

Banana Peel Applied to the Solid Phase Extraction of Copper and Lead from River Water: Preconcentration of Metal Ions with a Fruit Waste

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ABSTRACT: This article reports on an investigation into the ability of minced banana peel to extract lead and copper ions from water and the parameters involved in this process. The kinetics of copper and lead uptake reached equilibrium in 10 min and the extraction of metals ions was favorable above pH 3. The medium was characterized by FTIR, which showed absorption bands of carboxylic and amine groups at 1730 and 889 cm^{-1} , respectively. The adsorption isotherm fitted by Langmuir's model showed maximum adsorption capacities of 0.33 and 0.20 mmol g^{-1} (or 20.97 and 41.44 mg g^{-1}) for Cu(II) and Pb(II), respectively. Minced banana peel was applied in the preconcentration system and showed approximately 20-fold enrichment factor and the column was reused for 11 cycles without loss in the percentage of recovery. The proposed method was applied in the determination of Cu(II) and Pb(II) in a sample of raw river water and was validated by comparison with a standard reference material.

1. INTRODUCTION

Contamination of environmental compartments with organic and inorganic compounds such as metals and pesticides has motivated the development of purification and extraction methods. A wide variety of heavy metal species enters the aquatic compartment through atmospheric deposition, lixiviation of mining areas and cultivated fields, and industrial discharges, and these activities follow an upward curve in response to the world's ever growing population and its needs. Research into the contamination of water by metal species has attracted special attention due to the high dilution capacity of water, the possible accumulation of heavy metals in plants, fish, and sediments,^{1,2} and the need to protect all life forms.

Several technologies have been proposed to treat wastewater contaminated with metal species. Among several technologies, the extraction of metal ions using solid materials such as modified silica, alumina, activated carbon, and resins has been extensively investigated.^{3–7} These materials have been subjected to functionalization reactions to anchor molecules containing Lewis bases in its structure, which acts as a metal collector.^{8–14} In the case of silica, the main advantages are its high surface reactivity, the possibility to anchor molecules with desirable selectivity toward metals ions,^{15,16} and the high stability of ligand molecules on the silica surface, enabling the matrix to be used over a number of cycles.⁹

Despite these advantages, preparing modified silica gel with organic molecules is expensive because high-purity chemicals are required to enhance the efficiency of the reaction; moreover, the solvents used in the modification reaction are usually toxic. From

this standpoint, therefore, natural solid material can be considered more attractive, besides being aligned with the concepts of green chemistry.

Natural products usually considered waste, such as sugar cane bagasse, peanut shells, and apple waste, have been employed to extract metals from water.^{17–20} This is possible due to the presence of acid groups such as carboxylic and phenolic groups. This type of product can also be used in metal speciation, as in the case of Cr(VI) sorption by coconut coir.²¹

In the present work, minced banana peel was characterized by FTIR to identify the functional groups responsible for its capacity to coordinate metal ions. The material, which was tested in the extraction of copper and lead ions from water, was applied in column experiments to test its ability to preconcentrate copper and lead from raw river water. The accuracy of the preconcentration method was evaluated by comparison against a certified reference material (SRM 1643e).

2. EXPERIMENTAL PROCEDURES

2.1. Reagents and Equipment. All of the reagents used were of analytical grade. The metal ions solutions were prepared by dissolving an appropriate amount of their nitrate (Sigma-Aldrich Steinheim, Germany) in deionized water (Millipore, Direct-Q).

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The nitric acid solution used to acidify the metal ions solutions was predestilled in a quartz sub-boiling system (Marconi) and the metal standard solutions for the calibration curves were diluted from 1000 mg L⁻¹ stock solution (Merck Darmstadt, Germany).

The metal ions were determined by atomic absorption spectrometry (AAS, PerkinElmer AA700) using an air-acetylene flame and electrothermal atomization in a graphite furnace with 324.7 and 283.3 nm as resonance lines for copper and lead, respectively. Prior to their use, the graphite tubes were modified permanently with sodium tungstate solution²² and palladium nitrate (Sigma-Aldrich Steinheim, Germany) was used as a matrix modifier.

