



# SORPTION OF EUROPIUM AND COBALT USING THERMALLY MODIFIED WINERY WASTE

E. KAPASHI<sup>1\*</sup>, P. TSAMOS<sup>1</sup>, F. NOLI<sup>1</sup>

<sup>1</sup> DEPARTMENT OF CHEMISTRY, ARISTOTLE UNIVERSITY OF THESSALONIKI, GR-54124 THESSALONIKI

## INTRODUCTION

Radioactive contaminants in liquid waste pose significant threats to the environment and human health as they can contaminate water sources, soil and air. That is why they are a major concern when it comes to their management. They can be found in liquid wastes produced by various industries such as nuclear power plants, hospitals, mines, laboratories, etc. These types can include radioisotopes of uranium, thorium, barium, europium, cobalt, plutonium, etc. which are highly toxic and can cause long-term health conditions such as cancer and radiation sickness. Effective management of these pollutants is essential to prevent their harmful effects on living organisms and ecosystems.

One way to deal with this issue is to use biosorbents. Biosorbents are materials derived from natural sources. These materials have the ability to absorb and accumulate heavy metals, organic compounds and radioactive pollutants from liquid waste.

In this work the use of **thermally modified winery wastes** was studied for the removal of **Eu** and **Co** from aqueous solutions. Considering that 20% of the total weight of the grapes remains as pomace and the annual grapes production worldwide reaches almost 70 million tons, is estimated that more than 10 million tons per year are generated as grape pomace.

The results saw significant sorption capacity of the tested materials demonstrating their effectivity and possible use in nuclear waste treatment.

## 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 carbonized at 650 °C under N<sub>2</sub> -atmosphere (**GP-C**) and oxidized with 8M HNO<sub>3</sub> after carbonized to improve the adsorption capacity (**GP-C-OX**).

### Biosorption experiments

Batch technical,  
Solutions of metal concentration range (**Eu, Co**) 5-500 mg/L,  
**pH 4** and **8** for Eu and Co respectively  
dosage **1 g L<sup>-1</sup>**.

