

# **GREEN BIOSORBENTS PREPARATION FOR HEAVY METALS REMOVAL IN AQUEOUS MEDIA**

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UNIVERSITY OF PADOVA, 18<sup>th</sup> NOVEMBER 2022**



# WATER FOOTPRINT OF FOOD

How much water is used to produce what we eat?



185 LITERS



2400 LITERS



140 LITERS



135 LITERS



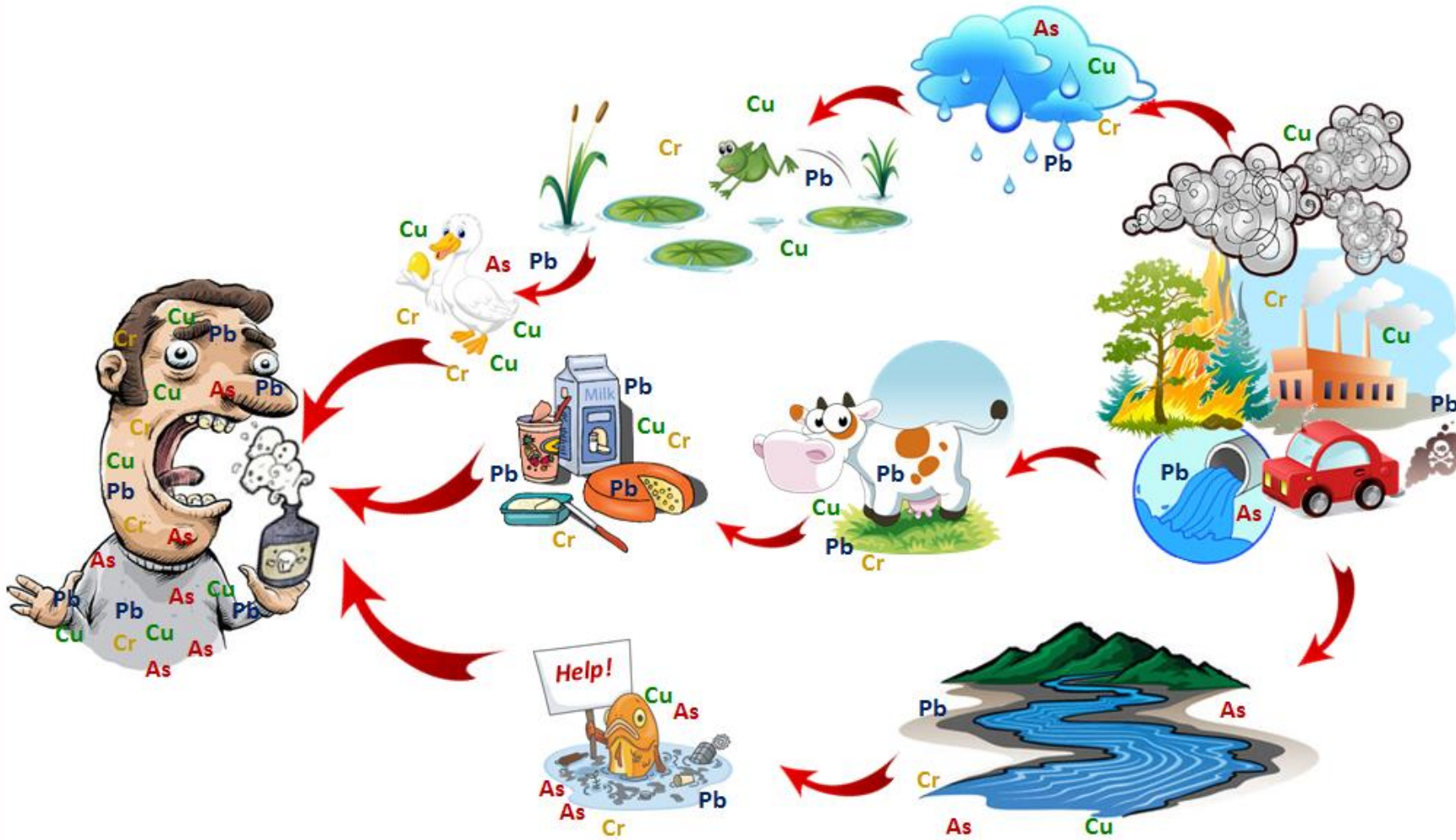
75 LITERS

1.4  
BILLIONS OF KM<sup>3</sup>



0.001%  
AVAILABLE FOR HUMAN USE

# BIOACCUMULATION



Some metals, issued by various points and diffuse sources, have the tendency to accumulate in the soil and then into the food chain, depositing in tissues and organs of living beings, causing serious diseases.



