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Removal of Copper and Lead from Water in The Mariana Mining Disaster Using Biomass Banana Peel and Rice Husk

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Abstract

The dumping of the mining tailings dam from Mariana, Brazil released about 34 million mining tailings in the Doce river basin, containing many toxic metals. The biomasses of banana and rice were used as adsorbents in the removal of Cu (II) and Pb (II) metals from contaminated water. Quantification of metals was performed using NexION 300D PerkinElmer (USA) ICP-MS. The pH effect studies indicated that the adsorption analyzed in the present work did not undergo significant changes with the variation of the pH values, thus for both banana and rice the best adsorption capacity of Cu (II), 34.11 mg g⁻¹ and 34.37 mg g⁻¹, was at pH 5. For Pb (II), the highest adsorption capacity was also at pH 5 with 36.06 mg g⁻¹ for banana and 36.04 mg g⁻¹ for rice. There was a rapid adsorption where, in all cases in the first 30 minutes of adsorption, more than 60% of the metals had already been adsorbed. Finally, tests were carried out using real samples from Doce river contaminated by the metals under study due to the Mariana disaster. The biomasses presented excellent performance in Cu (II) and Pb (II) removal, reaching concentrations close to zero after adsorption process.

Keywords: adsorption, metals, mining activity

1. Introduction

Pollution from toxic metals is a serious environmental problem all over the world. The intense technological and industrial development led to the excessive use of toxic metal ions and, thus, increased water pollution. These metals are often reported to be harmful to humans and other organisms because of their high toxicity and cumulative effects [1].

On November 5, 2015, Brazil faced its worst environmental disaster after an iron-ore mining waste dam collapsed releasing 34 million m³ of contaminated mud in a headwater region of the Doce River basin [2].

In a report from the Minas Gerais Water Management Institute [3], which monitored some elements in water samples from points in the Doce river Basin, high

concentrations of elements such as Pb and Cu, well above maximum value recommended by environmental legislation [4]. In this sense, it is necessary to develop technologies that can remove these pollutants, so that this water is properly used for human and animal consumption.

There are several methods to remove toxic metal ions from aqueous solutions which consist mainly of chemical, physical and biological techniques [5]. However, these technologies are not always economically viable for Water Treatment Plants.

A promising alternative is the use of biomass adsorption (biosorption). It has low cost, wide adaptation and selectivity in the removal of different types of toxic metals and stable performance in the purification of wastewater ($1-100 \text{ mg L}^{-1}$) [6]. The use of plant biomass to obtain raw material is one of the proposals of green chemistry. Green chemistry is an approach that aims to minimize the environmental impact through the creation, development and application of chemical products and processes for reduction or elimination of the use and the generation of toxic substances to the detriment of its treatment [7].

Biosorption is one of the most promising technologies for the remediation of aquatic areas polluted with toxic metal ions [8]. There are several compounds with promising characteristics for the treatment by the use of biosorption, among them rice straw and banana peel stand out. Rice straw contains large amounts of cellulose, hemicellulose, lignin and silica, these compounds provide binding sites for metals [9]. The banana peel has been used as a biosorbent for adsorption of copper, and it is readily available, inexpensive and ecologically correct [10].

The aim of this study was to evaluate and compare the adsorption capacity of the biomass of rice straw and banana peel in waters contaminated by Cu (II) and Pb (II) metals and application in contaminated waters due Mariana disasters.

2. Materials and methods

2.1 Origin of materials

The rice husk originates from the Muriaé region, in the state of Minas Gerais (Brazil) where it is widely grown and easy to obtain biomass. The banana peel was obtained in fairs of the city of Teófilo Otoni – MG (Brazil), these fairs are supplied by small producers of all region of the Mucuri Valley.

2.2 Preparation of biomass

2.2.1 *Banana peel*

The preparation of the biomass obtained from the banana peel was washed with ultrapure water, taken to the oven for drying at 70°C and ground by a SHOP63 01 industrial blender. After trituration the obtained product was sieved for Bertel granulometric analysis at 40 mesh.

2.2.2 *Rice husk*

The procedure for obtaining the rice husk biomass resembles the banana peel process. The rice husk was prepared by rinsing the husk with ultrapure water for the removal of particles, and was then taken to an oven at 70°C for 24 hours for drying. After drying, they were crushed in an electric mill and its product passed in a sieve for Bertel granulometric analysis with 40 mesh opening.

2.3 Characterization of materials

2.3.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images for biomass samples of banana peel and rice were obtained on a Zeiss (FEG-SEM) Sigma VP model.

2.3.2 Infrared spectroscopy with fourier transform (FT - IR)

IR-FT spectra were obtained on a Perkim Elmer FT-IR / NIR Spectrometer Frontier equipment at a frequency range of 4000 and 500 cm^{-1} . The examples were prepared using the KBr disk method.

2.3.3 Zeta potential

Zeta potential of banana peel biomass and rice straw were measured using a Zetasizer Nano-ZS (Malvern Instruments, UK).

2.4 Solutions of toxic metal ions

Solutions were prepared to be used in the isotherm, pH and kinetics tests. For each metal (Cu (II) and Pb (II)), a 1000 mg L^{-1} solution was used as the standard solution for other solutions of concentration: 0.5, 5, 20, 50, 100 and 200 mg.L^{-1} . The contaminating reagents used were Dehydrated Copper (II) Chloride - Sigma 99% and Lead (II) Nitrate - Cinética.

