POLITEHNICA UNIVERSITY OF BUCHAREST
FACULTY OF MATERIALS SCIENCE AND ENGINEERING
Doctoral School of Biotechnical Systems Engineering
Environmental Engineering Field

SUMMARY
PHD THESIS

VEGETABLE WASTES RECOVERY FOR HEAVY METALS REMOVAL PROCESSES FROM WATERS

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1. CURRENT STATE OF RESEARCH IN THE FIELD OF PLANT WASTE RECOVERY

In the past, the emergence of waste with the production and consumption of goods was considered a normal and necessary action. Today, there is a growing interest in the circular economy, zero waste, closed cycle, resource efficiency, avoidance of waste generation, reuse and recycling, all these terms being attributed to a responsible attitude towards resources, materials, products and the environment [1,2]. However, a holistic approach is needed to ensure that waste generation is not generated, and in this respect the focus is on the reuse and recycling of materials at every stage of their life cycle, but also with regard to the materials and energy used so that the design of the product protects the environment regardless of the recycling stage at which they are located, until the end of the life cycle [3].

Waste management at EU level can usually be described using the terms 'collection and storage', by collecting municipal and commercial waste streams and incinerating or storing them in the field. The European economy is mainly linear, disregarding the impact on the environment and human health, based on resource inefficient use and increased dependence on resources outside Europe. Unlike the circular economy, the current modes of production and consumption are outdated and can be defined using a linear principle. There are already alternative methods for the classical linear economy to reduce the consumption of resources and / or increase their efficiency. These are known as "3 R": Reduction (demand and/or consumption of resources, materials and products), Reuse and Recycling (return of materials to another life cycle). All these approaches support the concept of the circular economy which, as a whole, can be considered a fundamental alternative to the linear economic model [6]. The design of a circular product will require information and data from the waste management sector on how products or components can be remanufactured, disposed of and recycled, according to Figure 1.

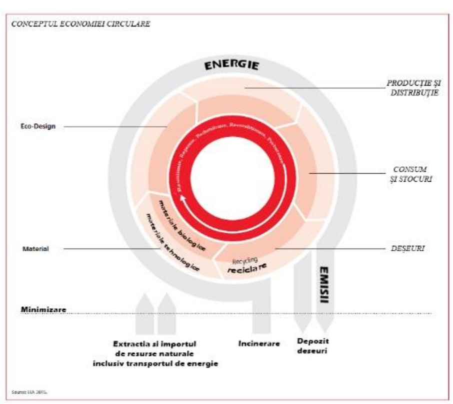

Figure0 The concept of the circular economy

According to EUROSTAT reports from 2018, the total amount of waste generated in the 27 EU Member States (EU-27) from all economic and household activities totals 2317 million tonnes. Figure 2 illustrates this classification in 2018 by activity [7]. In the EU-27, construction waste accounted for 36.0% of the total in 2018 and was followed by mining and extractive (26.2%), processing industry (10.6%), waste and water services (9.9%) and households (8.2%); the remaining 9.1% were waste generated by other economic activities, mainly services (4.2%) and energy (3.5%). [1] .

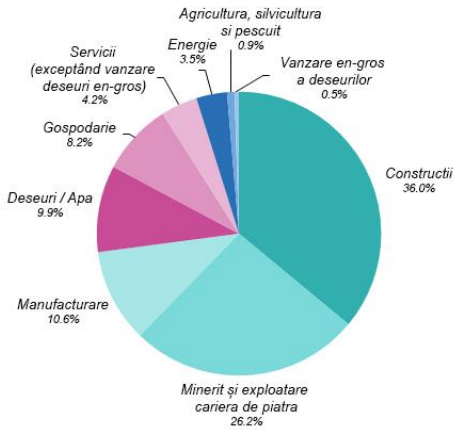

Figure 2 Classification of waste generation sectors by activity

Figure 3 shows the evolution of waste treatment methods in the EU-27 and the two main categories of treatment, recovery and disposal in the period 2004-2018.

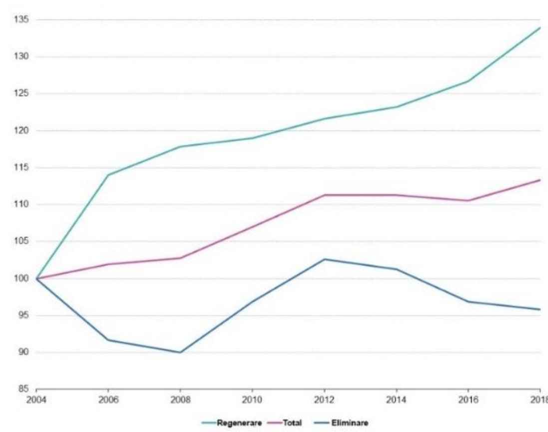

Figure 3 Waste treatment methods identified in the EU between 2004 and 2018

The amount of waste recovered, or recycled, used in excavated areas for the purpose of hill recovery or safety, or for technical purposes in spatial planning, or incinerated with energy recovery, increased by 33.9 % from 870 million tonnes in 2004 to 1165 million tonnes in 2018; as a result, the share of such a recovery in the total waste treatment increased from 45.9% in 2004 to 54.2% in 2018. The amount of waste subject to disposal decreased from 1027 million tonnes in 2004 to 984 million tonnes in 2018, which was a decrease of 4.2%. The share of disposal in total waste treatment decreased from 54.1% in 2004 to 45.8% in 2018.

Food waste is classified into 2 large groups: animal (dairy, coal, fish and seafood processing industry, etc.) and vegetable (with sources of different origins, from cereals, tubers, roots, to oilseed crops, fruits and vegetables), and their perishable character, combined with various external factors, make it difficult to capitalize on them.

Given the share that food waste has on the total amount of waste generated, today it exists in conventional management practices and emerging methods of its recovery. (Figure 4)

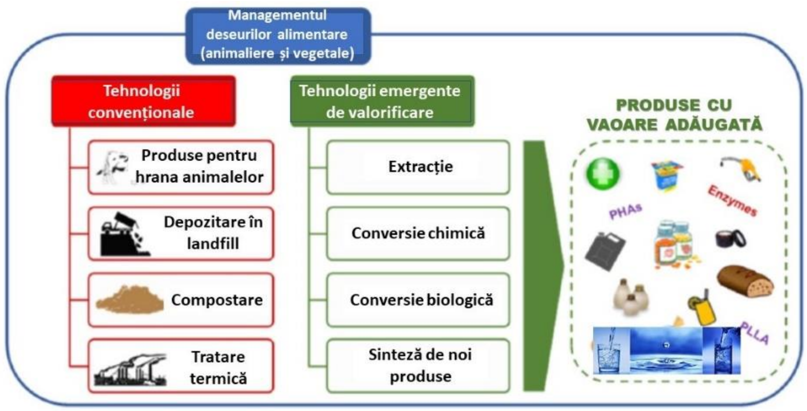

Figure 4 Food waste management strategies (animal and vegetable)

Emerging recovery technologies are preferred to conventional ones because they contribute to reducing the amount of waste and ultimately to recovering useful components and reintroducing them into the food chain or for other end uses (water purification, pharmaceutical, cosmetic, etc.).

Waste from inedible parts of the food consumed is directly related to certain physical properties of the product, such as the example of banana peels. In this case, it was found that bananas have an inedible fraction percentage of about 34-37%.

Adsorbents developed from vegetable matter, from fruit and vegetable waste and from agricultural waste in general are very popular raw materials for the manufacture of adsorbent materials due to their availability and cost-effectiveness [8]. Adsorbents derived from agricultural waste can be modified using different chemicals to increase the potential of functional clusters, thereby increasing the adsorption and capacity of adsorbents. Lignocellulose biomass is obtained from agricultural waste products and could be an effective raw material for the manufacture of carbonic materials, such as biochar (biomass activated coal), which has a large area, volume and pore distribution at least comparable to commercial activated carbon [9].