### Techniques

- Gamma- spectrometry using radioactive tracers

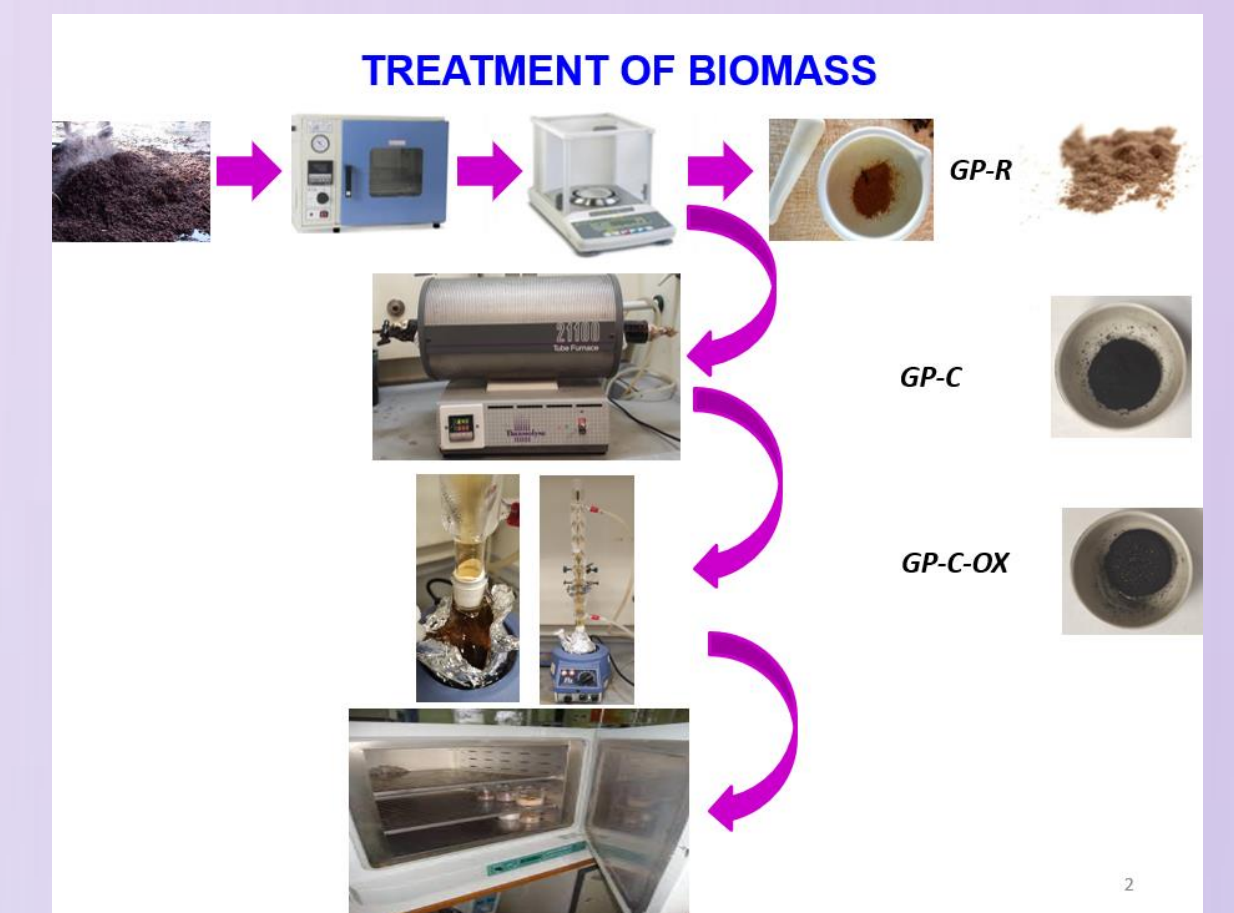
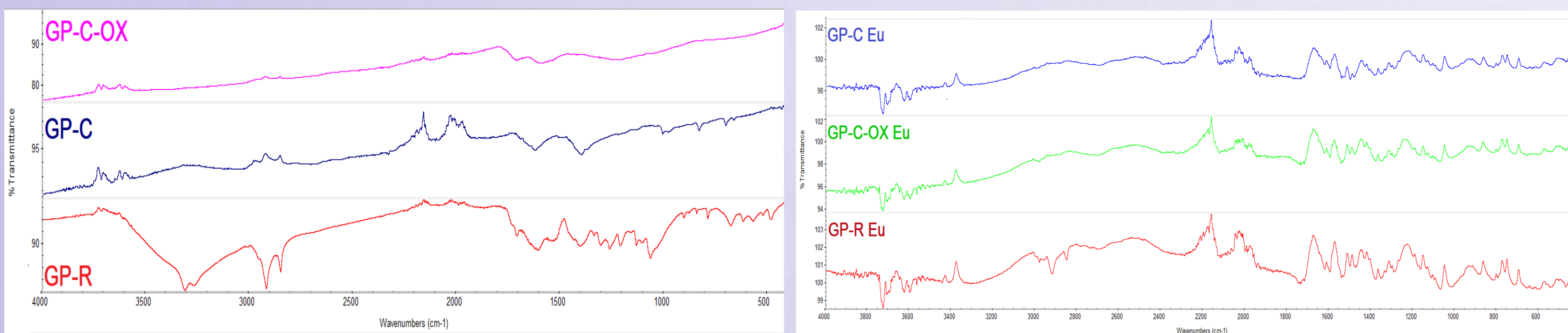


Fig.1: Treatment of biosorbent

## RESULTS AND DISCUSSION

### Spectroscopic Characteristics

FTIR spectra: GP-R, GP-C and GP-C-OX A) before sorption and after sorption with B) Eu C) Co



A)

