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Selective Electrochemical Recovery of Uranium from Fluoride-Complexed Aqueous Effluents in Tin presence

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1. Introduction

In recent years, there has been a growing push to expand electricity generation, with nuclear energy emerging as one of the safest options. Expanding domestic nuclear fuel production is therefore a strategic priority for the country. Furthermore, research reactors play a vital role in producing radioisotopes that meet critical societal needs, including applications in nuclear medicine, industrial processes, and other essential sectors. [1]. As a direct consequence of this operational increase, a proportional rise in the generation of radioactive waste and liquid effluents associated with nuclear fuel cycle processes is expected, reinforcing the need for effective technologies for treatment and environmental impact mitigation. Among the generated wastes, particular attention is given to the effluent originating from the precipitation step of uranium tetrafluoride (UF_4) from uranium hexafluoride (UF_6), characterized by the presence of dissolved uranium in a complex fluoridated medium, often associated with high concentrations of metallic species such as tin [2]. The chemical stability of the fluoride complexes present makes the treatment of this effluent particularly challenging, and no fully effective and operationally simple route is currently available for its decontamination and selective uranium recovery. In this context, electrochemical techniques, particularly selective electrodeposition processes, emerge as a promising alternative by exploiting differences in the redox behavior of the species present to simultaneously promote uranium removal and minimize secondary waste generation. Therefore, the present work investigates the application of pulsed electrochemical strategies for the selective treatment of this effluent, aiming at uranium recovery and environmental remediation.

2. Methodology

A model solution was prepared to simulate real effluent conditions. The synthetic solution contained 1 ppm uranium, 4 ppm tin and 300 ppm fluoride in 0.1 mol L^{-1} sodium sulfate (Na_2SO_4, ₄, ≥99%, Merck), the supporting electrolyte. All chemicals were of analytical reagent grade and used without further purification. Uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$, ≥98%, Sigma-Aldrich), tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, ≥98%, Merck), and hydrofluoric acid (HF, 48% w/v, Merck) were used to prepare the synthetic effluent. Deionized water (resistivity ≥18.2 MΩ·cm) was used for all solution preparations. Electrochemical investigations were conducted using a three-electrode configuration controlled by a PGSTAT 302 N potentiostat/galvanostat (Metrohm Autolab). Graphite electrodes (99.9% purity, 6 cm^2 geometric surface area) were employed as working electrodes. Prior to each experiment,

these electrodes were prepared by polishing with 600-grit SiC sandpaper, rinsing thoroughly with deionized water, and drying under nitrogen stream to ensure reproducible surface conditions. Platinum and Ag/AgCl (3.0 mol L^{-1} KCl) electrodes were used as counter and reference electrodes, respectively. To mitigate this interference and prevent tin co-deposition, an electrochemical pretreatment was implemented. The strategy consists of anodic pre-polarization at +0.8 V (vs. Ag/AgCl) for 15 minutes prior to uranium reduction. The influence of cathodic potential on selective metal removal was systematically evaluated by following the pre-oxidation with a pulsed electrodeposition protocol (cathodic pulse: −0.3 or −0.4 V for 1.5 s; anodic pulse: +0.2 V for 0.5 s; total electrolysis time: 20 min). The chosen cathodic potentials are optimized to reduce soluble uranyl fluoride complexes to insoluble uranium(IV) deposits [3, 4]. Metal quantification was performed using inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO BLUE FME26, AMETEK). Removal efficiency (%) was calculated as: $[(C_0 - Cf)/C_0] \times 100$, where C_0 and Cf represent initial and final metal concentrations, respectively. The electrodes were analyzed through scanning electron microscopy (SEM) using a JSM-IT700HR microscope (JEOL) equipped with a Schottky field-emission source operated at 15 kV accelerating voltage.

3. Results and Discussion

Figure 1 presents the ICP-OES analysis of post-electrolysis solutions. They revealed a strong potential-dependent selectivity: uranium removal reached 49% at −0.3 V and improved to 55% at −0.4 V. Concurrently, tin co-removal decreased from ~17% to 12.5%, demonstrating enhanced selectivity at more negative cathodic potentials. This inverse trend yielded a U:Sn removal selectivity ratio of 4.4 at −0.4 V, representing a significant improvement over the ratio of 2.9 observed at −0.3 V.

