



## Polymeric membranes grafted by ionizing radiation for uranium adsorption.

A. Cardoso<sup>1</sup>, R. L. Garcia<sup>1</sup>, E. F.U. de  
Carvalho<sup>1</sup>, M. Al Sheikhly<sup>2</sup> and Y.  
Kodama<sup>1</sup>

<sup>1</sup> *malinepc@gmail.com, Nuclear and Energy Research  
Institute – IPEN/CNEN, Brazil*

<sup>2</sup> *mohamad@umd.edu, University of Maryland, United  
States*

### 1. Introduction

Uranium recovery is of great interest due to the growing global demand for this element. Extracting uranium from seawater is an area of active research. An increase in nuclear power generation is expected, impacting uranium reserves. The recovered uranium is used in the manufacture of fuel elements [1].

The nuclear fuel cycle consists of the production, use and management of nuclear fuel. The enriched uranium-235 is transformed into powder, where the briquettes that constitute the core of the fuel element plates used in the IEA-R1 nuclear research reactor of IPEN/CNEN are assembled at CECON. The production of fuel elements generates various types of liquid waste, such as aqueous solutions resulting from the production of UF<sub>4</sub>, DUA, among others. These residues require appropriate treatment to minimize environmental impacts. This approach aims to integrate environmental conservation with industrial development, ensuring more sustainable practices [2], [3]. Adsorption is a key process for removing heavy metals from wastewater, with advantages like high selectivity and low environmental impact. Besides conventional methods for adsorbents production, ionizing radiation grafting (RIG) has been used to develop various adsorbents, including polymers and membranes, by introducing new properties through the incorporation of monomers. This method utilizes high-energy radiation, such as gamma rays or electron beam to initiate chemical reactions. The objective here is to synthesize and characterize polymeric membranes via RIG to enhance their ability to adsorb uranium from liquid effluents generated in the manufacturing process of nuclear fuel elements for research reactors. [4]–[6].

The monomer used in this study is Bis[2-(methacryloyloxy)ethyl] phosphate (B2MP). The method utilized is RIG polymerization, by direct method where the base polymeric film is irradiated together with the solution containing the monomer. Uranium adsorption test was carried out in liquid effluents from IPEN's nuclear fuel center (CECON) and cleaning effectiveness is evaluated using techniques such as hyperpure germanium (HPGe) detector and ICP-OES technique. For membrane characterization we used, Raman Spectroscopy (Raman) and Scanning Electron Microscope (SEM), These techniques provide essential data to understand the changes associated with grafting. Furthermore, the degree of adsorption was evaluated using a [7]–[9].

### 2. Methodology

This study focuses on the synthesis of adsorption membranes using RIG polymerization method and their application in the adsorption of uranium in liquid aqueous effluents. The hydrophilic monomer Bis[2-(methacryloyloxy)ethyl] phosphate (B2MP) is used in the synthesis of acrylic polymers, providing properties such as adhesion, fire resistance, and the ability to form ionic bonds. B2MP was acquired from Sigma-Aldrich. Tween 20 polysorbate acts as an emulsifier in several applications and was also acquired from Sigma-Aldrich [6], [7]. Mohr's salt (iron(II) ammonium sulfate) plays a crucial role as a reducing agent in chemical reactions and an inhibitor of homopolymerization during irradiation, acquired from Carlo Erba [8]. Winged polypropylene (WPP) is a thermoplastic polymer with different types for specific applications such as high-temperature resistance, impact resistance, and flexibility, was acquired from Alasso Industries by Maryland

University [9].

The fabric was cut with a scalpel, weigh and placed in tubes or plastic zip bags for irradiation. The grafting solution, 100 mL, contains 7.5 mL of B2MP, 632 mg Mohr's salt, ultrapure water, ethanol (50:50), and 2% Tween 20. Purge with inert gas for 20 min. to prevent homopolymer formation. Irradiation with cobalt 60 and/or electron accelerator (70-100 kGy) at CETER/IPEN. Clean grafted samples in water and ethanol with ultrasound. Calculate grafting degree by proportion of grafted groups to base polymer. Equation 1:

$$\text{Degree of grafting (\%)} = \frac{MI - MF}{MI} \times 100 \quad \text{Equation 1}$$

• *mi* → initial mass    • *mf* → final mass

The diagram in the Figure 1 illustrates the membrane grafting process and how they are organized for uranium adsorption.