2.5 Adsorption tests

2.5.1 Isotherm test

A quantity of 10 mg of the adsorbent were used in 10 ml samples of the metal solutions at concentrations of 0, 0.5, 5, 20, 50, 100 and 200 mg.L^{-1} . Afterwards, they were placed in a Thermo Scientific shaker model 4360 for 24 hours. After 24 hours, the samples were taken to a CIENTEC CT-6000R centrifuge for 3 minutes at 5500 rpm (4058 g) and the aliquot removed to dilute to 2% nitric acid. The initial and residual concentrations were analyzed by NexION 300D PerkinElmer (USA) ICP-MS and the adsorbed amount (q_e) was calculated by Eq. (1):

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where C_o and C_e (mg.L^{-1}) are the initial and equilibrium concentrations respectively, V is the volume of the solution (L) and m is the mass (g) of the adsorbent used in the experiments.

The Langmuir model (Eq. (2)) is used for a monolayer adsorption process on a homogeneous surface, in which the concentration occurs at specific sites in the adsorbent. The equation of the Langmuir isotherm is given by Eq. (2):

$$q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (2)$$

where Q_m ($\text{mg}\cdot\text{g}^{-1}$) and K_L ($\text{L}\cdot\text{mg}^{-1}$) are the maximum adsorption capacity and the Langmuir constant used for adsorption energy, respectively.

The adsorption is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Eq. (3)) [11].

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

The Freundlich model (Eq. (4)) is used to describe multilayer adsorption on heterogeneous surfaces.

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and $1/n$ are the Freundlich constants representing adsorption capacity and adsorption intensity, respectively.

2.5.2 pH test

For pH test, 10 mg of the adsorbent were used in 10 ml samples of the metal solutions at a concentration of 20 ppm of the metal solutions at pHs of 5, 7 and 9. With the pH corrected, the solutions were placed in the Thermo Scientific shaker model 4360 for 24 hours. After 24 hours of stirring, the samples were centrifuged in a CIENTEC CT-6000R centrifuge for 3 minutes at 5500 rpm (4058 g) for aliquot withdrawal, for further dilution in 2% nitric acid, and analysis by ICP-MS Nexion 300D PerkinElmer (USA).

2.5.3 Kinetic test

The metallic solution of 10 ml to $20 \text{ mg}\cdot\text{L}^{-1}$ was added to 10 mg of the adsorbent material (biomass of banana peel and rice). Soon after, the solutions had the pH corrected to 7 and placed in a Thermo Scientific model 4360 agitator, with variations in contact time of the biomass with the metallic solution: 0.5, 2, 4, 6, 12 and 24 hours. After the stirring time, the samples were centrifuged through CIENTEC CT-6000R for 3 minutes at 5500 rpm (4058 g) for aliquot extraction, dilution (2% HNO_3) and analysis of ICP-MS NexION 300D PerkinElmer (USA). The kinetic adsorption data were adjusted with the models of pseudo-first order [12] (Eq. (5)) and pseudo-second order [13] (Eq. (6)) models:

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

where q_e and q_t are the amounts of adsorbent ($\text{mg}\cdot\text{g}^{-1}$) in equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) are the equilibrium adsorption rate constants for pseudo-first and pseudo-second order adsorption, respectively.

2.6 Collecting contaminated water by metals in the Doce river basin

The water samples were collected in two different areas of the Doce river basin, in the state of Minas Gerais, in the years 2016, 2017 and 2018. The areas were chosen in relation to the contamination gradient. Two samples were collected at each point (**Figure 1**) whose latitude and longitude are described below: P1- 18° 52' 55.31 (S) 41° 57' 86" (W) and P2 - 18° 51' 22.54" (S) 41° 56' 10.55" (W). The first point is located in the water and sewage treatment system and the second point in the city center of Governador Valadares, Brazil.

The water samples were collected according to the procedure adopted by the Environmental Sanitation Technology Company [14]. Briefly, 1000 mL vials of Falcon BD® model polypropylene were contaminated free of contaminants were used for collection. Water samples were stabilized with ultrapure nitric acid (0.5% HNO₃). The concentrations of the metals in the samples were determined using ICP-MS according to EPA method 200.8 [15].