# THE IDEA

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Managing the water – resource is one of the biggest challenges that society is facing today on a global scale.



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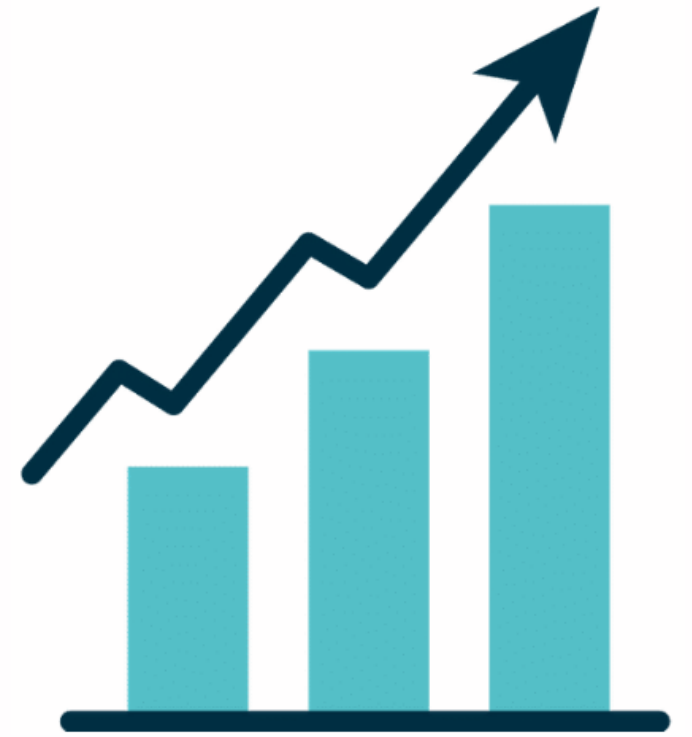
This project, which has led to the development of filtering devices, comes from the desire to propose a possible solution to the problem of water purification contaminated by heavy metals.



# THE IDEA: BIOSORBENTS FEATURES

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- Treat water and wastewater
- Easy availability
- Low-cost transformation of waste into a real asset
- High binding capacity
- No additional environmental impact
- Possibility of reusing without losing its effectiveness
- Be used on a large scale



# TRADITIONAL METHODS DISADVANTAGES

Method	Advantages	Disadvantages
Chemical precipitation / Filtration	Simply / Cheap	Required high concentrations; Use of chemical reagents; Difficult separation; Production of sludge
Redox	Mineralization	Use of chemical reagents
Electrochemical treatments	Recovery of the metals	Required high concentrations and pressures; High energy cost
Inverse Osmosis	Pure effluent for the re-use	High energy cost; Control of membranes
Ion exchange	Pure effluent for the re-use; Recovery of the metals	High cost of resins; Frequent maintenance
Active carbon	Conventional	Low yield of removal
Evaporation	Pure effluent for the re-use; Recovery of the metals	High energy cost; Production of sludge

**Drawbacks associated with the use of traditional methods and the legislation on environmental protection fostered research into the development of alternative technologies.**



# THE «METALS CATCHERS» DEVICES



The «Banana Pods»



The «Filtering Pipe»



The «Metals Catchers» Filter



# THE PRELIMINARY STUDIES

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Preliminary studies showed that:

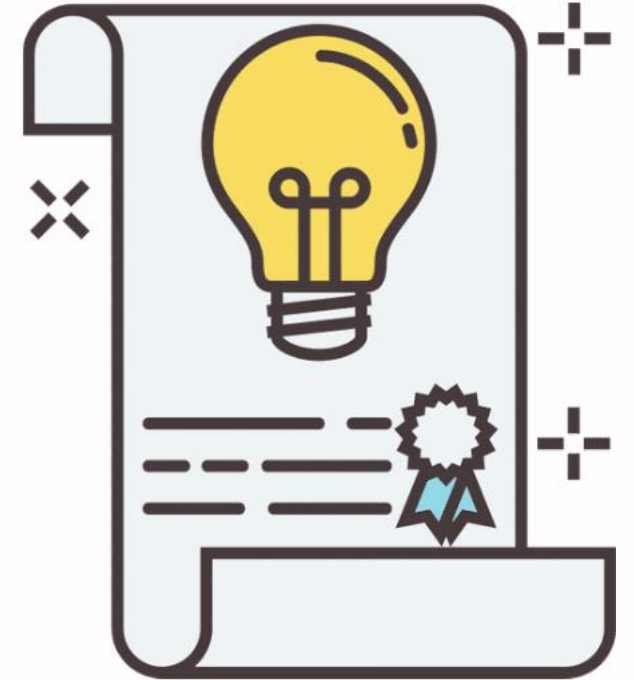
- The «Banana Peel Supremacy»
- Peel Swelling Phenomenon
- Peel Selectivity against some Heavy Metals and competitiveness in adsorption
- Optimization of the powder dimensions
- A more sustainable desorption process