Industrial (e.g. mining, paint, machine manufacturing, metal coatings and tanning) and agricultural activities (when using fertilizers and intense fungicidal sprays) are the main sources of waste containing heavy metals. Heavy metals are considered to be one of the most dangerous contaminants of water. According to the World Health Organization (WHO), among the most toxic metals are cadmium, chromium, copper, lead, mercury and nickel. In general, the decontamination of heavy metal wastewater using bio-charcoal "biochar" occurs through physical and chemical interactions, such as complexation of the outer and inner sphere, electrostatic attraction, ionic exchange and precipitation to the surface, as shown in Figure 5.

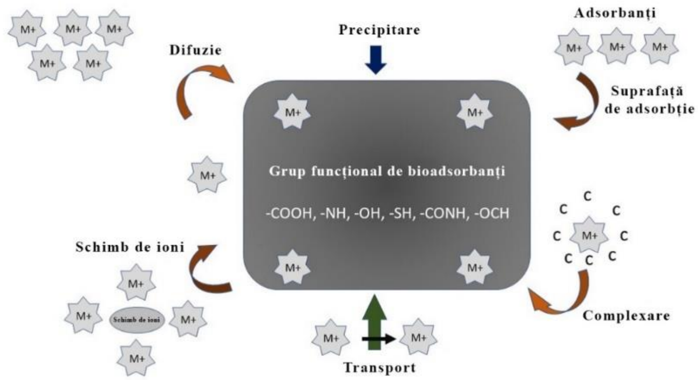

Figure 5 Schematic representation of decontamination processes using bioadsorbents

The internal and surface structure of biocaminate comprises a mixture of macropores, mesopores and micropores, through which heavy metals can be attracted both inside and on the surface of the pores. Fourier-transform infrared spectroscopy analyses (FTIR) have demonstrated that functional groupings of type -COOH and -OH are responsible for adsorption, e.g. they change before and after adsorption when complexed with Pb and Cd [8]. The O-metal bond causes the decrease of the electronic density of oxygen in the functional groups (O-O), which drastically reduces the binding energy of the oxygen-containing groups (O-O), leading to the stability of the O-metal fomate bond. The interaction of the metal in the bonding process can be diminished by the vibration energies of the C-C bond [12]. In addition, functional clusters that include oxygen (O-O) release H+ when they encounter metal ions, which leads to a reduction in the pH of the solution. The electrically charged properties of the bio-coal surface are indicators at the stage of choice of the raw material used in the process of electrostatic adsorption. The pH value and the redox potential play a crucial role in the adsorption of metals from wastewater [13].

The processes for activating coal consist of chemical and/or physical treatment [4, 5, 11, 14-16]. Both treatments are responsible for getting different shapes and sizes. With physical treatment, the precursors are initially charred, undergoing an activation process with steam or carbon dioxide.

Chemical treatment involves impregnating precursors with an activating agent, followed by a heating process in the atmosphere of inert gas [2, 11, 17-20]. The activating agents could dissolve the cellulosic composition of the precursor and lead to the process of crosslinking (Giraldo and Moreno-Piraján 2012).

Chemical activation has several advantages than physical activation. It requires low temperatures, produces high yields, large area of the specific surface, involves only one step for the development of micropores and the reduction of mineral matter content compared to physical activation. However, there are also disadvantages to chemical activation, such as the washing step required to remove impurities from the activating agents and also the corrosive properties of the agents [15].

Banana waste is of great interest in the field of research on waste recovery due to its adsorption capacity, availability and significant impact on water-soluble pollutants.

2. RESEARCH OBJECTIVES AND METHODOLOGY

The main objective of the thesis is the design and realization of sustainable eco-materials with a role in the decontamination of pollutants in water, using as a raw material a vegetable waste based on banana peels. The eco-materials obtained have adsorbent properties, are easy to integrate into the environment, can be regenerated, and the way of processing, applying different heat treatments and chemical activation, offers the possibility of obtaining two types of such materials: ash (CB) and activated charcoal (CBvid). The small size of these eco-materials leads to a possible risk of uncontrolled discharge into the environment, which is why their design also included a stage of immobilization on biopolymer supports (chitosan and alginate type), friendly environmentally and effective in the processes of reducing water pollution.

The use of banana peel waste as eco-materials with adsorbent properties is a way of capitalising on them, thus contributing to the concept of circular economy and the conservation of natural resources.

The results of this research paper were based on the realization of a complex study in the field of environmental protection and engineering, but also in the field of materials science. The approached topic has an obvious contribution in the field of vegetal waste recovery, by identifying the potential of their transformation into value-added products, useful in the decontamination of heavy metals of wastewater. This is how the protection of ecosystems is achieved by removing species of persistent pollutants (such as heavy metals) and reducing the amount of waste deposited.

The proposed topic contributes to the scientific research in the field of environmental engineering through:

- *reducing the risk of environmental pollution by: a) reintroducing into the natural circuit some vegetable waste (banana peels) in the form of eco-desorbents and b) decontaminating heavy metal wastewater with the help of eco-materials;*
- *designing a circular product as an integral part of the circular economy by converting a waste into products (eco-materials);*
- *substantiation of physico-chemical processes that favor the removal from the waters of persistent pollutants such as heavy metals;*
- *development and development of a complex programme for the recovery, characterisation and testing of eco-materials obtained from a waste also applicable to other types of waste with a view to converting them into products.*

In order to achieve the main objective of the thesis, the following scientific and technical objectives have been taken into account:

- ✓ Presentation of the concept of obtaining 2 eco-materials of the type ash and activated charcoal, using as raw material the waste from banana peels that has been heat treated and chemically activated.
- ✓ Establishment and evaluation of the qualitative and quantitative performances of the 2 eco-materials, based on the structural, surface and chemical characteristics, regarding the retention capacity of some heavy metal pollutants from synthetic aqueous solutions.
- ✓ Establishment and evaluation of the performance of the 2 eco-materials integrated into biopolymeric ecological matrices, using chitosan and alginate, thus reducing the risk of uncontrolled discharge into the environment.
- ✓ Demonstration of the concept presented by developing a complex program of morphological, structural, surface characterization in order to correlate with the evaluation of the performances regarding the retention of heavy metals from synthetic aqueous solutions.
- ✓ Validation and confirmation of performance in the retention of heavy metal pollutants using specific kinetic and isothermal adsorption mechanisms, including regeneration studies.

The research methodology was developed in order to obtain the 2 eco-materials of ash and activated coal type and of some fixed biopolymeric supports that would later integrate the 2 eco-materials, in order to reduce the risk of uncontrolled discharge into the environment, due to their small size. The information existing in the specialized literature on the current level of development in the field was the basis for the design of materials, their characterization and testing. There were studied methods of obtaining and the performances were analyzed from a qualitative and quantitative point of view, considering the technical as well as the economic aspects.

The research methodology, the work plan and the experiments were designed and carried out within the Environmental Protection Laboratory within the ECOMET Research and Expertise Center at the POLITEHNICA University of Bucharest.

Figure 6 shows schematically the methodology for obtaining ecomaterials, followed by their characterization and testing/validation.