The minced banana peel was separated from the supernatant of the metal solution in batch experiments, using a centrifuge (FANEM Excelsa II) operating at 3500 rpm for 7 min with 50 mL plastic tubes (Sarstedt). In column experiments, the flow was induced by a peristaltic pump (TECNOPON DMC 100) equipped with a tygon tube.

2.2. Surface Characteristics of Banana Peel. Dried banana peel was first minced in a ball mill using a FRITSCH Pulverisette 6 for 20 min and 500 rpm. After pulverization, the banana peel's particles were sieved and the fraction between 35 and 45 μm was selected for work. The banana peel's surface was characterized by diffuse reflectance infrared Fourier Transform (DRIFT) using a Nicolet Nexus 670 spectrometer equipped with a Smart Collector, using 200 scans, resolution of 4 cm⁻¹, and ambient atmosphere. In this procedure, a crucible, used in a reflectance apparatus, was filled with the banana peel's particles without dilution.

Specific surface area and pore size distribution were determined using a Micromeritics ASAP 2010 apparatus (Micromeritics Instrument Corporation) with 2.0 g of minced banana peel.

2.3. Batch Extraction Procedure. Aliquots of 10 mL of standard metal ions solution (10 mg L⁻¹) were transferred to 50 mL centrifuge tubes and 0.02 g of minced banana peel was added to each tube. The suspensions were stirred mechanically at 1–60 min intervals at room temperature (30 °C) to examine the kinetic reaction. The effect of pH on the extraction process was investigated in a range of 1–5 with diluted nitric acid and sodium hydroxide solutions. The adsorbent mass, solution concentration, and volume were the same as described above. The maximum amount of metals taken up (N_f) by minced banana peel was determined using aliquots of 10 mL in a concentration interval, according to the following equation:

$$N_f = (n_i - n_s)/m \quad (1)$$

where n_i is the initial number of moles of the metal ion in solution phase, n_s is the number of moles of metal ion in supernatant, after the extraction, and m is adsorbent mass used. The residual metal concentration in the supernatant was determined by FAAS.

Because this work aimed to preconcentrate a raw water sample, the influence of ions interfering in the extraction process was also investigated at three different concentrations, 10, 50, and 100 mg L⁻¹ of NO₃⁻, SO₄²⁻, Cl⁻. All experiments related to metal ion adsorption were performed with three replicates.

2.4. Solid-Phase Extraction Column Procedure. The preconcentration procedure was performed in a 1.2 cm long glass column with an inner diameter of 2.8 mm filled with 0.02 g of minced banana peel, and the volume of metal solution (0.01 mg L⁻¹) to be preconcentrated was set at 20 mL. The parameters investigated were the percentage recovery as a function of the eluant concentration in a range of 0.1–2.0 mol L⁻¹ of HNO₃, the eluant volume in a range of 0.5–2.0 mL, and the reusability of the

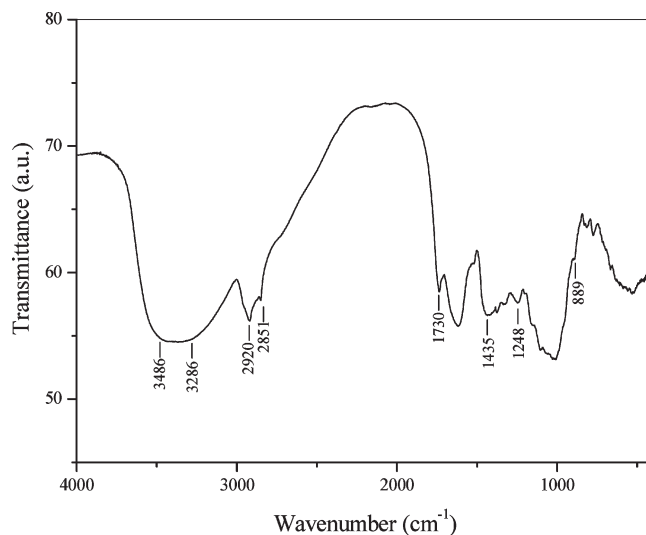


Figure 1. Infrared spectrum of minced banana peel obtained with 1 mg of adsorbent and 500 mg of KBr.

column as a function of number of cycles. In all of the investigated parameters, the eluant and sample flow rates were fixed at 1.0 mL min⁻¹. The operational conditions were adjusted initially using only Cu(II) solutions. All experiments related to column procedure were performed with three replicates.

