

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Use of Co-Products from the Processing of Cassava for the Development of Adsorbent Materials Aiming Metal Removal

Daniel Schwantes, Affonso Celso Gonçalves,
Marcelo Angelo Campagnolo,
César Ricardo Teixeira Tarley,
Douglas Cardoso Dragunski, Jéssica Manfrin and
Andréia Da Paz Schiller

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.71048>

Abstract

Nowadays the contamination of water resources by the most varied pollutants have been accelerated. Technologies of decontamination of water are too costly, however, the development of low cost adsorbents, have proven to be efficient, promising and cheap alternatives for this purpose. The use of adsorbents from cassava residues has shown great potential for use as an adsorbent. The productive chain of this crop involves the production and processing of its roots, generating a large volume of solid waste. Aiming the sustainability of production systems, productive chains should optimize the production of cassava barks residues, since these do not present significant uses or benefit. In this scenario, this chapter gathers information from the literature on the use of solid waste from the cassava agroindustry and its use as adsorbents, aiming the removal of toxic metals, as well as their potential for the treatment of other contaminants. Several authors have demonstrated through studies the potentiality of the use of agroindustrial cassava residues as adsorbents. Because of a range of characteristics observed these adsorbents present viability for large-scale use, being in very similar to activated carbon. Thus, the use of these adsorbent materials represents an extremely viable and sustainable alternative.

Keywords: cassava adsorbents, cassava wastes, cassava bark, cassava bagasse, adsorption of metals, biosorbents

1. Introduction

Cassava, *Manihot esculenta* Crantz, is a perennial and shrubby plant, native to the South American continent, probably from Brazil, since the Indians already cultivated cassava, when the country was discovered.

It is a plant well adapted to variations in temperature and rainfall, being found in areas of different edaphoclimatic conditions and between latitude of 30°N and 30°S. It is growing in regions from sea level up to 2300 m of the altitude and in areas considered marginal to other crops: soils with low fertility and annual rainfall less than 600 mm in the semi-arid or above 1500 mm in the humid and sub-humid tropics [1].

The residues produced by the industrialization of cassava roots do not have many destinations; the main purpose is being animal feed [1], which is an agroindustrial problem to be faced by the cassava production segment.

Another global problem that has been aggravating in the last decades concerns the organic and inorganic pollution of the waters, being the adsorption process is one of the most promising alternatives for the removal of these contaminants. In this context, commercial activated carbon is one of the most widely used adsorbents for a large variety of pollutants in water, but its high cost is one of its main disadvantages.

In this context, the adsorption of metallic pollutants is more promising when using natural adsorbents such as agroindustrial waste. These are a promising alternative for chemical remediation because of their high adsorption capacity, low cost, and high availability.

Several authors have been researching alternative biosorbents for the removal of metal ions from contaminated solutions, such as banana and orange barks [2], cocoa barks [3], dry mass of *Eichhornia crassipes* [4], mussel shells [5], and bagasse of natural and modified sugar cane [6]. However, few studies report the adsorptive capacity of the solid fraction of residues from the industrialization of cassava roots in the context of their use as natural or modified adsorbents in contaminated water.

It is important to emphasize some advantages of the use of plants residues to the treatment of wastewater. They are operational facility, low processing, good adsorption capacity, selective adsorption of metal ions, low cost, high availability, and easy regeneration [7].

The subsequent items will describe some of the characteristics of the cassava crop, its agroindustrial residues, as well as reports on the hydrological contamination by toxic metals, and some results from studies describe the use of natural and modified adsorbents obtained from cassava agroindustrial residues as a viable possibility.

2. Production chain of cassava

Brazilian annual production of cassava has remained at 23 million tons [8], while the harvested area has declined, giving way to the cultivation of other more profitable crops.

The consumption of natural cassava tends to lose space, as it moves away from the producer poles, because it is a perishable merchandise and it requires immediate consumption after harvest. **Table 1** shows the data of the quantity produced in tons of cassava in recent years.

Cassava processing in Brazil is concentrated in flour. It is estimated that 80% of the roots are intended for this purpose. About 3% can be counted as being destined for the extraction of starch and its modifications, with the rest probably destined for animal feed [1].

The processing of cassava roots generates solid residues called bark (bark + weaves), being the main destinations are animal feed and its use as biofertilizers. It is estimated, on average, that about 11 million cassava barks are produced annually only in Brazilian territory, and normally, the barks are disposed together with the bran/bagasse, which are supplied for animal feed or disposed to the soil for decomposition and incorporation of organic matter [9]. It should be noted that a greater amount of waste compose the cassava bagasse or bran, that represents the final residue of cassava starch extraction, and its main destination is animal feed.

| Region | 2013 | 2014 | 2015 | 2016 |
|-----------|------------|------------|------------|------------|
| North | 7,467,943 | 8,037,507 | 7,971,127 | 8,620,328 |
| Northeast | 4,803,212 | 5,668,126 | 5,311,813 | 5,787,657 |
| Southeast | 2,491,229 | 2,524,993 | 2,477,465 | 2,279,168 |
| South | 5,477,417 | 5,583,682 | 5,489,019 | 5,163,158 |
| Midwest | 1,244,417 | 1,427,756 | 1,507,383 | 1,207,362 |
| Brazil | 23,242,064 | 23,242,065 | 22,756,807 | 23,057,673 |

Source: SEAB [8].

Table 1. Brazilian production of cassava in metric tons from 2013 to 2016 by regions of Brazil.

3. Water contamination by metals

Only 0.8% of the water available on the planet can be easily used for public supply. Of this small fraction, only 3% is in the form of surface water, while the other 97% corresponds to groundwater. As important as the amount of available water is the water quality, because the quality of water around the planet has deteriorated more and more, especially in the last 50 years, mainly in the regions where industrial centers and high population density exist.

In fact, one of the major problems faced in the last decades is the water pollution, coming, in large part, to the inadequate management of pesticides, low quality of the water used in irrigation, and the indiscriminate disposition of industrial or domestic waste. This contamination can cause the

accumulation of substances that can be toxic to plants and, when entering the food chain, may become dangerous to animals and humans.

The industry contaminates water by eviction of disinfectants, detergents, solvents, toxic metal ions, radioactive waste, petroleum products, agrochemicals, and other compounds in rivers and lakes. Among the metals, some are strongly polluting and have several harmful effects on ecosystems, causing physical and chemical changes in water and a decrease in their quality and the mortality of flora and fauna, and consequently, human health.

The expression heavy metal applies to elements having a specific mass greater than 5 g cm^{-3} or having an atomic number greater than 20. Some metals are used in the biological metabolism, and in this way, they can be considered essential, as is the case of Cu^{2+} , Zn^{2+} , Ni^{2+} , and Cr^{3+} , and at higher levels, they can become toxic. On the other hand, Pb^{2+} and Cd^{2+} are considered toxic even at low concentrations [4].

For the treatment of contaminated water, there are several types of treatments considered conventional (physical, chemical, and biological), among which centrifugation, distillation, filtration, flocculation, sedimentation, ultrafiltration, electrodialysis, reverse osmosis, air entrainment, liquid-liquid extraction, catalysis, hydrolysis, neutralization, oxidation, reduction, precipitation, photolysis, ozonolysis, activated sludge, aerated lagoons, enzymatic treatments, and anaerobic digestion, among others can be mentioned. All these have advantages and disadvantages; however, it can be mentioned that the great majority is not always effective in the removal of small levels of metals without elevation of the costs.

In this scenario, the search for alternative adsorbents, which presents high availability and low cost of acquisition, can help and reduce the treatment of water and effluents with toxic metals. In the sequence, results from research that support this hypothesis will be presented.

4. Results from researches

4.1. Case of study: remediation of waters using solid wastes from the processing of cassava roots as biosorbents

The search for alternatives to conventional methods that have low cost and high efficiency pushed, in recent years, the research on the use of different biosorbents. Among the biosorbents that have been studied by several authors, cassava agroindustrial residues are also viable alternatives to their use as adsorbents. As presented by some authors, such as the studies, Schwantes et al. [9] applied the following solid residues of cassava: bark, bagasse, and the mixture of both, obtaining promising results for the use of these materials as natural adsorbents of Cu^{2+} and Zn^{2+} . Schwantes et al. [10] applied the biosorbents from bark, bagasse, and the mixture of both in the removal of Cr^{3+} from contaminated water. Or also, Schwantes et al. [11]

applied modified cassava barks with solutions 0.1 mol.L^{-1} of H_2O_2 , H_2SO_4 , and NaOH in the removal of Cd^{2+} , Pb^{2+} , and Cr^{3+} . Schwantes et al. [12] and Schwantes et al. [13] used cassava biomass in Pb^{2+} and glyphosate removal, among others.

As already commented in this chapter, the adsorption of metallic ions is extremely viable when using natural adsorbents such as, for example, industrial and agricultural waste. These adsorbents are a promising alternative for chemical remediation due to their great adsorption capacity, low cost, and high availability. In nature, there are a large number of biosorbents, which in their natural state and properly applied provide values of adsorption capacity similar or sometimes better than those presented by chemically modified materials.

In this way, it is known that the industrial processing of cassava generates significant quantities of waste that may cause serious environmental problems, and the correct treatment is rarely given to these residues. Some results of the literature will be demonstrated in the following items, which demonstrate the benefits of using cassava residues as adsorbents and their efficiency in the removal of pollutants from water.

4.1.1. Characterization of cassava residues and their possible use as adsorbents

It is usually observed that adsorbents with high capacity to remove pollutants from the environment have superficial structures varying from fibrous to spongy, with irregular structures and a large number of cavities on their surface.

Moreover, a good adsorbent is one that has a large number of active sites available for interaction with the species of interest. The sites are adsorption points constituted for one or more chemical functional groups distributed on the surface of the biosorbent. Clusters such as carboxyl, phenols, nitrogen groups, alkanes, and others may generate active sites that are favorable to adsorption of metallic species in addition to other pollutants.

Another outstanding characteristic in good adsorbents refers to textured parameters, such as high volume and varied pore diameters, aiming for adsorption of compounds with different ranges of hydration rays and perhaps the most outstanding characteristic and high-specific surface area.

According to the published studies [9–13], residues of the cassava crop have potential in the use of adsorption processes in function of physical, chemical, and morphological characteristics.

