REMOVAL OF LEAD, CADMIUM, COPPER, ZINC, AND MERCURY FROM WATER ON BANANA PEEL RESIDUES

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ABSTRACT

Industrial activities, inadequate waste disposal, and poor control of discharges generated by mining and domestic activities are the primary causes of water pollution with numerous chemical substances, including heavy metals. Several methods have been proposed for removing metals from water, such as precipitation, membrane separation, ion exchange, solid phase extraction, flocculation, and others to address this issue. The metal bio-adsorption using biomass from crops is an alternative that has shown excellent results in recent years. In this work, We studied the bio-adsorption of five metals present in water on biomass from ground banana peel. We evaluated the retention capacity of copper, lead, cadmium, zinc, and mercury on the bio-adsorbent material subjected to acid hydrolysis, basic hydrolysis, and the material without treatment. The material with the best-obtained results was selected to execute a 2^k experimental design. The factors were pH, adsorbent dose, and contact time between the adsorbent and the metal ion solution. We used the anodic stripping square wave voltammetry for the mercury determination and adsorptive stripping by square wave voltammetry for copper, zinc, cadmium, and lead quantification. The maximum adsorption capacity ranged from 20 to 30 mg for each gram of material used for the five studied metals. The optimum pH value for mercury was 3.0 while for copper, zinc, cadmium, and lead was 5.0. The optimum contact time was 15 minutes. Mercury is captured differently from the other metals. The materials were characterized using the techniques of Infrared Spectroscopy, Scanning Electron Microscopy, energy-dispersive X-ray Spectroscopy, and thermogravimetric analysis.

Keywords: banana peel, bio-adsorbent, biomass, heavy metal removal, *Musa paradisiaca* L., water pollution.

1. INTRODUCTION

Pollution of water sources is one of the most relevant environmental problems in the world today. The heavy metals present in water can affect the health of living beings due to their bioaccumulation and non-biodegradability [1]. Agricultural, mining, and industrial activities are the ones that contribute the most to this type of pollution. Different reports show the presence of metals such as copper, nickel, zinc, lead, cadmium, and mercury in bodies of water [2].

The human body needs small quantities of metals, such as copper and zinc, to perform different biological functions. However, an excessive or deficient amount of these elements can interfere with the organism's biochemical and physiological processes. On the other hand, heavy metals, such as cadmium, lead, and mercury, accumulate in various organs, causing damage to the nervous, circulatory, immunological, neurological, and cardiovascular systems [3].

Heavy metals can enter the human body through the food we consume, the air we breathe, or the water we ingest. Therefore, the scientific community continuously researches treatment systems to eliminate heavy metals in water. Conventional methods to remove heavy metals from water, including membrane filtration, electrodialysis, adsorption, chemical precipitation, coagulation, and flocculation [4], have proven to be effective in extraction percentages terms.

In recent decades, there has been an increasing trend in the use of natural materials, particularly those of plant origin, such as crop residues, residues or by-products of wood, and fungi, among the most studied [1]. Generally, these materials are referred to as biomass and have shown excellent results in removing different types of pollutants from water, including heavy metals [5]. Traditionally, biomass is not used in other applications apart from serving as fertilizer in crops. Biomass is the plant residue that remains after having harvested the economically or nutritionally helpful part of a plant and in some cases, it constitutes more than 80% of the total mass of the plant, in such a way that tens, hundreds, or thousands of tons of biomass can be generated, depending on the area and type of crop from which it comes.

Bioadsorption is a physicochemical process that involves a solid phase (bio-adsorbent) consisting of a material of natural origin derived from microorganisms, plants, or mushrooms and a liquid phase in which the species of interest is dissolved (adsorbate) [5]. This liquid phase is frequently water. Bioadsorption offers advantages such as efficiency, low cost, ease of operation, and the possibility of recovering the bio-adsorbent material using biomass, which is why it can be considered a sustainable alternative [6].

Several materials of plant origin have been studied as bio-adsorbents of metal ions present in water. Among these materials are grapefruit peel [7], potato peel [8], mangosteen peel [9], eucalyptus bark [10], agave bagasse [11], wood sawdust [12], cocoa pod [13], barley straw [14], peels of banana, granadilla and orange [15], melon peel[16], Jack fruit [17], Egyptian mandarin peel [18], sugarcane bagasse [19], and rice straw [20]. Other bio-adsorbent materials and their maximum adsorption capacities are listed in Table 1.

Table 1 Maximum Cu, Zn, Cd, Pb, and Hg adsorption capacity on different bio-adsorbent materials.