2.5. Preparation of the Raw Water Sample. The sample of raw water was subjected to a digestion procedure to oxidize organic substances such as humic acids, which can bind metal ions in solution and influence the preconcentration results.^{23,24} In this procedure, aliquots of 50 mL of water sample and 5 mL of concentrated HNO₃ were transferred to a beaker and slowly evaporated to a volume of about 15 mL on a hot plate. Five mL of concentrated HNO₃ were added to the evaporation residue and the beaker was covered with a watch glass and heated at 95 °C for 1 h. The pH of the digestion extract was adjusted to ~5.5 by the addition of a sodium hydroxide solution, the sample's volume was adjusted to 100 mL in a volumetric flask, and the digested sample was transferred to a polyethylene container. The results of the preconcentration system were compared with those obtained directly by graphite furnace atomic absorption spectrometry (GFAAS).

3. RESULTS AND DISCUSSION

3.1. Surface Characterization. An FTIR spectrum of minced banana peel (constituted by carbohydrates, proteins, lipids, and fibers) was recorded to identify functional groups responsible for the metal ion coordination. Figure 1 shows the FTIR spectrum of dried banana peel with a particle size of around 150 mesh. The bands in the region of 3486 and 3286 cm⁻¹ were assigned to O–H stretching, those at 2920 and 2851 cm⁻¹ to C–H stretching, and the band appearing at 1730 cm⁻¹ was attributed to the C=O bond of carboxylic acids.²⁵ The weak band in the region of 889 cm⁻¹ was attributed to amine groups.

The specific surface area, determined by the BET method,²⁶ was found to be 2.0 ± 0.01 m² g⁻¹ and pore diameters was 10.5 Å. The low surface area of banana peel's particles is a self-characteristic of carbonaceous materials (when compared with silica based materials) and its nitrogen adsorption and desorption isotherms can be seen in Figure 2.

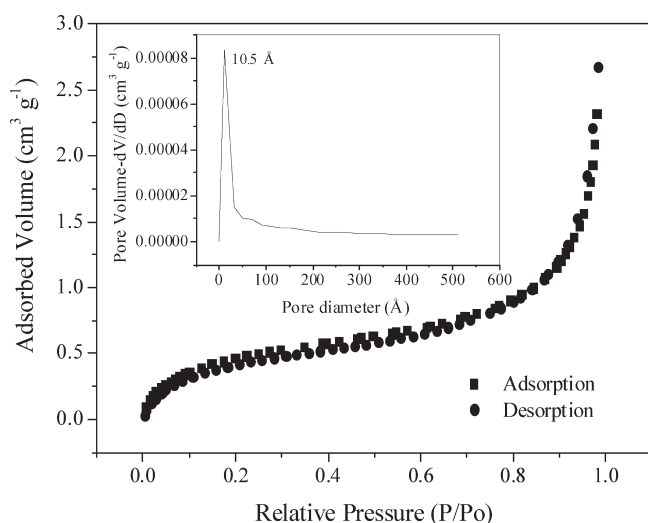


Figure 2. Adsorption and desorption of nitrogen isotherms and distribution of pore diameter and pore volume (inserted in figure).