When studying the morphology of the barks and bagasse of cassava, as well as the mixture of both, Schwantes et al. [9] and Schwantes et al. [10] observed that the surfaces of the biosorbents are endowed with fibrous and spongy aspect, with irregular and heterogeneous structure. Many of these cavities can be evidenced, demonstrating that the material presents characteristics that suggest favorable conditions for adsorption (**Figure 1**).

The infrared (IV) characterization contributes to the understanding of the dynamics or the adsorption mechanism, since it provides information about the functional groups present



Figure 1. SEM of the adsorbents originating of cassava residues: barks (3000×) bagasse (3000×), and mixture of both fractions (5000×). Source: Refs. [9, 10].

in the structure of the adsorbents [7]. The biosorption is the result of electrostatic interaction and formation of complexes between ions (pollutants) and functional groups of biomass [6].

In the case of cassava agroindustrial residues, barks, bagasse, and their mixture, all in their natural form, Schwantes et al. [9] when applied them in the removal of Cu^{2+} and Zn^{2+} and Schwantes et al. [13] when used in the removal of glyphosate from water found the following characteristic bands for the infrared spectra: 3440, 2920, 1730, 1650, 1420, and 1030 cm^{-1} , according to **Figure 2**.

According to **Figure 2**, the presence of a big and strong band at 3440–3330 cm^{-1} is observed, which can be attributed to the vibrational elongation of the O-H bond, possibly characterized by the vibrational stretching of the hydroxyl groups present in carbohydrates, fatty acids, proteins, lignin units, cellulose, and absorbed water [14], while the band at 2920 cm^{-1} can be attributed to a vibrational elongation of the C-H bond in alkanes.

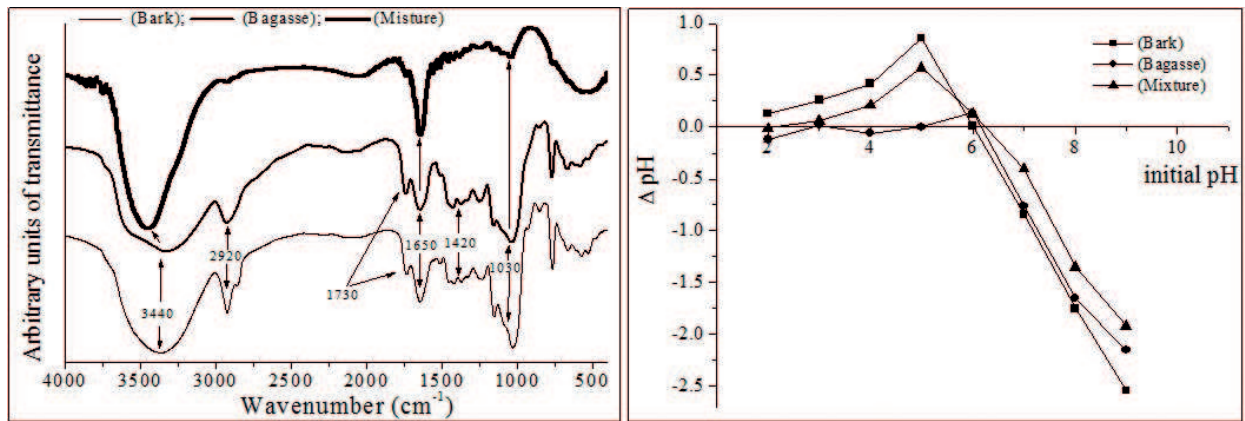


Figure 2. In the left: FT-IR to bark, bagasse, and mixture; in the right: pH_{pzc} in KCl 0.5 mol.L^{-1} to the adsorbents bark, bagasse, and mixture of both. Source: Refs. [9, 10, 13].

The bands in 1730 cm^{-1} are indicative of the presence of the starch, or the aldehyde and ketone functions present in lignin and holocellulose. Bands at $1420\text{--}1650\text{ cm}^{-1}$ can be attributed to the vibrational stretching of the C-O link of amides and carboxylic groups. Peaks at 1030 cm^{-1} can be attributed to the C-O stretch [14].

The adsorption of metals by residues of plants, natural materials, and agroindustrial residues can be attributed to the presence of some functional groups such as lignin, alcohols, carboxylic groups, proteins, and carbohydrates [15].

pH_{PZC} or point of zero charge, is defined as the pH at which the surface of the solid has a neutral charge [16]. When the $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of the adsorbent is electronegative, favoring the adsorption of cations; in case, if the $\text{pH} < \text{pH}_{\text{PZC}}$, the surface of the adsorbent is electropositive, and in this state, H^+ ions compete with the metallic cations, repelling them of the surface decreasing the adsorption. The characterization of the adsorbent in relation to its point of zero charge is very important, since it will be possible to predict the behavior of surface charges that vary with the pH of the medium and that, in one way or another, may influence the adsorption process of pollutants, favoring their removal from the environment.

According to authors Schwantes et al. [9], Schwantes et al. [10], and Schwantes et al. [13], the adsorbents originating of the cassava residues, bark, bagasse, and mixture of both, indicate that the pH corresponding to the equivalence point between positive and negative charges for the adsorbent bark is 6.00, for the bagasse material is 6.17, and for the mixture of both is 6.24 (**Figure 2**).

In this way, according to the cited authors, the adsorption of cations such as Cd^{2+} , Pb^{2+} , Cr^{3+} , Cu^{2+} , Zn^{2+} , and others should be favored by pH values higher than the values found for pH_{PZC} (6.00, 6.17, and 6.24 for bark, bagasse, and mixture, respectively).

It is important to remember that what is usually called the “cassava bark” in industry is the result of the cleaning of the roots in the moment of their reception in industry; in this time, the cassava barks are removed, as well as part what is denominated weaves. Both these residues constitute the first agroindustrial co-product. The average composition of the bark and bark + weaves (mixture), which configure the first agroindustrial residues related have the following composition (**Table 2**).

It is important to emphasize that the chemical composition of the adsorbent materials provides a basis for the verification of which chemical elements may possibly return the solution during the exposure of the adsorbent to the medium, since there is always the possibility of the occurrence of the inverse process called desorption.

Another very important aspect relative to the chemical composition of the materials is about the presence or absence of the component to be removed in the structure of the adsorbent. For example, a natural adsorbent whose composition is rich in Zn is possibly not efficient for the removal of this metal from solution and can increase the Zn concentration in the solution because of the diffusion of this from adsorbent to the medium.

| Parameters | Bark | Mixture | Parameters | Bark | Mixture |
|-----------------------|--------------------------------|---------|------------|--------------------------------|---------|
| | g.100 g ⁻¹ dry mass | | | mg.100g ⁻¹ dry mass | |
| Volatile solids | | 26.23 | Total CN | 0 | 23.9 |
| Ashes | 4 | 1.45 | Free CN | 60 | 120 |
| Soluble carbohydrates | | 7.86 | Phosphor | 110 | 60 |
| Starch | 0 | 32 | Sulfur | 18 | 320 |
| Lipids | 3 | 0.63 | Boron | | 18 |
| Nitrogen | 0.64 | 2.1 | | | |
| Fiber | 41 | | | | |
| Lignin | | 6.46 | | | |

Source: Alves [1].

Table 2. Mean values of several determinations carried out on cassava residues.

When evaluating the natural adsorbents from the residues of cassava roots, Schwantes et al. [9] and Schwantes et al. [10] found higher concentrations for K, Ca, Mg, Cu, Fe, Mn, and Zn in the cassava barks, when compared to bagasse and the mixture of both. This result is possibly because of the fact that the bagasse is the result of an industrial chemical and physical processing, where there is isolation and extraction of the starch, resulting in the removal of part of these chemical elements.

The authors also emphasize the presence of small concentrations of Pb in the adsorbent materials evaluated (**Table 3**), which according to the researchers may be an indication of the presence of this toxic metal in the soil, which was absorbed by the roots of cassava during growth and development of culture in the countryside.

It should be noted that soil contamination by toxic metals, such as Pb, could have different origin, for example, from inadequate disposal of Pb batteries, contaminated effluents, and disposal of contaminated waste in soil, atmospheric pollution originated of the burning fossil fuels containing Pb, pollution and atmospheric deposition from industries that work with Pb, and the use of fertilizers and agricultural inputs [17].

4.1.2. Experimental results involving natural adsorbents of cassava and remediation of toxic heavy METAS in waters

According to researchers in the literature that relate the use of adsorbent materials based on residual biomass of cassava and removal of metals from water, cassava biosorbents are efficient in the removal of metals such as Cd²⁺ [18], Pb²⁺ [12], Cr³⁺ [10], Cu²⁺, and Zn²⁺ [9]. The literature mention results where the influence of the pH of the medium is evaluated, the proportion between adsorbent and the volume of the adsorbate, adsorption kinetics,

| Adsorbent | K | Ca | Mg | Cu | Fe | Mn | Zn | Cd | Pb | Cr |
|-----------|--------------------|-------|---------------------|-------|-------|--------|-------|--------|-------|-------|
| | g.kg ⁻¹ | | mg.kg ⁻¹ | | | | | | | |
| Bark | 24.10 | 35.03 | 6.83 | 14.33 | 35.67 | 123.33 | 32.00 | <0.005 | 11.00 | <0.01 |
| Bagasse | 5.77 | 23.23 | 4.58 | 5.67 | 24.50 | 27.67 | 18.67 | <0.005 | 14.67 | <0.01 |
| Mixture | 7.77 | 22.58 | 5.12 | 6.00 | 26.00 | 34.00 | 17.00 | <0.005 | 3.33 | <0.01 |

ND: not detected by EAA/flame method; LQ (quantification limits): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01. Source: Refs. [9, 10].

Table 3. Chemical characteristics of adsorbent materials.

equilibrium studies, as well as the potential reuse of these materials in other sorption processes. Some of these results will be described further in the next items in this chapter.

4.1.2.1. Influence of the pH of the contaminant solution and the proportion between cassava biosorbents and adsorbate

The pH is one of the most important parameters in the adsorption process, because its interference occurs in the solid-solution interface, influencing the loads of the active sites of the biomass and in the behavior of the adsorbates. The pH controls the surface properties of the adsorbents, functional groups, and ionic state of the metallic species, affecting a lot the adsorption of metallic ions [15]. This occurs because in acidic pH, the H⁺ ions strongly compete between them and with the metals in solution by the active sites in the adsorbent. At basic pH, the connection sites may not be activated as a function of pH, or precipitation of these metals can occur, and it does not occur as contact between adsorbent/adsorbate.