# WHAT IS A PATENT?

A Patent is a legal act that:

- establishes the priority and the exclusive right of industrial exploitation of an invention;



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- establishes the priority and the exclusive right of industrial exploitation of an invention;
- excludes other subjects from the use and exploitation of the invention itself in the territory in which it was granted, for a certain period of time;

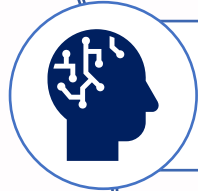


# THE PATENT REQUIREMENTS

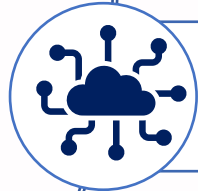
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**NOVELTY**



**INVENTIVE ACTIVITY (or ORIGINALITY)**



**INDUSTRIALITY**



**ADMISSIBILITY**



# NOVELTY REQUIREMENT

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**«THE INVENTION MUST BE NEW, IT MUST NOT BE INCLUDED IN THE STATE OF THE ART, IN ALL THE PRE-EXISTING TECHNICAL KNOWLEDGE, IN ITALY AND ABROAD»**

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Everything that is made accessible to the public before the application for the patent cancels the invention novelty feature (filing of previous applications, written and oral knowledge, lectures of predivulgation, articles on scientific papers, exposures in a catalog).

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Prior Art Searches: researches made in order to find the existence of equal earlier patents, carried out on databases of industrial and intellectual property.

# **INVENTIVE ACTIVITY REQUIREMENT**

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**«IT MUST DIFFER FROM THE STATE OF THE TECHNIQUE, A PERSON THAT HAS EXPERIENCE IN THAT PARTICULAR FIELD OF THE TECHNIQUE DOES NOT TURN OUT WITH SOMETHING ALREADY SEEN»**



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The assessment of originality takes place according to:

1. The identification of the invention sector;
2. The identification of the average specialist model;
3. The verification that the invention consist of an enrichment of the technical art state (a cost reduction, simplification of use, technical progress).

# INDUSTRIALITY REQUIREMENT

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**«THE INVENTION MUST HAVE AN INDUSTRIAL APPLICATION, THE INVENTION OBJECT CAN BE MANUFACTURED OR USED IN ANY TYPE OF INDUSTRY»**

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**«Industriality» is intended as industrial machinability or industrial usability of the invention;**



**Invention is not a simple intellectual process, but a feasible technique, capable of leading to an immediate result in the field of industrial technology, generating practical effects.**

# ADMISSIBILITY REQUIREMENT

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**«THE GRANTING OF THE PATENT IS ALLOWED ONLY IF THE  
OBJECT DESIGNED CAN BE USED LAWFULLY,  
THE IMPLEMENTATION OF WHICH IS IN FAVOR OF PUBLIC  
ORDER AND MORALITY»**



# HOW PATENTS ARE MADE

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## PATENT TYPOLOGY

- FOR INDUSTRIAL INVENTION
- FOR UTILITY MODEL

## STRUCTURE

- DESCRIPTION
- CLAIMS
- DRAWINGS

# PATENT TYPOLOGY

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It has a duration of 20 years from the date of filing of the application and may not be renewed on its expiry



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It has a duration of 10 years from the date of submission of the application

# THE PATENT STRUCTURE

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## DESCRIPTION

It contains the main features of the invention, what problems can be solved, how these problems can be overcome, the specification of state of the previous technique, summarising all the patented and non-patented technical knowledge.



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## DRAWINGS

They promote the understanding of the patent, providing a clear and immediately usable representation; they have the task of specifying the components of the invention or summarizing process steps.