Bio-adsorbent	Maximum adsorption capacity **(mg/g)**						**Ref**
	Cu (II)	**Zn (II)**	**Cd (II)**	**Pb (II)**	**Hg (II)**	**Others**	
Rice shell (RS)	9.59						
Wheat shell (WS)	9.51						[28]
Lentil shell (LS)	8.98						
Pomelo peel (PP) and Depectinated Pomelo peel (DPP)	PP = 19.70 DPP = 21.10						[7]
Barley straw (BS) and Barley Straw modified with citric acid (CA-BS)	BS = 4.64 CA-BS = 31.71						[14]
Potato Peels	10.70						[8]
Dried sugar beet pulp	28.50						[29]
Pomegranate peel	19.70						[30]

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Jackfruit peel (JP), Jackfruit peel modified with HCl (HJP), Jackfruit peel modified with NaOH (NaJP)	JP = 7.41 HJP = 13.55 NaJP = 38.46	NaJP=39.5				[17]
Banana peel (BP) Granadilla peel (GP) Orange peel (OP)		BP=25.59 GP=27.48 OP=16.61				[15]
ground wheat stems			11.60			[31]
Rice straw			13.90			[32]
Corncobs				43.40		[33]
Unripe papaya				6.45		[34]
Banana peel				359		[26]
Rice straw					209.65	[35]
Egyptian mandarin peel (MP) Egyptian mandarin treated with NaOH (MNa), Carbonized Egyptian mandarin (MC)					MP = 19.01 MNa = 23.26 MC = 34.84	[18]
Sugarcane bagasse					35.71	[36]
Mangosteen shell					49.75	[9]
Olive stone	2.03		7.73	9.26	Ni (II) 2.13	[37]
Watermelon	39.2			116.2		[38]
Cocoa pod husk	4.69		4.42	4.83	Fe (II) 4.16	[13]
Coffee residues	31.20	13.40	39.50	19.50	Ni (II) 11.00	[39]
Green coconut shells	20.26	7.32	11.96	17.90	Ni (II) 3.12	[40]
Bacterial biomass	0.25	0.17				[41]
Grass Pea			52.8		Ni(II) 23.6	[42]
Agave bagasse		8.00	14.00	36.00		[43]
Orange peel		18.51	10.05		Ni(II) 21.81 Co(II) 20.87	[44]
Cassava Peel					V(III) 132.8 Cr(III) 116.2 Co(II) 99.6	[45]
Rice straw	2.54	2.61	4.50		8.02	[46]

Banana peel is the main by-product of banana cultivation and constitutes 35 to 40% of its weight. Its composition includes fiber, proteins, essential amino acids, and polyunsaturated fatty acids. The crude fiber present in the husk contains 60% lignin, 25% cellulose, and 15% hemicellulose [21]. The biomass, composed of lignin, cellulose, and hemicellulose, is known as lignocellulosic material. Its main component, lignin, is responsible for promoting the adsorption process of other substances because its composition contains functional groups such as hydroxyls, carbonyls, methoxy, carboxyls, and sulfonates [22], facilitating the uptake of metal ions.

Traditionally, banana peels are employed in composting processes to obtain organic fertilizers. This material has been studied without modifications as a bio-adsorbent for lead [23] and modified for zinc [15] and copper [24], in addition to other types of contaminants [25]. An outstanding performance of biochar derived from banana peels treated with phosphoric acid and hydrothermal carbonization resulted in a high lead removal efficiency of 359 mg/g [26]. In addition, many other uses have been found for this type of biomass, making it a promising material for many applications. Kumar et al. [27] summarize other uses of banana plants in different technological fields.

In this study, we evaluated the ability of unmodified banana peel to absorb heavy metals such as copper, zinc, cadmium, lead, and mercury from water.

2. EXPERIMENTAL PROCEDURE

Acetic acid, copper sulfate, cadmium standard solution, sodium acetate, nitric acid, sodium hydroxide, mercury chloride, zinc sulfate, and lead standard solution, was purchased from Sigma-Aldrich. Hydrochloric acid, phosphoric acid, and hydrogen peroxide were obtained from Fisher Scientific. Type I water was employed for electrolytic cells and dilution of metal solutions.

Pretreatment of banana peel

The banana peel (*Musa paradisiaca* L.) was removed from the fruit, washed with plenty of water, and divided into small pieces of approximately 0.5 x 0.5 cm^2, then dried under the sunlight for 15 days. The dried material was then crushed and sieved to a size of 1.0 mm and oven-dried for three days at 60 °C. It was then grounded again to a particle size of 0.25 mm and kept in the oven at 60 °C for three days.