According to Mimura et al. [16], the adsorption of metallic species in the positive form will be favored at the pH in which negative species predominate on the adsorbent surface. As verified in **Figure 3**, proportions between adsorbent/adsorbate higher than 4 g.L⁻¹ do not result in high removal of ions. Also can be observed that there is a little variation of the % removal in the studied pH range; however, it should be considered that metals such as Cd and Pb present an easy precipitation in pH ranges close to neutrality, making the adsorption process impracticable under these chemical conditions.

The authors of **Figure 3** mention that these tests were executed in low concentrations (10 mg.L⁻¹), being, therefore, the adsorbent materials bark, bagasse, and mixture capable of almost completely removing the contents of Cd²⁺ and Pb²⁺ from contaminated solutions. It can be observed that in the studied pH range, the removal reached values higher than 90% in all materials, especially the adsorbent consisting of “bark + bagasse,” which almost completely removed the metals contained in the contaminant solution. According to the authors of this study, 4 g of adsorbent per liter of solution contaminated with Cd²⁺ or Pb²⁺ is the ideal ratio between adsorbent and adsorbate.

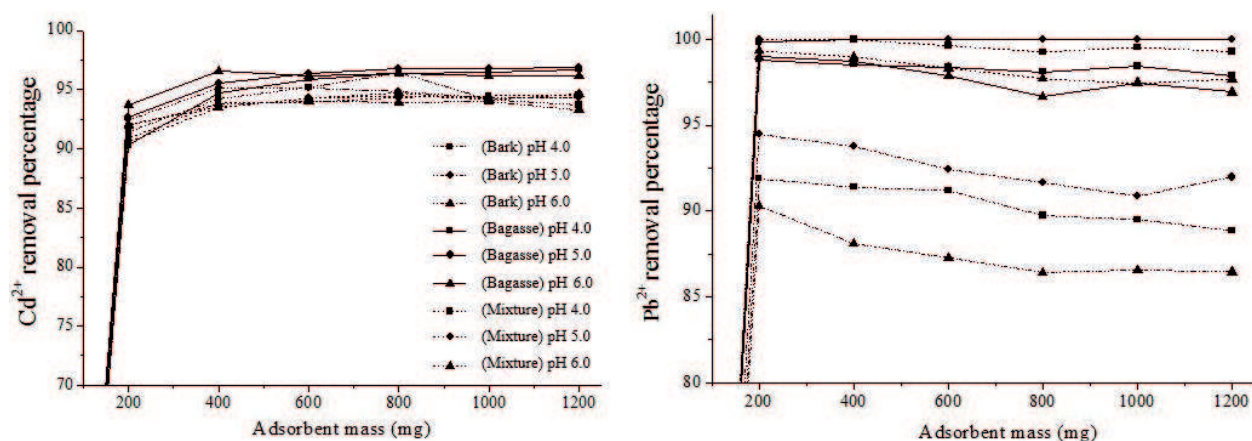


Figure 3. Adsorbent mass and pH of solution on the % of removal of Cd^{2+} [18] and Pb^{2+} [12] for the adsorbents barks, bagasse, and mixture of cassava. The values in the x-axis corresponding to the proportion adsorbent/adsorbate: 200 mg (4 g.L^{-1}), 400 mg (8 g.L^{-1}), 600 mg (1.2 g.L^{-1}), 800 mg (1.6 g.L^{-1}), 1000 mg (2.0 g.L^{-1}), and 1200 mg (2.4 g.L^{-1}).

Other authors also verified removal percentages of varied metals similar to those found for cassava adsorbents, and the pH range studied, because it was slightly acidic, did not cause great influences in the adsorption process, for example, in the case of the adsorbent materials using barks of *Pinus elliottii* [19], rice barks [10], peanut barks [20], among others.

4.1.2.2. Contact time influences between cassava biosorbents and metals

Another relation that must be observed because of its importance is the influence of the contact time between adsorbent and adsorbate also called adsorption kinetics. The kinetics of this process is dependent on the relative velocity between four successive stages: transport within the solution, transport by diffusion, transport through the pores, and adsorption.

In the **Figure 4**, it is possible to observe that, independent of the metal ion, Cd^{2+} or Pb^{2+} , or adsorbent material studied, occurs an increase in the adsorption process with the passage of time, and that in general, after 20 min of agitation, the system enters into dynamic equilibrium, indicating a quick adsorption. It is also possible to observe that the material denominated mixture presents adsorption superior for Cd^{2+} and Pb^{2+} , demonstrating that even in low concentrations, the mixture of the two materials (barks + bagasse) produces superior results than acting in isolation.

By linearizing these results according to the Pseudo-second order [21] and intraparticle diffusion models, as cited by Yang and Al-Duri [22], we have the following results.

According Ho and McKay [21], the pseudo-second-order model presents a good fit for many adsorbent and polluting materials, which are not different for cassava biosorbents studied by Schwantes et al. [12], Schwantes et al. [13], and Schwantes [18]. These authors suggest

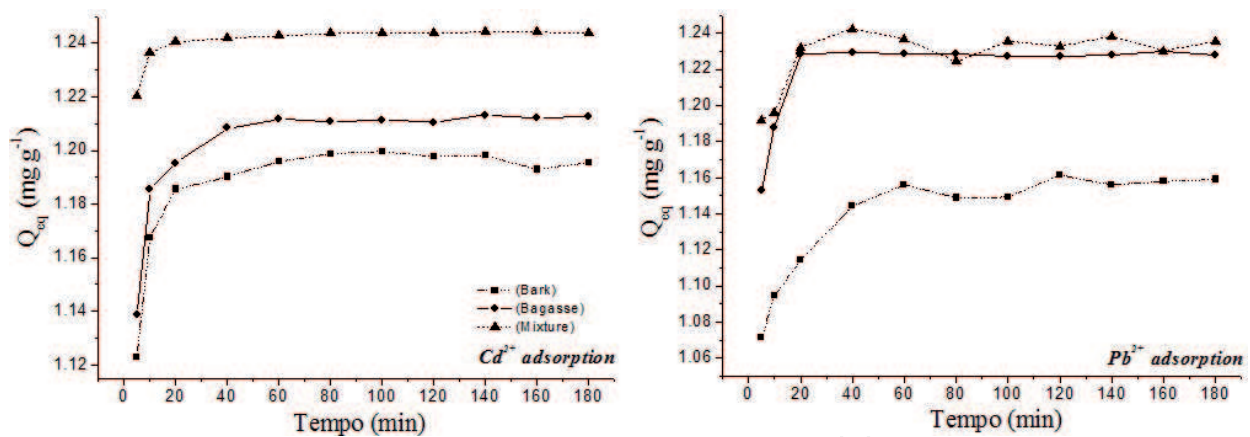


Figure 4. Effect of time on the amount of adsorbed ions (mg.g^{-1}) of the ions Cd^{2+} [18] and Pb^{2+} [12] for the adsorbents bark, bagasse, and mixture.

predominance of chemical adsorption of Pb^{2+} , that is, with the occurrence of chemical bonds between the polluting metal and the adsorbent biomass.

Figure 5 can be observed that the author Schwantes [18] fragmented the contact time between adsorbent and adsorbate and their close relationship with the adsorption capacity of Cd^{2+} in several lines, searching for multilinearity. According Neta et al. [23], when performing the fragmentation for the data, there is the possibility of graphically observing the phenomenon of movement of adsorbate into adsorbent particle.

In the case of adsorbents based on cassava residues, for Cd^{2+} adsorption, we can observe two to three phases in the retention process of this metal, the first phase being represented by the boundary layer effect, with external mass transfer, in that Cd^{2+} ions are rapidly adsorbed by

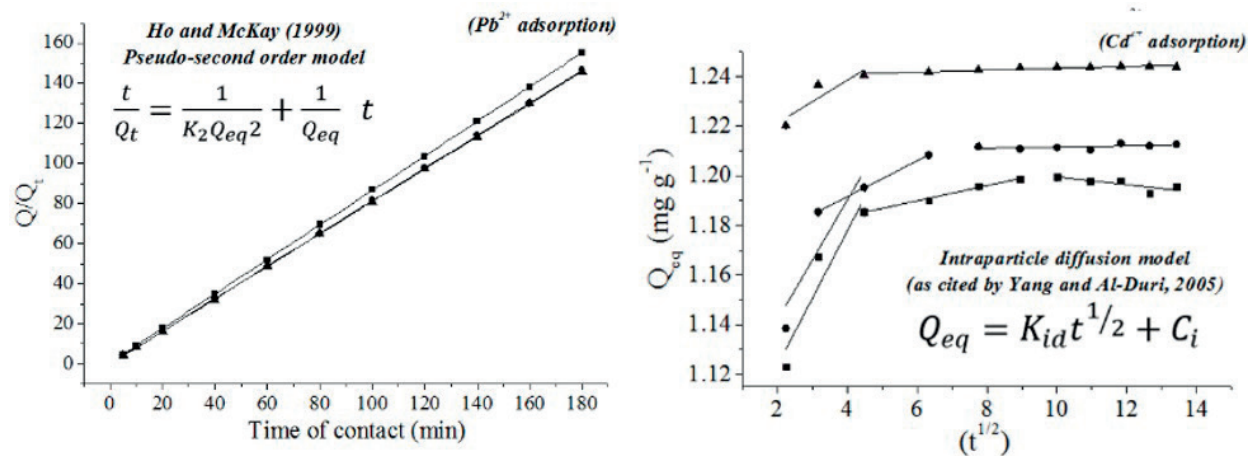


Figure 5. Linearization by the pseudo-second order model for adsorbed amount of Pb^{2+} by natural cassava adsorbents [12] and linearization by intraparticle diffusion model for Cd^{2+} quantity adsorbed [18] by natural adsorbents of cassava solid wastes.

the cassava adsorbents. After a certain time, the adsorption velocity decreases, resulting in the second phase that refers to the diffusion of the molecules to the adsorption sites inside the adsorbent [23]. Finally, in the third and last phase, equilibrium is observed, that is, the intra-particle diffusion begins to decay because of the low concentration of solute in the solution as well as a lower availability of sites for adsorption.