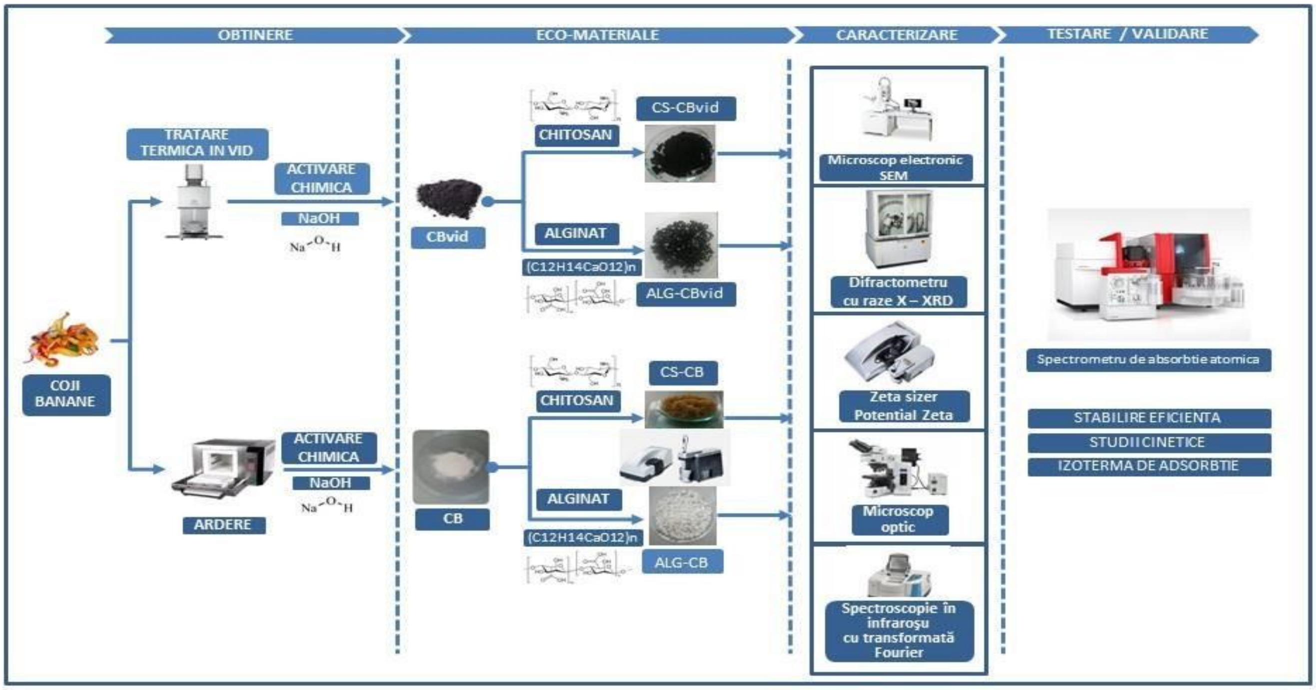

Figure 6 Schematic representation of the work plan

2.1. Methods of analysis and equipment used

1 Table.1 Equipment and working methods

No.	Working stages	Equipment/Laboratory instruments used
1. Ash Obtaining and Characterization (CB)		
1.	Scales of banana peels waste	Laboratory glassware Analytical balance (Ohaus Explorer)
2.	Drying banana peels, (i) naturally 3 days, (ii) 105°C, 4h.	Laboratory oven (Memmert)
3.	Heat treatment- combustion (i) 700°C, 1h(ii) added NaOH (iii) 800°C, 1h	Heat treatment furnace (Microterm 1206) Laboratory glassware Analytical balance (Ohaus Explorer)
4.	Wash with acidified distilled water with HCl 0.1N for neutral pH	Laboratory glassware (Berzeliu beakers, filtration funnels, Buchner vacuum filtration system) Phenolphthalein 1% solution pH-meter Consort C931
5.	Drying 105°C	Laboratory oven (Memmert)
6.	Morphological, strcutural, surface and stability characterization	Scanning Electron Microscope (FEI, QUANTA 450 FEG) equipped with energy dispersive spectrometer (EDS) X-ray diffractometer (PANalytical, Model: X'Pert PRO MPD X) ZetaNanosizer (Malvern, Model: Zetasizer Nano ZSP) FTIR Spectrometer (INTERSPECTRUM Estonia, Model: Interspec 200-X)
2. Obtained and characterized activated charcoal (CBvid)		
7.	Scales of banana peels waste	Laboratory glassware Analytical balance (Ohaus Explorer)

8.	Drying banana peels, (i) naturally 3 days, (ii) 105°C, 4h.	Laboratory oven (Memmert)
9.	Heat treatment vacuum carbonization (i) 700°C, 1h (ii) added NaOH (iii) 800°C, 1h	Vacuum sintering furnace (Caloris CD 1016) Laboratory glassware Analytical balance (Ohaus Explorer)
10.	Wash with acidified distilled water with HCl 0.1N for neutral pH	Laboratory glassware (Berzelius glasses, filter funnels, Buchner vacuum filtration system) Phenolphthalein 1% solution pH-meter Consort C931
11.	Drying 105°C	Laboratory oven (Memmert)
12.	Morphological, strcutural, surface and stability characterization	Scanning Electron Microscope (FEI, QUANTA 450 FEG) equipped with energy dispersive spectrometer (EDS) X-ray diffractometer (PANalytical, Model: X'Pert PRO MPD X) ZetaNanosizer (Malvern, Model: Zetasizer Nano ZSP) FTIR Spectrometer (INTERSPECTRUM Estonia, Model: Interspec 200-X)
3. Obtaining CS, CS-CB, CS-CBvid, systems characterization		
13.	Obtaining CS 1%: dissolving in 25% acetic acid solution, magnetic stirring, 60 °C. Obtaining CS – CB 1:0,2 and 1:1 by dispersion of CB powder in suspension CS 1%, magnetic stirring, 30 minutes, 50% (Glu), filtration, drying. Obtaining CS – CBvid 1:1 by dispersion CBvid powder in suspension CS 1%, magnetic stirring, 30 minutes, 50% (Glu), filtration, drying.	Reagents: Chitosan, Sigma Aldrich, Acetic acid 25%, Glutaraldehyde 50% Laboratory glassware Analytical balance (Ohaus Explorer) Buchner vacuum filtration system Magnetic stirrer with hob Ultrasonic Device Laboratory oven (Memmert)
14.	Morphological, strcutural, surface and stability characterization	Olympus optical microscope (BX 51 M) Scanning Electron Microscope (FEI, QUANTA 450 FEG) equipped with energy dispersive spectrometer (EDS) FTIR Spectrometer (INTERSPECTRUM Estonia, Model: Interspec 200-X)
4. Alg, Alg-CB, Alg-CBvid, systems characterization		
15.	Alg: dissolving Alginate Na (1%) in hot distilled water, stirring, 90°C, 4 h, 200 rpm. Alg-CB 1:1 and Alg-CBvid 1:1: DISPERSING CB and CB vacuum powder into AlgNa, drip into cacl2 bath 2%.	Reagents: Sodium Alginate, BioChemica, CaCl2 2%, Laboratory glassware Analytical balance (Ohaus Explorer) Magnetic stirrer with hob Ultrasonic Device Laboratory oven (Memmert) Pumping system TL-BM-300
16.	Morphological, strcutural, surface and stability characterization	Olympus optical microscope (BX 51 M) Sem scanning electron microscope (FEI, QUANTA 450 FEG) equipped with energy dispersive spectrometer (EDS) FTIR Spectrometer (INTERSPECTRUM Estonia, Model: Interspec 200-X)

5. Qualitative testing of CB, CBvid eco-materials and systems formed with support matrices CS and Alg		
17.	Preparation of multielement solutions, laying characteristics (pH, conductivity)	Laboratory glassware pH-meter Consort C931 Multimeter CONSORT C 835 Merck multilement solutions (KGaA, Darmstadt, Germany), 1.0907 g/cm3 (20°C), ~1000 mg element / L
18.	Qualitative analysis of multielement solutions, before and after contact with the cross-materials and systems obtained	Laboratory glassware Atomic Absorption Spectrometer, ContrAA 800D, AnalytikJena AG Germany
6. Quantitative testing of cb, CBvid eco-materials and matrix systems formed with support matrices CS and Alg		
1.	Preparation of Solutions Pb and Cu, laying characteristics (pH, conductivity)	Laboratory glassware pH-meter Consort C931 Multimeter CONSORT C 835 Merck solutions (KGaA, Darmstadt, Germany), 1.0907 g/cm3 (20°C), ~1000 mg element / L
2.	Setting parameters: efficiency, contact time, kinetic and adsorption studies, regeneration	Laboratory glassware Atomic Absorption Spectrometer, ContrAA 800D, AnalytikJena AG Germany

3. EXPERIMENTAL RESEARCH ON OBTAINING AND ESTABLISHING THE PERFORMANCE OF VALUE-ADDED ECO-MATERIALS OBTAINED FROM BANANA PEEL WASTE

In this chapter, the results obtained by making integrated use of the waste from banana peels are presented, namely:

- Vacuum heat treatment and chemical activation of banana peels in order to obtain an adsorbent material (CBvid) with added value through the large specific area, capable of retaining metal ions at the same time;
- Controlled combustion, in an oxidizing atmosphere, of banana peels in order to generate heat with obtaining as waste an activated ash (CB), subsequently used in the process of retaining metal ions from aqueous solutions.