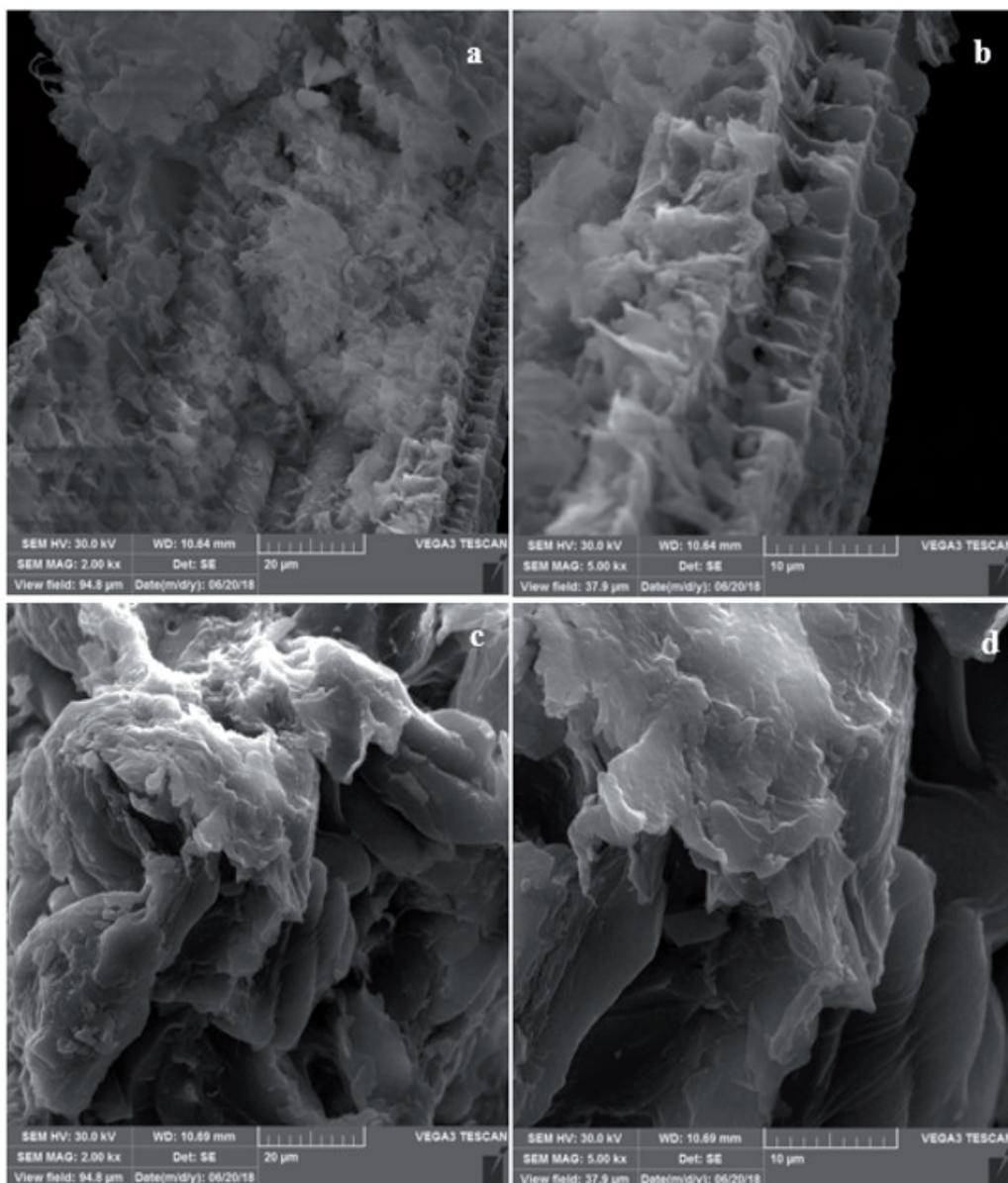


Figure 1. Scanning electron microscopy image of (a - b) rice (c - d) banana biomass expand 2,000 and 5,000 times.

3. Results and discussion

3.1 Characterization

3.1.1 Scanning electron microscopy

The **Figure 1(a)** and **(b)** shows the scanning electron microscopy of rice biomass, with magnification of 2.000 x in (a) and 5.000 x in (b). In (c) and (d), it shows the banana biomass, with an image enlarged from 2.000 x in (c) to 5.000 x in (d). In all the images it is possible to observe a porous structure, being able to be susceptible to adsorption of metals on its surface.

3.1.2 Infrared spectroscopy with fourier transform

The main adsorption bands were observed in the infrared region (500-4000 cm^{-1}) and compared with the literature.

In **Figure 2**, the banana peel biomass presents: the absorption band of 3200 cm^{-1} can be attributed to the O-H bond stretch, characteristic of functional groups of alcohols and phenols. Pino [16] as well as the presence of H_2O molecules. The wavenumber 2930 cm^{-1} corresponds to the axial deformation of aliphatic and hydro aromatic carbon sp^3 carbon bonds found in cellulose and hemicellulose [17]. In the vicinity of the range 1620 cm^{-1} indicates the lignin, due to the functional group C=O [18]. Finally, the peak near 1000 cm^{-1} is assigned to the C-O group stretching than can be observed in cellulose, hemicellulose and lignin. Thus, it can be concluded that groups alcohols/phenols, carboxyl, carbonyl, alkane, aromatic groups are present in banana bark [19].

Rice bark biomass shows major bands in the bands of 3369 cm^{-1} indicating O-H elongation, revealing a hydrogen bond, this structure may be due to the presence of acids or alcohols [20]. The wavelength 2900 cm^{-1} , as well as in banana biomass,

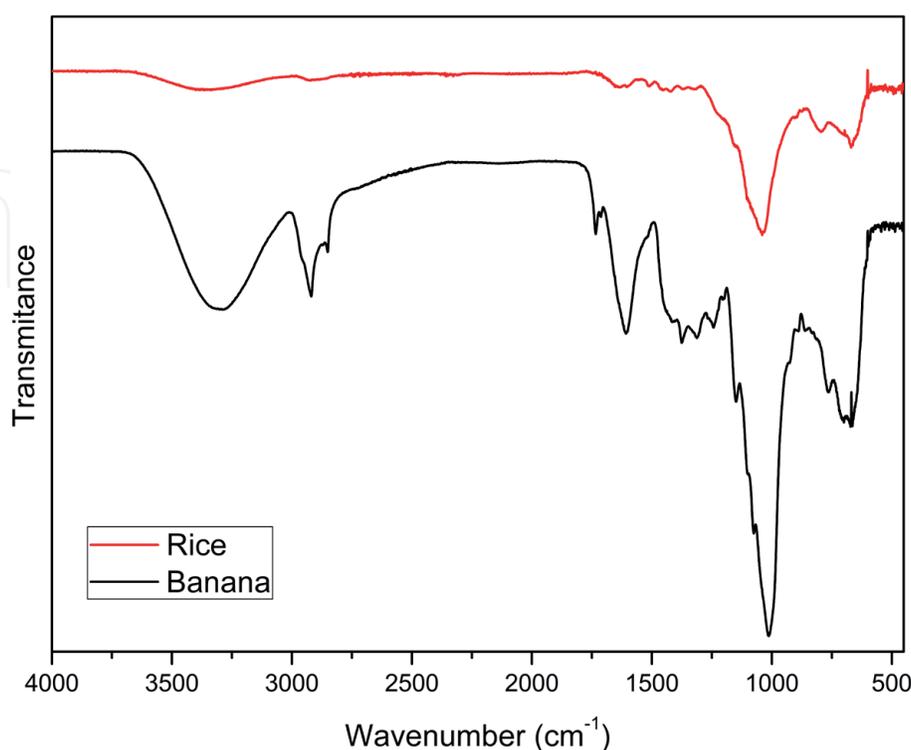


Figure 2.
Results of the Fourier transform infrared analysis of rice and banana biomass.