4.1.2.3. Adsorption equilibrium studies in cassava biosorbents

According to published studies [12, 18], the adsorbent materials based on natural cassava, under some specific conditions, may present efficiency close to that of activated carbon (**Figure 6**). It is important to emphasize that commercial activated carbon is the result of physical and chemical modifications, and the production costs of this material are high, while the natural adsorbents present low cost and high availability, since they rarely have a final destination that adds value to the product; in most cases, they are only agroindustry waste.

As presented in **Figure 6**, in relation to the adsorption of Cd^{2+} , it is observed that the adsorption capacity of the biosorbents decreases significantly with the increase in the initial concentration (C_0), whereas the adsorbent activated carbon (AC) also decreases, however, in a smaller proportion.

According to authors Schwantes et al. [12], the adsorbents based in cassava (barks, bagasse, and mixture) showed high values of Q_{eq} for the metal ion Pb^{2+} (**Figure 6**), comparable to the adsorbent activated carbon, which removed Pb^{2+} to below the limit of quantification ($LQ = 0.01 \text{ mg.L}^{-1}$) of the used method (FAAS—Flame atomic absorption spectrometry). The results presented in **Figure 6** also can be graphically studied through the construction of adsorption isotherms, which are presented in the **Figure 7**.

According to Giles [24], the isotherms in the **Figure 7** fit in the “L group” (of Langmuir) and in the subgroup “1,” this subgroup indicates slow saturation of the surface and characteristics of adsorbent materials of high adsorption capacity. Langmuir, Freundlich, and

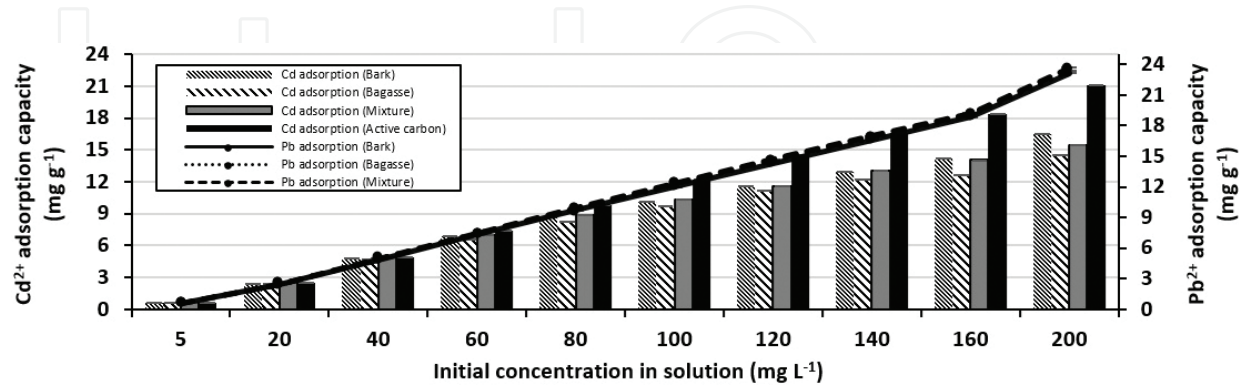


Figure 6. Adsorbed quantity (Q_{eq}) of the ions Cd^{2+} and Pb^{2+} by adsorbents barks, bagasse, mixture, and activated carbon, in increasing initial concentrations (C_0), varying from 5 to 200 mg.L^{-1} , $n = 3$. Limit of quantification (LQ): $\text{Cd} = 0.005 \text{ mg.L}^{-1}$; $\text{Pb} = 0.01 \text{ mg.L}^{-1}$. Source: Refs. [12, 18].

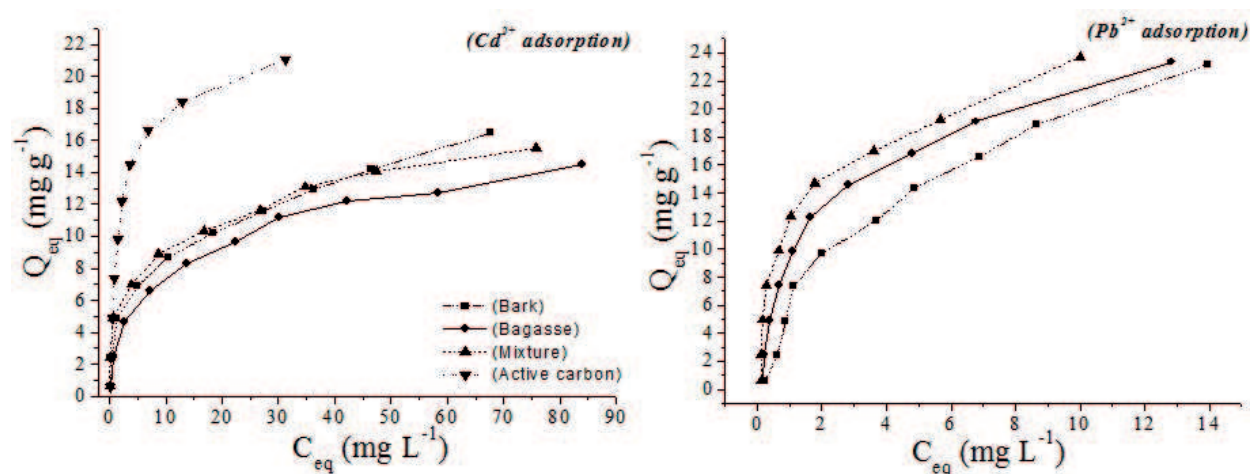


Figure 7. Adsorption isotherms of Cd^{2+} and Pb^{2+} from adsorbents (C_0 : 5–200 $\text{mg}\cdot\text{L}^{-1}$; 400 mg; pH 5.5, 60 min; 200 rpm; 25°C). Source: Refs. [12, 18].

Dubinin-Radushkevich (D-R) models linearized the results presented in the isotherms in **Figure 7**, for Schwantes [18] and Schwantes et al. [12], presented in **Table 4**.

It can be observed that cassava bark shows adsorption of Cd^{2+} in monolayers, as adjusted by Langmuir. However, the materials bagasse and mixture presented better adjustment for the Freundlich model, suggesting, in this case, adsorption in Cd^{2+} predominantly in multilayers.

Some results presented by Schwantes [18] are remarkable, as the parameter “ Q_m ” of Langmuir, which measures the maximum amount of adsorption, was observed values of the order of 16.66, 14.88, and 15.45 mg of Cd^{2+} per liter of contaminated solution, for the adsorbents bark, bagasse, and mixture. These values are close from the values obtained for activated carbon (22.69 $\text{mg}\cdot\text{L}^{-1}$), suggesting that the natural adsorbents of cassava, even if they constitute residual biomass, present great potential in the removal of this metal toxic.

The model of Dubinin-Radushkevich (D-R), according Schwantes [18] and Schwantes et al. [12], explains satisfactorily the adsorption of Cd^{2+} and Pb^{2+} by the cassava adsorbents, presented a good fit (R^2) (**Table 4**). According to **Table 4**, the values of “ E ” in the majority of the cases assume values superior to 8 $\text{KJ}\cdot\text{mol}^{-1}$, suggesting predominance of chemical adsorption [7] to cassava biosorbents. It indicates that the quantity of the toxic metal adsorbed by cassava biomass, in normal conditions, rarely returns to the solution, being this result, according to the interpretation of the authors of this chapter, a great advantage to decontamination of the waters containing toxic metals.

4.1.2.4. Possibility of reuse of the cassava biosorbents

The desorption phenomenon, according to Mimura et al. [16], corresponds to the removal of the metal from the connecting site of the surface of the adsorbent; for this, usually, it used acids in solution containing the adsorbents after sorption, so that H^+ ions can replace the

| Linear models | | Bark | Bagasse | Mixture | Activated carbon | Bark | Bagasse | Mixture |
|---|-------|--------------------------------|---------|---------|------------------|--------------------------------|---------|---------|
| | | Adsorption of Cd ²⁺ | | | | Adsorption of Pb ²⁺ | | |
| Langmuir [25] | Q_m | 16.66 | 14.88 | 15.45 | 22.69 | 29.26 | 25.16 | 24.81 |
| $\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m b} + \frac{C_{eq}}{q_m}$ | K_L | 0.025 | 0.034 | 0.017 | 0.005 | 0.052 | 0.003 | 0.002 |
| | R_L | 0.168 | 0.128 | 0.226 | 0.506 | 0.489 | 0.628 | 0.746 |
| | R^2 | 0.983 | 0.982 | 0.979 | 0.984 | 0.961 | 0.989 | 0.983 |
| | | | | | | | | |
| Freundlich [26] | K_f | 9.949 | 4.863 | 3.479 | 4.400 | 3.814 | 6.180 | 8.643 |
| $\log q_{eq} = \log K_f + \left(\frac{1}{n}\right) \log C_{eq}$ | n | 4.246 | 3.684 | 3.049 | 3.331 | 1.224 | 1.449 | 1.704 |
| | R_2 | 0.920 | 0.995 | 0.993 | 0.991 | 0.870 | 0.772 | 0.712 |
| D-R [27] | Q_d | 0.0004 | 0.0003 | 0.0003 | 0.0004 | 0.0015 | 0.0006 | 0.0004 |
| $\ln Q_{eq} = \ln Q_d - B d \varepsilon^2$ | E | 12.004 | 12.461 | 13.814 | 16.807 | 10.733 | 13.245 | 14.712 |
| | R^2 | 0.984 | 0.992 | 0.994 | 0.979 | 0.997 | 0.984 | 0.991 |

Q_m (mg.g⁻¹): maximum adsorption capacity; K_L or b (L.mg⁻¹): constant related to the adsorbent/adsorbate interaction forces; R_L : Langmuir constant; R^2 : determination coefficient; K_f (L.mg⁻¹): related to the adsorption capacity; n : related to the heterogeneity of the solid; Q_d (mol.g⁻¹): maximum adsorption capacity; E (Kj.mol⁻¹): mean sorption energy. Source: Refs. [12, 18].

Table 4. Linearization of the data by Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) to the biosorption process of Cd²⁺ and Pb²⁺ by bark, bagasse, and mixture and activated carbon.

adsorbed cations by the ion exchange mechanism. For this practice, it is fundamental knowledge of the interaction characteristics between the adsorbate and the adsorbent for their resistance for reuse purposes in new adsorption processes.