3.1. Obtained activated charcoal from banana peels (CB) vacuum

The procedure for obtaining activated charcoal consists of carbonisation followed by the activation of carbonic material of plant origin [10]. Carbonization is a heat treatment that takes place at 400-800°C through which raw materials are converted into activated carbon by minimizing the volatile material content and increasing the carbon content in the material. This increase leads to an increase in the hardness of the material and the creation of an initial porous structure that is necessary if the material is to be activated. An increase in temperature leads to increased reactivity, but at the same time to a decrease in the volume of pores. The decrease in the volume of pores is due to an increase in condensation of the material at high temperatures specific to carbonization [10]. After the porous structure has been created by carbonization, an activation (oxidative or chemical) is required to create micropores, which can reach up to 2 nm, these being the majority of the pores that contribute to the carrying out of the adsorption process [10, 23]. Figure 7 schematically depicts the process of obtaining activated charcoal from banana peels (CBvid).

Figure 7 – The process of obtaining activated charcoal from banana peels – CBvid

In the first stage, the material was heated to 700°C for 1 hour with a heating speed of 3°C/min. The intermediate product obtained (carbonic and mineral mass) was chemically treated with NaOH at a weight ratio of 1:3 (NaOH:intermediate product) to remove the intermediate compounds, partially carbonised, followed by a heating process to 800 °C for 1 hour in the same vacuum furnace. Weight loss is the mass of volatile substances, as seen in Table 2. After going through these steps resulted activated charcoal CBvid. The resulting activated charcoal was washed several times with distilled water in order to remove excess NaOH (check with the phenolphthalein indicator) and then dried in the oven.

Table 2 – properties of the CBvid biomaterial

Properties of banana peel	CBvid	References	
		[24]	[21]
Humidate	19,56%	11,4%	5,2%
Volatile	72%	83%	78,83%
Fixed charcoal (activated)	6%	0,43%	5,95%
Intermediate product (mineral and carbonic mass)*	8,44%	5,1%	15,73%

3.2. Obtaining ash from banana peels (CB)

The production of ash (denoted CB) using banana peels as a raw material was achieved by heat treatment of waste in order to obtain a biofuel and a stable product in the form of ash that activated can be used as an adsorbent material in the waste burning process to generate energy, the organic components decompose with the release of a certain amount of gases with small molecules, such as CH4 and CO, and the remaining remaining mineral residue can be harnessed according to the composition [25]. In Figure 8 schematically the process of obtaining ash is shown.

Figure 8 – The process of obtaining ash from banana peels - CB

To obtain CB ash, the banana peels were dried in the oven at a temperature of 140°C for 4 h. The result was dried banana peels (water absorption of about 88%) which were then subjected to two-stage combustion in a calcination furnace. In the first stage, at the temperature of 700°C, for 1h, an amorphous ash was obtained. The product was activated by treatment with NaOH at a weight ratio of 1:3 (NaOH:ash), followed by a heating process to 800°C for 1 h. After completing these steps resulted CB, washed several times with distilled water to remove excess NaOH (check with the indicator phenolphthalein) and then dried in the oven. According to the absorption of water, banana peels, before the burning process, have about. 88.49% humidity, ash production efficiency, relative to the amount of dry matter is 9.5%, and the percentage of volatiles is about 90.44% as seen in Table 3.

Table 3 - properties of cb biomaterial

Bpineapple peel characteristics	**CB**	**References**	
		[22]	**[27]**
Humidity*	88,49%	9,64%	50,5
Volatile	90,44%	N.A.	49,5
Ash	9,5%	18,98%	8,8

For both material, the characteristic functional groups were identified, using fourier FT-IR transformed infrared spectroscopy with totally attenuated ATR reflection.

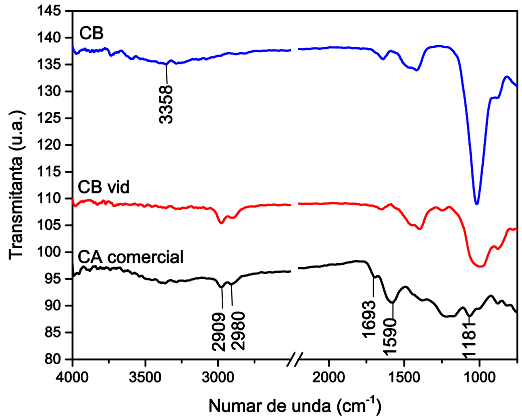

Figure 9 ATR-FT-IR SPECTRE on the identification of functional groups present in coal made from banana peels (CB and CB vacuum) compared to the spectrum of commercial activated carbon (CA)

Both materials, CB and CBvid, were characterized by the following methods:Identification of functional clusters characteristic of CB and CBvid samples

- Determination of particle sizes and stability in CB and CBvid samples
- Morphological, structural and dimensional characterization of materials obtained from banana peel waste

The performances regarding the retention capacity of some metal ions using coal (vacuum CB) and ash (CB) obtained from banana peels have been established, with the following results:

- Experimental results on the removal of metal ions from multielement aqueous solution using activated charcoal of type CBvid, the conclusions being as follows:
  - An obvious affinity has been recorded for ionic species of type Pb, Co, Zn, Cd and Cu, and for species of type Fe, Mn, Cr no changes in absorbance values are observed even after 60 minutes of contact with different amounts of PB, Co and With the changes occur after 15 minutes of contact and are maintained in time up to 60 minutes, a phenomenon demonstrating the retention capacity of CBvid material for these species.
  - From the qualitative information regarding the absorbance values recorded, it was found that in the first 15 minutes they decrease significantly, by over 50% compared to the initial absorbance value. Using a smaller amount of material, 0.05 g, it was found that the optimal time is reached at 60 minutes, while for 0.5 g CB vacuum, the retention is over 80%.

- High efficiency, at an optimal time of 15-30 minutes, can be achieved at an adsorbent amount of 0.5 g that can ensure retention over 80% of Cu and Pb and below 30% for Co, Cd and Zn.

The recovery yield of the CBvid material was 30%, the losses thus influencing the high retention efficiency of the material for Cu and Pb. Experimental results on the removal of metal ions from multielement aqueous solution using CB ash, the conclusions being as follows:

- After the contact at 30 minutes between the multielement solution, at different amounts of CB there is a significant decrease in the absorbance values, reaching after 60 minutes the total removal of the metal ions from the analyzed systems, a phenomenon that demonstrates a high retention capacity of the CB material.
- From the qualitative information on the absorbance values recorded, it was found that in the first 15 minutes they decrease significantly, by over 50% compared to the initial absorbance value, and at 30 minutes the decrease is over 95%, reaching 100% at 60 minutes.
- Using a smaller amount of material, of 0.05 g, it was found that the optimal time is reached at 45 minutes, with the total retention of Cd, Co and Cu.
- A high efficiency, at an optimal time of about 15-30 minutes can be achieved at an adsorbent amount of 0.5 g, with a good efficiency for most of the competitive ions studied.
- The recovery yield of the CB material is about 25%, the losses thus influencing the high efficiency of the material.