indicates groups of C-H, from carbon sp^3 , connecting to the presence of cellulose and hemicellulose. The spectral band around $1500-1640\text{ cm}^{-1}$ attributes to the functional group carbonyl (C=O) elongation associated with lignin [21]. The bands near 1100 and 800 cm^{-1} are characteristic of the O-Si bond in polymorphic silica, SiO_2 [22].

The adsorption mechanism of the copper and lead ions in the studied biomass can be associated with the presence of functional groups that have oxygen in their constitution [23]: a two-step process: (i) the metal ions hydrolyze in the solution to form a hydrolyzed metal ion (ii) the positively charged halves interact with oxygen-containing functional groups, leading to better contact with biomass and high adsorption capacity.

3.1.3 Zeta potential

Figure 3 show the zeta potentials of the banana and rice peel. The original peels exhibit a negative zeta potential and the used particles possess a less negative potential. All these results reveal that the waste peels had adsorbed the metal ions. The isoelectric point for banana was $6.6 - 7.0$ and for rice $6.6 - 7.3$.

3.2 Adsorption tests

3.2.1 Isotherm test

3.2.1.1 Copper

In order to determine and compare the adsorption capacity of copper by the banana and rice biomass, **Figure 4** shows two graphs of the Cu (II) equilibrium concentration (C_e) as a function of the adsorption capacity (Q_e) of the biomasses. **Figure 4(a)** shows a marked increase in the isotherm, indicating that the free sites of the banana biomass were empty and available for Cu (II) adsorption. While **Figure 4(b)** shows some initial oscillation in the adsorption capacity but soon after the free sites reach the saturation and, consequently, a balance in the adsorption capacity of the rice biomass.

The Langmuir and Freundlich isotherm models were tested for information on Cu (II) adsorption by banana and rice biomasses. These models describe the interaction between the adsorbent and the adsorbed material. The Langmuir model considers that the adsorption process occurs in a monolayer on a homogeneous

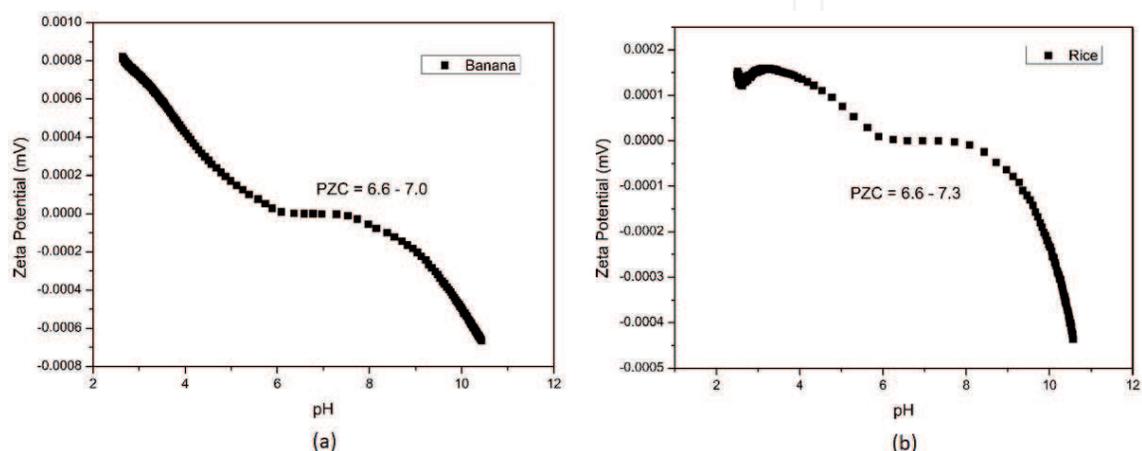


Figure 3.
Zeta potential curves obtained for (a) banana peel and (b) rice rusk.

