

Environment

Submissão 04/10/18 Aprovação 31/10/19 Publicação 24/06/20

Biosorbent material for the removal of potentially toxic metals from water supply systems

Material biossorvente para remoção de metais potencialmente tóxicos em água de abastecimento

Beatriz de Castro^I, Guilherme Junqueira Jerônimo^{II}, Julio Cesar de Souza Inácio Gonçalves ^{III}, Mário Sérgio da Luz ^{IV}, Deusmaque Carneiro Ferreira Correio^V

ABSTRACT

The aim of this study was to evaluate the potential of green coconut shell powder in the biosorption of metal ions (Pb2+ e Ni2+) found in public water supply systems. The univariate method was used to optimize the biosorption process. Freudlich and Langmuir isotherms were used to evaluate the physical or chemical characteristics of the adsorption material. Results shows that for pH=4, biosorption time = 25 minutes and fiber granulometry at 60 mesh was enabled to remove 97% of Pb2+and 95% of Ni2+, using a biosorbent material concentration of 25 gL-1. The isotherms, adsorption results was better adjusted to the Freundlich model, which is related to a physical adsorption. Thus, based on our results, the coconut shell fiber presents appropriate characteristics for lead and nickel biosorption processes. This biosorbent material can be used in combination with classic water treatment processes focused on the removal of potentially toxic metals.

Keywords: Adsorption isotherms; Green coconut fiber; Biosorption

RESUMO

O objetivo desse trabalho foi avaliar o potencial do pó da casca de coco verde no processo de biossorção de íons metálicos (Pb2+ e Ni2+) presentes na água de abastecimento público. Empregou-se o método univariado para otimizar o processo de biossorção. As isotermas de Freundlich e Langmuir foram empregadas para avaliara característica física ou química do material. Os resultados mostraram que em pH igual a 4, tempo de 25 minutose granulometria da fibra de 60 mesh ocorreram as maiores remoções, na faixa de 97% para Pb2+ e 95% para Ni2+. Com relação à concentração inicial da biomassa, observou-se que a concentração de 25 gL-1 do material biossorvente foi suficiente para uma máxima remoção dos íons metálicos em estudo. Com relação às isotermas, foi possível identificar, a partir dos resultados de adsorção, que as espécies metálicas se ajustaram melhor ao modelo de Freundlich, adsorção física. Dessa forma, os resultados apresentados mostram que a fibra da casca de coco apresenta características apropriadas para o processo de biossorção de chumbo e níquel. Esse material biossorvente pode ser utilizado juntamente com os processos clássicos de tratamento de água para remoção de metais potencialmente tóxicos.

Palavras-chave: Isotermas de adsorção; Fibra de coco verde; Biossorção

^{II} Mestrando do Programa de Pós-Graduação em Ciência e Tecnologia Ambiental, Universidade Federal do Triângulo Mineiro. guijunj@hotmail.com III Docente do Programa de Pós-Graduação em Ciência e Tecnologia Ambiental da Universidade Federal do Triângulo Mineiro.

julio.goncalves@uftm.edu.br

^v Docente do Programa de Pós-Graduação em Ciência e Tecnologia Ambiental da Universidade Federal do Triângulo Mineiro. <u>deusmaque.fe</u>rreira@uftm.edu.br



¹ Engenheira Ambiental pela Universidade Federal do Triângulo Mineiro. beatriz17castro@hotmail.com

¹ Docente do Programa de Pós-Graduação em Ciência e Tecnologia Ambiental da Universidade Federal do Triângulo Mineiro. mario.luz@uftm.edu.br

1 INTRODUCTION

Traditional technologies applied to treat water used for human consumption purposes comprise stages such as coagulation, flocculation, decantation, filtration and disinfection (DI BERNARDO; DANTAS, 2005). However, these technologies are not overall fully efficient in removing traces of potentially toxic metals soluble in water (FRANCISCHETTI, 2004).