The recovery yields of CB and CBvid having very low values of 25% and 30%, respectively, the possibility of incorporating these materials into biopolymeric ecological matrices of chitosan and alginate type was studied.

3.3. Obtaining nanostructures from coal of type CBvid and CB ash embedded in chitosan CS matrix

In order to incorporate CB vacuum coal and CB ash, with the aim of stabilizing the powders obtained and reducing the risk of uncontrolled disposal into the environment, the chitosan powder (CS) which was soiled in acetic acid was used as a support material. CS is known as an eco-friendly flocculant, used in water treatment applications due to its ability to remove a wide range of organic and inorganic particles from waters [28].

The advantages of using CS, with the role of biopolymer are: eco-friendly flocculant, ability to remove a wide range of organic and inorganic particles from the waters [28], removal of solid suspensions, paints, heavy metals and other pollutants by applying chitosan derivatives, high efficiency in acid, neutral or alkaline pH conditions [29], can be removed by filtration or sedimentation, resulting in clean, treated water without other chemical compounds [30].

Schematically, the process of obtaining the CS-CB microspheres is shown in Figure 10.

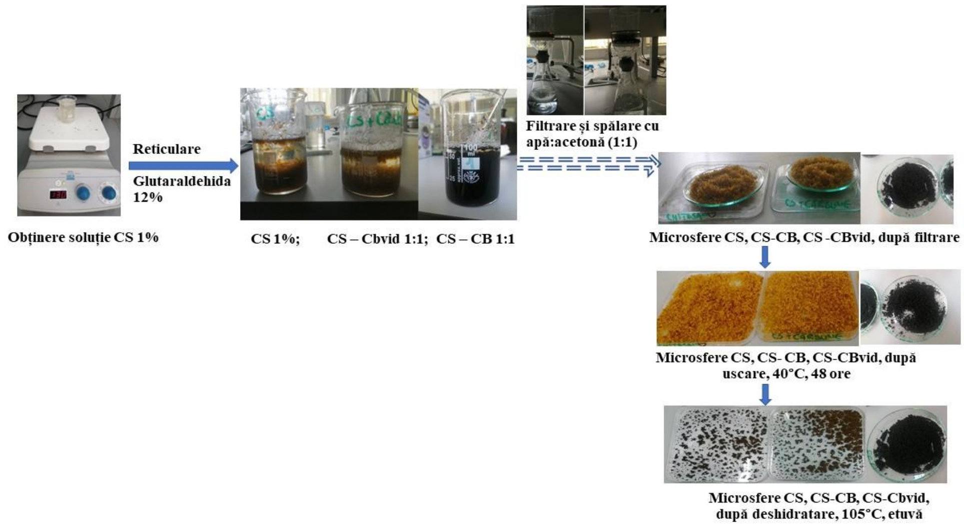

Figure 10 Schematic representation of the stages of obtaining microspheres of 0.2% CB and CS cross-cross-related with Glutaraldehyde

Several experimental variants were used, using CS, CB and CBvid. The experimental variants are given in Table 4.

Table 4 Experimental variants using CS-CB microspheres

Na.	Codification	Solution Volume (ml)	S.C. (g)	CBvid (g)	CB (g)
1	CS-CBvid 1:1	100	1	1	-
2	CS-CB 1:0,2	100	1	-	0,2
3	CS-CB 1:1	100	1	-	1

Both materials, CB-CS and CBvid-CS, were characterized by the following methods:

- Identification of functional groups characteristic of samples of type CS, CB-CS and CBvid-CS
- Determination of particle sizes and stability in samples of type CS, CS-CB and CBvid-CS
- Morphological, structural and dimensional characterization of the samples of CS, CS-CB and CBvid-CS

The performances regarding the retention capacity of some metal ions using the materials CS, CS-CB, CS-CBvid have been established, having the following results:

- The results obtained for the formulation CS-CB 1:0,2 were inconclusive and thus the evolutions of the absorbance values recorded for the materials CS-CBvid 1:1 and CS-CB 1:1, respectively, were presented.
- Although the quantities of CBvid and CB, respectively, are kept when incorporated into the CS matrix, a better retention is found on the plain CS material, the incorporation into the CS of CBvid and CB leading to the appearance of possible links between CBvid and CB with the functional groups of the amino and carboxyl type CS, which reduces the active reaction sites in the CBvid and CB structure.
- The retention trend is higher on CS and CS-CB, respectively.
- For CS-CBvid about 30% is retained Cr after 30 minutes, reaching over 40% after 60 minutes
- The simple CS material has affinity for Co and Cu of about 30% and Cd of about 25% respectively.
- In the case of CS-CB, Fe is retained about 80% after 30 minutes reaching 99% at 60 minutes, and for the other elements as follows: Pb about 45% after 60 minutes, Zn over 20% after 60 minutes and Mn respectively about 20% after 30 minutes, a trend that disappears at 60 minutes.
- The incorporation of CB and CBvid materials into the CS, leads to a stability of the material, but also to a reduction of the reaction centers through possible links established between the CS and CB and CS-CBvid groups, respectively.

In view of the fact that although the stability of the material was better following the incorporation of CB and CBvid biomaterials into cs but at the same time there was a reduction in reaction centers, we considered it necessary to study the possibility of incorporating activated charcoal (CBvid) and ash (CB) into alginate.

The advantages of using alginate as a biopolymer are: it is natural polyelectrolyte, used as an alternative to synthetic polyelectrolytes, has high efficiency in removing heavy metals, is colloidal hydrophilic carbohydrate extracted from brown algae species, offers safety in operation, does not affect health and is effective in the flocculation process.

The process of obtaining alg-CB and Alg-CBvid materials is shown schematically in Figure 11.

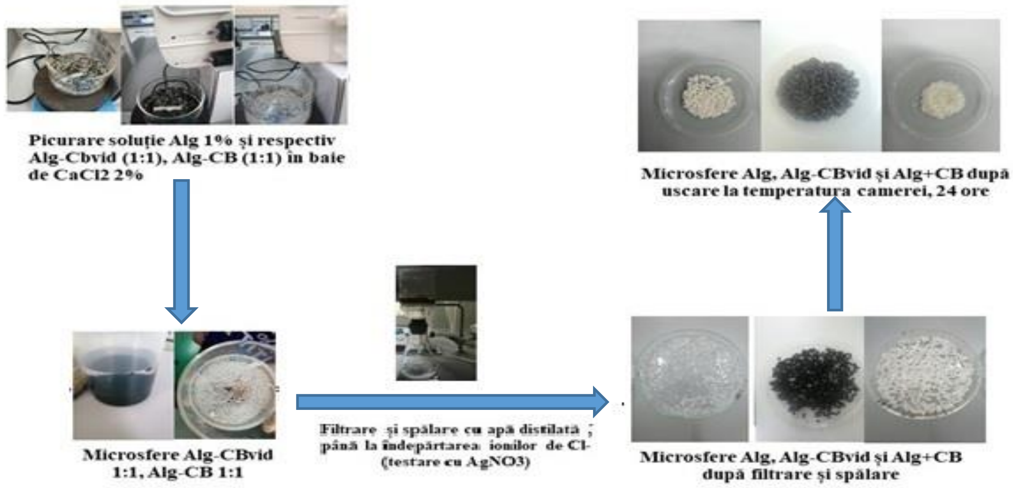

Figure 11 Schematic representation of the alg-CB and Alg-CBvid material production steps

Both materials, CB-Alg and CBvid-Alg, were characterized by the following methods:

- Identification of functional groups characteristic of alg, CB-Alg and CBvid-Alg samples
- Determination of particle sizes and stability in alg, CB-Alg and CBvid-Alg samples
- Morphological, structural and dimensional characterization of alg, CB-Alg and CBvid-Alg samplesS-established the performances regarding the retention capacity of some metal ions using the materials Alg, CB-Alg and CBvacuum-Alg, had the following results:

  - ➢ Alg has high efficiency after 15 minutes and the downward trend is maintained at 60 minutes as well.
  - ➢ Alg-CB shows high adsorbent values especially for Cr, Fe and Pb.
  - ➢ In the case of Alg-CBvid, the highest absorbance values are observed in the case of Pb, followed by Cu, Co, Cd, after the first 15 minutes.