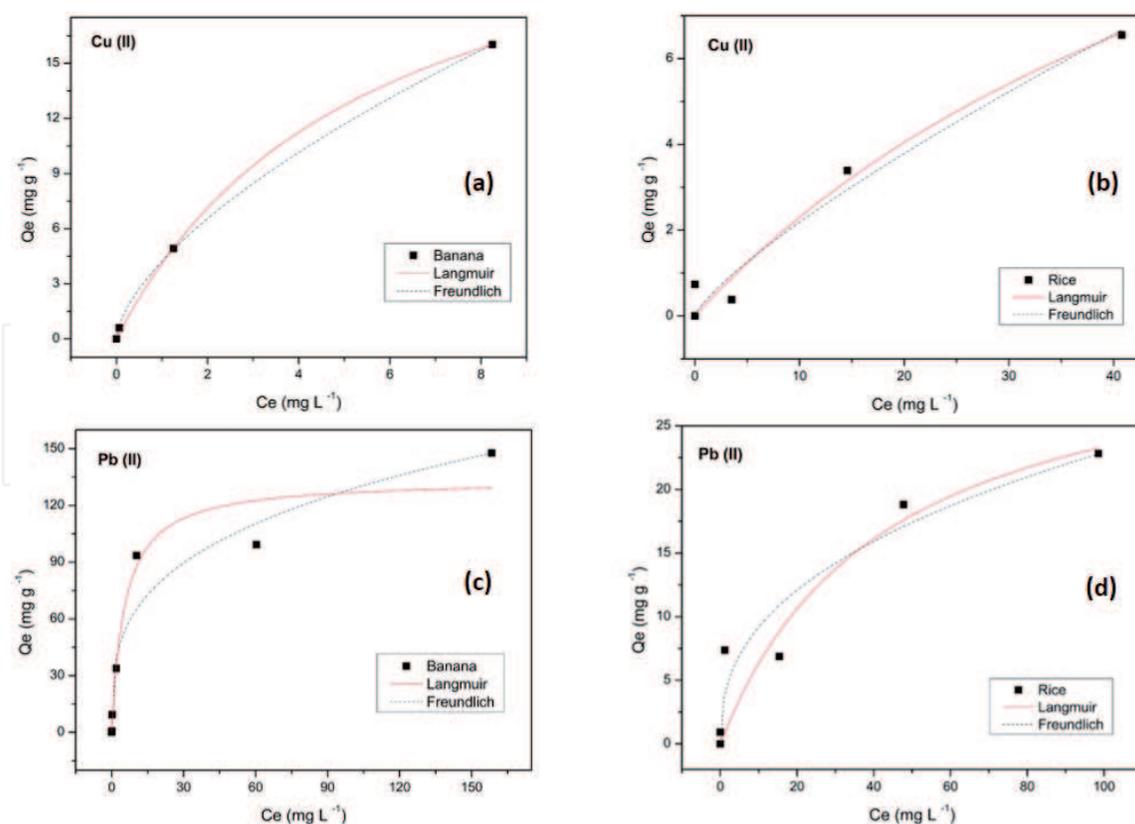


Figure 4.

Adsorption isotherm of Cu (II) (a) by banana, (b) by rice and of Pb (II) (c) by banana, (d) by rice. Adsorbent dose: 10 mg; shaking speed: 200 rpm; pH 7 ± 0.3 ; temperature: $25 \pm 0.3^\circ\text{C}$.

surface, that is to say, with active sites with identical energy and availability and without interaction between the adsorbed molecules [24].

The Freundlich isotherm differs from the Langmuir isotherm model, which describes multilayer adsorption on heterogeneous surfaces [25]. In the Freundlich model, when the $1/n$ exponent value for this model equals 1, the adsorption is considered linear, with identical adsorption energies at all sites. The higher the value of $1/n$, the stronger the interaction between adsorbent and adsorbate [26].

Table 1 shows the values of the parameters obtained by nonlinear regression of the Cu (II) adsorption by the banana and rice biomass applied to the Langmuir and Freundlich isotherm. For banana biomass, the Langmuir and Freundlich isotherms presented very close adaptations when comparing the values of the correlation coefficient (R^2): 0.99 (Langmuir) and 0.99 (Freundlich). In addition, the R_L value is between 0 and 1, indicating that the Langmuir model is favorable, but Freundlich is also an accepted model for this adsorption since the value of $1/n$ is less than 1. For rice biomass, the Langmuir model was more favorable, with $R^2 = 0.96$ and $R_L = 0.99$.

3.2.1.2 Lead

The **Figure 4(c)** and **(d)** illustrates the experimental data obtained in the adsorption of Pb (II) by banana and rice biomasses applied to the Langmuir and Freundlich models. For both banana and rice biomass, there was an increase in the adsorption capacity, indicating the occupation of the free sites in the material.

The adsorption of Pb (II) by banana biomass was favorable to the Langmuir isotherm model with $R^2 = 0.95$ and $R_L = 0.92$. For rice biomass the Freundlich model presented $R^2 = 0.91$, but another parameter, $1/n$, indicates that this model is not adequate because it has a value higher than 1. With this, the Langmuir model is the most favorable model.

Isotherm	Parameters	Biomass	
		Banana	Rice
Cu (II)			
Langmuir	Q_m (mg g ⁻¹)	26.68	16.80
	K_L (L mg ⁻¹)	0.18	0.02
	R^2	0.99	0.96
	R_L	0.92	0.99
Freundlich	K_F (L g ⁻¹)	4.23	0.35
	1/n	0.63	0.79
	R^2	0.99	0.95
Pb (II)			
Langmuir	Q_m (mg g ⁻¹)	133.71	33.33
	K_L (L mg ⁻¹)	0.18	0.02
	R^2	0.95	0.86
	R_L	0.92	0.99
Freundlich	K_F (L g ⁻¹)	32.21	3.67
	1/n	0.30	2.52
	R^2	0.93	0.91

Table 1.

Parameters obtained by nonlinear regression adjustment of Langmuir, Freundlich, for Cu (II) and Pb (II) isotherms by adsorption in biomass of banana and rice husk. Q_m : Maximum adsorption capacity, K_L : Langmuir constant, R_L : Balance parameter, K_F : Freundlich constant, 1/n: Adsorption intensity.

3.3 pH test

3.3.1 Copper

The effect of pH on copper (II) adsorption by banana and rice biomass at pH values of 5.0, 7.0 and 9.0 is described in **Figure 5(a)**. The adsorption capacity of the metal by the banana is higher at pH 5.0 (34.16 mg g⁻¹) than pH 7.0 (33.80 mg g⁻¹) and 9.0 (31.02 mg g⁻¹). In agreement, the rice presents similar behavior where the capacity of adsorption undergoes a slight decrease with the increase of the pH, pH 5.0 (34.37 mg g⁻¹), pH 7.0 (33.70 mg g⁻¹) and pH 9.0 (30.81 mg g⁻¹). As in the literature [27], the rate of Cu (II) removal has little effect on pH.