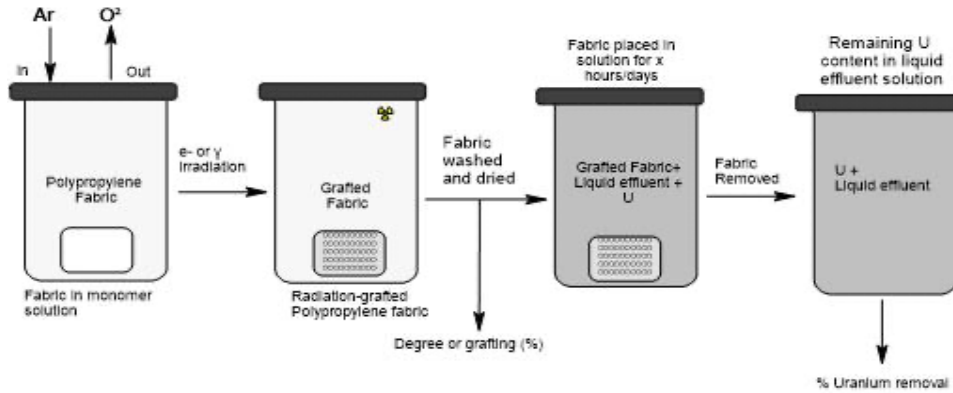


Figure 1: Diagram illustrating all stages of membrane preparation from grafting to adsorption.

Raman spectra were recorded on a Horiba JobinYvon, model XploRA-PLUS spectrometer with a laser wavelength 785 nm, power of 85 mW, objective lens 50 x 0.50 N.A., HORIBA Instruments Incorporated/Syncrity™ CCD Detector and a resolution of 4 cm<sup>-1</sup>, software LabSpec6.

The solution of liquid effluent containing uranium tetrafluoride was provided by the Center for Nuclear Fuel (CECON)/IPEN. The membranes were then immersed in the solution for at least 24 hours. The detection of the amount of adsorbed uranium was done through ICP-OES and Hyperpure Germanium Detector.

### 3. Results and Discussion

Variations in the degree of grafting were observed in the graph below (Figure 2), carefully adjusting the amounts of surfactant, monomer and Mohr's salt in the membrane synthesis solution, together with the absorbed radiation dose. Doubling the amount of B2MP monomer resulted in significant grafting levels, exceeding 100% for the base polymer. Reducing the amount of Mohr's salt by half showed remarkable grafting results for polypropylene membranes.

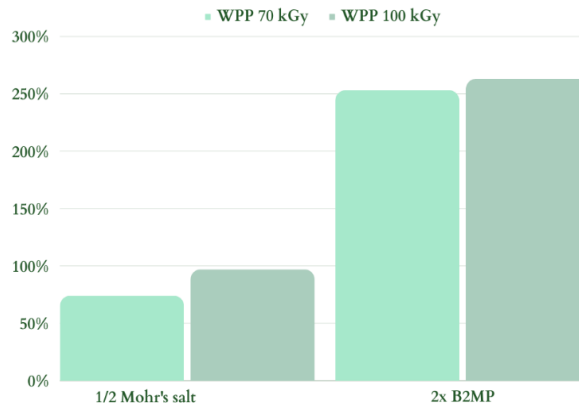


Figure 2: Graph of the degree of grafting of Winged Polypropylene grafted with 70 and 100 kGy.

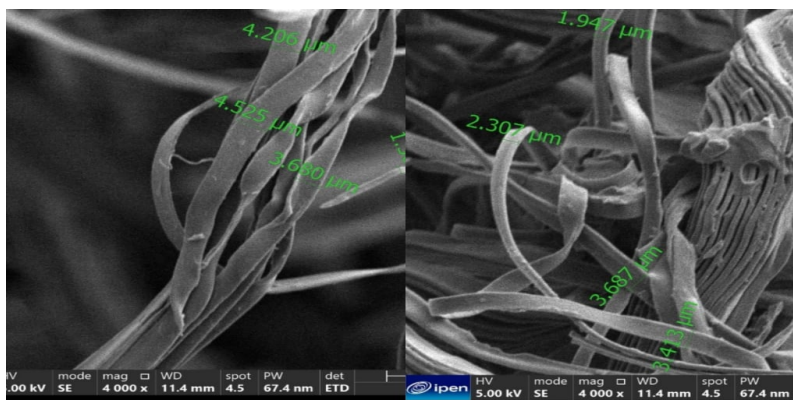


Figure 3: SEM image of the pristine WPP fiber (left) and the WPP-g-polyB2MP fiber (right).