# BACHELOR'S DEGREE RESEARCH THESIS

## «GREEN GRAPE MARC BIOSORBENT PREPARATION FOR MERCURY REMOVAL IN AQUEOUS MEDIA»

Italy has been the largest wine-producing nation in the world at least in the last four years [OIV]

Wine – production waste abundant and easily available (Life Cycle Assessment, Circular Economy)

Heavy metals have the highest bearing on water contamination among Persistent Organic Pollutants (POPs)

Mercury – Hg (II) – has the biggest impact on water contamination among Heavy Metals

Development of an eco-sustainable, economical and efficient treatment protocol to prepare bioadsorbents from organic waste

# GRAPE MARC APPLICATION

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➔ For the production of grape spirits (ethanol) to be used in beverage industry, animal feed, biofertilizers (due to its organic and nutrient values)

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- For the recovery of tartaric acid following different extraction methodologies
- For monomeric sugars production that can be employed as a fermentation substrate for the production of various products (lactic acid, enzymes, protein, antioxidants, biosurfactants)

# MERCURY POLLUTANT

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- Mercury is as hazardous as it is important: due to its chemical and physical characteristics, it is crucial for industries such as pharmaceutical, oil refinery, electroplating, battery manufacturing and mining activities;



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- **Mercury ions and organomercury compounds are easily solubilized in water and living tissues and are capable to bioaccumulate in the human body;**





# MERCURY SOURCES

1

**PRIMARY NATURAL SOURCES:** natural weathering of mercury containing rocks, geothermal and volcanoes activity

2

**PRIMARY ANTHROPOGENIC SOURCES:** which involve coal burning, mining activity for various metals and cement production

3

**SECONDARY ANTHROPOGENIC SOURCES:** the accumulation of exhausted products in landfills or incinerators, secondary steel industry, industrial and artisanal gold mining, chlor-alkali industry and the production of vinyl chloride monomer



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- One of the main problems related to the mercury contamination of aquatic systems is the methylmercury formation, a potent neurotoxin that rapidly biomagnifies in the living beings organism;
- It's important to focus interventions on the pre-existing mercury jointly on reducing emissions on a global scale: when an aquatic system accumulates sufficient amounts of mercury, further increases become secondary if compared to the amount already stored in the system.



# EXPERIMENTAL SECTION

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Biosorbent  
collection and  
preparation

Preliminary  
tests

Hg(II)  
adsorption  
isotherms

FTIR and  
kinetic study  
of the  
biosorbent

Comparative  
adsorption  
study and  
reusability



# BIOSORBENT PREPARATION



Winery industry



Fresh Grape Marc

Air Drying

Grinding and Sieving

Ethanol

Polar Extractives

GM – CA  
BIOSORBENT

Drying

Water

Citric Acid (pH 2)

GM – HCl  
BIOSORBENT

Drying

Water

HCl pH 1



# PRELIMINARY TESTS RESULTS

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Preliminary tests, that have been carried out using the analytical technique of Inductively Coupled Plasma Mass Spectrometry (ICP – MS), showed the following results:

→ GM-CA and GM – HCl have shown a good adsorbing capacity with numerous elements, including Mercury

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- ➔ The sample treated with an aqueous solution of lemon juice has not provided satisfying absorption results concerning mercury, but appreciable absorption results have been achieved as regards Chromium, Copper, Vanadium, Cadmium, Cobalt, Zinc;

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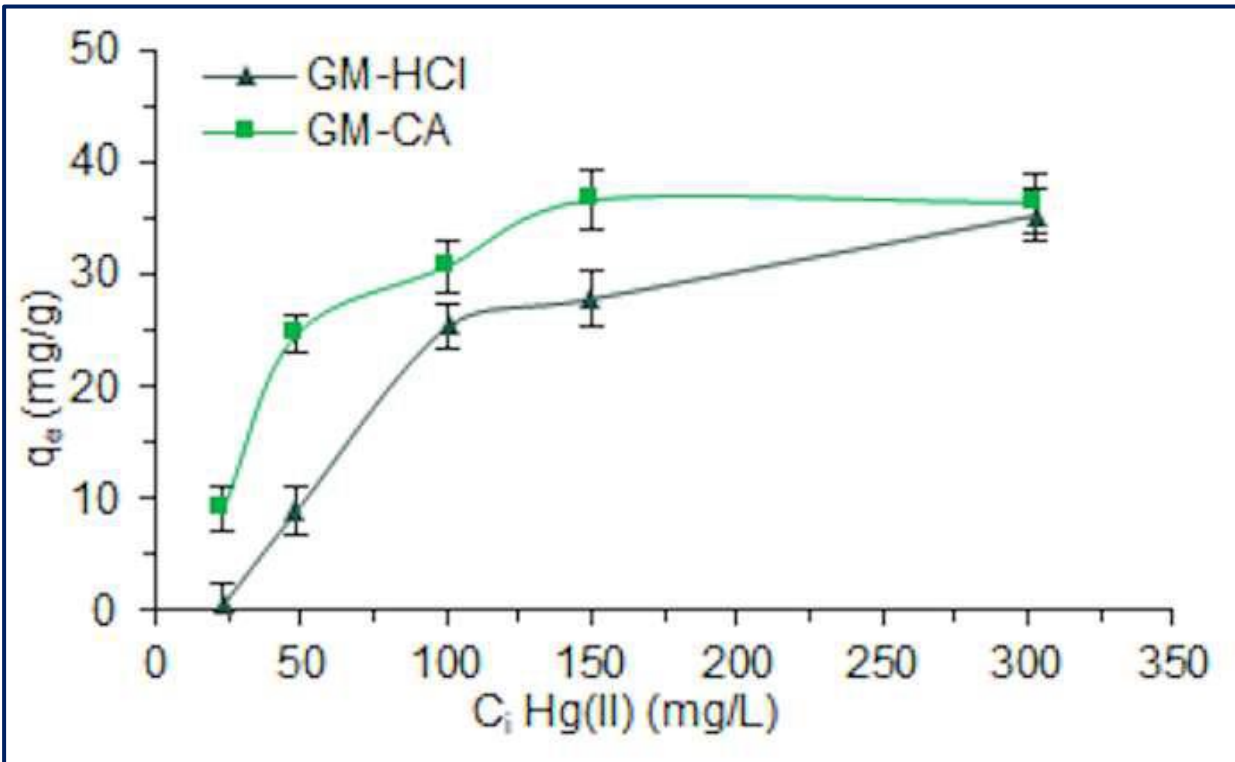
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Preliminary tests, that have been carried out using the analytical technique of Inductively Coupled Plasma Mass Spectrometry (ICP – MS), have shown the following results:

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- ➔ The sample treated with an aqueous solution of lemon juice has not provided satisfactory absorption results as regard mercury, but appreciable absorption results have been achieved as regards Chromium, Copper, Vanadium, Cadmium, Cobalt, Zinc;
- ➔ Copper and Nickel have been chosen as secondary elements on which to conduct test by the marc samples to evaluate their selectivity.

# Hg (II) ADSORPTION ISOTHERMS

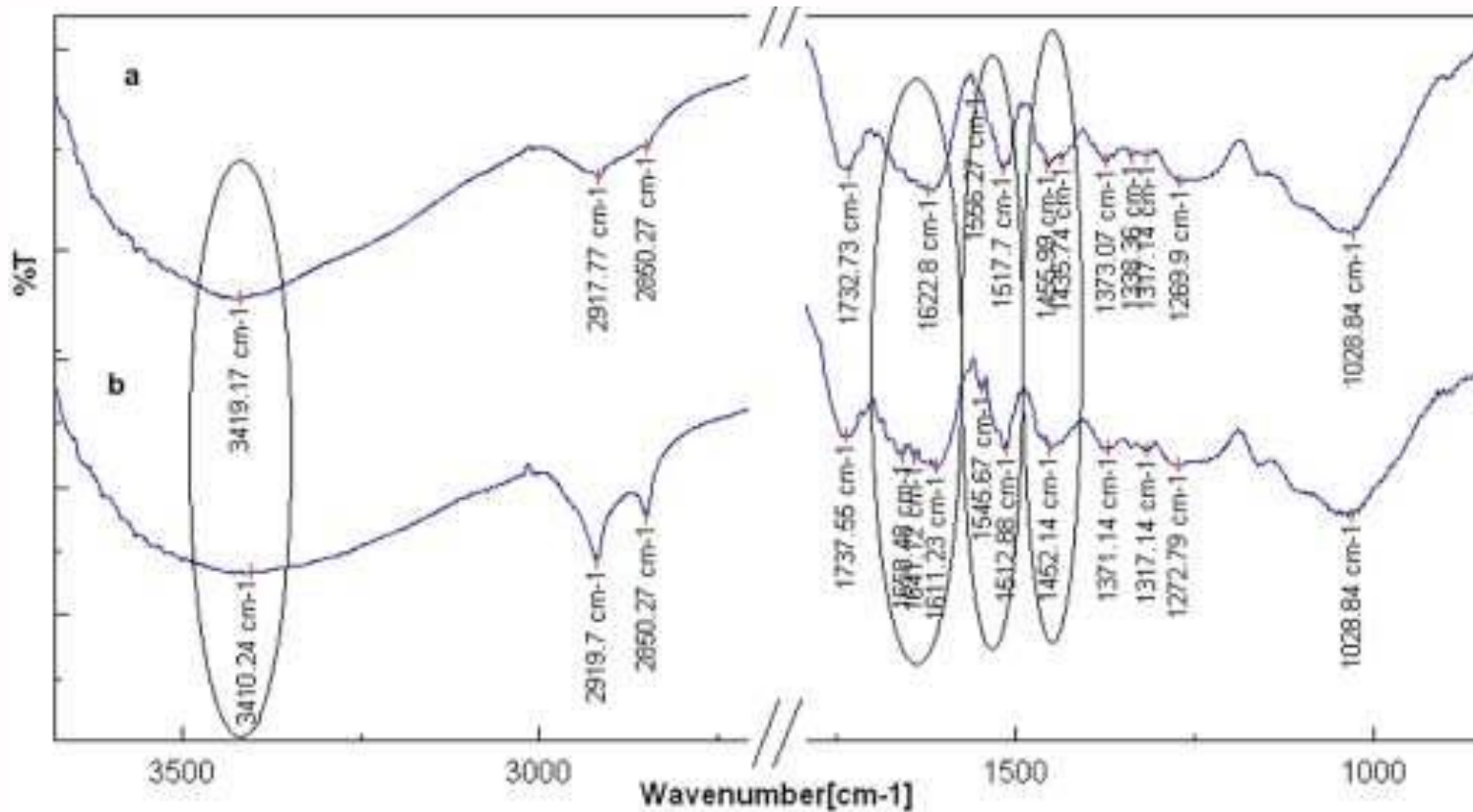
The purpose of this work is to obtain a specific green biosorbent able to bind Hg(II) in a water solution with neutral pH, in order to avoid additional chemical pretreatments, which have high environmental impact