3.3.2 Lead

Figure 5(b) shows the effect of pH on the adsorption of Pb (II) by banana and rice biomasses. Banana biomass presented a removal rate of 91.21% (36.46 mg g⁻¹) at pH 5, 93.88% (37.53 mg g⁻¹) at pH 7.0 and 94.46% (37.76 mg g⁻¹) to pH 9.0. As for banana, the adsorption capacity for rice did not have a significant effect, since at pH 5.0 it removed 93.61% (37.42 mg g⁻¹) from Pb (II) 94.85% (37.91 mg g⁻¹) and 95.68% (38.25 mg g⁻¹) to pH 7.0 and 9.0, respectively.

The behavior shown where the adsorption capacity has a small increase together with the pH value is justified by the PZC values of banana biomass (6.6 - 7.0) and rice (6.6 - 7.3) and a study [28] where it states that the negative surface charge leads to deprotonation of functional groups of the biomass as H⁺ (aq) and H₃O⁺ (aq) are

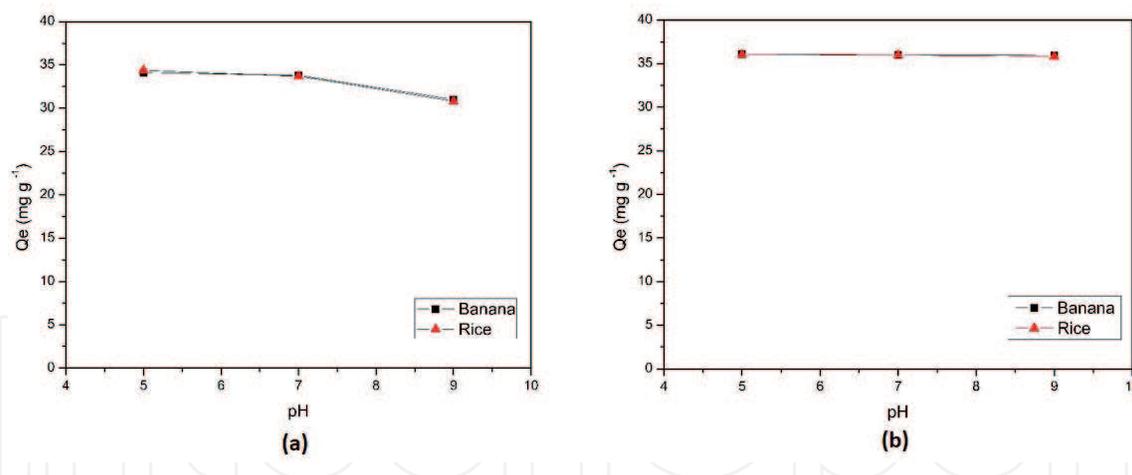


Figure 5. Effect of pH on (a) Cu (II) and (b) Pb (II) adsorption by banana and rice biomass. Initial $[Cu^{2+}]$ and $[Pb^{2+}]$: 20 mg L^{-1} ; adsorbent dose: 20 mg ; shaking speed: 200 rpm ; temperature: $25 \pm 0.3^\circ\text{C}$.

released from them. Thus, these deprotonated functional groups serving as binding sites become readily accessible to metal ions causing better sorption.

3.4 Kinetic test

3.4.1 Copper

The results obtained from the kinetic copper adsorption test for banana and rice biomass are presented in **Figure 6(a)** and **(b)**. At pH 7.0, the results indicate a rapid removal in the first 30 minutes of contact, with approximately 53.16% for banana and 69.66% for rice. The maximum removal rate was reached at 120 minutes for banana, with 64.73% and 360 minutes for rice, with 91.72%.

The kinetic adsorption data were fitted with a pseudo first order model [12] and pseudo second order model [13].

The kinetic pseudo-first order model does not adjust to copper adsorption by banana and rice biomasses. While the pseudo-second order model based on the adsorption capacity of the solid phase shows the processes of adsorption studies in all time bands.

The kinetic data presented linearity (**Figure 6(b)**), with a correlation coefficient of 0.99 for banana and 0.99 for rice. The q_e calculated with values close to experimental q_e . For banana, the values q_e (14.05 mg g^{-1}), K_2 (0.0012 L mg^{-1}) and q_e (29.41 mg g^{-1}), K_2 (0.0026 L mg^{-1}) were obtained from the slope and intersection of the straight line of the graph t/q_t as a function of t , according to **Figure 6(b)**.

3.4.2 Lead

Figure 6(c) and **(d)** shows the results obtained for the kinetic test at the times of 30, 120, 360, 720 and 1440 minutes. At pH 7.0, the data indicate a rapid adsorption of lead by banana biomass in the first 30 minutes of contact, with approximately 83% removal. While the biomass of rice removed about 75.9% in the first 120 minutes.

