.7 mg/g for uranium (U(VI)), significantly outperforming untreated biochar. Similarly, Guilhen et al. [10] found that activated biochar derived from macauba endocarp removed up to 99.2% of U(VI) from aqueous solution, demonstrating a marked increase in adsorption efficiency after activation. Furthermore, Liao et al. [11] developed bismuth-impregnated biochar, which exhibited a removal efficiency of 93.9% for U(VI) and a high adsorption capacity of 516.5 mg/g.

The modifications in biochar composition, such as the introduction of functional groups and increased surface area, have been shown to enhance the interaction with U(VI), as described in studies by Li et al. [12] and Ahmed et al. [13], where modifications led to substantial improvements in uranium adsorption. These findings collectively underscore the biochar potential as a sustainable and effective adsorbent for uranium remediation in aqueous wastes [9-13].

In parallel, covalent organic framework membranes (COF) are a class of advanced membrane materials composed of highly ordered, porous organic polymers. Key features of COF membranes include tunable pore size, structure and functionality at the molecular level, depending on the monomers [14].

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

Experimental set-up

The effluent generated in the UF_4 precipitation step was subjected to an initial chemical treatment, where Sn^{2+} and F^- ions were removed through the sequential addition of sodium carbonate (Na_2CO_3) and calcium oxide (CaO), promoting the precipitation of these species as tin (VI) hydroxide ($Sn(OH)_4$) and calcium fluoride (CaF_2). Simultaneously, uranium, which is in the form of uranyl (VI) fluoride (UO_2F_2), is partially precipitated as calcium diuranate (DUCA, CaU_2O_7).

The pre-treatment results in a solution that meets the industrial effluent discharge standards in Brazil of for Sn and F [6]. However, the uranium concentration in solution still remains too high for regular sewage discharge (approx. 5 mg/L). To reduce the uranium concentration even further, the resulting solution was subjected to two parallel adsorption experiments: 1) adsorption experiment with activated biochar (BC) and 2) adsorption with COF.

Adsorption experiment with activated biochar (BC)

BC was placed in contact with a U solution at 5 mg/L using a dosage of 10g of biochar per liter of solution. The system BC-solution was kept under 120 rpm agitation for 3h in room temperature conditions.

BC was prepared from macauba endocarp, an organic agricultural residue, using a pyrolysis furnace at 350 °C (therefore called ″BC350″). Subsequently, this material was subjected to physical activation using CO_2 at 850 °C (″BC350-A″) in order to increase its specific surface area and, consequently, its adsorption capacity [15]. The macauba palm is native to various regions of South America, including Brazil, and is known for its versatility and ecological benefits. The endocarp, or the hard shell surrounding the seed within the fruit, is typically discarded as waste after the fruit is processed for various purposes, such as extracting oil. Repurposing the endocarp is not only interesting for reducing waste and mitigating environmental impacts, but also adds value to an otherwise underutilized agricultural residue.

Adsorption experiment with COF

The production process of the COF membrane is described in [14]. 10 mL of the uranium solution were subjected to permeation through the membrane in a 10 mL Amicon stirred cell. The driving force for permeation was provided by compressed nitrogen gas. U concentrations in solution before and after the adsorption processes were determined using inductively coupled plasma optical emission spectroscopy, ICP OES (Spectro Analytical Instruments Co, Kleve, Germany, model Arcos).

After the adsorption experiment, the saturated biochar was subjected to micro-energy dispersive X-ray fluorescence (μ-EDX) analysis to confirm the presence of uranium adsorbed on BC350-A. This analysis was performed using the QUANTAX Micro-XRF system from Bruker. The tube voltage was set at 15 kV, with automatic current adjustment, and an incident beam diameter of 50 μm. The scanning time for the measurements was of 100 seconds per point.

Results and discussion

The tank where part of the UF_4 effluent is stored in CECON is shown in Fig.1. The contaminants concentrations before and after the initial chemical pre-treatment are listed in Table 1. This pre-treatment proved successful as it effectively reduced the concentration levels for Sn and F, meeting the accepted standards for effluent discharge in Brazil [6].

Fig. 1. UF_4 effluent tank at the installation

Table 1. Concentration of Sn, F and U before and after initial chemical treatment

Contaminant	Concentration before treatment [mg/L]	Concentration after treatment [mg/L]
Sn	50	< 0.9*
F	56	5.7**
U	76	5.1

Maximum allowable limit for *Sn is 4.0 mg/L and for **F is 10.0 mg/L

The remaining solution was then subjected to the adsorption experiments for U removal:

1) With physically activated biochar (BC350-A), the U concentration decreased from 5.1 mg/L to 0.11 mg/L [10]. This observation confirms the effectiveness of BC350-A adsorption, meeting the criteria outlined in CNEN-NN-8.01 Standard [5].