A portion of the obtained solid was subjected to acid hydrolysis. For this, 40 g of the material was kept in contact with 200 mL of 30% H_3PO_4 for 24 hours. The mixture was filtered, and the solid was washed using type I water. The resulting product was placed in the oven for eight days at 40 °C before being used as an extracting agent. A second portion of the material was subjected to basic hydrolysis. 0.5 F NaOH was used instead of H_3PO_4, and the procedure was the same as indicated before. Finally, a third portion of the material was left untreated. All three types of material were stored separately in sterilized plastic containers for later use to test their capability to remove metal ions from water.

Selection of the type of material

Five portions of 0.250 g acid-treated material (ATM) were put in contact with 10.0 mL of 10 mg/L solutions of each of the metals Cu, Zn, Cd, Pb, and Hg separately. After 120 minutes, the mixtures were filtered under vacuum, and the filtrates were taken to an electrochemical cell to determine the concentration of the corresponding metal. The same procedure was applied for the base-treated material (BTM) and the untreated material (UM).

Metal quantification

The technique employed for quantification of the metals Cu, Zn, Cd, and Pb was the square wave voltammetry in an electrochemical cell consisting of a mercury drop electrode as the working electrode, an Ag/AgCl reference electrode, and platinum as the counter electrode. The square wave voltammetry technique was also used for the mercury quantification but with a gold working electrode. The volume of the solution in the cell for all measurements was 20.0 mL. The electrochemical cell was bubbled with grade 5.0 nitrogen gas before each analysis to eliminate the oxygen from the solution. The quantification method employed for metal ions consisted of standard addition calibration curves. For the construction of each curve, increasing volumes of standard solutions of 10 mg/L metals of interest were added to the measuring cell. The system was controlled by an Autolab M-204 potentiostat-galvanostat along with the 663 VA Stand Metrohm module using the Nova 2.1.5 software.

Experimental design

Using the material that removed the highest percentage of metal in the previous stage, this study investigated the effects of pH, adsorbent dose, and contact time

to determine the best conditions to extract as much as possible of each metal. To do this, we applied a 2^k experimental design with star points and a central point, with k=3 corresponding to the three mentioned factors. The response variable was the percentage of metal removed from 10 milliliters of 10 mg/L solution of each metal. The software STATGRAPHICS Centurion XVI.I was used to developing the experimental design. The conditions established for the low and high levels of the design were: pH 2.0 and 6.0, adsorbent dose 0.1 and 0.5 g, and contact time 15 and 45 s. The adjustment of the pH value before contact with the bio-adsorbent material was made with HNO_3 for Cu, Zn, Cd, and Pb solutions and with HCl for Hg solution. The pH measurement was performed with a Thermo Scientific Orion Star A211 pH meter.

The experiments consisted of placing the bio-adsorbent material in contact with 10 mL of the solution of each metal for the time and quantities established in the design for each analysis. To ensure a rapid and constant interaction between the material and the metal ions, stirring at 500 rpm was used with a Heidolph MR Hei-standard iron. To calculate the removal efficiency, We determined the concentration of the solutions of each metal before and after its contact with the bio-adsorbent material using the current signals generated by the successive additions of the standards to the electrochemical cell, which allowed the construction of each calibration curve.

The extraction percentage (%E) of each metal was calculated using the equation 1.

$$\%E = \frac{C_i - C_f}{C_i} x\ 100 \qquad \text{Ec. 1}$$

Where C_i is the initial concentration of the metal in the working solution before its contact with the bio-adsorbent material, determined experimentally by square wave voltammetry, and C_f is the final concentration of the metal, determined after its contact with the bio-adsorbent material.

Isotherms

Adsorption isotherms of the five metals were obtained by measuring metal concentration after contact with the bio-adsorbent. The concentration of employed solutions ranged from 10 to 1000 mg/L at 22 °C. The points of the isotherms were obtained according to the working conditions described in section 2.3.

Characterization

The bio-adsorbent material was characterized by infrared spectroscopy using a Nicolet iS 10 spectrophotometer from Thermo in Totally Attenuated Reflectance mode. Surface changes were observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using a Phenom Pro X scanning electron microscope.

The material-thermal stability was studied by thermogravimetric analysis (TGA) using a Q50 model calorimeter from TA Instruments. Applying a heating ramp of 20 °C/min up to 600 °C in a nitrogen atmosphere at 90 mL/min flow.

3. RESULTS AND DISCUSSION

Selection of Material Type

Table 2 presents the removed metal quantity by a gram of bio-adsorbent using the three types of the obtained material. The results show that UM presented better behavior since the removal percentages for Cu, Pb, Cd, and Hg were higher than with ATM and BTM. BTM removed a higher quantity of Zn (0.094 mg/g). Nevertheless, because UM removed a high Zn quantity too (0.086 mg/g), UM was the material selected to execute the planned experimental design.