- ➢ In terms of embedding capacity, the results in the case of alg use are superior compared to CS, thus presenting the advantage of immobilizing the nanosized particles of CBvid and CB, while maintaining the performance, through the qualitative evaluation, related to the evolution of the absorbances of the competitive elements analyzed within 60 minutes.
- ➢ Analyzing the obtained efficiencies, an increased affinity of the Alg-CB material (1:1) can be observed for Fe, Pb, Cr and Cu, after 30 minutes, leading to separation efficiencies from the system of over 95%, and increasing the contact time to 45 minutes, the separation from the system with efficiencys of over 95% also occurs for Zn, Fe, Pb, With and Cr.

- In the case of Alg-CBvid, for carbonic material with porous structure, the maximum efficiency occurs at 15 minutes, for Pb of about 90% and Cu of about 22%.

 Compared to plain Alg and Alg-CBvid, the Alg-CB microspheres show higher efficiencies attributed to both CB and alginate in the composition.

3.4. CONCLSIONS

Qualitative tests on heavy metal retention were performed, using different quantities of material type CB, CBvid, Alg-CB, Alg-CBvid, CS-CB and CS-CBvid comparing the absorbance values specific to the analyzed elements, before and after contact with materials. It was found that the optimal value is 0.5 g at 30 minutes, with efficiency of over 90% for heavy metals in the systems studied for CB, Alg-CB.

Although the performance of CB and CBvid materials is promising, the material losses of about 36% at the stage of removal from the system, due to the small size of the particles, led to the study of its behavior in polymer matrices of chitosan and alginate type.

The use of chitosan as an embedding material results in a better stability of the CB material, but according to the results, a reduction of the reaction centers is also observed through possible links established between the CS and CB groups. Using amounts of CB embedded in the CS matrix it is found that the best efficiencies are obtained when using 1g CS-CB 1:1 (i.e. 0.25 g CB), and in the case of using alginate as incorporation material for CB, it can be seen that the retention efficiency occurs for the Alg-CB type system (1:1).

Comparatively, the efficiency of materials, relative to all metal elements studied in aqueous solutions is as follows: CB (efficiencies over 99% after 30 minutes) > Alg-CB (efficiencies over 98% after 30 minutes) > Alg (efficiencies over 96% after 30 minutes) > CS-CB (efficiencies over 95% after 30 minutes) > CS (efficiencies over 94% after 30 minutes) > CA (efficiency over 90% after 30 minutes). An affinity for metals of the type Fe, Pb, Cr, Zn is found, depending also on the materials studied.

The results obtained based on the evolution of the absorbance values specific to the studied elements over time, allowed the evaluation of the removal efficiency using different binary systems of type CS-CB and Alg-CB, in order to reduce the loss of CB material. The qualitative performance of the materials for the retention of metals was assessed, thus identifying the possibility of reuse of the waste from banana peels, thus contributing to the circular economy, by reducing the amount of vegetable waste and identifying ecological materials used in water scrubbing.

Based on the results obtained in this chapter, further experiments on kinetic studies, the ionic desication/exchange mechanism responsible for the retention of the studied metals from aqueous solutions, and water samples containing metals were further tested.

4. STUDIES AND RESEARCH ON THE ESTABLISHMENT OF COMPETITIVE ION RETENTION MECHANISMS USING AS ADSORBENT MATERIALS HEAT-TREATED WASTE FROM BANANA PEELS

The process of desication of heavy metal species in the waters is a phenomenon thatinvolves physicalor chemical processesorfor which there is a needfor kinetic investigation of these phenomena, this being closely related to the subsequent design of the adsorption system, as well as to the correct choice of the sequence of the reaction mechanism that defines the process. The processes of adsorption are also found in the natural environment. There are multiple possible mechanisms of heavy metal adsorption, which are shown schematically in Figure 12.

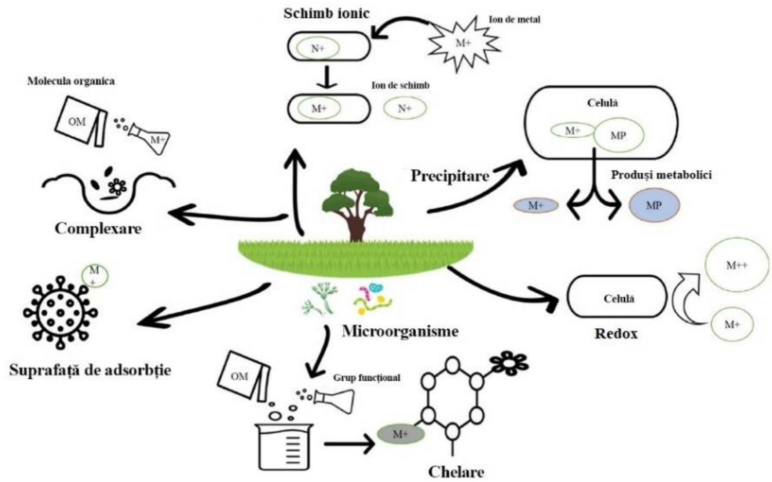

Figure 12 Possible mechanisms of heavy metal adsorption

Process modeling involves kinetics and the reaction mechanism to establish the reaction at the molecular level. Thus, the experimental stages taken within the PhD program were the following:

- establishing the optimal working parameters in order to evaluate the performance of adsorbent materials of type CB. CBvid, CB-Alg and CBvid-Alg;
- the study of the adsorption kinetics of the Cu and Pb type metallic species using the above-mentioned materials for the determination of the prevailing kinetic mechanisms, the determination of the apparent speed constants and the half-life;

- establishing the mechanisms underlying the adsorption process and the possibility of material regeneration.

4.1. Comparative desisorption tests on the retention efficiency of Pb and Cu from synthetic solutions usingad sorbent systems CB, Cbvid, Alg-CB and Alg-CBvid

The retention process has been studied for Pb and Cu solutions to assess the competitive effect of ions. The solutions of the studied elements had initial concentrations of Pb (1004±10 mg/L) and Cu (1005±10 mg/L, respectively. From these solutions were prepared working solutions of concentrations 0,25; 1 and 2 mg/L of each element, the working volumes being 100 mL.

According to the data obtained by drawing the calibration curves, a correlation coefficient of R^2 data of 0,9999 is found for both metals studied, which indicates a good accuracy of the detector response from the atomic absorption spectrometer with which the following metal retention experiments will be carried out.

Inthe 60-minute interval, during the experiments, in the case of Pb, concentrations of 0.25 and 1 mg/L can be removed from the stem usingCBvid with an efficiency of about 90%, after the first 15 minutes, at concnetratias of 2 mg/L, the efficiencys decrease to about 67%, for Cu.

It can be found that in the field of concentrationstudied (0.25 – 2 mg/L),for 60 minutes,theperformances exceed 65%, and as a general trend it is found that the best results are obtained at small concen tratia of 0.25 mg/L for Pb, where 90% is reached after 15 minutes contact with alg-CBvid material, noting a slight decrease in efficiency over time, but not falling below 75%.

It can be found that for elemental Cu the same trend is observed, the highest efficiency being at 15 minutes for 0.25 mg/L and decreasing to 70% for 2 mg/L.

Also, in the case of CB and Alg-CB, a high efficiency can be found, especially for 0.25 mg/L Pb, after 30 minutes, the efficiency increasing to about 99%. The same trend can be observed with the use of Alg-CB, where the efficiencies keep high values of about 90% in the first 30 minutes, for 0.25 mg/L Pb and 0.25 mg/L Cu, respectively.

The efficacy values are slightly low when using Alg-CB and due to the possible bonds that form between the oxidic components of the CB with the carboxylic functional groups of the alginate, thus reducing the active centers on the CB surface, necessary for the adsorption process.