The conventional treatment applied to wastewater containing metals involves physical (evaporation, reverse osmosis, ultrafiltration and distillation) and chemical (chemical precipitation, organic redox reactions, the use of ion-exchange resins and acid-base neutralization) processes. The application of these processes leads to high costs, as in the case of the membrane and ion exchange processes, and it can also introduce residues, due to oxidation and chemical precipitation, which make the treatment process even more laborious (MONTEIRO, 2009).

Wastewater containing potentially toxic metals is released into the environment without proper treatment on a daily basis, fact that leads to irreparable environmental impacts. Therefore, the use of biosorbent materials as low-cost alternative to treat such water can be environmentally, economically and socially feasible (MONTEIRO, 2009).

Potentially toxic metals, such as lead and nickel, are bio accumulative; thus, the effect on contact with these contaminates is unpredictable, since they do not decomposes (MAGRO et al., 2013).

Lead is a metal found in many industrial products such as batteries, photographic materials, paints and pigments, fuels, as well as in automotive, aeronautical and steel industries (JALALIET et al., 2002; SEKHAR et al., 2004). The main lead release forms resulting from anthropogenic activities are associated with emissions from foundries and battery factories. Water contamination often happens through industrial effluents, mainly generated by steel industries (CETESB, 2012).

According to the World Health Organization, the maximum lead concentration in water used for human consumption purposes cannot exceed 0.01 mg L⁻¹ (WHO,

2006). The chronic exposure to lead can lead to gastrointestinal, neuromuscular and central nervous system disorders, besides changing the human blood pressure and negatively affecting the liver and renal system (SCHIFER; BOGUSZ; MONTANO, 2005).

Nickel is widely used to produce stainless steel and other corrosion-resistant alloys, as well as to produce coins and batteries (UNESP, 2016), and is released into the atmosphere due to the burning of fossil fuels and the incineration of solid waste. According to Brazilian Ministry of Health, the maximum nickel concentration allowed in the water is 0.07 mg L⁻¹, in order to ensure potability standards (BRASIL, 2011). This metal is harmful to human health because it can cause lung, larynx and prostate cancer (LENNTECH, 2016).

Biosorption is an adsorption process associated with the passive bonding of metal ions through living or dead biomass (MONTEIRO; BONIOLO; YAMAURA, 2012). According to Pino (2005), the capture of metal ions by biomass is a passive and independent energy process that happens through physical-chemical interactions between the ions and the functional groups on the biomass surface.

lons are attracted to the active sites on the biomass surface, where different functional groups such as phosphate, carboxyl, sulfide, hydroxyl and amine are responsible for their interaction. This process continues until the equilibrium between captured and dissolved ions is reached (VOLESKY, 2004).

Langmuir's and Freundlich isotherms are the most used models to describe the biomass adsorption phenomenon (MOREIRA, 2010) and were used to classify physical or chemical adsorptions.

According to Moreira (2010), the Langmuir model is characterized by the monoatomic approximation to a limiting adsorption amount, which is assumed to correspond to monolayer formation. The Langmuir isotherm enables the maximum metal adsorption capacity through the biomass, whereas the K_{ads} coefficients linked to the ion-substrate interaction energy (SHUMAN, 1988).

The Langmuir Isotherm expression is given by the Equation 1.

$$q = \frac{q_{max}K_{ads}C}{1 + K_{ads}C} (1)$$

wherein:

q is the amount of adsorbate (metal) retained in the solid at equilibrium (mg g⁻¹); q_{max}is the Langmuir parameter linked to the adsorption capacity (mg g⁻¹); K_{ads}is the Langmuir constant linked to the adsorption energy (L mg⁻¹ or L mmol⁻¹); C is the ion concentration (in mg L⁻¹) in the solution at equilibrium.

 K_{ads} and q_{max} values can be graphically determined by rearranging Equation 1 into Equation 2.