Table 2 Metal removal results on ATM, BTM, and UM using an adsorbent dose of 0.2500 g and contact time of 2 hours in a 10 mg/L solution of each metal

	Amount of metal removed per gram of bio-adsorbent (mg/g)				
	Cu	**Zn**	**Cd**	**Pb**	**Hg**
ATM	0,085	0,055	0.090	0.089	0,078
BTM	0,072	0,094	0.083	0.079	0,071
UM	0,091	0,086	0.097	0.094	0,091

Characterization of the bio-adsorbent material

Analysis was carried out using infrared spectroscopy at the ATR mode to identify the functional groups on the surface of each of the materials. The superimposed spectra for the ATM, BTM, and UM, appear in Figure 1. The FTIR spectrum of UM coincides with the spectrum presented by Kovo et al. for this same type of material [25]. The signals observed between 3000 and 3350 cm^{-1} correspond to the OH group. Cellulose, hemicellulose, and lignin, which are part of the composition of banana peel, have high amounts of the -OH group. For this reason, it appears as a broad and intense band. Signals below 3000 cm^{-1} are characteristic of C-H bonds. These bonds are part of the skeleton of lignocellulosic compounds. The signal for the C-O bond can be seen in the interval between 1010 – 1080 cm^{-1}. The C-O bond is present in carboxylic acids, esters, and ethers. On the other hand, the presence of hemicellulose has been identified through signals observed at 1424, 1044, and 897 cm^{-1} [47]. In our samples, it appears as a low-intensity band at 1420 cm^{-1}. The characteristic bands of the presence of lignin have been reported at 1510 and 1600 cm^{-1}, which correspond to the vibrations of the aromatic ring [48]. In the spectra of Figure 1, signals appear around 1600 cm^{-1}, which confirms the presence of this type of compound. The differences between the spectra for the three types of materials are related to the intensity of the bands, such as those of the OH group. This signal is more intense for the UM than for ATM and BTM. The latter could be associated with the treatment applied to the material. The greater amount of OH groups may explain why UM removes a higher amount of metal than ATM and BTM.

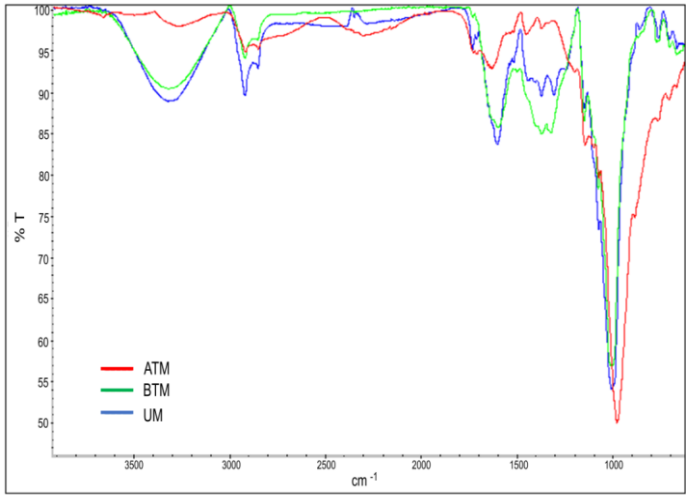

Figure 1: FTIR spectra for acid treatment material (ATM), basic treatment material (BTM), and untreated material (UM).

Thermogravimetric analysis

The thermal characterization of the banana peel was carried out to identify the thermal profile in which the degradation processes of the different components of the peel occur. In Figure 2, thermograms appear for the three material types, ATM, BTM, and UM. The UM thermogram matches that Castro et al. presented for the same material type [15]. Three areas stand out in these thermograms.

Zone 1: Includes room temperature up to 100 °C, a zone in which a decrease in the mass of all materials is observed. This zone corresponds to the elimination of water. Next, the minimal mass variation between 100 and 230 C is due to the material's degradation of small molecules or impurities, creating a stable zone.

Zone 2: Between 230 °C and 380 °C. It covers the decomposition of cellulose and even lignin associated with cellulose in small quantities. The difference in lost mass between UM and the other two materials comes from the difference in water content, such that the three materials present the same cellulose losses, so we can infer that acidic and basic treatments do not generate degradation of the material.

Zone 3: Temperatures higher than 380 °C. It includes progressive loss of mass, attributed mainly to lignin degradation, the majority component of banana peel.