→ The citric acid (CA) acidic treatment is suitable for obtaining an efficient biosorbent for Mercury removal



# FTIR STUDY OF «GM – CA» BIOSORBENT



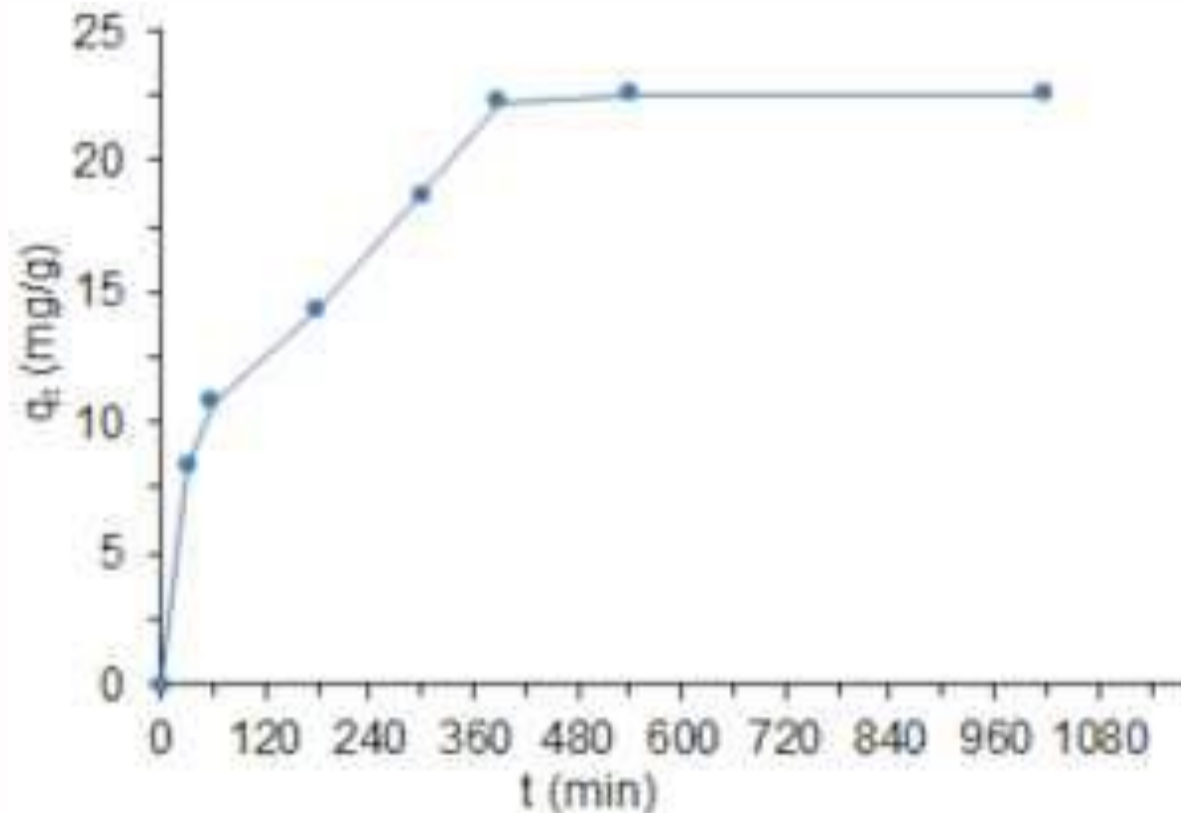
FTIR spectra of biosorbent GM-CA before Hg(II) ions loading (a) and after Hg(II) loading (b).

