SORPTION OF RADIO(TOXIC) METALS ONTO BIOCHARS WITH AND WITHOUT ACTIVATION VIA OXIDATION

ELEFTHERIA KAPASII, PANAGIOTIS TSAMOS, FOTINI NOLI

DEPARTMENT OF CHEMISTRY, ARISTOTLE UNIVERSITY, THESSALONIKI, GR-54124 THESSALONIKI

INTRODUCTION

RADIOACTIVE CONTAMINANTS FOUND IN LIQUID WASTE POSE MAJOR RISKS TO THE ENVIRONMENT AND HUMAN HEALTH BECAUSE THEY CAN POLLUTE WATER, SOIL, AND AIR. THEY CAN BE FOUND IN LIQUID WASTES FROM A VARIETY OF INDUSTRIES, INCLUDING NUCLEAR POWER STATIONS, HOSPITALS, MINES, AND LABORATORIES, AND CAN CAUSE LONG-TERM HEALTH PROBLEMS DUE TO THEIR TOXICITY AND RELEASED RADIATION. AS A RESULT, IT IS CRITICAL TO REMOVE THEM FROM THE ENVIRONMENT USING A VARIETY OF APPROACHES, INCLUDING BIOSORPTION.

IN THIS STUDY THE SORPTION OF **U(VI), TH(IV), BA(II), CO(II), EU(III), CS(I), I(I)** AND **TC(VII)** ONTO BIOCHARS PRODUCED FROM WINERY WASTE AFTER THERMALLY MODIFICATIONS WITH AND WITHOUT ACTIVATION VIA OXIDATION, WAS EXPLORED USING A BATCH TECHNIQUE IN AQUEOUS SOLUTIONS OF DIFFERENT INITIAL CONCENTRATIONS. THE SORPTION CAPACITY OF THE BIOSORBENTS WAS INVESTIGATED UNDER BATCH CONDITIONS AT ROOM TEMPERATURE (20 ± 1 ^{O}C) AND DOSAGE 1 G L^{-1} IN THE CONCENTRATION RANGE 5–500 MG L^{-1} AT PH=3 FOR U(VI) AND TH(IV), PH=4 FOR EU(III) AND CS(I), PH=6 FOR BA(II) AND PH=8 FOR CO (II). FOR ANIONIC SPECIES OF I(I) AND TC(VII) THE CONCENTRATION RANGE WAS 10-2500 MG L^{-1} AND THE PH=3. THE INVESTIGATION WAS PERFORMED WITH GAMMA-SPECTROMETRY USING RADIOACTIVE TRACERS AS WELL AS UV-PHOTOMETRIC METHODS.

THE RESULTS SHOWED SIGNIFICANT SORPTION CAPACITY OF THE MATERIALS FOR THE INVESTIGATED METALS DEMONSTRATING THEIR EFFECTIVITY AND POSSIBLE USE IN MANAGEMENT OF NUCLEAR WASTE.

EXPERIMENTAL

Materials and Methods

− **Winery Waste**

Constitution: ethanol, citric acid, polysaccharides, polyphenols, lignin, proteins, anthocyanins and tannins compose the grape pomace. This material is a complex substrate of 30% neutral 20% acid pectic substances, 15% insoluble proanthocyanidins, and phenols. All the above comprise the active groups on the biosorbent surface.

− **Winery Waste modified**

The material (**GP-R**) were also treated with carbonized at 650 °C under N_2 -atmosphere (**GP-C**) and part of the carbonized material was oxidized with 8M HNO_3 (**GP-C-OX**).

Biosorption experiments

Batch technical, Solutions of metals concentrations:

dosage **1 g L^{-1}**

$UO_2(NO_3)_2.6H_2O$-> 5-500 mg L^{-1}, pH 4

Th -> 5-500mg L^{-1}, pH 4

$CsNO_3$-> 5-500 mg L^{-1}, pH 4

$CoSO_4$-> 5-500 mg L^{-1}, pH 8

$BaCl_2.2H_2O$-> 5-500 mg L^{-1}, pH 6

$EuCl_3.6H_2O$-> 5-500 mg L^{-1}, pH 4

NaI-> 10-5000 mg L^{-1}, pH 3

NH_4ReO_4 -> 10-5000 mg L^{-1}, pH 3

Techniques

Optical spectroscopy (UV-Vis) using Arsenazo III (**U(VI), Th(IV)**)