Figure 8 shows that the recuperation of the material in acid solution (HCl) is high, varying by 60% to near of 90% to cassava adsorbents used in the removal of Cd²⁺ [18], Pb²⁺ [12], Cu²⁺, and Zn²⁺ [9]. However, it is observed that, when using the adsorbents of cassava to

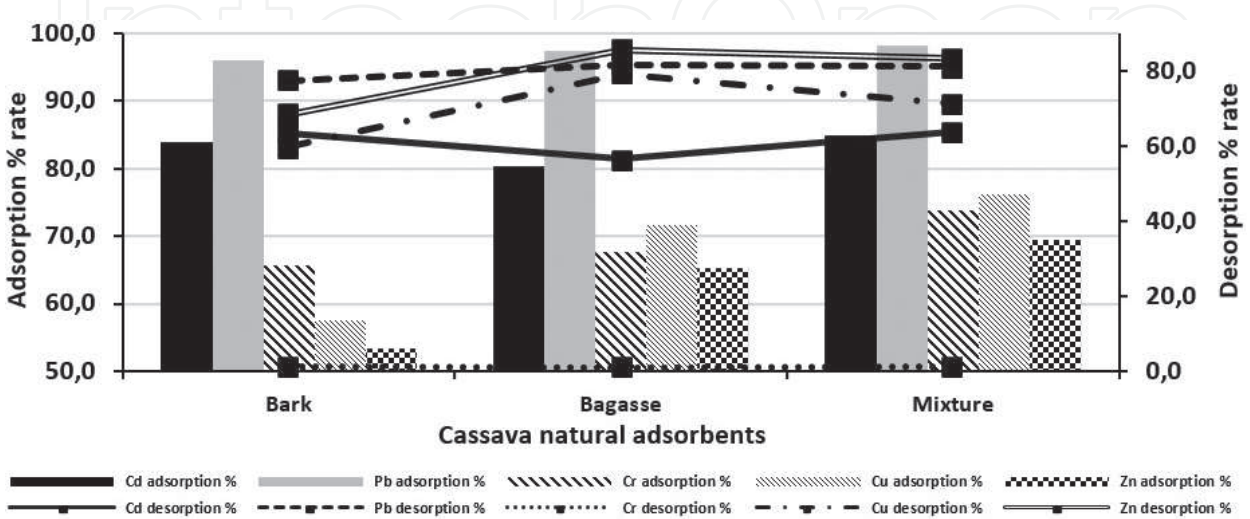


Figure 8. Possibility of cassava adsorbents reuse to new cycles of metallic ions sorption. Source: Refs. [9, 10, 12, 18].

remove Cr^{3+} , desorption rates are 1%, that is, recovery of cassava biosorbents is compromised, which according to Schwantes et al. [10] is a strong indicative of chemical adsorption of this metal with referred natural adsorbents.

4.2. Case studies: chemical modifications to cassava biosorbents and their use in the removal of toxic metals in waters

As already mentioned in this chapter, a good adsorbent is one that has a large number of active sites available for interaction with the polluting species of interest. The sites are adsorption points consisted of one or more chemical functional groups distributed on the surface of the biosorbent. It is important to emphasize that some biosorbents may have their surfaces chemically modified in order to increase the amount of active sites and, consequently, to increase the adsorption capacity of metallic ions.

As mentioned above, it is not novelty to use modifying agents in improving the characteristics of the adsorbents. The literature reports the use of chemically modified adsorbents and their use in the removal of metals, agrochemicals and other pollutants from liquid solution, such as modified adsorbents with HCl [28], jute fiber modified with H_2O_2 in the removal of Cu^{2+} , Ni^{2+} , and Zn^{2+} [29], wheat barks treated with H_2SO_4 in the removal of Cu^{2+} [30], and bagasse ashes modified with H_2O_2 in the removal of Pb^{2+} [31], among other examples.

The principal modifications included delignification, esterification of carboxyl and phosphate groups, methylation of amine groups and hydrolysis of carboxylate groups, acid treatments, basic treatments, and peroxide treatments, among others cited in the literature.

The aforementioned modifications aim to eliminate the coloration, turbidity, and other unfavorable characteristics of the treated water (after adsorption), as well as increase the adsorptive capacity of metals and other pollutants [7].

In contrast, when using acid treatments to plant biomass, such as sulfuric acid, hydrochloric, or nitric acid, all in their diluted form, the hydrolysis of cellulose is accelerated, resulting in a higher capacity of adsorption of the resulting adsorbents.

It is important to mention that this whole modification process generally does not overtax the final product, that is, this process results in adsorbents of greater adsorption capacity without generating great costs to the final adsorbent.

Related to the use of modified cassava adsorbents, the literature is scarce. Schwantes et al. [11] realized chemical modifications to the cassava barks through H_2O_2 , H_2SO_4 , and NaOH solution of 0.1 mol.L^{-1} in the proportion of 7 g of biosorbent per liter of modified solution. The authors kept the biosorbents in contact with the modifying solution for 6 h in a Dubnoff system, with shaking at 150 rpm at 60°C . Subsequently, successive washes were carried out on the material with distilled and deionized H_2O to remove eventual remnants of the modifying agent, resulting in three modified adsorbents, nominated by the authors according to the modification applied in M. H_2O_2 , M. H_2SO_4 , and M. NaOH.

Without these citations, the literature presents failures (with the exception of the methods to production of activated carbon), while other chemical and/or physical modifications applied

to biosorbents originated from cassava agroindustry, being necessary for more studies about this topic. In the subsequent items, the physical, chemical, and morphological characteristics obtained by the authors aforesaid to the adsorbents M. H_2O_2 , M. H_2SO_4 , and M. NaOH, as well as the adsorption capacity of various polluting ions will be described.

4.2.1. Characterization of the cassava-modified adsorbents and their possible utilization in the removal of toxic metals

According to Schwantes et al. [9] and Schwantes et al. [10], the micrographs observed in **Figure 9a**, to the adsorbent M. *in natura*, showed a surface with spongy and fibrous aspect, with irregular and heterogeneous structure. Some spheres present in the micrograph can be noted, possibly indicating the presence of residual starch granules from the originating material. It is also observed that the modified adsorbents (**Figure 9b–d**) have a surface that remind the originating material (**Figure 9a**), however, with some differential aspects depending on each treatment applied.

As can be seen in **Figure 9b–d**, corresponding to the chemical modifications of the chemical reagents H_2O_2 , H_2SO_4 , and NaOH, respectively, the modified adsorbents retain the characteristics of their precursor (M. *in natura*, **Figure 9a**), however, with some marked modifications. In these cases, structures that remember the cells of the original plant are observed.

Hydrogen peroxide, a powerful oxidizing agent, caused some changes in the surface of the adsorbent M. H_2O_2 . It is observed in **Figure 9b** that M. H_2O_2 presents with heterogeneous surface, remembering the form of scales. In **Figure 9c**, referring to M. H_2SO_4 , unlike the others, a relatively homogeneous surface is observed, with a flat structure, apparently little porous, reminding the shape of scales, also presenting some prominent cracks, possibly because of the dehydration from sulphuric acid, which is a powerful dehydrator.

Caustic soda is a strong, highly soluble, and recognizably corrosive base that, upon contact with the cassava barks, caused changes in its surface structure, as shown in **Figure 9d**, which illustrates an irregular, heterogeneous surface with cracks (breaks) of the adsorbent, with a surface that reminds scales.

As previously mentioned in this chapter, one of the main objectives of the application of chemical modifications in biosorbents is the promotion of new functional groups, aiming to increase the adsorption capacity by the modified biomass. According to the observation in

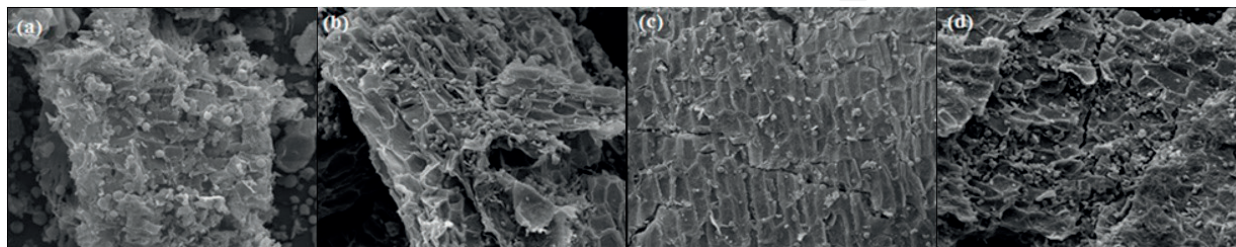


Figure 9. Micrographs of the adsorbents M. *in natura* (a) [9, 10], M. H_2O_2 (b), M. H_2SO_4 (c), and M. NaOH (d) in 800, 400, 400 and 400 \times , respectively. Source: The authors.

the studies of Schwantes et al. [9] and Schwantes et al. [10], the infrared spectra of the natural adsorbent, when superimposed on the modified cassava adsorbents, contrast with the appearance of some peaks, such as in 2855, 1161, and 579 cm^{-1} , as well as the peaks obtained in 1019 cm^{-1} , specifically for the M. H_2SO_4 adsorbent.

The peaks obtained in 1161 cm^{-1} possibly indicate the presence of the vibrational stretches of C-O connections present in carboxylic acids, one of the main responsible for the formation of active sites on the adsorbent surface. Peaks at 2855 cm^{-1} may be indicative of the vibrational elongation of C-H connections present in aldehydes [32]. Peaks at 579 cm^{-1} suggest groupings with S-S connections, suggesting the presence of amino acids like cysteine "[$\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$] $_2$ ", lipolic acids " $(\text{C}_8\text{H}_{14}\text{O}_2\text{S}_2)$ ", and others.

In general, the authors corroborate that the results obtained in the infrared spectra suggest that solutions of H_2O_2 , H_2SO_4 , and NaOH caused modifications of cassava barks, forming functional groups that may provide adsorbents with good sorption characteristics.

In the treatment of biomass of cassava barks with modifying solutions, changes in the point of zero charge occur because the material M. *in natura* presented pH_{PZC} of 6.02 [9, 10], and after modifications, this value was changed to 3.98 in the modification with H_2O_2 , 2.05 for modification with H_2SO_4 , and about 7.07 for modification with NaOH [11] (**Figure 10**).