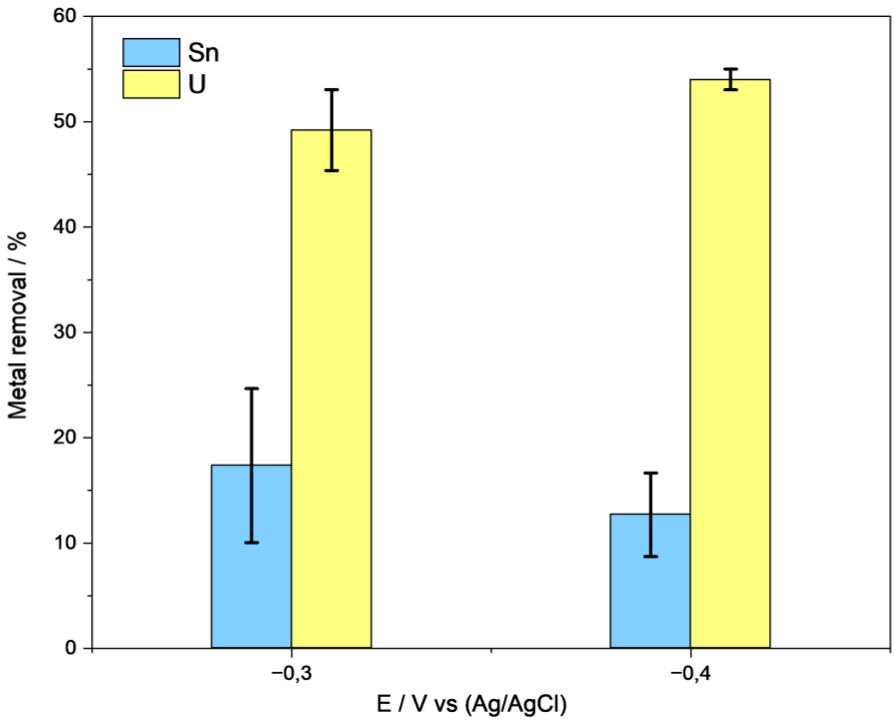


Figure 1: Removal efficiency (%) of U and Sn as a function of applied cathodic potential during pulsed chronoamperometry. Data obtained by ICP-OES analysis after 20 minutes.

This behavior aligns with the principles of kinetically controlled cathodic polarization, where deeper negative potentials favor the multi-electron reduction of uranyl-fluoride complexes ($[UO_2F_3]^-$, $[UO_2F_4]^{2-}$) to insoluble U(IV) species such as UO_2(s) or U_3O_8 precursors, while the electrochemical inertness of hexafluorostannate(IV) persists due to its high kinetic barrier [5, 6]. This complex is both thermodynamically stable and kinetically slow toward electrochemical reduction compared to SnF_2,

effectively passivating tin species and significantly reducing the probability of competitive co-deposition during subsequent uranium reduction. The intermediate anodic pulse (+0.2 V, 0.5 s) likely mitigates surface passivation by selectively dissolving incidental SnO deposits, which exhibit faster anodic dissolution kinetics than uranium oxides [6]. This selective anodic stripping prevents accumulation of undesired tin deposits without resolubilizing the more stable uranium (IV) deposits, maintaining high selectivity throughout the pulsed cycles.

Electrodes utilized were characterized by SEM, providing direct visualization of electrodeposited material morphology and insights into the mechanism of metal immobilization. The graphite surface exhibited the characteristic granular texture and well-defined lamellar structures of the graphitic material (Fig. 2a). After electrolysis at −0.3 V, discrete deposit islands distributed uniformly across the surface were observed (Fig. 2b). At higher magnification, these deposits displayed a compact morphology with finely granular texture and a network of microcracks (Fig. 2c)—a typical signature of internal stress build-up associated with growth dynamics in pulsed electrodeposition of metal and metal-oxide coatings.