Gamma- spectrometry using radioactive tracers

^{137}**Cs**, ^{60}**Co**, ^{133}Ba, ^{152}**Eu**, ^{123}I, and ^{99m}Tc

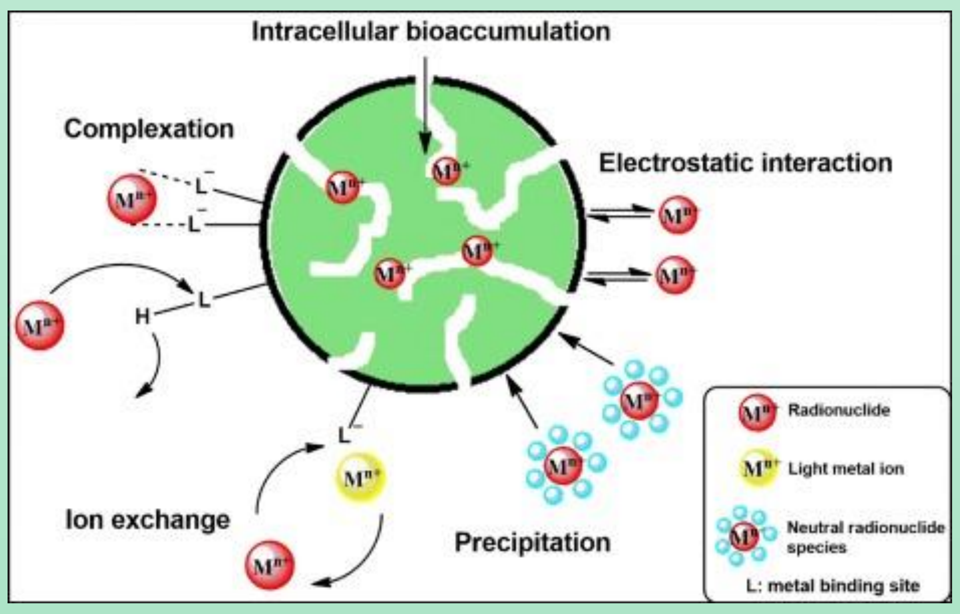


Fig 1: *Biosorption mechanisms*

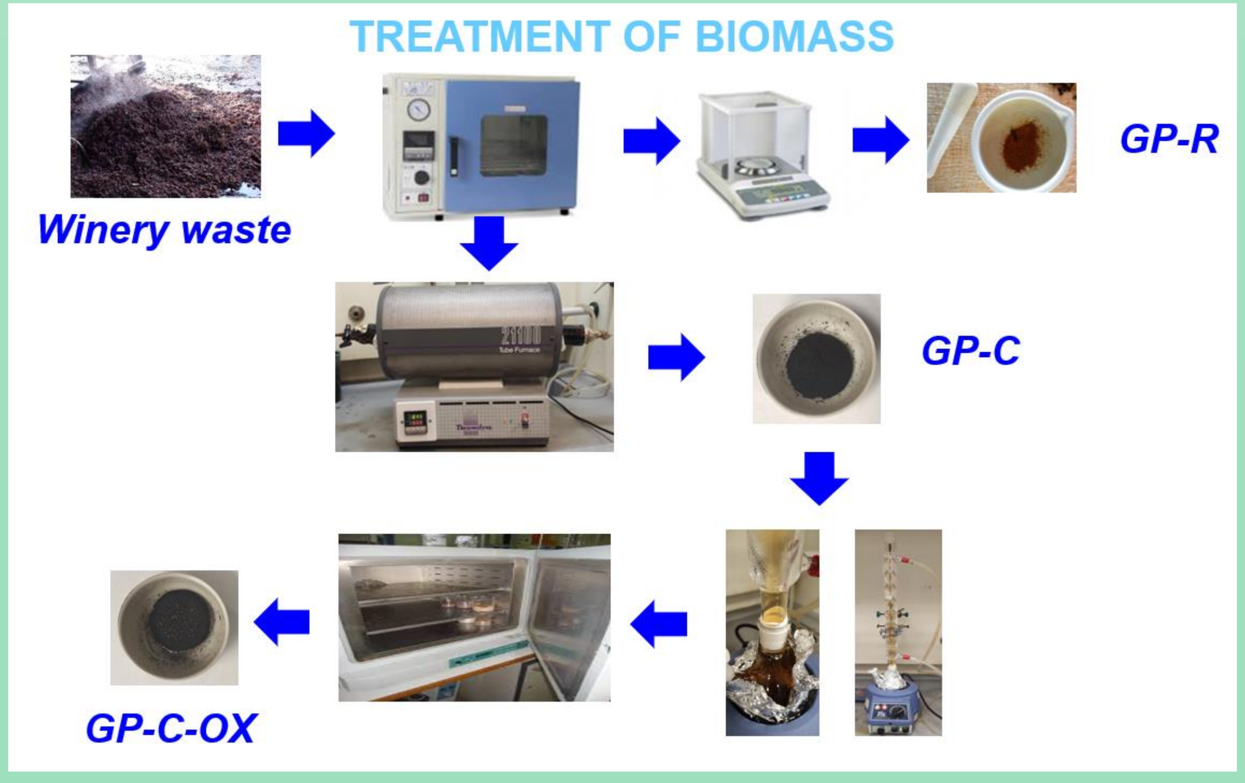
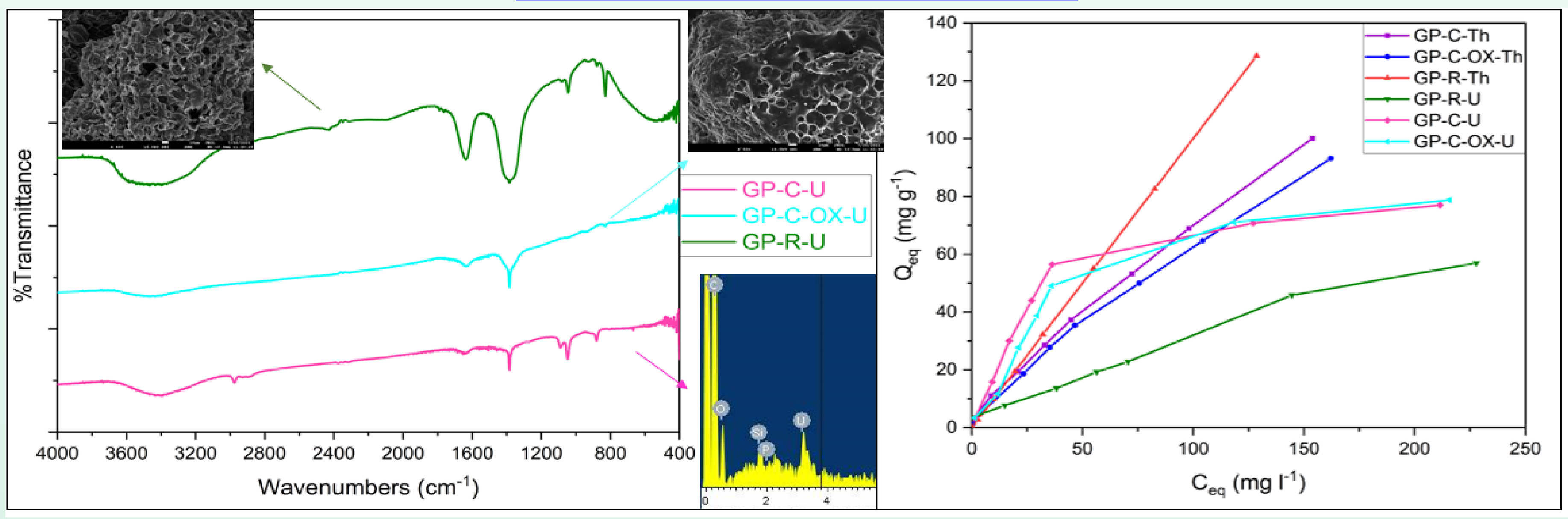