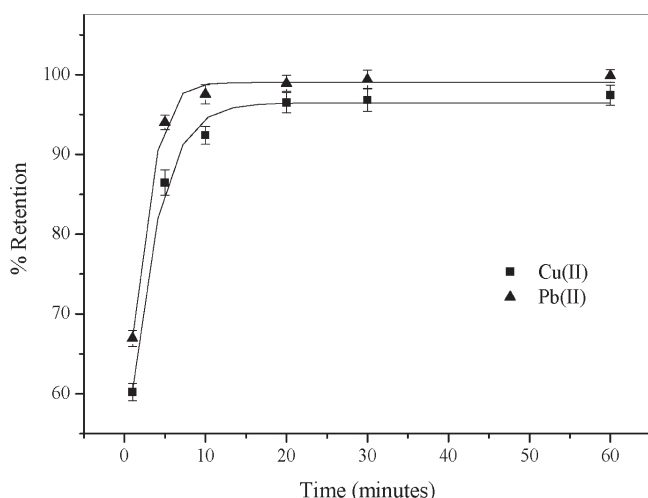


Figure 3. Retention percentage as a function of time for Cu(II) and Pb(II) in aqueous medium using 0.02 g of minced banana peel.

The adsorption and desorption isotherms are characteristic of a low surface area material that is predominantly microporous, which can be seen from the distribution of pore diameter graph, inserted in Figure 2.

3.2. Batch Extraction Experiments. An important aspect of this material applied in preconcentration experiments is the time required for the extraction process to achieve equilibrium. Figure 3 plots the retention percentage of Cu(II) and Pb(II) as a function of time and, as can be observed, the kinetics is fast, reaching equilibrium in about 20 min.

The effect of pH was investigated by varying the pH of metal solutions subjected to extraction experiments with diluted solutions of NaOH and HNO₃. Figure 4 plots the retention percentage as a function of pH for Cu(II) and Pb(II). As can be seen in Figure 4, this material can be applied easily in extraction experiments in acidic medium, because it showed more than 90% retention in pH 3 and about 98% retention in pH 4 and 5. At pH below 3, the main group responsible for metal extraction, carboxylic acids,^{27,28} is protonated due to the high

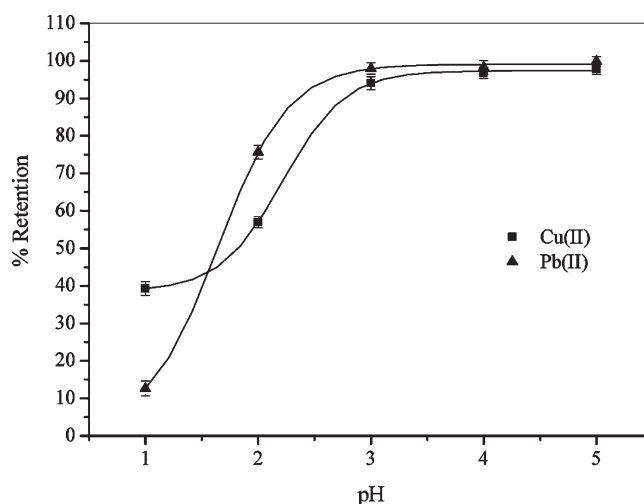


Figure 4. Effect of pH solution on the extraction of Cu(II) and Pb(II) onto surface of minced banana peel.

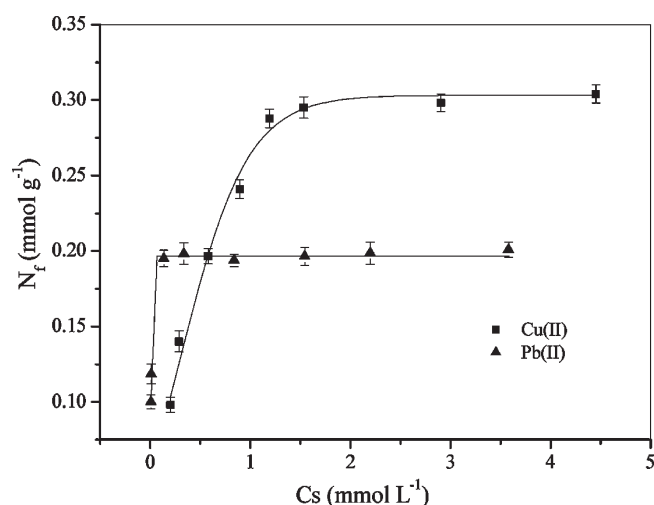


Figure 5. Adsorption isotherms of Cu(II) and Pb(II) from aqueous solution.

concentration of H⁺ species. Metal solutions with pH above 5 were not used in view of the risk of hydrolysis.