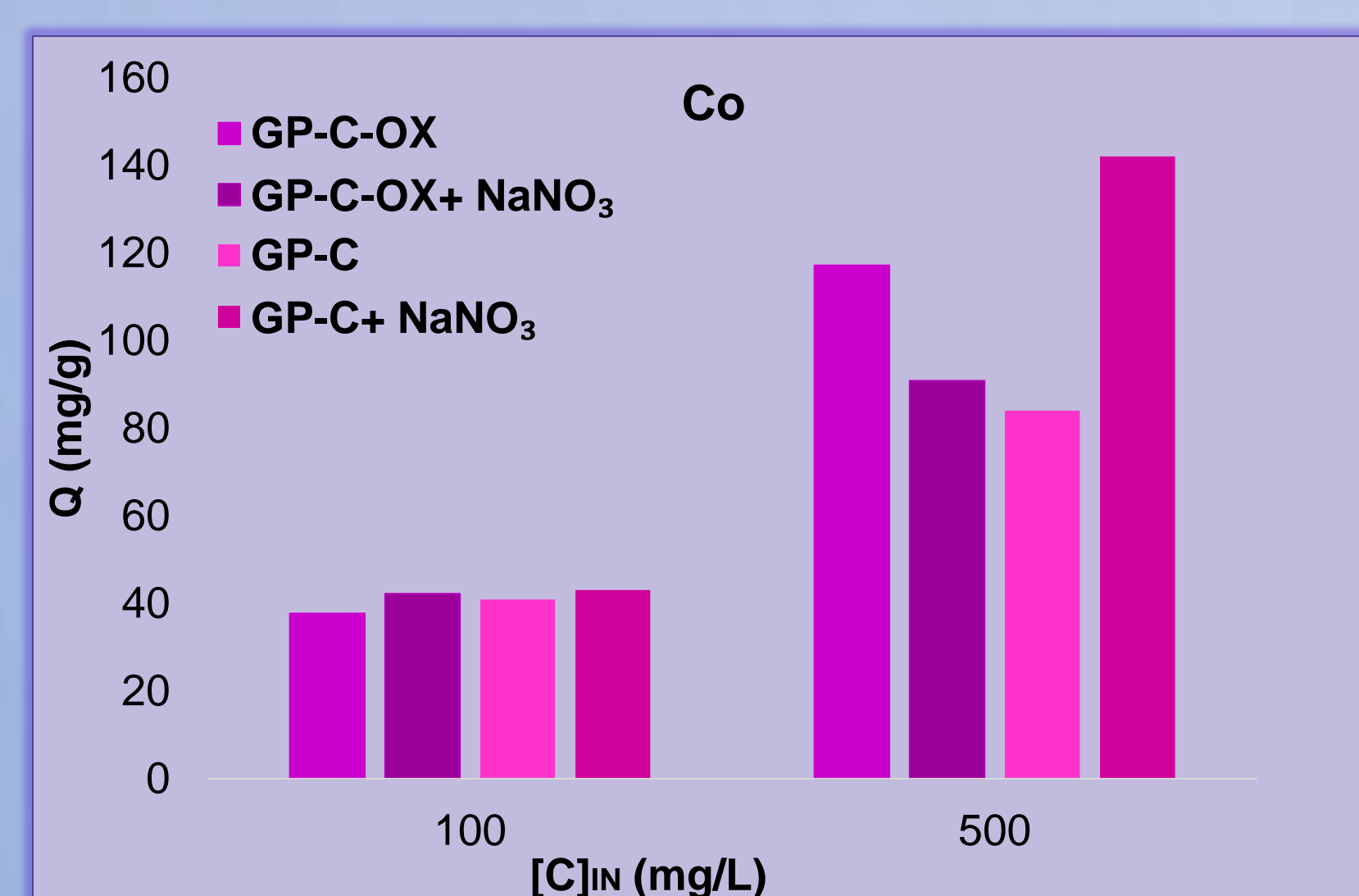
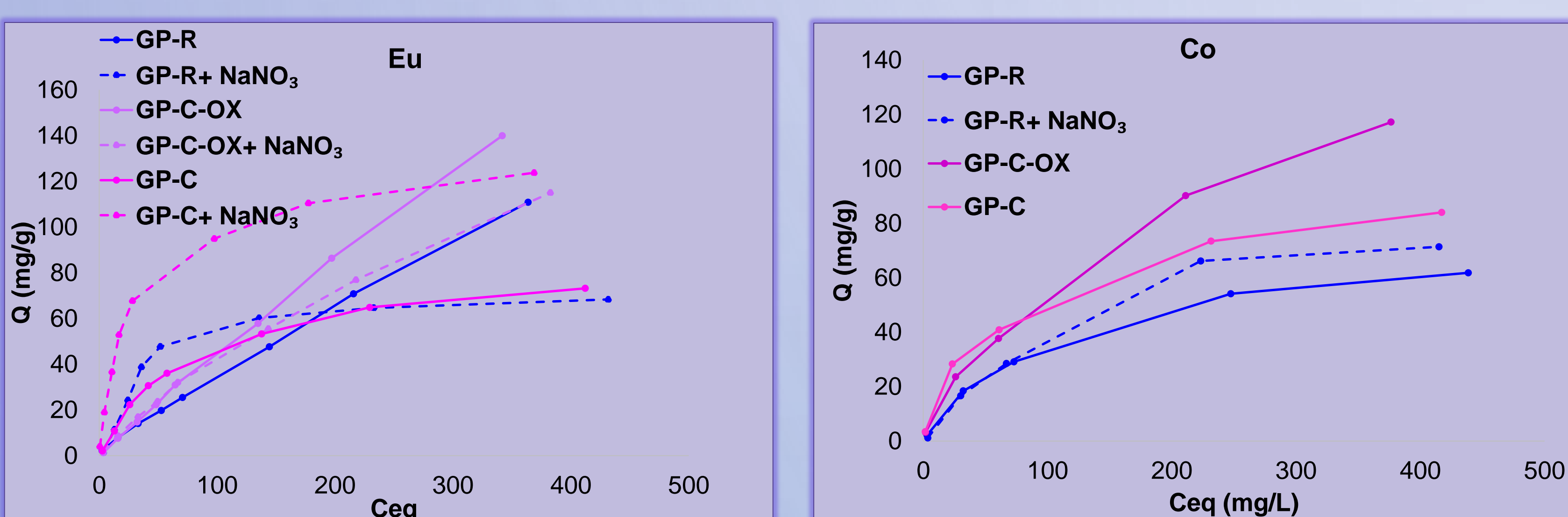
B)