The adsorption of metal cations is favored when they are in solutions in which the pH values are higher than pH_{PZC} , because in these cases, the surface of the adsorbent presents predominance of the negative charges. These results suggest that the simple washing of the adsorbent materials of cassava can change the point of zero charge of the adsorbent; in other words, the point of zero charge of an adsorbent can be handled, according to the need for values higher or lower than the biosorbent of origin.

Another curious fact is the simple washing of the cassava biosorbent with modifying solutions caused extraction of part of the constituent elements of the biomass, as evidenced in **Table 5**.

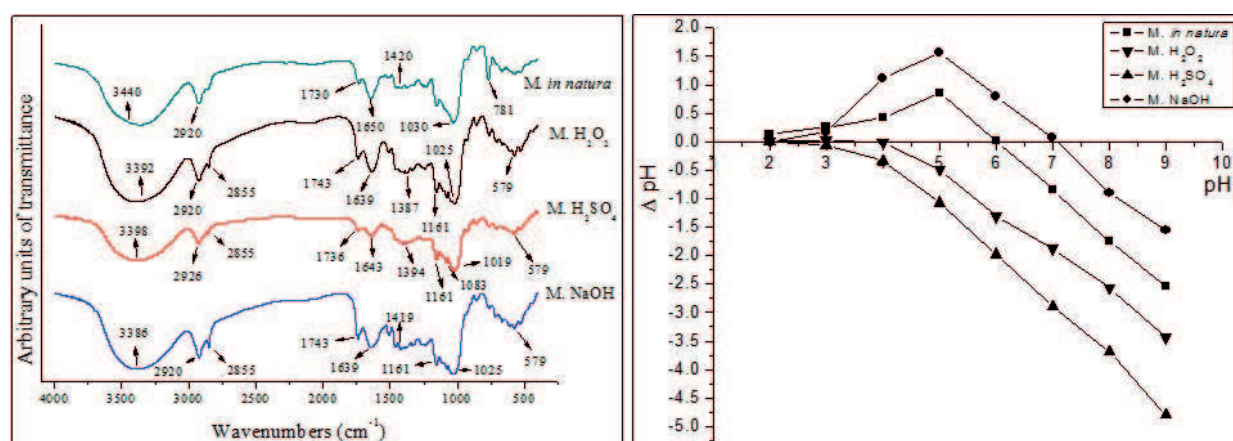


Figure 10. In the left: infrared spectra for adsorbents based in natural cassava barks [9, 10] and modified with H_2O_2 , H_2SO_4 , and NaOH. Source: The authors. In the right: pH_{PZC} of adsorbents M. *in natura* [9, 10], M. H_2O_2 , M. H_2SO_4 , and M. NaOH [11].

| Adsorbents | K | Ca | Mg | Cu | Zn | Mn | Fe | Cd | Pb | Cr |
|--|--------------------|---------------------|------|-------|-------|--------|--------|-----|-------|-----|
| | g.kg ⁻¹ | mg.kg ⁻¹ | | | | | | | | |
| M. <i>in natura</i> [9, 10] | 24.10 | 35.03 | 6.83 | 14.33 | 32.00 | 123.33 | 335.66 | <LQ | 13.00 | <LQ |
| M. H ₂ O ₂ [11] | 7.84 | 5.68 | 1.27 | 10.60 | 32.20 | 121.50 | 333.70 | <LQ | 10.40 | <LQ |
| M. H ₂ SO ₄ [11] | 5.78 | 3.41 | 0.43 | 4.30 | 20.40 | 115.70 | 330.90 | <LQ | 5.10 | <LQ |
| M. NaOH [11] | 11.22 | 6.52 | 1.49 | 4.80 | 32.60 | 122.00 | 331.60 | <LQ | 11.50 | <LQ |
| LQ (limit of quantification): K = 0.01; Ca = 0.005; Mg = 0.005; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005; Cd = 0.005; Pb = 0.01; Cr = 0.01 (mg kg ⁻¹). | | | | | | | | | | |

Table 5. Average values of element concentrations in the studied adsorbents.

According to Schwantes et al. [11], the modifying agents act as extractors of the metallic elements in the biosorbent, with reduction of K (67%), Ca (84%), Mg (81%), Cu (70%), Fe (1%), and Pb (20%) to the cassava adsorbent modified with H₂O₂. As for the adsorbent modified with H₂SO₄, it can evidence the reduction of K (76%), Ca (90%), Mg (94%), Cu (70%), Zn (36%), Mn (6%), Fe (1%), and Pb (61%), while for the adsorbent modified with NaOH, it resulted in reduction of K (53%), Ca (81%), Mg (78%), Cu (67%), Mn (1%), Fe (1%), and Pb (12%).

This possibly occurs in function of the actions of modifying solutions (H₂O₂, H₂SO₄, and NaOH), in addition to the loss of these metals caused by the postmodification washing, eliminating a good part of these elements. It is important to emphasize the high reductions of the metal contents when using the modifying solution of H₂SO₄, a strong acid, recognized as a potent dehydrator [11].

As previously quoted in this chapter, one of the many characteristics of a good adsorbent is the high-specific surface area, as well as considerable values for the pore volume parameters and a good distribution to the average diameters of these values.

In the **Table 6**, it can be seen that the specific surface area (SSA) of the cassava adsorbents is generally small when compared to the activated carbon. Among the values obtained, it is important to highlight the adsorbent M. H₂O₂, which presents the highest values for SSA (0.91 m².g⁻¹), followed by M. NaOH (0.70 m².g⁻¹) and M. H₂SO₄ (0.46 m².g⁻¹).

It can be observed that SSA of the modified cassava is small when compared to values obtained for activated carbon originated from coffee barks (130 a 391 m².g⁻¹), but similar to the other residues of low economic value, such as Oliveira et al. [33], which obtained 0.46 m².g⁻¹ for

| Parameters | M. <i>in natura</i> | M. H ₂ O ₂ | M. H ₂ SO ₄ | M. NaOH |
|---|---------------------|----------------------------------|-----------------------------------|---------|
| Superficial area (m ² .g ⁻¹) | 0.5583 | 0.9156 | 0.4637 | 0.7017 |
| Pore volume (cm ³ .g ⁻¹) | 0.001137 | 0.00307 | 0.00179 | 0.00146 |
| Pore diameter (nm) | 1.922 | 1.734 | 3.295 | 1.924 |

Source: The authors.

Table 6. Texture of the cassava adsorbents.

rice bran. Also, Penha et al. [34], that even using chemical treatment of the rice barks, do not obtain higher values than $1.13 \text{ m}^2 \cdot \text{g}^{-1}$, with mean pores volume equal to $1.94 \text{ cm}^3 \cdot \text{g}^{-1}$ and mean diameter of the pores equal to 6.9 nm, that is, predominance of mesoporous.

The volumes of the pores obtained in this research (0.0031 and $0.0018 \text{ cm}^3 \cdot \text{g}^{-1}$ to M. H_2O_2 and M. NaOH) are similar to those obtained for Penha et al. [34] in modified rice barks ($0.0019 \text{ cm}^3 \cdot \text{g}^{-1}$). Pores with diameter situated between 2.0 and 50.0 nm are considered mesoporous, being the cassava adsorbents are predominantly microporous and, to a lesser degree, mesoporous (Table 6).

Although low surface area and low pore volume, which are initially disadvantages the adsorption process, this is not the only determining condition in a high-pollutant remediation capacity of the adsorbent.

4.2.2. Experimental results involving modified adsorbents of cassava and remediation of toxic metals in waters

4.2.2.1. Influences of the pH of the contaminant solution and the proportion between the cassava-modified adsorbents and metallic adsorbents

Schwantes et al. [11], when evaluating the influence of different pH ranges and modified adsorbent mass on the removal of Cd^{2+} , Pb^{2+} , and Cr^{3+} , observed significant difference in relation to the amount of mass of the adsorbents studied.

These results demonstrate that the adsorbents of cassava in their natural form and modified with H_2O_2 , H_2SO_4 , and NaOH depend closely on the amount of adsorbent used but did not show this relationship with the pH variable in the range studied by the authors, which was 3.60–7.00. The removal of metals from the solutions was higher for the lower masses tested by the authors (close to $4 \text{ g} \cdot \text{L}^{-1}$), according to Figure 11.

In a similar study, in which activated carbon with ZnCl_2 was produced from residues of cassava bark, with the purpose of using it to remove Pb^{2+} from contaminated water, there was also an increase in the removal efficiency of Pb^{2+} as the doses of mass of the adsorbents studied by the authors increased, reaching efficiency of 74% [35].

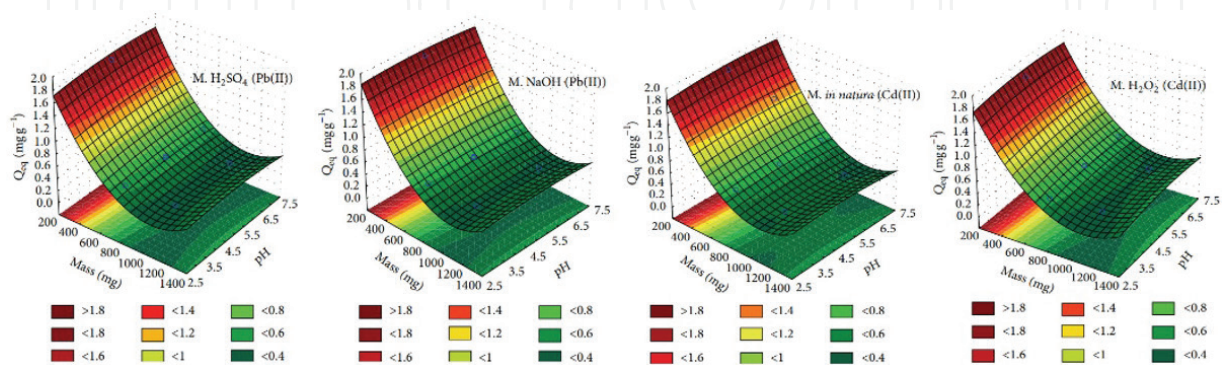


Figure 11. Response surfaces for interaction between the mass of the natural cassava adsorbent and modified with H_2O_2 , H_2SO_4 , and NaOH, in the removal of Cd^{2+} and Pb^{2+} . Source: Schwantes et al. [11].