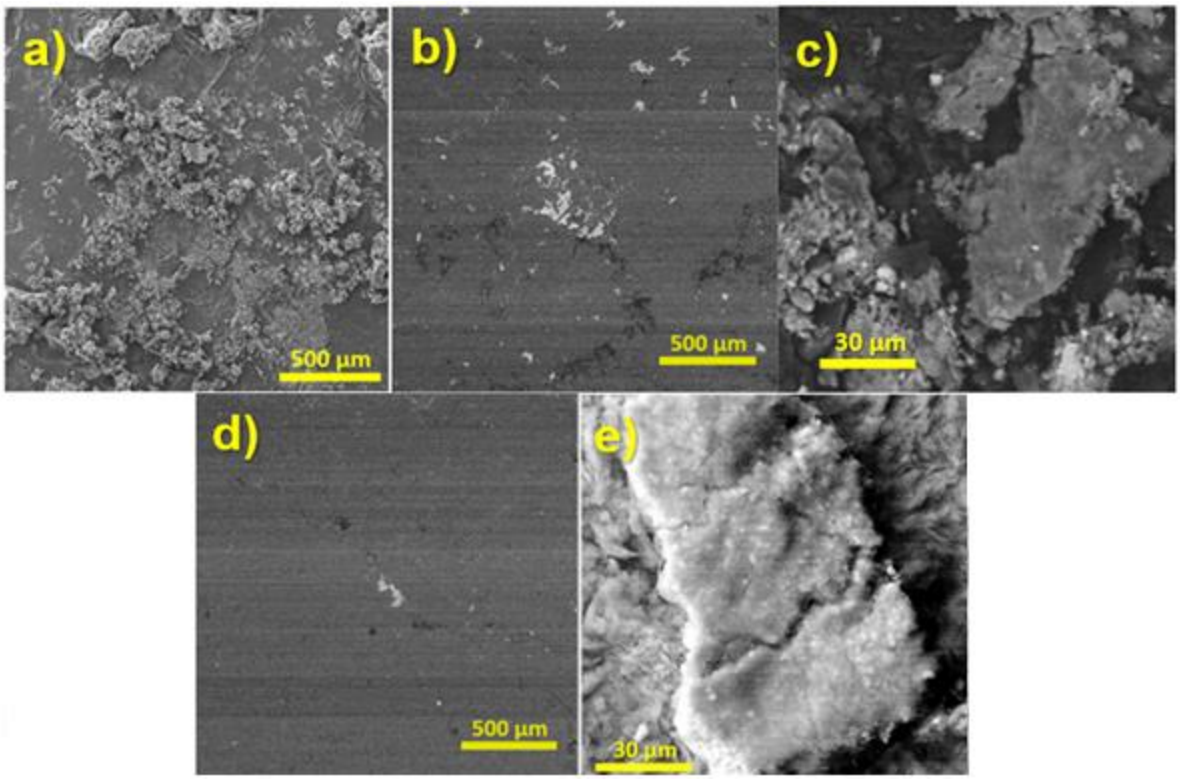


Figure 2: SEM micrographs of graphite electrode surface: (a) Pristine; (b-c) After pulsed electrolysis at −0.3 V; (d-e) After pulsed electrolysis at −0.4 V.

For the −0.4 V condition in the first stage, the morphology changed significantly (Fig. 2d-e). Greater spacing between islands and apparently higher surface porosity were observed. This texture is consistent with a selective anodic dissolution mechanism during positive potential pulses, where more oxidized and soluble phases (such as tin oxides/hydroxides) are preferentially removed, while the UO_2 phase is more efficiently retained on the electrode surface. The islands exhibit considerable volume and height, visually corroborating the significant removal of both metals during this initial stage, as quantified by ICP-OES analysis.

These results highlight that the −0.4 V condition optimizes uranium recovery from this hazardous fluoride-complexed effluent while minimizing tin co-deposition in a single-stage electrochemical operation. Uranium can be easily stripped from the electrodes in order to be reinserted in the nuclear fuel cycle. The achieved selectivity represents a significant advancement for treating real-world effluent, offering both environmental remediation and resource recovery.

4. Conclusions

This study demonstrates that selective electrochemical strategy applied for uranium removal from fluoride-complexed tin effluents through anodic Sn^{2+} pre-oxidation followed by pulsed cathodic-anodic electrodeposition presented promising results. Further research could improve the efficiency of the process through electrochemical refinement, an increase in the electrode's active area, and the addition of removal steps. The proposed methodology provides a practical route for environmental remediation and uranium recovery from contaminated tin effluents, converting a radioactive liability into a strategic material. Its operational simplicity, based on graphite electrodes, controlled potential cycling, and periodic electrode replacement, supports potential industrial application without requiring complex chemical treatments or generating secondary hazardous waste.

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