The maximum extraction capacity of Cu(II) and Pb(II) was determined by the saturation condition of the isotherms shown in Figure 5, which were 0.30 and 0.20 mmol g⁻¹ for Cu(II) and Pb(II), respectively. The higher extraction capacity of Cu(II) ions can be explained by the fact that carboxylic groups, which are considered hard bases,²⁹ have a stronger affinity for hard or intermediate acids such as Cu(II) ions. Pb(II) ions are considered soft due to their large ionic radius and high polarizability, which cause their extraction to occur to a lesser extent.

To evaluate the maximum adsorption capacity (N_s) of banana peel, a modified Langmuir equation was applied as proposed by a series of systems.^{27,30}

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b} \quad (2)$$

In this expression, C_s is the concentration of solution in equilibrium (mmol L⁻¹), N_f is the concentration of metal ions sorbed on the surface (mmol g⁻¹), N_s is the maximum amount of

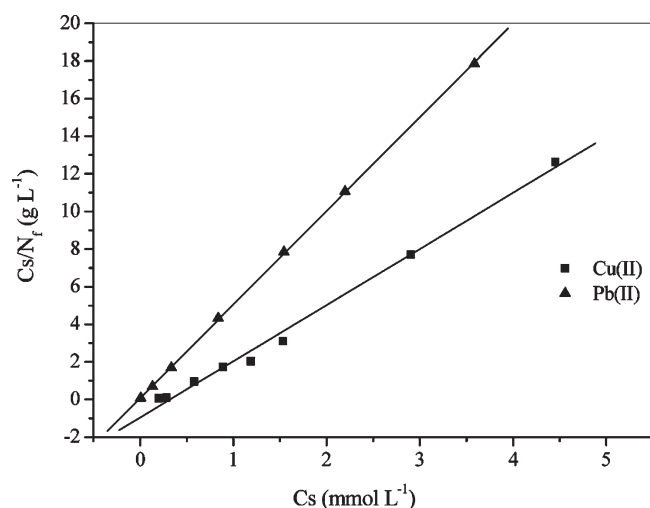


Figure 6. Linear shape of adsorption isotherms of Cu(II) and Pb(II).

Table 1. Influence of Some Anions Found in the Extraction Process from Raw River Water, ($n = 3$)

interfering ions	Concentration (mg L^{-1})		
	10	50	100
	% retention of Cu(II)		
SO_4^{2-}	97.9 ± 1.3	96.2 ± 1.4	94.2 ± 1.3
Cl^-	96.5 ± 0.4	96.2 ± 1.0	92.5 ± 0.3
NO_3^-	98.3 ± 0.3	96.4 ± 1.9	94.0 ± 1.1
	% retention of Pb(II)		
SO_4^{2-}	97.67 ± 1.2	96.4 ± 1.3	93.1 ± 0.8
Cl^-	96.0 ± 0.5	95.7 ± 1.0	90.7 ± 1.2
NO_3^-	97.6 ± 1.4	97.1 ± 0.4	95.5 ± 0.7

metal ions sorbed per gram of sorbent (mmol g^{-1}), which depends on the number of adsorption sites, and b is a constant. Thus, the adsorption studies were based on the linearized form of the sorption isotherm derived from C_s/N_f as a function of the C_s plot. The values of N_s , 0.33 and 0.20 mmol g^{-1} (or 20.97 and 41.44 mg g^{-1}) for Cu(II) and Pb(II) respectively were determined from these data, which are depicted in Figure 6.

The interaction between metal species and adsorption sites can be related to a covalent bond formation due to the small difference from N_f to N_s values and this way the adsorption process can be classified as a chemical adsorption.