 $\frac{C}{q} = \frac{1}{q_{max}K_{ads}} + \frac{C}{q_{max}}(2)$

The graphical representation of C/q is a linear function whose slope is equal to $1/(q_{max}$, whereas the intersection with the C/q axis is equal to $1/(q_{max}K_{ads})$. Therefore, the angular coefficient can be used to calculate q_{max} , which is the maximum adsorption capacity based on the monolayer coverage; based on this value, the linear coefficient can be used to calculate the value of the Langmuir adsorption constant - K_{ads} (PINO, 2005).

The Freundlich isotherm describes the equilibrium on heterogeneous surfaces; therefore, it does not assume a monolayer adsorption capacity. This isotherm suggests that the adsorbate concentration on the adsorbent material surface increases as the adsorbate concentration in the solution also increases (SUKSABYE; THIRAVETYAN; NAKBANPOTE, 2008).

The mathematical expression of the Freundlich isotherm is given by the Equation 3.

 $q = kf.X^{1/n}(3)$

Wherein:

q is the amount of adsorbate (metal) retained in the solid at equilibrium (mg g⁻¹); X is the adsorbate concentration (in mg L⁻¹) at equilibrium; K_f and n are constants. The expression in Equation 3 is often used in linear form. Thus, we have Equation 4.

$$logq = \frac{1}{n}logC + logK_f(4)$$

The graphical representation of log q is a linear function whose slope is equal to 1/n, whereas the intersection with log axis q is equal to log Kf. Therefore, the angular coefficient of the line can be used to calculate n, whereas the linear coefficient can be used to find Kf (PINO, 2005).

The pursuit of new technologies focused on treating wastewater and public water supply systems is based on the use of biomass as biosorbent material; besides, these technologies have been gaining credibility in recent years due to their good performance (MONTEIRO, 2009).

Cocos nucifera L., commonly known as green coconut, was used as biosorbent material in this study. The species is highly distributed in the Brazilian territory and is easy to produce. In addition, there is imminent need to reuse its wastes, since its material is not easily decomposed it takes more than 8 years to decompose (CARRIJO; LIZ; MAKISHIMA, 2002). The use of green coconut as biosorbent material is also justified by its high organic matter content, which is mainly composed of lignin (approximately 35% to 45%) and cellulose (approximately 23% to 43%) (CARRIJO; LIZ; MAKISHIMA, 2002).

The aim of this study was to evaluate the potential of the green coconut fiber in the biosorption of metal ions such as Pb²⁺ and Ni²⁺ in public water supply systems.

2 METHODOLOGY

2.1. Biosorbent material obtainment process

The first stage comprised the fragmentation of the biosorbent material, in which we removed the external (shell) and inner parts, as well as the chestnut, and left only the mesocarp, which is the part which contains the desired fibers (FERREIRA et al., 2012).

The mesocarp was cut into small pieces and left to dry in oven under forced air circulation at 60°C for 24 hours to reduce the initial moisture content from 85% to approximately 15-20% (ROSA et al., 2001).

Next, the material was ground using a knife mill (WillyeSTAR FT 50).

The mean particle size recorded after the fiber was ground was not greater than 1.0 mm. The powder obtained in the mill was selected in a set of 45, 60 and 80-mesh sieves -which corresponded to 0.355 mm, 0.250 mm and 0.180 mm, respectively - in order to assure a homogeneous contact surface.

2.2. Standard solutions preparation

The multielementar solutions containing the metals ions Pb²⁺ and Ni²⁺ at 200 mg.L⁻¹ was prepared using chloride salts of these metals: PbCl₂ (Vetec, 99%) and NiCl₂.6H₂O (Vetec, 99%). Next, 0.10 mol L⁻¹ of sodium hydroxide solution (Vetec, 99%) was used in the biosorbent material preconditioning step; this procedure aimed at increasing the adsorption capacity of the material (VOLESKY, 2004). Subsequently, the adsorbent material was placed in an oven under forced air circulation, at 60°C, for 3 hours.