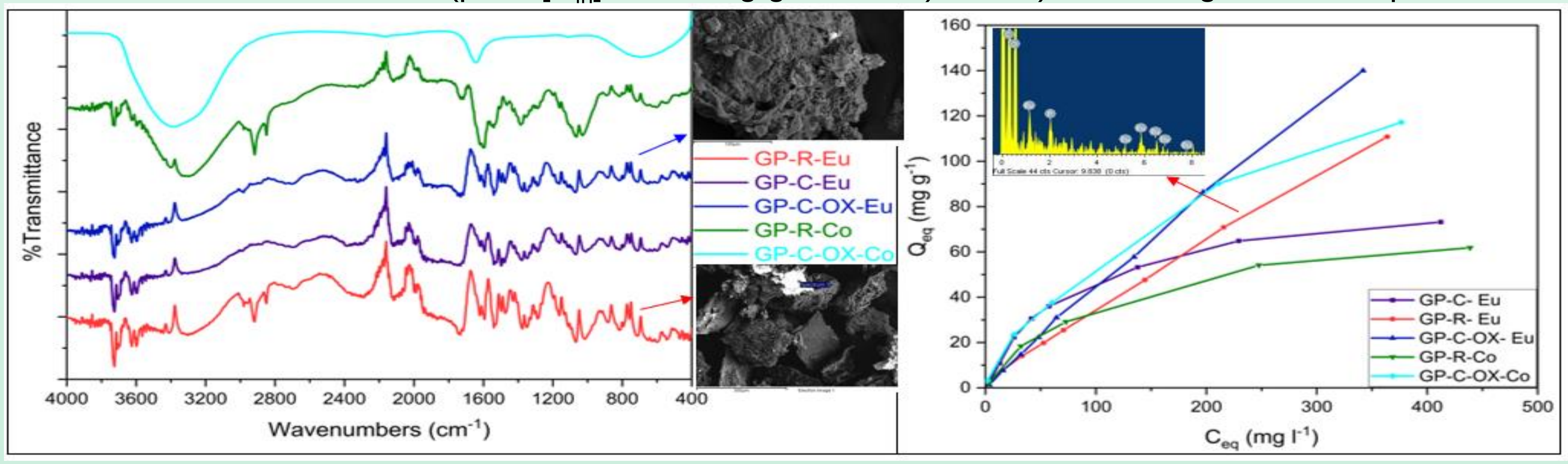
Fig. 2: *Treatment of Biomass*

RESULTS AND DISCUSSION



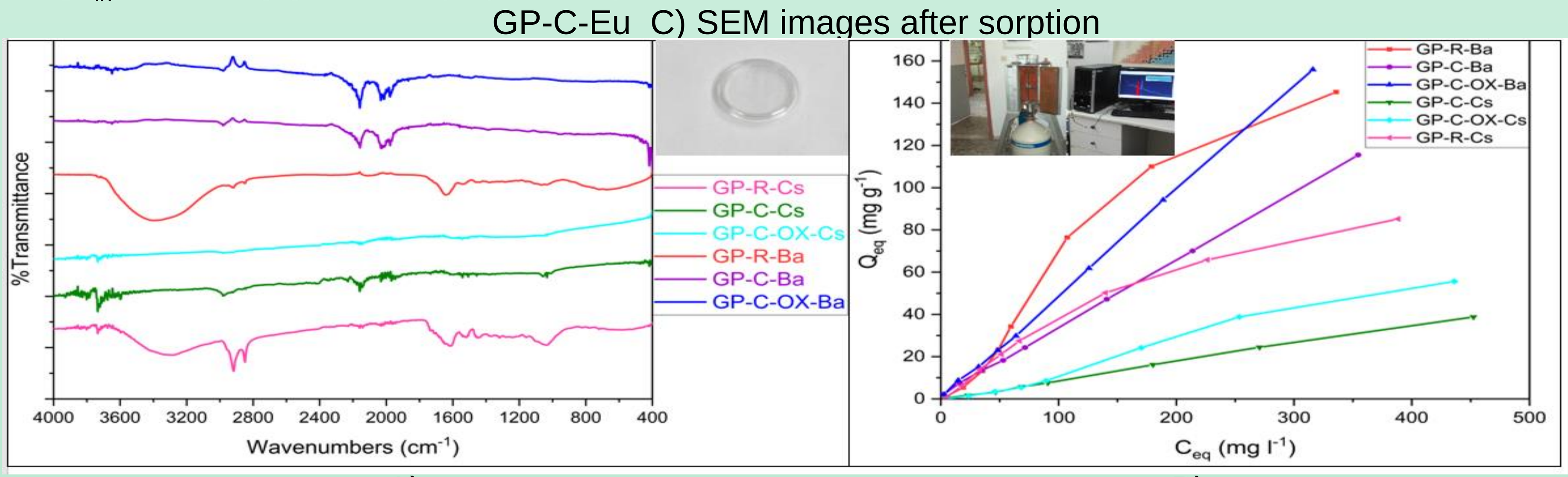
A) B)