In the analysis of the pure monomer, one of the most significant peaks in the spectrum was located at wavenumbers of  $\sim 1627\text{ cm}^{-1}$  and  $\sim 1717\text{ cm}^{-1}$ . As for the spectra corresponding to Winged Polypropylene, peaks are observed at wavenumbers of  $\sim 1610\text{ cm}^{-1}$  and  $\sim 1450\text{ cm}^{-1}$ . In the spectrum of the grafted membrane, we observe the same wavenumbers ( $\sim 1627\text{ cm}^{-1}$ ,  $\sim 1717\text{ cm}^{-1}$ ), clearly indicating successful grafting, as they correspond to the ethyl and ester functional groups present in B2MP. Figure 4 provides further insight into the Raman results.

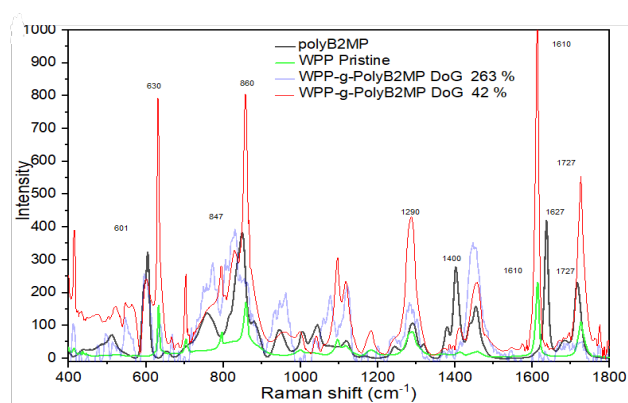


Figure 4: Raman spectrum of B2MP (black), pristine WPP (green), WPP grafted with DoG 263% (blue), and WPP grafted with DoG 42% (red).

The adsorption of Uranium was evaluated using the results from ICP-OES, located at CECON/IPEN. The Uranium concentration in each sample was measured to be less than  $0.1\text{ mg L}^{-1}$ . For a more precise evaluation of the results, assays using the Hyperpure Germanium detector are currently underway.

Table I: Determination of Uranium Concentration in Samples Analyzed by ICP-OES.

SAMPLE IDENTIFICATION	U Concentration ( $\text{mg L}^{-1}$ )
YK-1	<0.1
YK-2	<0.1
YK-3	<0.1
YK-4	<0.1
YK-5	<0.1
YK-6	<0.1
YK-7	<0.1
YK-8	<0.1
YK-9	$0.15 \pm 0.02$
DS-1	<0.1

#### 4. Conclusions

The doubling of B2MP resulted in high grafting levels, while reducing Mohr's salt showed promising results for winged polypropylene. However, increasing Tween 20 was ineffective for winged nylon. Regarding the variation in radiation dose, the range from 70 kGy to 100 kGy was explored. It's worth mentioning that 70 kGy already proved to be sufficient for achieving satisfactory grafting outcomes. New Raman spectra will be obtained to further analyze the structural modifications during grafting. Experiments with the germanium detector are underway to assess the uranium concentration in the adsorption membranes and the parent effluent solution. The aim is to optimize membrane grafting by varying doses and concentrations of Bis[2-(methacryloyloxy)ethyl] phosphate (B2MP), Mohr's salt, Tween 20, and other reagents. Future work should focus on evaluating the membranes' applicability and environmental sustainability in nuclear fuel manufacturing processes.

#### Acknowledgements

Authors are grateful to IAEA for financial support through TCBRA2019 and RC 23708, CNPq and CAPES for students' scholarships. Also, would like to acknowledge Bianca S. Balbino, Carolina F. A. Sepulbeda, Catharina J. Costa, Fernanda B. S. Vieira, Gustavo B. Campos and Laura N. Nakashima for experimental development. "We thank the support given by the Radiation Technology Center at IPEN/CNEN for providing the facilities for the conduction of the experiments and data analysis. The XploRA-PLUS was financially supported by Financiadora de Estudos e Projetos (Finep) – Grant: 01.18.0073.00".

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