Comparing the spectra, some of the signals are slightly modified in terms of shape, intensity or wavenumber as a result of mercury interaction.

Thus, it is clear that the interaction of the Hg(II) involves mainly lignocellulosic part, which is the main component of the biosorbent.

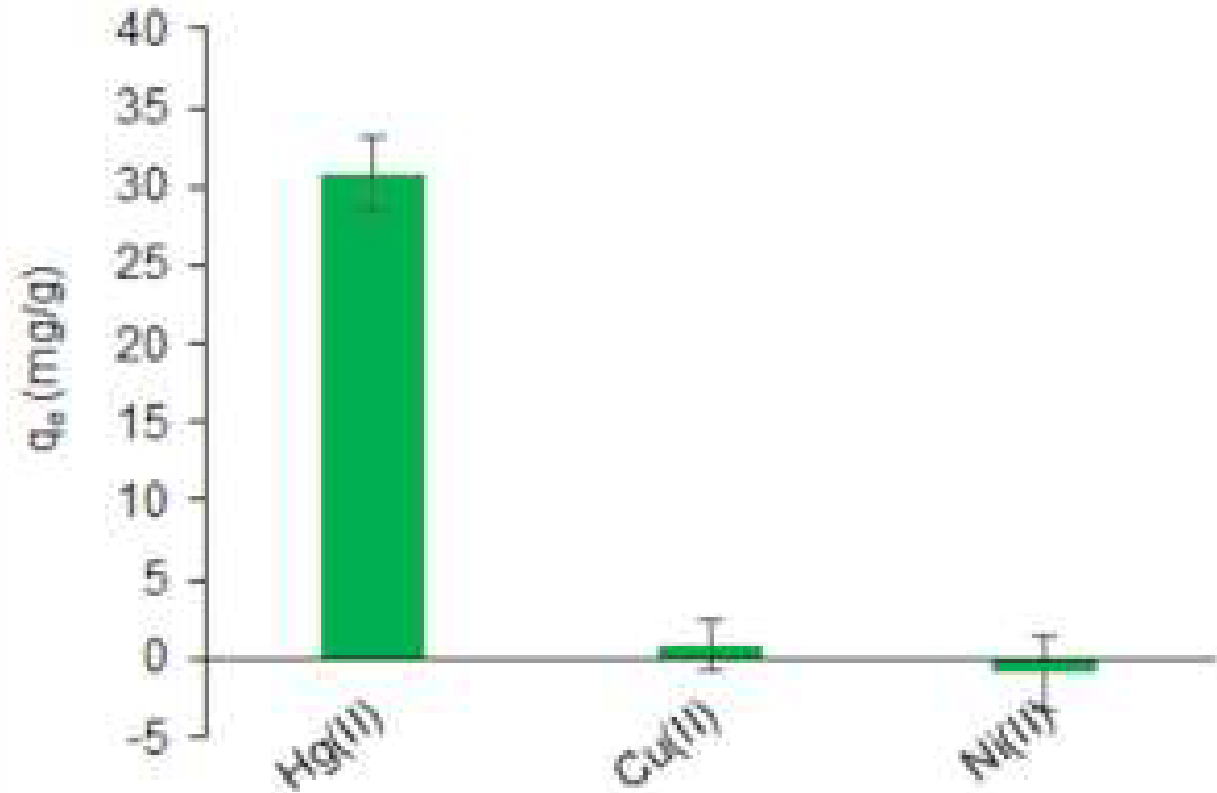


# KINETIC STUDY OF «GM – CA» BIOSORBENT



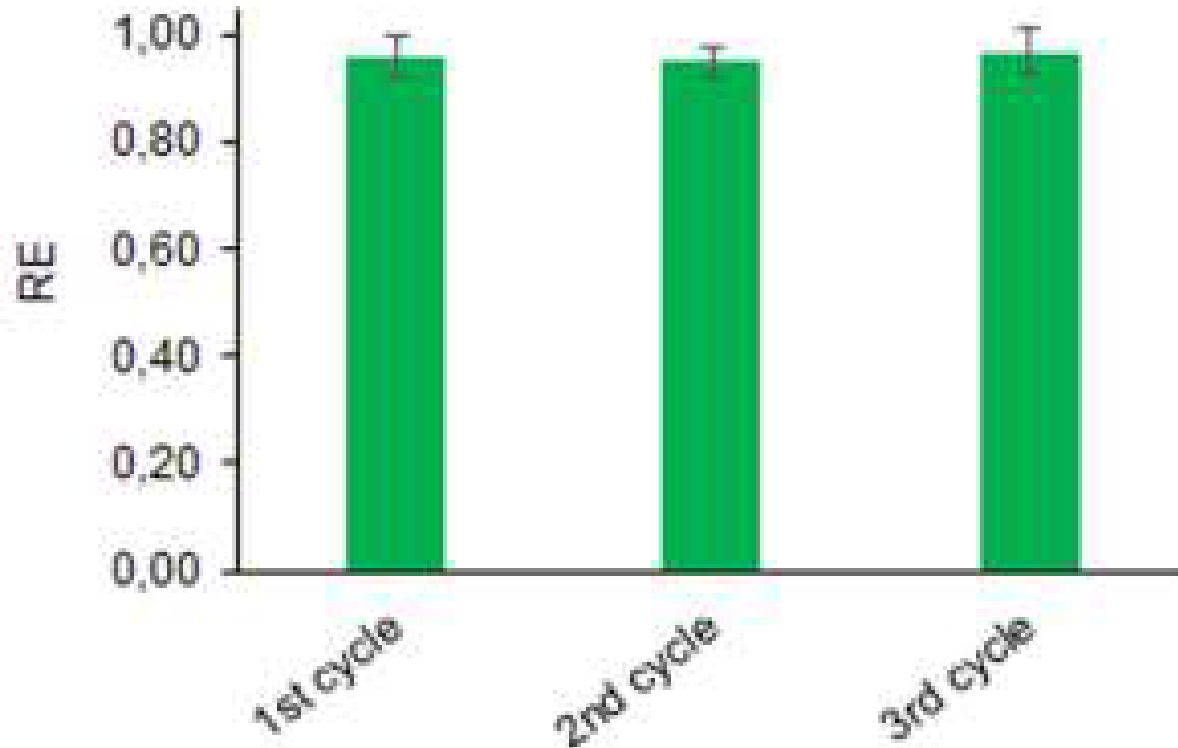
Seven different solutions containing the same initial amount of mercury were prepared: bioadsorbent and mercury-containing solution were put in contact together and taken at different times to study the influence of contact time on adsorption. At different time intervals the bioadsorbent was removed from the solution and the solution analysed at the ICP-MS to quantify the residual mercury remaining after mercury uptake.

# COMPARATIVE ADSORPTION STUDY



The adsorption capacity of GM-CA biosorbent for other two bivalent metal ions, using aqueous solution of  $100 \text{ mg L}^{-1}$  of Cu(II) and Ni(II). Almost no adsorption was found for both Cu(II) and Ni(II) metal ions: these results can be justified taking into account the complex structure typical of the grape biomaterial and also the different composition of each grape variety in addition to the modification of its structure during the biosorbent preparation steps.

# REUSABILITY PROCEDURE



In order to demonstrate the reusability of grape-marc based biomaterial, after an adsorption experiment of GM-CA with Hg(II) aqueous solution at 100 mg/L, the mixture was centrifuged to remove the solution and the biomaterial was treated with HCl for desorption of Hg(II) ions, trapped into the biosorbent and again reused for another adsorption experiment. The regeneration efficiency has been proven for three cycles of adsorption/desorption experiments and remains higher than 93%.