A) FTIR spectra: GP-R- U, GP-C-OX-U and GP-C-U B) Sorption isotherms: U and Th onto GP-R, GP-C-OX and GP-C (pH:4 [C_{in}] 5-500 mg.g^{-1} Θ:25^{o}C) and C) SEM images after sorption



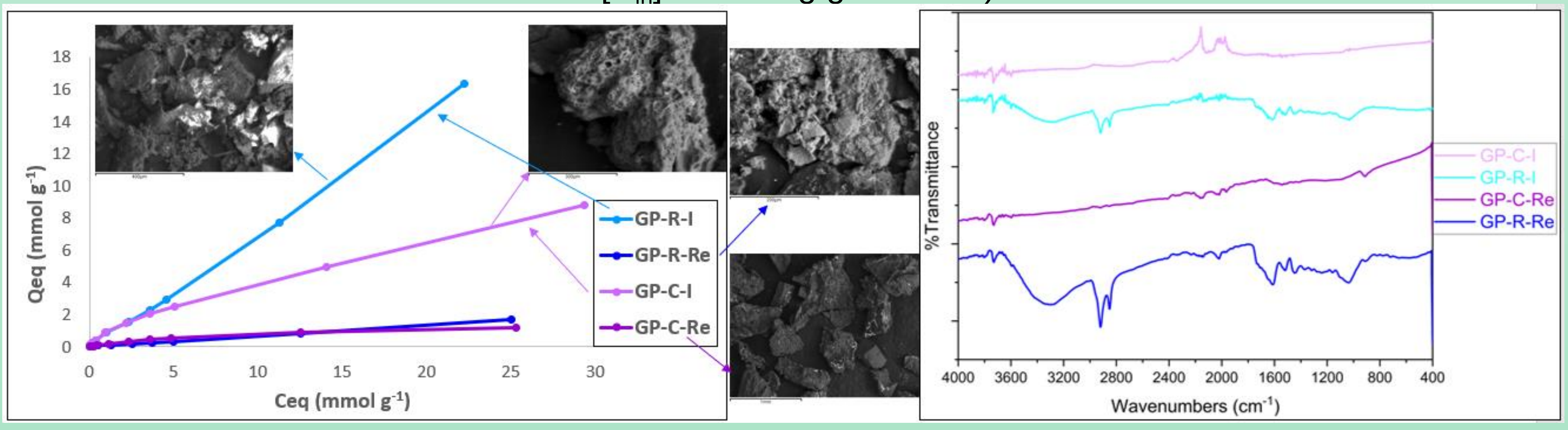
A) B)

A) Sorption isotherms: Eu and Co onto GP-R, GP-C-OX and GP-C (pH:4 and 8 respectively, [C_{in}] 5-500 mg.g^{-1} Θ:25^{o}C) B) FTIR spectra: GP-R- Eu, GP-R-Co, GP-C-OX-Eu, GP-C-OX-Co and GP-C-Eu C) SEM images after sorption



A) B)