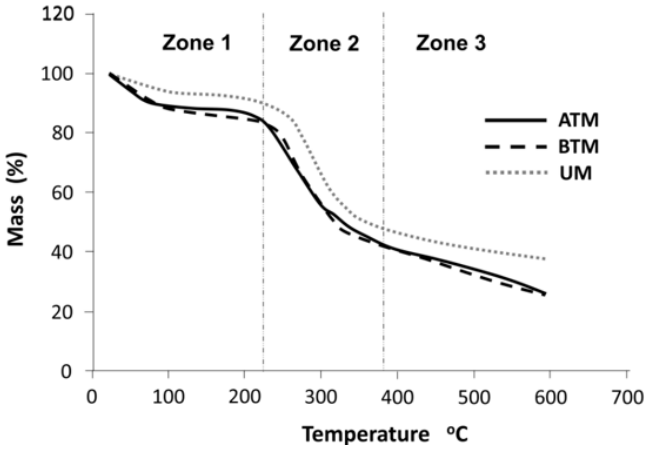

Figure 2: Thermogravimetric curves for ATM, BTM and UM.

Surface analysis by Scanning Electron Microscopy (SEM)

The study of the surface of the bio-adsorbent was carried out before and after being in contact with the metal solutions. Figure 3A shows the micrography corresponding to the UM before contact with the metals. It is possible to observe a surface with amorphous, agglomerated granules and a certain roughness, which could be related to the material porosity resulting from the drying and crushing process of the banana peels. The analysis by energy dispersion of X-rays (EDX) indicates carbon, oxygen, and potassium as the major elements. Figure 3(B-F) shows the Micrographs of the material after it comes in contact with the solution of each of the metals.

The heterogeneous surfaces have granular and smooth areas. The EDX analysis results for the same material after its contact with Pb^{2+}, Cd2+, Cu2+, Zn2+, and Hg2+ solutions presented in Table 3 show the metal concentration values in different zones on the UM surface. Lead and cadmium are present in low concentration over much of the surface and in higher concentration (close to 50% for lead and close to 30% for cadmium) in small zones (white zones in Figures 3 B and C). Zinc and Copper are homogeneously distributed on the UM surface and appear in all sampled points. Finally, mercury is deposited only in small areas with a concentration greater than 98% (white zones in Figure 3F). That is why a non-uniform distribution occurs on the material's surface. This characteristic differs from that observed in the SEM micrographs for the material with lead, cadmium, zinc, and copper in which it is clear that the metal is distributed more homogeneously on the bio-adsorbent surface. Additionally, the presence of mercury clusters does not agree with the results of D. Anitha et al. (2021) [9] who removed mercury using bicarbonate-treated mangosteen shell carbon and found that mercury deposited homogeneously on the material surface. The aforementioned indicates that the metal–bioadsorbent interaction mechanism differs depending on the metal type and the type and treatment of bio-adsorbent.

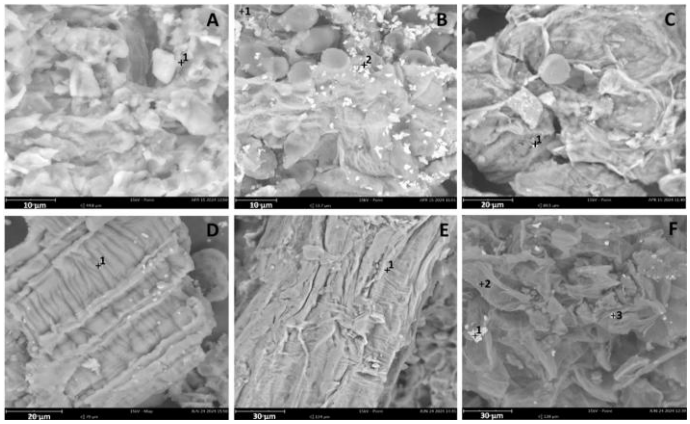

Figure 3: SEM micrographs for the UM before (A) and after contact with a metal solution of lead (B), cadmium (C), zinc (D), copper (E), and mercury (F).

Metal Extraction

The development of the experimental design allowed us to evaluate the effects of the variables pH, bio-adsorbent dose, and contact time on the uptake of the metal ions Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Hg^{2+} to optimize the conditions to achieve effective removal.

Quantification of Metals

The voltammograms recorded during metal quantification show a high linearity of the generated current signal as a function of the metal concentration. Although the technique allows the simultaneous quantification of four of the metals studied, the determination was carried out in two groups: in the first one, Cd and Pb were quantified, and in the second one, Cu and Zn. Concerning Hg, it was quantified separately on a gold electrode. The voltammograms for each of the metals appear in Figure 4. The calibration curves obtained for each metal appear in Figure 5.