These authors point out that the higher dosage of adsorbents increases adsorption, and this is mainly because the greater number of surfaces and functional groups of the adsorbents, with which the metal can interact, as well as to an improvement in the dissolved oxygen value and a reduction in the electrical conductivity of the wastewater, that may occur as a function of higher doses of the adsorbent used.

According to Ilaboya et al. [35] that tested pHs between 2 and 12, observed that the metallic ions removal of the samples they evaluated were related to the pH of the samples, observing that the amount of Pb^{2+} ions removed raised to pH 8 and then began to decrease, they considered that the pH together with the temperature were the most effective variables for adsorption of ions of this metal.

The elevation of Pb^{2+} removal as the pH is high may be related to the lower occurrence of hydrogen ions and the decrease of positive charges on the surface of the adsorbent, resulting in lower electrostatic repulsive forces between the surface and the ions of the metal.

According to Schwantes et al. [11], the fact that in their studies, the pH range studied did not influence the adsorption process is an excellent result, because the adsorbents proposed by the authors can be used in waters and effluents with different pH values, without affecting the removal efficiency of these pollutants.

The fact that the results observed by Ilaboya et al. [35] and Schwantes et al. [11] differ in the behavior of removal as a function of pH may have relation with the form of activation of the material used (cassava barks). In addition, Ilaboya et al. [35] used physical activation through pyrolysis, which changes the characteristics of the adsorbent, demonstrating that adsorbent materials from cassava barks have several possibilities of use. In addition, it should be remembered that the activation reagent in these cases differed.

Although the differences occurred in both works, it is possible to observe that the use of adsorbents of cassava barks is efficient in cases when it is activated only chemically and in cases where physical and chemical activation occurs, that is, with addition of pyrolysis.

It is important to emphasize that in all the researches mentioned above, the proportion between the adsorbent mass and the volume of contaminated water is one of the great differentials of this technology, since the higher adsorption efficiencies of metals occur with values around 4–5 g of adsorbent per liter of adsorbate.

4.2.2.2. *Contact time influences between modified cassava adsorbents and toxic metals*

According to study conducted by published by Schwantes et al. [11], showed in **Figure 12**, it can be observed that after 20–40 min of contact time with the modified cassava adsorbents, in solutions containing 10 mg.L^{-1} of Cd^{2+} and Pb^{2+} , the system enters in dynamic equilibrium. The process of adsorption of these metals by the modified cassava adsorbents is a fast process, easily applicable in large scale.

Schwantes et al. (2016) applied the results obtained in **Figure 12** the linear model of Pseudo-second order, proposed by Ho and McKay [21], being observed good mathematical adjustments (R^2), suggesting in this way the occurrence of chemical adsorption of Cd^{2+} and Pb^{2+} by the adsorbents of cassava modified with H_2O_2 , H_2SO_4 , and NaOH.

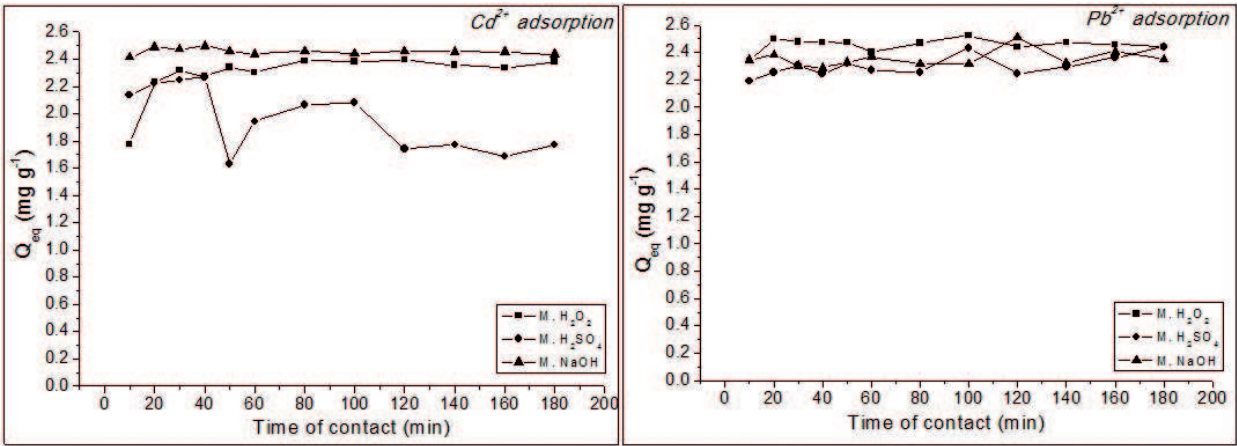


Figure 12. Adsorbed amount of metals Cd^{2+} and Pb^{2+} in function of contact time between modified cassava adsorbents. Source: Schwantes et al. [11].

4.2.2.3. Equilibrium studies of adsorption in modified cassava adsorbents

In the studies of Schwantes et al. [11], the adsorption isotherms of Cd^{2+} , Pb^{2+} , and Cr^{2+} were linearized by the mathematical models of Langmuir and Freundlich. These authors observed a predominance of good adjustments for the Langmuir models, suggesting the occurrence of adsorption in monolayers for cassava bark modified with H_2O_2 , H_2SO_4 , and NaOH in the adsorption of Cd^{2+} , H_2O_2 , and NaOH in the adsorption of Pb^{2+} (Table 7).

Comparing the results published by Schwantes et al. [12] and Schwantes et al. [11], increases in the maximum capacity of adsorption of Cd^{2+} and Pb^{2+} by cassava barks about 17 and 45%, respectively, can be observed, when compared to the unmodified adsorbent.

| Models and parameters | | M. <i>in natura</i> [18] | M. H ₂ O ₂ [11] | M. H ₂ SO ₄ [11] | M. NaOH [11] | Activated carbon [18] | M. <i>in natura</i> [12] | M. H ₂ O ₂ [11] | M. H ₂ SO ₄ [11] | M. NaOH [11] |
|--|-------|--------------------------------|---|--|--------------------|-----------------------------|--------------------------------|---|--|--------------------|
| | | Adsorption of Cd ²⁺ | | | | | Adsorption of Pb ²⁺ | | | |
| Langmuir [25] | Q_m | 16.66 | 13.420 | 7.058 | 19.539 | 22.696 | 29.265 | 21.678 | 24.004 | 42.463 |
| | K_L | 0.025 | 0.026 | 0.017 | 0.006 | 0.0049 | 0.005 | 0.022 | 0.019 | 0.002 |
| | R_L | 0.165 | 0.163 | 0.224 | 0.467 | 0.506 | 0.489 | 0.188 | 0.207 | 0.667 |
| | R^2 | 0.967 | 0.993 | 0.980 | 0.996 | 0.984 | 0.961 | 0.994 | 0.938 | 0.996 |
| Freundlich [26] | K_f | 9.949 | 1.967 | 1.565 | 3.634 | 4.400 | 3.814 | 2.510 | 1.692 | 3.393 |
| $\log q_{eq} = \log K_f + \left(\frac{1}{n}\right)$ $\log C_{eq}$ | n | 4.246 | 2.287 | 1.020 | 1.678 | 3.331 | 1.224 | 1.764 | 1.488 | 0.762 |
| | R^2 | 0.920 | 0.934 | 0.977 | 0.902 | 0.991 | 0.870 | 0.980 | 0.977 | 0.931 |

Q_m (mg.g⁻¹): maximum capacity of adsorption; K_L ou b (L.mg⁻¹): constant related to the adsorbent/adsorbate interaction forces; R_L : Langmuir constant; R^2 : coefficient of determination; K_f (L.mg⁻¹): related to the adsorption capacity; n : related to the heterogeneity of the solid.

Table 7. Parameters referring to the Langmuir and Freundlich linear models for adsorption of Cd^{2+} and Pb^{2+} by cassava adsorbents.

Moreover, it is observed that the modification of the cassava bark with NaOH generated an adsorbent with adsorption capacity of Cd^{2+} similar to the commercial activated carbon tested by Schwantes et al. [12]. This result is an unprecedented and very interesting result from the point of economic view, since the cost of acquiring commercial activated carbon is several times higher than that of the modified adsorbent of cassava barks. In addition, these authors observed good adjustments for the Freundlich model, which suggests multilayer adsorption of Cd^{2+} for M. H_2SO_4 and M. H_2O_2 and H_2SO_4 in the adsorption of Pb^{2+} .

The models of Langmuir and Freundlich also were studied by Omotosho and Sangodoyin [36] to linearize the adsorption data obtained by investigating the efficiency of the cassava bark carbon activated with zinc chloride at the activation levels of 1:3, 2:3, and 1:1 in the removal of NO_3^- wastewater from cassava processing.

The results linearized by Langmuir for the four levels of activation of that author show that all had coefficients values (R^2) between 0.972 and 0.994. These results demonstrate, as verified by Schwantes et al. [11], which the material followed the assumptions of Langmuir theory, that is, the carbon surface was adsorbing at specific monolayer sites, the authors concluded that this characteristic implies that the activated carbon of cassava barks without and with chemical activation are effective adsorbents.

4.2.2.4. Possibility of reuse of the cassava-modified adsorbents

When evaluated the possibility of reuse of the cassava-modified adsorbents, Schwantes et al. [11], when proceeding the acid elution with HCl 0.1 M, obtained the follow rates of desorption to Cd^{2+} : M. H_2O_2 (60%); M. H_2SO_4 (62%) and M. NaOH (74%); to desorption of Pb^{2+} : M. H_2O_2 (65%); M. H_2SO_4 (53%) and M. NaOH (56%); and to desorption of Cr^{3+} : M. H_2O_2 (1%); M. H_2SO_4 (3%); and M. NaOH (1%).

According to the authors, the results about the desorption of the metallic ions confirm the possibility of reuse of the adsorbents through the action of a strong acid solution, which promotes the extraction of these elements from the active site, as observed for the use of adsorbents of cassava for Cd^{2+} and Pb^{2+} .

However, it is observed that when the modified adsorbents are used in Cr^{3+} adsorption cycles, low desorption values are observed, which, according to Schwantes et al. (2016), is a strong indication that this ion is adsorbed by chemical bonds (chemisorption), which makes it impossible to reuse them in new sorting cycles. This effect was observed for other authors noted by the literature, such as jatropha seed pie [37], cassava barks in their natural form [11], and others.