The kinetic adsorption data were fitted with a pseudo first order model and pseudo second order model. The pseudo-first-order kinetic model does not fit the adsorption of lead by banana or rice biomass. While the pseudo-second order model

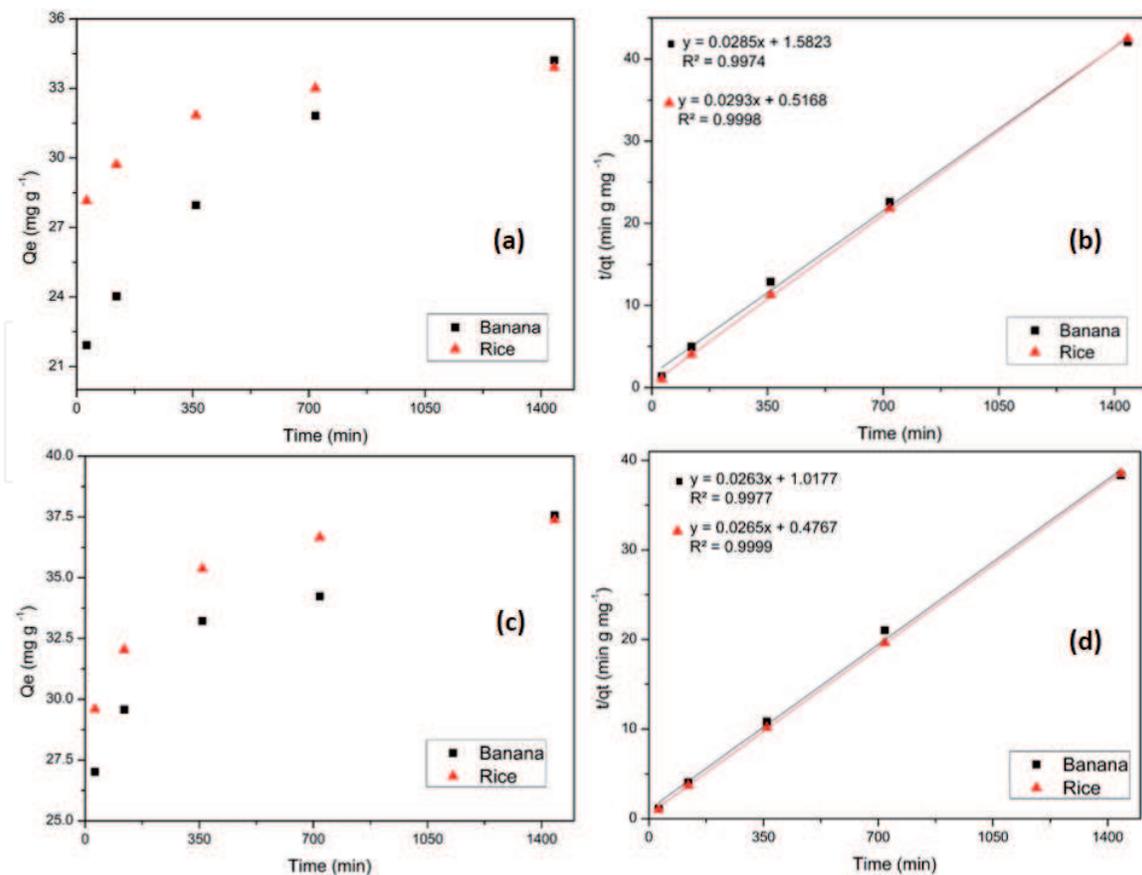


Figure 6. (a) Kinetics of Cu (II) adsorption by banana and rice biomass (b) pseudo-second order kinetic model of Cu (II) adsorption by banana and rice biomass (c) kinetics of Pb (II) adsorption by banana and rice biomass (d) pseudo-second order kinetic model of Pb (II) adsorption by banana and rice biomass. Initial $[\text{Cu}^{2+}]$ and $[\text{Pb}^{2+}]$: 20 mg L^{-1} ; pH: 7.0 ± 0.3 ; shaking speed: 200 rpm ; temperature: $25.0 \pm 0.3^\circ\text{C}$.

based on the adsorption capacity of the solid phase shows the adsorption process in all time bands.

The kinetic data for the adsorption of lead by banana biomass present a high linearity (**Figure 6(d)**), with correlation coefficient close to 1 (0.99) and calculated Q_e (26.60 mg g^{-1}) with values close to experimental Q_e (26.96 mg g^{-1}). The values of calculated Q_e and K_2 (0.0014 L mg^{-1}) were obtained from the slope and intersection of the straight line of the graph t/qt as a function of t .

For the rice biomass, the correlation coefficient is also close to 1 (0.99), the calculated Q_e (23.81 mg g^{-1}) presented a value close to the experimental Q_e (23.92 mg g^{-1}) at the end the K_2 , through the 0.0006 L mg^{-1} slope of the line.

The adsorption capacities of copper and lead in banana and rice biomass are compared with the studies on the types of materials of organic origin (**Table 2**). In addition to the efficiency of the removal, it is easy to obtain and handle the adsorption capacity. Considering this, it is noticed that the studied materials present great efficiency in the removal of metals from contaminated water. Worked biomasses are cheap and easy to prepare because they are reused materials from common productive activities in various regions, making this technology accessible to various social levels.

Comparing the biomaterials of this study with the values found in the literature (**Table 2**), the biomasses of banana peel and rice present better adsorption capacities, thus confirming the great potential of applying the material with real water samples.

Adsorbent	Adsorption Capacity (mg.g^{-1})	pH	Reference
Cu (II)			
<i>Aspergillus niger</i> -treated rice straw	23.80	4.0 – 6.0	[29]
Pine sawdust	9.59	7.0	[30]
Treated laterite	7.25	5.0	[31]
Hazelnut husk	6.64	5.7	[32]
Irish peat moss	17.60	4.5	[33]
Banana peel	26.68	7.0	Present study
Rice husk	16.80	7.0	Present study
Pb (II)			
Organo-mineral complex	1.59	7.0	[34]
Cucumber peel	133.60	5.0	[28]
Palm biomass	98.90	5.5	[35]
F. andina fibers	31.50	7.0	[36]
Biofilm on F. andina	35.90	7.0	[36]
Banana peel	133.71	7.0	Present study
Rice husk	33.33	7.0	Present study

Table 2.
Comparison between the adsorption capacities of different materials in copper and lead removal.