The results presented low standard deviations, the highest being 0.41 for Zn and the lowest being 0.08 for Hg. The aforementioned confirms the high reproducibility of the analysis method used. Additionally, the relative error values were also low, the lowest being 0.60 for Cu and the highest being 5.40 for Hg, which corroborates the accuracy of the analysis method. The detection limits for each of the metals studied were 1.0 µg/L, 2.0 µg/L, 1.28 µg/L, 1.86 µg/L, and 2.0 µg/L, for Cu, Zn, Cd, Pb, and Hg respectively

Table 3 EDX analysis results for UM and UM after contact with five metal solutions

Material	Point	Element Symbol	Atomic Concentration	Weight Concentration
UM	1	C	74.20	66.91
		O	24.60	29.55
		K	1.20	3.54
UM-Pb	1	C	63.32	37.95
		O	33.25	26.54
		Pb	3.43	35.50
	2	C	63.90	30.17
		O	28.54	17.96
		Pb	6.19	50.41
		Al	1.37	1.46
UM-Cd	1	C	49.38	27.79
		O	39.07	29.30
		Cd	5.68	29.93
		Ca	5.31	9.97
		In	0.56	3.01
UM-Zn	1	C	64.23	52.18
		O	32.36	35.02
		Zn	2.13	9.42
		K	1.28	3.37
UM-Cu	1	C	62.52	40.32
		O	28.62	24.59
		K	4.15	8.70
		Cu	2.98	10.16
		Am	0.96	12.49
UM-Hg	1	Hg	98.08	99.78
		C	1.33	0.08
	2	C	63.52	52.50
		O	34.77	38.28
		K	1.26	3.39
	3	Hg	94.14	99.58
		C	4.81	0.30
		O	0.78	0.07

Effect of pH

The Pareto diagram of Figure 6A shows that the pH value of the solution is the factor that exerts the most relevant effect on the extraction of Cu. The same behavior was observed for Cd, Zn, and Pb. The effect of pH is critical for the extraction of copper and zinc, although not for the cadmium and lead extraction.

In the case of mercury (Figure 6B), the pH of the solution is the factor that had the lowest effect of the three factors studied on the extraction of metals in water. Increasing the pH value of the solution improves the extraction percentage of Pb, Cd, Zn, and Cu. Figure 7 A-D shows the response surface graphs for the variables studied and their effects on the metal removal percentage. The results confirm that to achieve the highest extraction percentage of Pb, Cd, Zn, and Cu with UM, the pH value of the solution must be kept close to 5.0. The aforementioned is because the hydroxyl, carboxyl, carbonyl groups, and other components of the lignocellulosic material are protonated at low pH values, preventing their interaction with the metal ions of the working solution. On the other hand, the high pH values facilitate the formation of hydroxides or oxides of the metals in the solution.

For mercury, the highest removal is observed at acidic pH values (close to 3.0), although, in the latter case, there are no significant differences when the pH is higher. This behavior is contrary to that reported by Ghodbane and Hamdaoui (2008) [10], who studied eucalyptus bark for mercury removal and found that mercury adsorption presents better performance at pH values greater than 8.0. In contrast, they observed low metal adsorption at acid pH values on the material. This can be attributed to the differences in the composition and treatment performed on the material compared to the material used in the present study. On the other hand, it is not sufficiently clear whether the pH value is responsible for facilitating the mercury trapping mechanism observed by SEM-EDX (Figure 3F), which allows the metal to be deposited and concentrated only in small, well-defined areas.

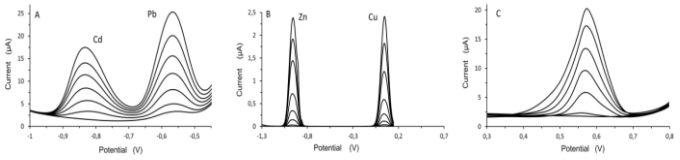

Figure 4: Square wave voltammograms for quantification of A) Cd and Pb, B) Cu and Zn, and C) Hg.

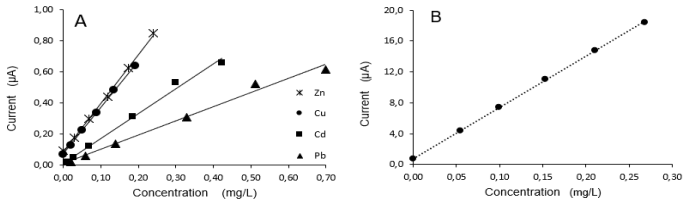

Figure 5: Calibration curves for quantification of A) Cu, Zn, Cd, and Pb, B) Hg.