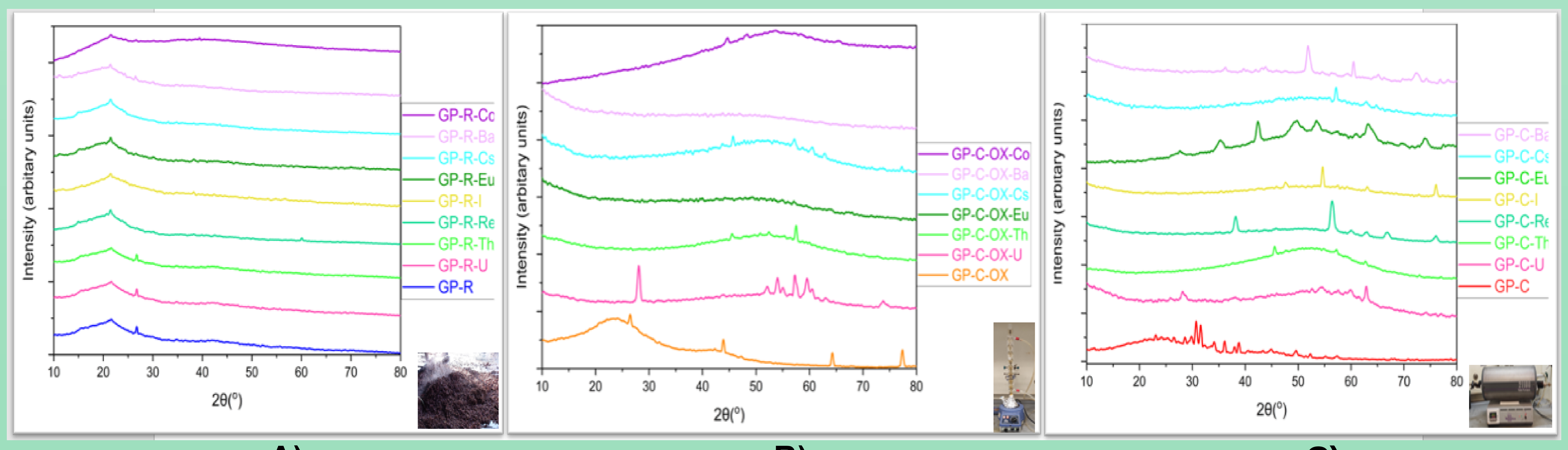
A) FTIR spectra: GP-R- Ba, GP-R-Cs, GP-C-OX-Ba, GP-C-OX-Cs, GP-C-Ba and GP-C-Cs B) Sorption isotherms: Ba and Cs onto GP-R, GP-C-OX and GP-C (pH: and respectively, [C_{in}] 5-500 mg.g^{-1} Θ:25^{o}C)



A) B)

A) Sorption isotherms: Re and I onto GP-R, and GP-C (pH:3 [C_{in}] 10-5000 mg.g^{-1} Θ:25^{o}C) B) FTIR spectra: GP-R- ReO_4^-, GP-R-I^-, GP-C-ReO_4^- and GP-C-I^- C) SEM images after sorption

XRD Characterization



A) **B)** **C)**

XRD spectra A) GP-R B) GP-C-OX and C) GP-C RAW AND METAL SORPTION respectively

CONCLUTIONS

- Potential application of these low-cost materials as bioadsorbents for the removal of both cationic and anionic Toxic Metals
- The modification of the materials into biochar, with and without activation, significantly improved their sorption capacity.
- Sorption is strongly influenced by pH, temperature and contact time.
- Analysis of SEM-EDS and FT-IR data indicated the involvement of complex mechanisms, combining ion exchange, physisorption, and surface complexation through the formation of outer-sphere complexes. Additionally, in certain cases, a combination of ion exchange and chemisorption was observed.
- The concentration of metals in the leachates indicates the safe environmental disposal of the spent material.
- Finally, the high adsorption capacity of the tested materials for all studied ions clearly demonstrates their potential as promising adsorbents in environmental technology, particularly for applications in radioecology involving the removal of radionuclides from radioactive wastewater.

LITERATURE

- P. Rajec, O. Rosskopfova, M. Galambos, V. Fristak, G. Soja, A. Dafnomili, F. Noli, A. Dukic, Lj. Matovic, (2016), Sorption and desorption of pertechnetate on biochar under static batch and dynamic conditions, J Radioanal Nucl Chem, 310:253–261, DOI 10.1007/s10967-016-4811-8
- F. Noli, E. Kapashi, M. Kapnisti, Biosorption of uranium and cadmium using sorbents based on Aloe vera wastes, J. Environ. Chem. Eng. 7 (102985) (2019) 1–10.
- E. Kapashi, M. Kapnisti, A. Dafnomili, F. Noli, Aloe Vera as an effective biosorbent for the removal of thorium and barium from aqueous solutions, Journal of Radioanalytical and Nuclear Chemistry, (2019) 321(1), pp. 217–226
- Hui Hu, Chenguang Lv, Anqi Hu, Tian Wang, Huijuan Lu, Influence of torrefaction intensities on bamboo (Acidosasa longiligula) shoot shell-derived biochar and its application for Tc(VII) reductive immobilization, (2020), Journal of the Taiwan Institute of Chemical Engineers 116, 266271
- F. Noli, E. Kapashi, I. Pashalidis, A. Margellou, D. Karfaridis, The effect of chemical and thermal modifications on the biosorption of uranium in aqueous solutions using winery wastes, Journal of Molecular Liquids 351 (2022) 118665