3.5 Application of the materials in real samples from environmental mariana disaster region

The **Figure 7** shows the concentration of metals (a) Cu (II) and (b) Pb (II) before and after adsorption by using banana and rice biomasses at two points collected in the city of Governador Valadares - MG in the years of 2016, 2017 and 2018. For copper, the concentration at point 2 is higher when compared to point 1 in the

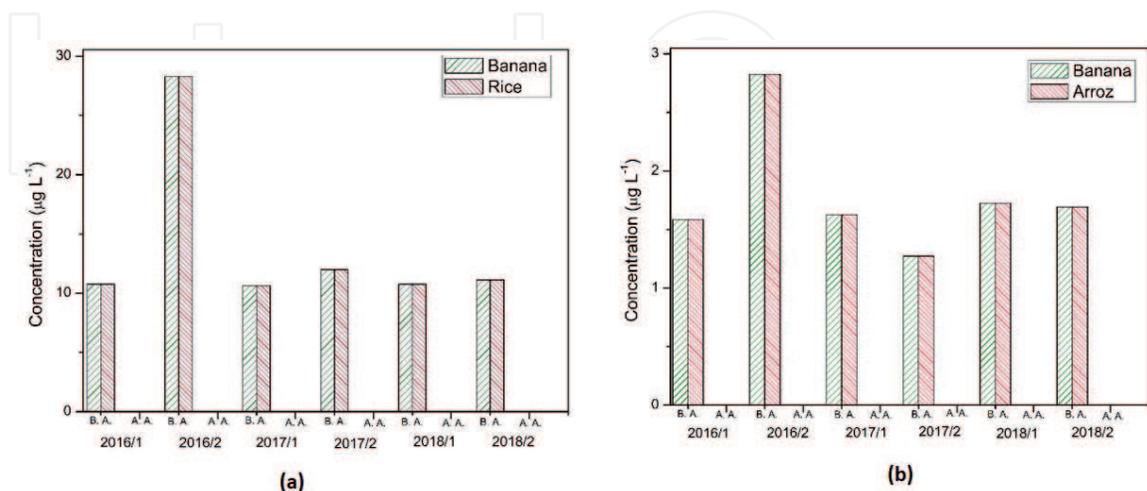


Figure 7.
(a) Adsorption of Cu (II) onto banana and rice biomass in samples collected from two points of a river in the region of Governador Valadares, state of Minas Gerais, Brazil, (b) adsorption of Pb (II) onto banana and rice biomass in samples collected from two points of a river in the region of Governador Valadares, state of Minas Gerais, Brazil, (B.A- before adsorption; a.A- after adsorption; 2016/1- sample collected in 2016 at point 1; 2016/2- sample collected in 2016 at point 2; 2017/1- sample collected in 2017 at point 1; 2017/2- sample collected in 2017 at point 2; 2018/1- sample collected in 2018 at point 1; 2018/2- sample collected in 2018 at point 2).

same year, 2016: p1 ($10.75 \mu\text{g.L}^{-1}$) and p2 ($28.29 \mu\text{g.L}^{-1}$), 2017: p1 ($10.63 \mu\text{g.L}^{-1}$) and p2 ($11.98 \mu\text{g.L}^{-1}$), 2018: p1 ($10.75 \mu\text{g.L}^{-1}$) and p2 ($11.13 \mu\text{g.L}^{-1}$). For lead, with the exception of the year 2016, p1 ($1.58 \mu\text{g.L}^{-1}$) and p2 ($2.82 \mu\text{g.L}^{-1}$), the same trial was observed, 2017: p1 ($1.62 \mu\text{g.L}^{-1}$) and p2 ($1.27 \mu\text{g.L}^{-1}$), 2018: p1 ($1.72 \mu\text{g.L}^{-1}$) and p2 ($1.6911 \mu\text{g.L}^{-1}$).

Point 2, in all years, presented higher concentrations when compared to point 1, for both Cu (II) ($28.29 \mu\text{g.L}^{-1}$) and Pb (II) ($2.82 \mu\text{g.L}^{-1}$). According to the US EPA, the maximum limits for copper and lead are $1300.00 \mu\text{g L}^{-1}$ and $15.00 \mu\text{g.L}^{-1}$, respectively. In spite of this, the concentrations of the studied metals reached very close to zero after the treatment with banana and rice biomasses.

Seen this, the studied material shown efficiency in removal of copper and lead in contaminated water even in real samples with several parameters outside the ideal that cannot be controlled and altered. With this, these biomaterials have application in real situations of contamination by metals with high removal rate and low cost [37].

4. Conclusion

Finally, it can be concluded that the studies presented achieved results beyond expectations, with high adsorption capacity. Isotherm studies demonstrate that the Langmuir model is the most applicable in all analyzed cases. Studies of the effect of pH indicated that the adsorption analyzed in the present work did not undergo significant changes with the variation of pH values. Where, for both banana and rice, the best Cu (II) adsorption capacity, 34.11 mg.g^{-1} and 34.37 mg.g^{-1} , respectively, was at pH 5. For Pb (II), the highest adsorption capacity was also at pH 5 with 36.06 mg.g^{-1} for bananas and 36.04 mg.g^{-1} for rice. In the kinetics studies, there was a fast adsorption, in all cases, in the first 30 minutes of adsorption more than 60% of the metals had already been adsorbed. For tests on real samples, the biomasses showed excellent performance in removing Cu (II) and Pb (II), reaching concentrations close to zero after adsorption, indicating efficiency in environmental remediation. In view of this, the biomasses studied can be used to purify water contaminated by mining or other sources. For future studies, the application of biomass in the form of filters will be analyzed.

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