C)

- The spectra of the loaded materials, they displayed a shift of the band at 3400 cm<sup>-1</sup> to 3430- 3450 cm<sup>-1</sup>
- Different depictions were presented by the band at 1620 and 1425 cm<sup>-1</sup>, indicating that carboxyl and hydroxyl groups participate in the binding to metal ions.

### Sorption isotherms

- Eu and Co onto GP-R, GP-C and GP-C-OX (pH:4 and 8 respectively, 0.01 mg, [C] 5-500 mg/L)
- The thermal and oxidized modified have better sorption capacity than raw material

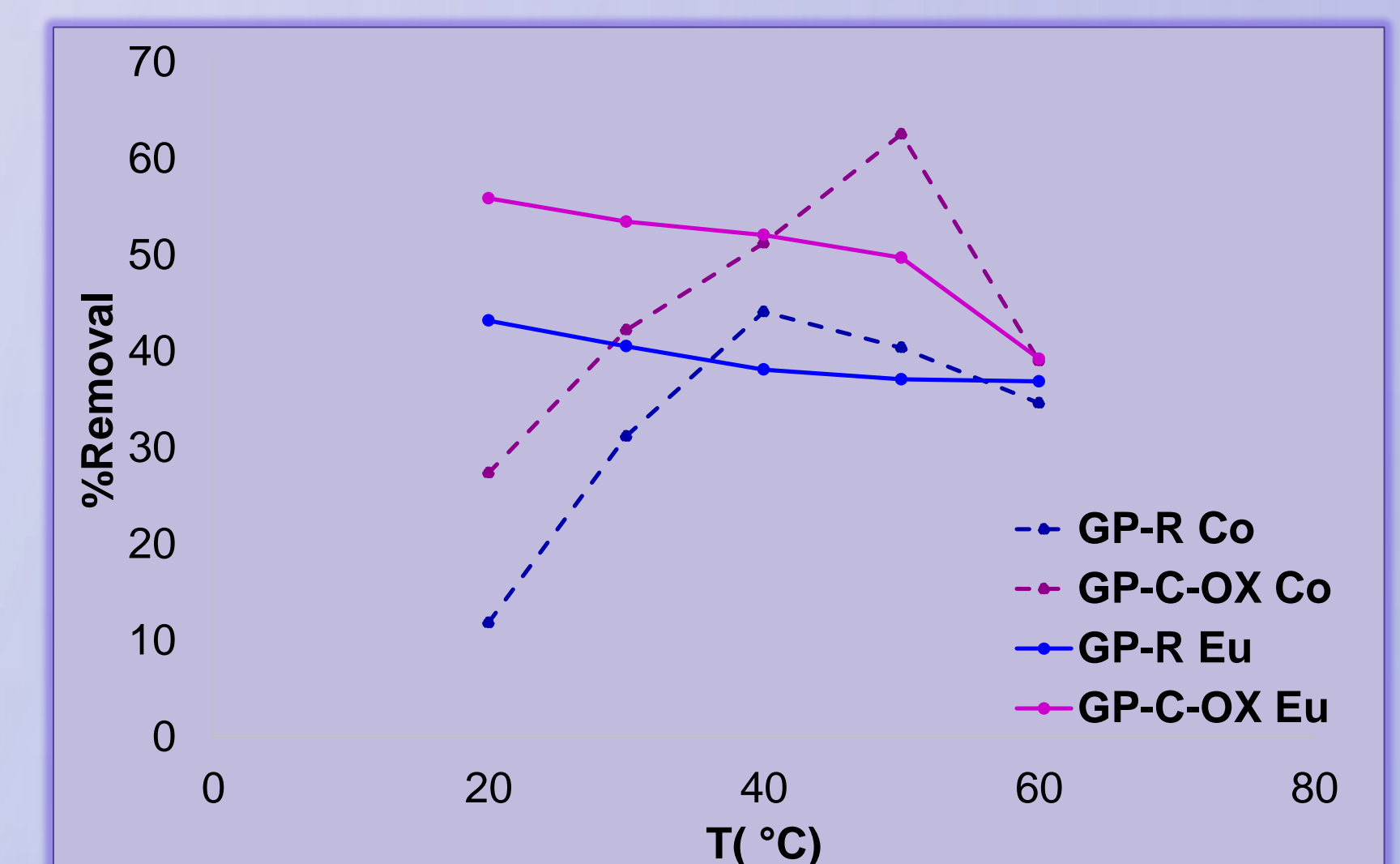
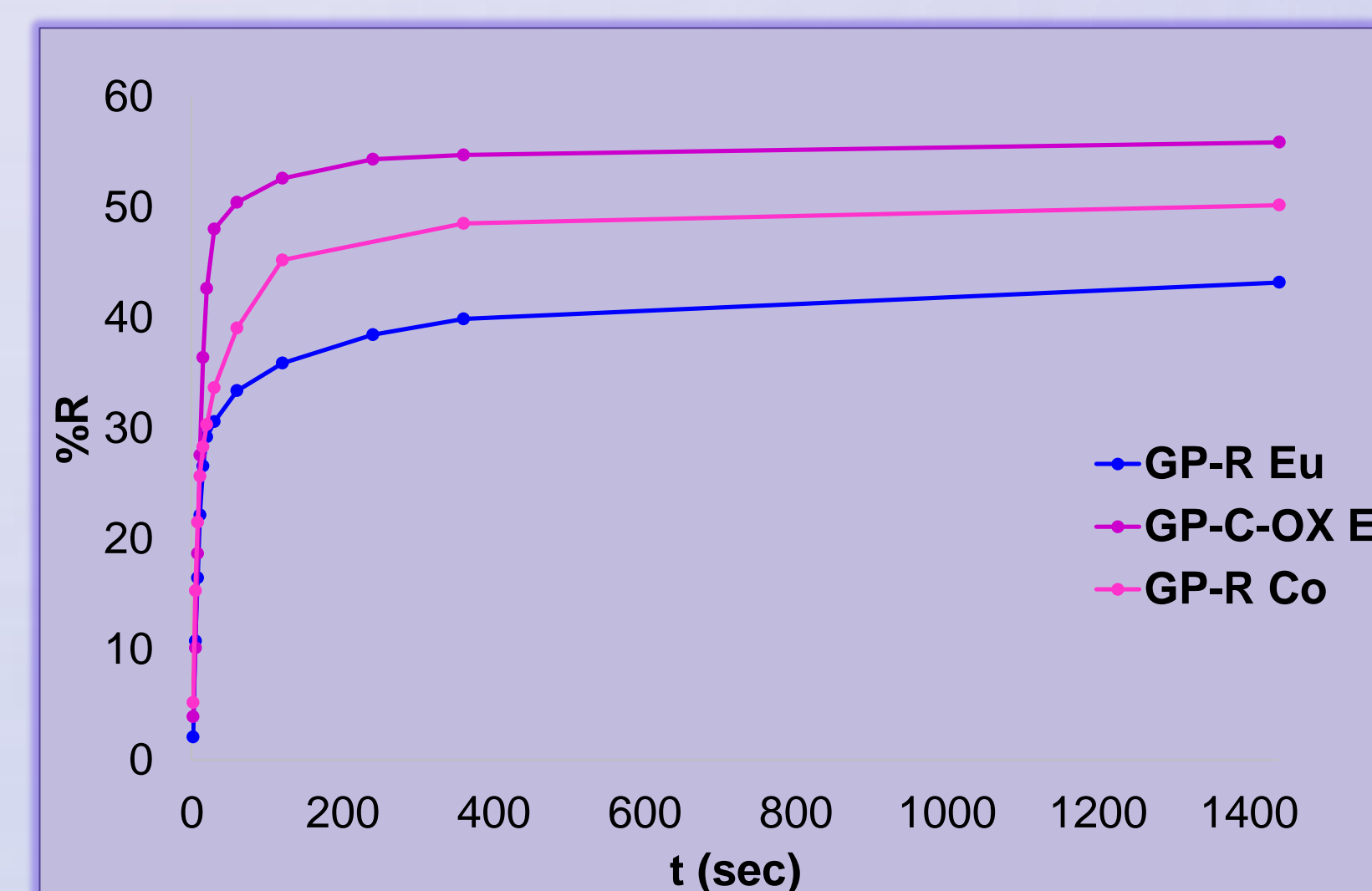