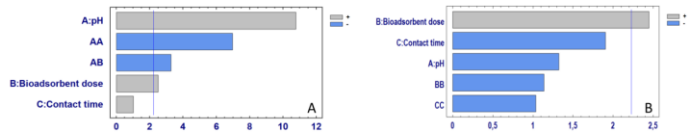

Figure 6: Pareto chart for the effects of three factors on the removal of A) Cu and B) Hg using an untreated banana peel bio-adsorbent.

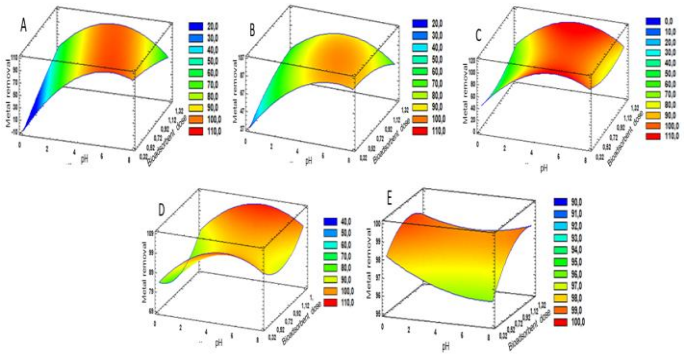

Figure 7: Response surface diagrams for removal conditions of A) Cu, B) Zn, C) Cd, D) Pb, and E) Hg using a banana peel bio-adsorbent.

Effect of the bio-adsorbent dose

The second most relevant effect on the extraction of Pb, Cd, Zn, and Cu and the first for the extraction of mercury is the dose or amount of bio-adsorbent material. However, it registers a critical value only for Cu (Figure 6A). The above suggests that, at the pH values studied, mercury can be uptake more efficiently than other metals by the UM and that the extracted amount of this metal is limited mainly by the amount of UM. The latter confirms the results obtained in the material selection stage, in which the extraction of Hg reached the highest percentage along with that of Cu.

The response surface graphic (Figure 7) shows that the adsorbent dose has less effect than the pH of the solution, obtaining slightly higher removal percentages with amounts greater than 0.3200 g of UM when the metal solution concentration was 10 mg/L. Complementary, the greater the amount of UM, the greater the percentage of metal removal. The optimal values of the three variables studied in the removal process of the metal ions appear in Table 4.

Table 4 Optimal adsorption conditions of metals on banana peel biomass from 10 mg/L metal solutions.

Metal	pH	Adsorbent Dose (g)	Contact time (min)
Cu, Cd, Pb	5.0	0.3300	15
Zn		0.3500	
Hg	3.0		

Contact time effect

The contact time demonstrates that it is a factor that has little effect on metal extraction. The contact time required was the shortest applied in this study for all five metals. That suggests a rapid and easy interaction between metal and UM.

The adsorbent dose and the contact time caused a moderate change in the response variable. For this reason, we decided to use a contact time of 15 minutes for further experiments. In the case of Hg, the graph indicates superior results with a contact time of 15 minutes and pH close to 3.0. However, the removal percentage differences for every pH value studied are small in this case.

Adsorption isotherms

The concentration of the five metals Pb, Cd, Zn, Cu, and Hg for the construction of the adsorption isotherms ranged from 10 to 1000 mg/L. We worked with the conditions of pH, adsorbent dose, and contact time recorded in Table 4. The graphs for each isotherm, relating the adsorbed amount/bio-adsorbent mass (mg/g) vs the concentration of each metal in the solution, are presented in Figure 8 A-E.

Figure 8 shows that the adsorption of the metals Cu, Zn, Cd, Pb, and Hg fits the type II isotherm (IUPAC classification), where the metals form a monolayer on the surface of the bio-adsorbent. Once the surface is saturated, the adsorption process continues in multilayers. This isotherm shows two sections: region 1 (Figure 8A), which includes from the beginning of the formation of the first monolayer until its saturation. In this monolayer, the heteroatoms of the lignocellulose bond the metal ion (chemical adsorption). This section of the isotherm depends on the nature of the adsorbate and adsorbent. It fits the Langmuir mathematical model in most cases. It agrees with what was reported by Gupta et al. [23] regarding the adsorption of lead on banana peels and other bio-adsorbents.

In the five isotherms presented, this behavior is evident up to the saturation point; this occurs because the surface of the adsorbent contains a limited number of active sites in which it can bond with metal ions. In Region 2, multilayer adsorption begins, consisting of the aggregation of metal ions that interact electrostatically with the substrate formed by the UM and the first layer of ions (physical adsorption).

On the other hand, although the above description agrees well with the observed behavior, region 1 of the mercury isotherm presents a higher amount of adsorbed metal than the different metals. As mentioned above, the adsorption mechanism of mercury differs from that of lead, cadmium, zinc, and copper, but the isotherms follow a similar behavior. This issue should be studied in more detail.