2) Using the COF, the concentration of uranium decreased to 0.14 mg/L. This result can also be considered effective, meeting the national standard criteria.

Considering that an average estimated volume of 400 L of UF_4 effluent is annually produced at IPEN and this volume should be six-folded in the following years, the use of tested materials as adsorbents for U removal from this effluent represents an important alternative for treating aqueous waste containing uranium.

Besides its superior performance, the biochar presents various advantages over COF's for uranium removal, including ease of fabrication and cost effectiveness. Its disposal as solid waste, consisting of the biochar adsorbent -adsorbate system (BC350-A/U), is also governed by CNEN-NN-8.01 Standard [5] and takes into account the limit of activity concentration for the disposal of solid materials (kBq/kg).

The disposal limit for U enriched up to 20% is 100 kBq/kg, and the specific activity of U enriched at 19.75% is 25.789 kBq/g (19.75% of 80.011 kBq/g and 80.25% of 12.445 kBq/g). Therefore, to calculate the maximum allowed concentration for the disposal of solid waste containing U enriched to 20%, if 25.789 kBq corresponds to 1 gram, then 100 kBq/kg corresponds to "x" grams. Thus, "x" stands for 0.039 g/kg. This means that, if the solid waste is composed of the adsorbent associated with 20% enriched U, the concentration limit for its disposal would be about 0.04 g of U per kilogram of waste.

Considering the initial concentration of 5.1 mg/L and a remaining concentration in the liquid effluent of 0.107 mg/L, 4.993 mg/L is the concentration adsorbed on the biochar. Since the experiment was conducted in 10 mL of solution, it can be considered an adsorbed amount of 0.049 mg for every 100 mg of biochar (adsorbent dose) or 490 mg for every kilogram of biochar. This amount (0.49 g/kg) exceeds the disposal limit (0.04 g of U for every kg of waste) by more than 12 times.

Thus, for long-term storage, this waste inertization through its immobilization in a matrix is necessary. At IPEN, the monitoring and storage of solid wastes adequately immobilized are the responsibility of the Radioactive Waste Management Center (CERER), according to the CNEN-NN-6.09 Standard [16].

Despite the complexities outlined, it's important to note that significant volume reduction is achievable. Storing the waste in this solid form not only enhances safety, but also considerably simplifies management of the final waste.

The micro-energy dispersive X-ray fluorescence (μ-EDX) spectrum of the remaining biochar is shown in Fig. 2.

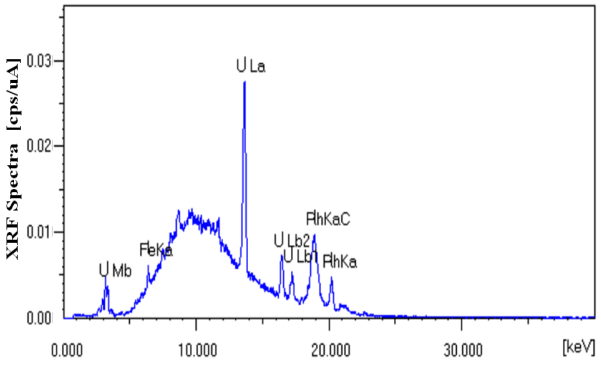

Fig. 2. XRF spectrum of the biochar after adsorption experiment with uranium-contaminated solution

The graph shows the characteristic peaks of Lα, Lβ and Mβ of uranium. Moreover, a Kα emission line from Fe can also be identified, probably due to a biochar contamination. Rh lines presence was expected due to the X-ray anode of the equipment. μ-EDX analysis provided an efficient means to identify the presence of uranium in the adsorbent and, thereby, validate the effective adsorption of this metal by BC350-A [10]. μ-EDX technique was chosen due to the sample small size and low uranium concentration, what could be difficult to analyze using the conventional XRF technique.

Conclusions

The utilization of biochar and COF has demonstrated to be effective in reducing the uranium content from contaminated aqueous solutions. More tests should be performed in order to upscale the procedure to a routine basis.

This method not only shows considerable promise in reducing radioactive liquid wastes, but also provides an encouraging path for improving the sustainability of waste management techniques in nuclear fuel manufacturing.

Through the use of biochar technology, this process presents a more eco-friendly and economically viable option for uranium cleanup, laying the groundwork for a more effective and environmentally aware strategy to tackle radioactive wastes.

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