The regenerated biomaterial showed similar adsorption capacities at least for three cycles.

# CONCLUSION

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For the first time the adsorption capacity of Hg(II) was demonstrated for a green and cheap grape marc – based biosorbent

This is an alternative method for the removal of metal ions from aqueous media that can be effective, cheap and with zero environmental impact in order to protect human health, ecosystems and food resources

The method allows us to take advantage of a widely available waste, thus making it a resource. Italy ranks first among wine-producing countries and produces large amounts of grape marcs as a waste of wine production process

The method is an intervention strategy to face mercury pollution which can undergo long-range transport in the atmosphere, can be persistent in the environment, can accumulate in the food chain, and pose severe consequences on the human and ecosystem health due to its toxicity

**LAST BUT NOT**

**LEAST...**

**FUTURE TRENDS!**



**Creation of composite nanohydrogel that can exploit adsorbent capacity of different materials**

**Creation of hybrid nanostructures to increase SSA and the number of available binding sites**

**AVAILABLE AND READY PRODUCT BY 2024**

**Engineering the surface with Ag nanoparticles (antibacterial function)**

**Porosity optimization to improve the interaction with the adsorbent surface**

**Swelling control to facilitate exploitation in pre-existing devices**

**THANKS FOR  YOUR ATTENTION!**