Metals ions in raw river water may be in contact with anions and this interaction may decrease the extraction efficiency. Therefore, experiments with NO_3^- , SO_4^{2-} , and Cl^- were performed at three different concentrations: 10, 50, and 100 mg L^{-1} of each.

As can be seen in Table 1, the extraction efficiency at an anion concentration of 10 mg L^{-1} was about 97–98%, and at higher concentrations the extraction diminished only slightly, suggesting that banana peel can be applied to remove metals from raw water and wastewater samples.

3.3. Comparison of the Adsorption Capacity of Minced Banana Peel and Other Materials. Table 2 compares the Cu(II) and Pb(II) ion adsorption capacity of minced banana peel with other materials. As this table shows, minced banana

Table 2. Comparison of the Adsorption Capacity of Minced Banana Peel and Other Materials Employed in Metal Ion Extraction

type material	Adsorption Capacity (mmol g^{-1})		reference
	Cu(II)	Pb(II)	
Na-bentonite	0.108		31
AMP-modified silica gel	0.447	0.380	14,32
herbicide-modified silica gel	0.442		27
modified peanut husk	0.159	0.140	33
sawdust	0.104	0.106	33
expanded perlite (EP)	0.136	0.064	34
minced banana peel	0.330	0.200	this study

Table 3. Influence of Eluant Volume on the Recovery and Enrichment Factor in the Column Mode for Three Replicates ($n = 3$)

eluant volume (mL)	% recovery	enrichment factor (E_f)
0.5	77.9 ± 4.6	31.2
1.0	100.8 ± 2.1	20.1
1.5	99.1 ± 1.0	13.2
2.0	100.1 ± 3.4	10.1

peel has a higher adsorption capacity than several other natural and synthesized products.

3.4. Column and Preconcentration Experiments. The first parameter investigated in the column mode was the eluant volume required to strip all metal adsorbed on banana peel particles. Aliquots of 0.5–2.0 mL of a 2.0 mol L^{-1} HNO_3 solution were used and the results are presented in Table 3.

As this table indicates, the metal ions adsorbed on the column were completely eluted when eluant volumes equal to or higher than 1.0 mL were used. Despite the higher enrichment factor observed when using 0.5 mL, this volume did not show a good recovery rate. An eluant volume of 1.0 mL was chosen because higher volumes diluted the metal ions and thus reduced the enrichment factor.

The eluant concentration was also investigated in the range of 0.1–2.0 mol L^{-1} aiming to avoid using excessive acid and thus ensure the column's reuse. As Figure 7 indicates, a volume of 1.0 mL of eluant 1.0 mol L^{-1} was enough to strip quantitatively the metals adsorbed on banana peel particles. A column reusability experiment was performed using 1.0 mL of 1.0 mol L^{-1} HNO_3 solution as eluant and the material showed good stability over 11 cycles, as indicated in Figure 8. The decrease in metal ion recovery was attributed to the oxidation of coordination sites existing on the surface of the material.¹³

After optimizing the parameters of the preconcentration system, it was employed to preconcentrate Pb(II) in the same conditions as those applied to Cu(II). This experiment also showed a 20-fold enrichment factor.

3.5. Determination of Trace Metal in Raw Water. The proposed preconcentration method was applied to preconcentrate trace metals in a sample of raw river water after the mineralization procedure. Aliquots of 20 mL of mineralized water were subjected to the preconcentration system and the metals adsorbed on banana peel particles were eluted with 1.0 mL of 1.0 mol L^{-1} of HNO_3 solution. The eluate was analyzed directly by flame atomic absorption spectrometry (FAAS) and