The maximum adsorption capacity for Pb, Cd, Zn, Cu, and Hg was 28.28, 29.22, 26.24, 20.81, and 24.75 mg for each gram of UM used, respectively. These results indicate that UM from banana peel surpasses in its metal adsorption capacity many of the materials from different biomass sources reported for the removal of copper, zinc, cadmium, lead, and mercury, which report removal values less than 20 mg/g in untreated materials or those that report removal only for one metal. (see Table 1). On the other hand, materials such as barley straw (31.71 mg/g Cu) [14], jackfruit peel (39.5 mg/g Zn) [17], corn cob (43.40 mg/g Pb) [32], mangosteen peel (49.75 mg/g Hg) [9] have high metal adsorptive capacity but require additional chemical treatment with citric acid, sodium hydroxide, methanol, and sodium bicarbonate respectively. That confirms that UM is a promising material for heavy metal extraction.

Desorption tests

Desorption tests were conducted to determine how much metal could be desorbed from the bio-adsorbent used for metal extraction. The bio-adsorbent was dried for 72 hours at 110°C and then introduced into a 1.0 M HCl solution. After 24 hours, the concentration of metal in the solution was measured. This process was repeated for the same sample, and the amounts of metal recovered in the two procedures were added together. The recovery percentages ranged between 50% and 75%, with the lowest average for Cu^{2+} (52.6%) and the highest average for Zn^{2+} (73.6%). The recovered metal is associated with that deposited by physisorption in the second region of the isotherm. In contrast, the non-desorbed metal can be attributed to that chemisorbed at UM and related to the first region of the isotherm.

A second desorption test was performed by digesting the bio-adsorbent used for the metal extraction in a solution of concentrated HNO_3 and H_2O_2 in a 3:1 ratio. In this case, the lowest recovery percentage was again for Cu^{2+} at 86.43% and the highest for Hg^{2+} at 93.18%.

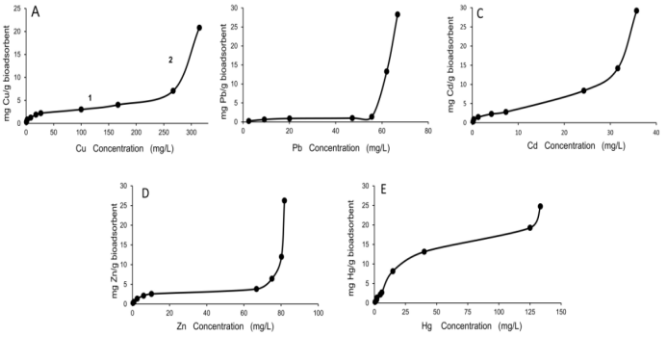

Figure 8: Adsorption isotherms for A) Cu, B) Pb, C) Cd, D) Zn, and E) Hg on untreated material from banana peel.

CONCLUSIONS

The bio-adsorbent derived from the banana peel (*Musa paradisiaca L.*) showed satisfactory efficiency in removing Pb, Cd, Zn, Cu, and Hg. The experimental design executed with the untreated material gender a maximum removal capacity of 28.28, 29.22, 26.24, 20.81, and 24.75 mg for each gram of the bio-adsorbent used for Pb, Cd, Zn, Cu, and Hg, respectively. No additional treatment apart from grinding and drying is necessary to obtain a material with excellent metal adsorptive properties. The results allow us to assert that the banana peel material constitutes an efficient alternative for its application as an adsorbent material for removing polluting metals from water.

The adsorption mechanism for all five metals fits the Langmuir model. Nevertheless, the mercury adsorption mechanism differs from the other four metals because it is concentrated in small regions well-differentiated from the bulk of the material. The distribution of Zn and Cu on the material surface is more homogeneous. On the other hand, lead and cadmium are captured over the entire surface, with small areas of higher concentration of the metal.

The pH value of the working solution was the factor with the most relevant influence on the extraction process of Pb, Cd, Zn, and Cu, with the untreated material derived from banana peel. The dose of bio-adsorbent was the most influential factor for Hg extraction. The optimal adsorption conditions are pH = 5.0 and an adsorbent dose of 0.3300 g (Cu, Cd, and Pb) and 0.3500 g (Zn). In the case of Hg, a pH of 3.0 and an adsorbent dose of 0.3500 g are the best conditions for treating 10 mL of solution with a concentration of 10 mg/L of the metal.

The isotherms and desorption tests show that two types of interaction exist between the bio-adsorbent and the metal. Chemisorption occurs in the first stage, followed by physisorption in the second stage.

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DECLARATION OF INTEREST

The authors have no conflicts of interest to declare relevant to this article's content.

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