### Isotherm parameters for Eu and Co sorption obtained by linear regression

Parameters	Eu			Co	
	GP- R	GP- C	GP- C- OX	GP- R	GP- C- OX
<b>Langmuir</b>					
$g_{max}$ (mg g <sup>-1</sup> )	232.56	90.09	2500	76.92	156.25
$K_L$ (L mg <sup>-1</sup> )	0.002	0.011	0.000	0.009	0.007
$R^2$	0.5669	<b>0.9936</b>	0.0495	<b>0.9986</b>	0.9462
<b>Freundlich</b>					
$1/n$	0.79	0.697	1.012	0.683	0.684
$K_F$	0.95	1.66	0.42	0.79	0.45
$R^2$	<b>0.9952</b>	0.9289	<b>0.9967</b>	0.9647	<b>0.9962</b>

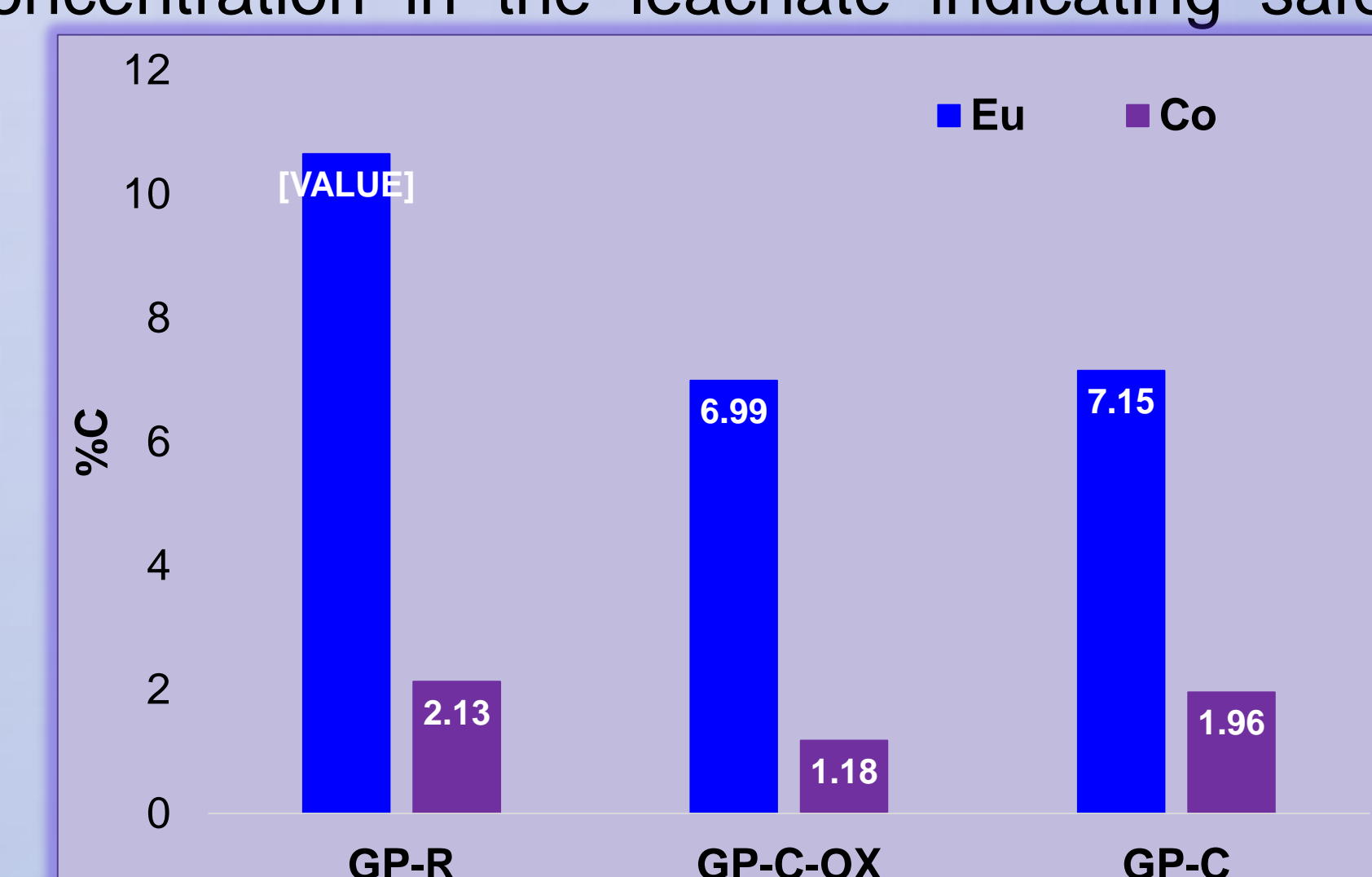
### Sorption kinetics and effect of T °C