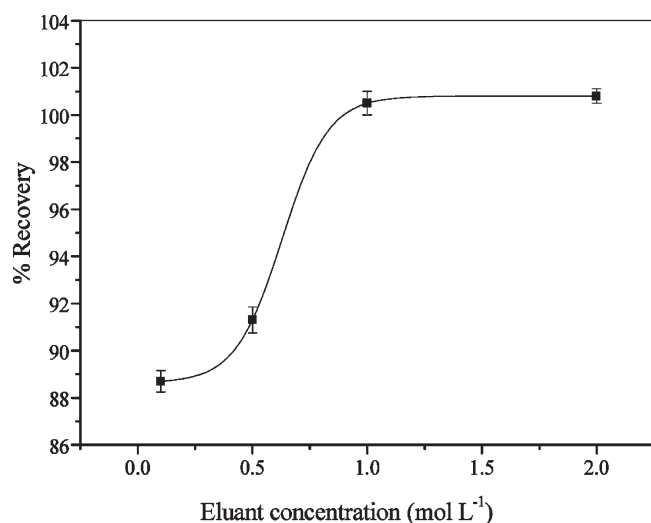


Figure 7. Recovery percentage as a function of HNO₃ concentration.

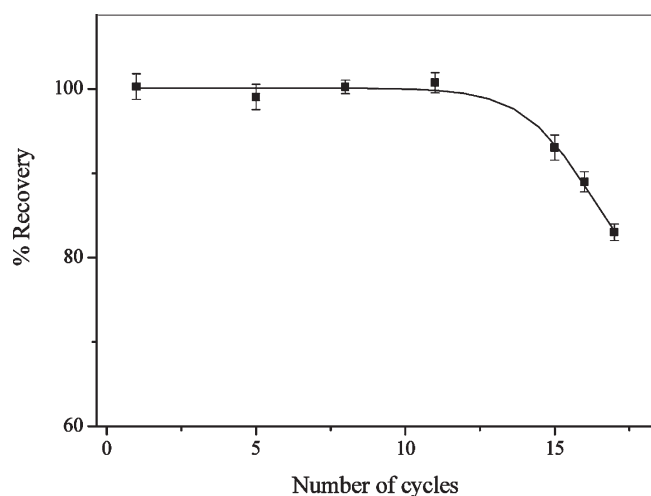


Figure 8. Metal ion recovery percentage as a function of number of cycles.

the results were compared with those obtained by GFAAS. The graphite tubes were modified permanently with sodium tungstate and the samples were injected with palladium nitrate as a matrix modifier. Table 4 presents the results of the water preconcentration and the standard reference material.

An analysis of the data in Table 4 for Cu(II) and Pb(II) with and without preconcentration indicates that the results are in agreement with the 20-fold enrichment factor determined experimentally. The analysis of the SRM water is also consistent with the enrichment factor, proving that the system using banana peel particles can be applied easily for the determination of trace metal ions in raw water samples.

CONCLUSIONS

The high retention percentage of Cu(II) and Pb(II) in acid medium, pH 3, is an important aspect of the adsorption process because it can be applied to the purification of wastewater. In our opinion, this biomaterial is also very attractive due to its low cost and the fact that it does not require modification reactions such as those required by other materials used in this type of work. This

Table 4. Metal Ion Concentrations in River Water with and without Preconcentration ($n = 3$)

metal species	Determination Module	
	nonpreconcentrated samples ($\mu\text{g L}^{-1}$)	preconcentrated Sample ($\mu\text{g L}^{-1}$)
Cu(II)	5.1 ± 0.2^a	105.1 ± 4.3^b
Pb(II)	4.2 ± 0.3^a	81.7 ± 3.8^b

Standard Reference Material		
metal species	reference values ($\mu\text{g L}^{-1}$)	preconcentrated standard ($\mu\text{g L}^{-1}$)
Cu(II)	22.7 ± 0.3	459.5 ± 6.2^b
Pb(II)	19.6 ± 0.2	400.2 ± 7.1^b

^a Analyzed by GFAAS. ^b Analyzed by FAAS.

study led to the conclusion that minced banana peel can be applied in the extraction and preconcentration of metal ions in raw river water with an enrichment factor of approximately 20-fold, and that, in the conditions described here, it can be used with good stability over 11 cycles. Our analysis of the SRM water allows us to conclude that the system can be applied in the determination of trace metal species in raw water samples.

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