The mechanism of adsorption will be evaluated by kinetic studies and specific models of adsorption, presented in the following subchapters.

4.2. Kinetic aspects regarding the retention mechanism of Cu and Pb species on materials of type CBvid and Alg-CBvid

Kinetic studies were conducted to determine the equilibrium time and how to bind pb and cu ions to the materials studied. Thus, studies help not only to determine the equilibrium time of the adsorption process but also to design treatment/treatment systems that are based on the reaction speed.

The sampling was carried out from 10 minutes to 60 minutes, based on the preliminary results, so that about 3-4 mL of the sample were taken at different times, the volumes being filtered through a syringe with a filter membrane of 0.2 µm.

In the case of second-order kinetics,for Pb and Cu tested for retention on CBvid, the R2 correlation coefficients describing the model have values of 0.9994 for Pb and 0.9996 for Cu, respectively.

Table 5 shows the speed constants (K) and the quantity at equilibrium (q_{e}),obtained from thelinearization of the kinetic model of the ii order. It can be seen that the RMSE error values are small, especially for Alg-CBvid, the q_e values are higher in the case of the use of CBvid for Pb and Cu respectively, and K for Cu retained on CBvid and Pb retained on Alg-CBvid, both cases indicating a chemical adsorption on the surface of the materials [23].

Table 5 Parameters of the model of order II

Element/material	q_e, mg/g	K_2	R^2	RMSE, mg/g
Pb CBvid	0.0771	5.8954	0.9994	0.00012
With CBvid	0.0837	6.1621	0.9996	0.00027
Pb AlgCBvid	0.0409	13.1957	0.9937	0.00024
With AlgCBvid	0.0289	33.2460	0.9962	0.00016

The results indicate a phenomenon that occurs not only on the surface of the material, being possible both a chemical adsorption and a diffusion between the particles of the material, but also an ionic exchange, due in the case of Alg-CBvid, to the Ca^{2+} ions in the alginate structure [23].

Ccorrelation coefficients are satisfactory in the case of Pb (R2 = 0.8959 for CBvid and 0.6661 for Alg-CBvid), and for Cu, the values are consistent with the analyzed model (R^2 = 0.9983) for Alg-CBvid, which indicates a good correlation with the interparticles model.

4.3. Kinetic aspects regarding the containment mechanism of Cu and Pb species on CB and Alg-CB materials

The application of the kinetic model of order I indicated low values for R^2 from linearization, for both types of materials, CB as well as Alg-CB for Pb and Cu (below 0.1), so that a correlation between the data obtained according to this kinetic model cannot be established.

The kinetic model of order II indicates a correlation regarding the Cu ions for the cb material (R^2 = 0.9979) and Alg-CB (R^2 = 0.9676), respectively, but also for Pb (R^2 = 0.9601), which indicates a higher affinity for the Alg-CB type material compared to CB, where the agglomeration trend prevails.

Table 6 The constants specific to the kinetic model of order II

Element/material	q_e, mg/g	K_2	R^2	RMSE, mg/g
Pb CB	0.064	31.44	0.7838	0.0011
With CB	0.051	46.54	0.9979	0.0012
Pb AlgCB	0.051	125.11	0.9621	0.0031
With AlgCB	0.082	42.28	0.9679	0.0037

4.4. Equilibrium isotherms used to evaluate the retention process of Pb and Cu on materials CBvid, CB, Alg-CBvid and Alg-CB

Adsorption isotherms are useful in quantitatively evaluating and establishing process performance, binding capacity and affinity for different metal concentrations and adsorbent doses. The Langmuir and Freundlich isotherms are most commonly used due to their simplicity and ease of interpretation [31, 32].

4.4.1. Models of isothermal adsorption when used as adsorbent materials of CBvid and Alg-CBvid

Isotherms were obtained by varying the initial metal concentration from 0.25 to 2 mg/L, the equilibrium time was 60 minutes. A good correlation of the experimental data can be observed, in particular in the case of Pb retained on CBvid and Cu on CB vacuum respectively, in the concentration range analysed. The coefficients of 0,9997 for retention Pb on CBvid and 0,9992 for Cu retention on CBvid respectively are consistent with the model studied, asalso seen in Table 7.

Table 7 Parameters specific to langmuir and freundlich isotherm models

Isothermal	Parameters specific to Langmuir and Freundlich models		R_L	R^2	RMSE
Langmuir CBvid	KPb (W/w) = 0.3168	qmaxPb (mg/g) = 0.5087	0.9928	0.9997	0.0121
	KCu = 0.1603	qmaxCu = 0.4067	0.9870	0.9992	0.0282
Langmuir Alg-CBvid	KPb = 2.0935	qmaxPb = 0.2393	0.9604	0.9997	0.0156
	KCu =1.8700	qmaxCu = 0.2694	0.9055	0.9944	0.0245
Freundlich CBvid	K_fPb = 0.2951	nPb = 3.9463	-	0.9985	0.0014

	K_fCu = 0.3416	nCu = 2.5239	-	0.9971	0.0032
Freundlich Alg-CBvid	K_fPb = 0.3249	nPb = 2.9958	-	0.9949	0.0056
	K_fCu = 0.4387	nCu = 0.5158	-	0.8113	0.0045

Lower values of the corlation coefficients are observed when using Alg-CBvid (0.9987 for Pb and 0.9966 for Cu, respectively) but the values indicate a homogeneous trend in the ability of the analyzed materials to retain metalions.

The obtained values show that the surface of the solids studied as adsorbent materials (CBvid and Alg-CBvid respectively) has a specific number of places, each being able to react and bind ionic molecules / species from the solution (adsorbate).

From the data obtained it can be seen that the best correlation coefficients are for Pb (0.9985) and Cu (0.9971) when retained on CBvid.

R^2 for the Isotherma Langmuir is higher compared to Freundlich, indicating better correlation with this model. The R_L values indicate for the Langmuir isotherm that the process that takes place is favorable ($0 < R_L < 1$).

4.4.2. Models of isothermal adsorption when used as adsorbent materials of CBvid and Alg-CBvid

The models developed with the use of CB ash and alginate ash (Alg-CB) material were langmuir and freundlich. The concentration range studied was between 0.25 - 2 mg/L for each metal (Pb and Cu respectively), and the equilibrium time was 60 minutes. The following is shown in Table 8 the parameters specific to the 2 types of models of adsorption isothermal models.

Table 8 Parametry specific to the 2 types of models of adsorption isothermals.

Isothermal	Parameters specific to Langmuir and Freundlich models		R_L	R^2	RMSE
Langmuir CB	KPb (W/w) = 98.4285	qmaxPb (mg/g) = 7.2568	0.9972	1	0.0126
	KCu = 83.8235	qmaxCu = 7.0175	0.9966	0.9999	0.0274
Langmuir Alg-CB	KPb = 51.0892	qmaxPb = 3.4953	0.9889	1	0.0258
	KCu=16.0434	qmaxCu = 2.7100	0.9954	1	0.0275
Freundlich CB	K_fPb = 0.8616	nPb = 0.0942	-	1	0.0294
	K_fCu = 0.8150	nCu = 12.0048	-	0.9973	0.0336
Freundlich Alg-CB	K_fPb = 0.5243	nPb = 9.47867	-	1	0.0356
	K_fCu = 0.4207	nCu = 4.6598	-	1	0.0445

Correlation coefficients of 1 for Pb and Cu can be observed when using Alg-CB and for Pb when using CB, and for Cu retained on CB, the value is 0.999.

Se observes values indicating a good adsorption capacity of THE CB, which is also maintained in the case of incorporation in Alg.

The data presented above, high values of the maximum adsorption capacities can be found for Pb (98.4285) and Cu (83.8235), which demonstrates a strong affinity of the material for these types of ionic species, values that are also maintained in the case of incorporation of porous CB material into alginate (51.0892 for Pb and 16.0434 for Cu).