- Sorption kinetics for Eu onto GP-R, GP-C-OX and Co onto GP-R (T:20°C, Cin:75mgL<sup>-1</sup> pH 4 and 8 respectively).
- Effect of T °C for Eu and Co onto GP-R and GP-C-OX (Cin :75mgL<sup>-1</sup>) in 20, 30, 40, 50 and 60°C.
- As the temperature increases, the sorption capacity increases until 40 °C for GP-R and 50 °C for GP-C-OX. After that temperature the sorption capacity decreases.



### Leaching experiments using the TCLP method

- The thorium concentration in the leachate indicating safe disposal of the loaded material



## CONCLUSIONS

- Possibility of applying the specific materials low cost as biosorbents and their thermal modification as a method of improvement of their sorption capacity
- Sorption process was considerably affected by sorbent mass, competitive ions, as well as temperature and contact time.
- Oxidation increases the sorption capacity as mentioned in the literature due to increase of porosity and removal of water-soluble substances.
- A complex adsorption mechanism emerges from thermodynamic data. Also they show that the biosorption was feasible, endothermic, spontaneous and physical in nature.
- If we also consider the data from SEM- EDS and FT-IR led to the conclusion that a complex mechanism takes place, combining ion exchange, physical sorption and surface complexation via formation of outer sphere complexes.
- Finally, the safety in disposal of loaded material was tested making evident that the investigated sorbents could be promising in environmental technology.

## LITERATURE

- EPA Test Method 1311-TCLP (Toxicity characteristic leaching procedure)
- Kapashi E., Kapnisti M., Dafnomili A., Noli F., (2019). *Aloe Vera as an effective biosorbent for the removal of thorium and barium from aqueous solutions*. J Radioanal Nucl Chem 321:217-226.
- Noli F., Busari Nasiru M. S. A., Tsamos P., Pavlidou E., (2022). *Eu (III) removal from aqueous solutions using raw and modified pomegranate peel as biosorbents*. International Journal of Environmental Science and Technology Noli F., Kapashi E., Kapnisti M., (2019). *Biosorption of uranium and cadmium using sorbents based on Aloe vera wastes*. J Environ Chem Eng.
- Noli F., Kapashi E., Pashalidis I., Margellou A., Karfaridis D., (2022). *The effect of chemical and thermal modifications on the biosorption of uranium in aqueous solutions using winery wastes*. J. of Mol.. Liq. 351, 118665
- Noli F., Kapnisti M., Buema G., Harja M., (2016). *Retention of barium and europium radionuclides from aqueous solutions on ash-based sorbents by application of radiochemical techniques*. Appl Radiat Isot 116:102- 109
- Prodromou M., Pashalidis I., (2016). *Europium adsorption by non-treated and chemically modified Opuntia ficus indica cactus fibres in aqueous solutions*. Desalin Water Treat 57:5079-5088.