5. Final considerations

The use of these adsorbent materials from cassava residual biomass is a viable alternative in the removal of water pollutants, since they represent an important increase in the cassava agroindustrial chain. The reuse of these materials is in according to the sustainability, since

such residues can be used in remediation of environmental compartments contaminated with toxic metals such as Cd, Pb, Cr, Cu, Zn, and others.

The results of the researches presented in this chapter demonstrate that cassava agroindustrial residues have potential for use in the form of adsorbents, and they can be used in their natural or modified form, presenting high efficiencies and comparable to conventional commercial adsorbents, however, with a lower cost of production.

The authors of this chapter also reiterate that although the barks, bagasse, and other solid residues from the processing of the cassava roots have proven potential for adsorption of several contaminants (especially metals), further research on these materials is still needed, especially related to pesticides, POP, and other pollutants.

Author details

Daniel Schwantes¹, Affonso Celso Gonçalves^{2*}, Marcelo Angelo Campagnolo³, César Ricardo Teixeira Tarley⁴, Douglas Cardoso Dragunski⁵, Jéssica Manfrin² and Andréia Da Paz Schiller²

*Address all correspondence to: affonso133@hotmail.com

1 Department of Engineering and Exact Sciences, Federal University of Paraná, Palotina, Paraná, Brazil

2 Program of Post-Graduation in Agronomy, State University of Western Paraná, Marechal Cândido Rondon, Paraná, Brazil

3 Department of Environmental Engineering, Pontifical Catholic University of Paraná, Toledo, Paraná, Brazil

4 Department of Chemistry, Londrina State University, Londrina, Paraná, Brazil

5 Program of Environmental Sciences, State University of Western Paraná, Toledo, Paraná, Brazil

References

- [1] Alves AAC. Fisiologia da mandioca. In: Aspectos socioeconômicos e agrônômicos da mandioca. 1st ed. Cruz das Almas – BA: EMBRAPA Mandioca e Fruticultura Tropical, Cap. 7; 2006. pp. 139-169
- [2] Annadurai G, Juang RS, Lee DJ. Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology*. 2002;**47**(1):185-190
- [3] Meunier N, Laroulandie J, Blais JF, Tyagi RD. Cocoa shells for heavy metal removal from acidic solutions. *Bioresource Technology*. 2003;**90**(3):255-263

- [4] Gonçalves AC Jr, Selzlein C, Nacke H. Uso de biomassa seca de aguapé (*Eichornia crassipes*) visando à remoção de metais pesados de soluções contaminadas. *Acta Scientiarum Technology*. 2009;**31**(1):103-108
- [5] Peña-Rodríguez S, Fernández-Calviño D, Nóvoa-Muñoz JC, Arias-Estévez M, Núñez-Delgado A, Fernández-Sanjurjo MJ, Álvarez-Rodríguez E. Kinetics of hg (II) adsorption and desorption in calcined mussel shells. *Journal of Hazardous Materials*. 2010;**180**:622-627
- [6] Dos Santos VCG, Souza JVTM, Tarley CRT, Caetano J, Dragunski DC. Copper ions adsorption from aqueous medium using the biosorbent sugarcane bagasse in natura and chemically modified. *Water, Air, and Soil Pollution*. 2011;**216**:351-359
- [7] Wan Ngah WSW, Hanafiah MAKM. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*. 2008;**99**(10):3935-3948
- [8] SEAB. Secretaria de Estado da Agricultura e do Abastecimento. Available from: http://www.agricultura.pr.gov.br/arquivos/File/deral/Prognosticos/mandiocultura_2013_14.pdf [Accessed: May 2017]
- [9] Schwantes D, Gonçalves AC Jr, Miola AJ, Coelho GF, Dos Santos MG, Leismann EAV. Removal of cu (II) and Zn (II) from water with natural adsorbents from cassava agroindustry residues. *Acta Scientiarum Technology*. 2015;**37**(3):409-417
- [10] Schwantes D, Gonçalves Jr AC, Casarin J, Pinheiro A, Pinheiro IG, Coelho GF. Removal of Cr(III) from contaminated water using industrial waste of the cassava as natural adsorbents. *African Journal of Agriculture Research*. 2015;**10**(46):4241-4251
- [11] Schwantes D, Gonçalves AC Jr, Coelho GF, Campagnolo MA, Dragunski DC, Tarley CRT, Miola AJ, Leismann EA. Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater. *Journal of Chemistry*. 2016;**2016**:1-15
- [12] Schwantes D, Gonçalves AC Jr, Strey L, Schwantes V, Nacke H. Reuse and recycling techniques: Kinetics, equilibrium and thermodynamics of the adsorption process of lead using cassava industry wastes. In: Bártolo H, Duarte JP, editors. *Green Design, Materials and Manufacturing Processes*. 1st ed. Vol. 1. Boca Raton: CRC Press Taylor & Francis Group; 2013. pp. 417-422
- [13] Schwantes D, Gonçalves AC Jr, Coelho GF, Casarin J, Stangarlin JR, Pinheiro A. Reuse and recycling techniques: Equilibrium of the adsorption process of glyphosate using wastes from the cassava industry. In: Bártolo H, Duarte JP, editors. *Green Design, Materials and Manufacturing Processes*. 1st ed. Vol. 1. Boca Raton: CRC Press Taylor & Francis Group; 2013. pp. 423-428
- [14] Han R, Zhang L, Song C, Zhang M, Zhu H, Zhang L. Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydrate Polymers*. 2010;**79**:1140-1149
- [15] Pehlivan E, Altun T, Cetin S, Bhanger MI. Lead sorption by waste biomass of hazelnut and almond shell. *Journal of Hazardous Materials*. 2009;**167**(1-3):1203-1208

- [16] Mimura AMS, Vieira TVA, Martelli PB, Gorgulho HF. Utilization of rice husk to remove Cu^{2+} , Al^{3+} , Ni^{2+} and Zn^{2+} from wastewater. *Química Nova*. 2010;**33**(6):1279-1284
- [17] Gonçalves AC Jr, Nacke H, Schwantes D, Coelho GF. Heavy metal contamination in Brazilian agricultural soils due to application of fertilizers. In: Hernández-Soriano MC, editor. *Environmental Risk Assessment of Soil Contamination*. 1st ed. Vol. 4. Rijeka: InTech; 2014. pp. 105-135
- [18] Schwantes D. Kinetics, Equilibrium and Thermodynamic of the Adsorption Process of Metallic Ions Using Wastes from the Cassava Industry as Biosorbents. 18-02-2013. 103p. Universidade Estadual do Oeste do Paraná. Campus de Marechal Cândido Rondon, PR: Dissertação de Mestrado; 2013
- [19] Gonçalves AC Jr, Strey L, Lindino CA, Nacke H, Schwantes D, Seidel EP. Applicability of the Pinus bark (*Pinus Elliottii*) for the adsorption of toxic heavy metals from aqueous solutions. *Acta Scientiarum Technology*. 2012;**34**(1):79-87
- [20] Runping H, Han P, Cai Z, Zhao Z, Tang M. Kinetics and isotherms of neutral red adsorption on peanut husk. *Journal of Environmental Sciences*. 2008;**20**:1035-1041
- [21] Ho YS, McKay G. Pseudo-second order model for sorption processes. *Process Biochemistry*. 1999;**34**:451-465
- [22] Yang X, Al-Duri B. Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. *Journal of Colloid and Interface Science*. 2005;**287**(1):25-34
- [23] Neta JJS, Silva CJ, Moreira GM, Reis C, Reis EL. Removal of the reactive blue 21 and direct red 80 dyes using seed residue of *Mabea fistulifera* Mart. As biosorbent. *Revista Ambiente & Água*. 2012;**1**:7
- [24] Giles CH, Macewan TH, Nakhwa SN, Smith D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society*. 1960. p. 3973-3993
- [25] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*. 1918;**40**:1361-1403
- [26] Freundlich H. Adsorption in solution. *Physical Chemistry Society*. 1906;**40**:1361-1368
- [27] Dubinin MM, Radushkevich LV. Equation of the characteristic curve of activated charcoal. *Chemisches Zentralblatt*. 1947;**55**:331-337
- [28] Argun ME, Dursun S. Removal of heavy metal ions using chemically modified adsorbents. *Journal of International Environmental Application & Science*. 2006;**1**(1-2):27-40
- [29] Shukla SR, Pai RS. Adsorption of $\text{Cu}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ on modified jute fibres. *Bioresour Technology*. 2005;**96**:1430-1438
- [30] Ozer A, Ozer D, Ozer A. The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): Determination of the equilibrium and thermodynamic parameters. *Process Biochemistry*. 2004;**39**:2183-2191

- [31] Gupta VK, Ali I. Removal of lead and chromium from wastewater using bagasse fly ash – A sugar industry waste. *Journal of Colloid and Interface Science*. 2004;271-321
- [32] Stuart BH. *Infrared Spectroscopy: Fundamentals and Applications*. Hoboken, New Jersey: John Wiley and Sons; 2004;1:224
- [33] Oliveira EA, Montanhera SF, Andrade AD, Nóbrega JA, Rollemberg MC. Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. *Process Biochemistry*. 2005;40:3485
- [34] Penha RS, Santos CC, Cardoso JJF, Silva HAS, Santana SAA, Bezerra CWB. Chemically treated Rice husk as low-cost adsorbent for metal ions uptake (Co^{2+} and Ni^{2+}). *Revista Virtual Química*. 2016;8(3):588-604
- [35] Ilaboya IR, Oti EO, Ekoh GO, Umukoro LO. Performance of activated carbon from cassava peels for the treatment of effluent wastewater. *Iranica Journal of Energy & Environment*. 2013;4(4):361-375
- [36] Omotosho OA, Sangodoyin AY. Production and utilization of cassava peel activated carbon in treatment of effluent from cassava processing industry. *Water Practice Technology*. 2016;8:215-224. DOI: 10.2166/wpt.2013.023
- [37] Gonçalves AC Jr, Nacke H, Daniel S, Campagnolo MA, Miola AJ, Tarley CRT, Dragunski DC. Adsorption mechanism of chromium(III) using biosorbents of *Jatropha curcas* L. *Environmental Science and Pollution Research*. 2017;1:1-13