Analyzing the n values, a betterefficiency is due to the use of alg-CB type material for the 2 ionic species.

RMSE values are higher in the case of the isotherm Freundlich which leads to the conclusion that this type of isothermal model does not most accurately indicate the type of phenomenon that occurs when materials are contacted with Pb and Cu.

4.5. Studies on the regeneration of adsorbents CB, CBvid, Alg-CB, Alg-CBvid

Studies on the desorption and regeneration of the studied materials were conducted using 25 mL HCl 0.1 M as a washing solution. Before each reuse, the materials were subsequently washed with distilled water. Resultsare presented in Table 9,highlighting, comparatively, the retention efficiency and recovery yield of materials, without affecting the adsorption capacity for Pb and Cu.

Table 9 Retention efficiency and recovery yield of the material

No. Regeneration Cycles	Pb/Cu concentration (mg/L) before adsorption	Concentration Pb/Cu (mg/L) after adsorption	Adsorption (%)	Amount desorbed after washing with 0.1M HCl	Recovery (%)
	Alg -CBvid				
1	0.25	0.0217/0.0329	91.32%/86.34%	0.190/0.184	83.22%/ 84.75%
2	0.25	0.0289/0.032	88.44%/87.20%	0.171/0.166	77.37%/76.14%
3	0.25	0.0415/0.0518	83.40%/79.28%	0.158/0.124	75.77%/62.56%
4	0.25	0.0647/0.0842	74.12%/66.32%	0.106/0.082	57.20%/49.45%
	Alg-CB				
1	0.25	0.013/0.023	94.80%/90.80%	0.185/0.182	78.05%/80.17%
2	0.25	0.025/0.029	90%/88.40%	0.176/0.176	78.22%/79.63%
3	0.25	0.041/0.051	83.60%/79.60%	0.179/0.152	85.64%/76.38%
4	0.25	0.076/0.098	69.6%/60.8%	0.142/0.108	81.60%/71.05%
5	0.25	0.105/0.114	58%/54.4%	0.112/0.089	77.24%/65.4%
6	0.25	0.136/0.139	45.6%/44.4%	0.096/0.043	84.21%/38.73%

It can be noted that in the case of Alg-CBvid, for Pb and Cu a maximum of 4 regeneration cycles can be maintained, after the last the recovery yield falls below 57% for Pb and below 50% for Cu, respectively. Thefailure to remove ionic species from the solution is starting to decrease, to about 74% for Pb and 66% for Cu.

In the case of Alg-CB, after 6 cycles of using the material, it loses efficiency and the recovery efficiency drops below 40% after 6 washing cycles.

5. FINAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS AND FUTURE PERSPECTIVES

5.1. Conclusions

Within the phd thesis on "Recovery of vegetal waste in processes of retention of heavy metals from water", studies and researches have been carried out on obtaining "low-cost" adsorbents coming from vegetable wastes of banana peel type, as a sustainable solution for the treatment of wastewater. Also, in the context of the circular economy, by using waste as products of added value, it has been achieved the reduction of the amount of this waste generated in the environment and the transformation into a circular, efficient and cheap eco-material. Given the performance recorded, it was also studied the capacity that these eco-materials can have by incorporating into biopolymers in order to reduce the losses that could occur due to the small size that ensures an increased reactivity.

Based on the study in the specialized literature it was found that:

- vegetable waste successfully replaces activated carbon, after application of chemical and/or physical treatments, in order to obtain morphologies and dimensions leading to the development of adsorbent properties;
- banana fruits are one of the most popular and nutritious fruit crops grown in the world, and the amount of waste generated by more than 34%, which needles can cause over time to accumulate in the environment;
- banana waste, compared to other biomass wastes used as adsorbents, has affinity for cationic, anionic and neutral pollutants, and the material studied is usually obtained by heat treatment and physical or chemical activation;
- waste banana peels can lead to combustion in order to obtain biofuels to produce a ash with adsorbent potential;
- banana peel powder was used in pre-concentration experiments and an enrichment factor was determined almost 20 times, and the column could be reused in 11 cycles without having large losses in recovery.

In order to achieve the main objective of the thesis, it was taken into account:

- obtaining eco-materials using banana peel waste as a raw material;
- characterization of these eco-material in order to validate the structure, morphology, surface properties, by applying optical microscopy (OM) and scanning electronics (SEM) techniques coupled with X-ray dispersive energy (EDS), X-ray diffraction (XRD), IR spectrometry (FTIR) and Zeta potential;

- integration of the eco-materials obtained in the retention processes of metal ions, highlighting the adsorbent properties of these eco-materials;
- testing and validation of the performance of eco-materials in multi-nutrient solutions, with the establishment of removal efcienţe and retention mechanisms.

The experimental research activities carried out throughout the doctoral training stage have highlighted performances that the waste from banana peels can perform as an adsorbent for pollutants present in wastewater. The results obtained indicated:

- heavy metal removal efficiency of over 80% for Cu and Pb and below 30% for Co, Cd and Zn from monoelement solutions, after about 15-30 minutes, using 0.5 g CBvid;
- efficiency of over 90% for the competitive ions studied, at an optimal time of about 15-30 minutes using an amount of adsorbent of 0.5 g CB;
- material recoveries of about 30% for CBvid and 25% for CB for material regeneration;
- superior c-orporation capacity when using Ca Alginate compared to chitosan, for both types of CBvid and CB materials;
- in the case of testing the retention capacity of metal ions on material of type CS-CBvid and CS-CB, compared to CS, higher efficiency is found for CS (especially for Co and Cu, of about 30%) and CS-CB respectively (eg: Fe retention of about 80% after 30 minutes and 99% after 60 minutes and Pb of about 45%), respectively, the CS-CBvid material having the lowest effectiveness;
- the alg-CB test efficiency (1:1) is over 95 % for Fe, Pb, Cr and Cu after 30 minutes;
- in thecase of useas an adsorbent material of Alg-CBvid, the maximum efficiency is at 15 minutes, for Pb of about 90% and Cu of about 22%;

5.2. Original contributions

Through the research activities carried out, the original contributions made to the field of environmental engineering are supported by the stages carried out within this doctoral internship, as follows:

- carrying out an extensive documentary study from the specialized literature on the possibility of capitalizing some vegetal wastes that represent today a critical quantity that can influence the environment and the quality of life, thus identifying elements of originality with scientific value regarding the heat treatment and the activation of these types of waste in order to transform them into eco-carbonic materials (activated coal) and minerals (ash);

- the development of an integrated method of vacuum-slurs and combustion respectively in the case of a banana-shell waste in order to double capitalise on it: the production of activated charcoal (CBvid) and ash (CB) respectively;
- designing and obtaining sustainable eco-materials by incorporating CBvid and CB respectively into chitosan (CS) and alginate (Alg) biopolymeric masses, respectively, in order to reduce the risk of material loss after its use in aqueous systems contaminated with metal ions;
- selection and testing of metallic species representing major pollutants of aqueous systems in order to test the performance of the eco-materials obtained;
- elaboration of a plan of investigations and characterizations for the validation of the structures obtained by valuing the banana peel waste in the form of eco-materials, using morphological, structural and dimensional characterization techniques, including the establishment of the chemistry of the surface of the eco-materials obtained;
- the development and implementation of a work plan on the experimental programme in order to establish the specific optimal working parameters by using kinetic studies, adsorption isotherms and regen capacity investigations;
- validation of performances and establishment of mechanisms that led to the performances of the eco-materials obtained regarding the retention of some metallic species.

5.3. Future prospects

- identification and recovery of other types of vegetal waste with potential for use in water treatment processes in the context of the requirements of the circular economy and the protection of natural resources;
- simultaneous testing of eco-materials obtained on inorganic and organic pollutant species in order to integrate them into existing treatment processes
- the transfer to pilot level of the proposed concept in order to demonstrate technological maturity.

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