Then, 0.10 mol L⁻¹ hydrochloric acid solution (Merck) and 0.10 mol L⁻¹ sodium hydroxide solution were used to adjust the pH. The pH values (3 to 5) were chosen based on lead (II) and nickel (II) hydroxide solubility values in order to avoid the chemical precipitation of Pb²⁺ and Ni²⁺ in the form of hydroxides.

2.3. Biosorption experiments

Biosorption experiments were performed in batches, based on the univariate method, which estimates one variable at a time. The analyzed variables was contact time (10, 25 and 40 minutes), pH (3, 4 and 5), metal concentrations (10, 55 and 100 mg L⁻¹), biomass concentrations (10, 25 and 40 g L⁻¹) and granulometry (45, 60 and 80 mesh). Biosorption experiments were carried out at constant temperature in order to find the adsorption Langmuir's and Freundlich isotherms. A BOD-type incubator (120L capacity), model SP-500/120-SPLABOR was used for temperature control purposes.

Langmuir's and Freundlich were chosen from among several possible models because its parameters have a straightforward physical and chemical interpretation.

It is worth to emphasizes that we decided to use standard solutions of low Pb²⁺ and Ni²⁺ concentrations, since the main aim of this study was to develop an alternative method to remove lead and nickel from public water supplies. This type of water presents Pb²⁺ and Ni²⁺ concentrations lower than 100 mg L⁻¹(PINO, 2005).

The fixed values applied to each variable in the univariate analysis were based on data available in the literature, which presented the best biosorption results in previous studies (FERREIRA et al., 2012; MONTEIRO, 2009; MONTEIRO; BONIOLO; YAMAURA, 2012). Thus, the fixed values were: contact time = 25 minutes, pH = 4, biomass concentration = $25g L^{-1}$, metal concentration = $100 mg L^{-1}$ and granulometry= 60 mesh.

After the analyses based on the standard multielementar solutions, two tap water samples was used to check the coconut fiber ability to remove ions from commercial water samples. The first sample comes from CODAU (Operational Center for the Development and Sanitation of Uberaba County - sanitation company); the second sample came from a tubular underground water collected at Federal University of Triângulo Mineiro (UFTM) in Uberaba County (MG). Both water samples were analyzed in order to identify the metals in them, as well as to calculate the removal rate of these metals based on the use of green coconut fiber.

2.4. Analytical metal determinations

The content of the metal species (in mg L⁻¹) was determined through air/acetylene flame atomic absorption spectrophotometry (Perkin Elmer, model ASS 3300), based on the direct and background correction method (Welz, 1985). The standards used for the calibration curves and wavelengths of each metal are presented in Table 1.

Table 1 – Atomic absorption spectrometer parameters used for Pb and Ni

determination

Parameters	Metals		
(units)	Pb	Ni	
λ (nm)	217.0	232.0	
Slot (nm)	1.0	0.5	
HCL (mA)	6	3	
Ar (L min ⁻¹)	10.0	10.0	
Acetylene (L min ⁻¹)	2.0	2.0	
Calibration curve (mg L ⁻¹)	1.0 a 10.0	0.1 a 4.0	

Source: authors

3 RESULTS AND DISCUSSION

3.1. Evaluating the biosorption potential of the coconut fiber

Ph is one of the most important parameters in the biosorption of potentially toxic metals, since metal speciation in the solution and the charge of active sites on the biosorbent material surface can vary depending on the solution pH (VOLESKY, 2004).Table 2 shows the results of Pb²⁺ and Ni²⁺ removal by the coconut fiber based on pH variation.

Table 2 - Pb^{2+} and Ni^{2+} removal efficiency based on the pH of the multielement solution

Pb ²⁺ removal (%)	Ni ²⁺ removal (%)
90.35 ± 0.23	91.05 ± 0.63
97.34 ± 0.33	95.17 ± 0.44
91.75 ± 0.27	89.12 ± 0.39
	Pb ²⁺ removal (%) 90.35 ± 0.23 97.34 ± 0.33 91.75 ± 0.27

Source: authors

According to Table 2, the highest Pb^{2+} and Ni^{2+} removal took place at pH = 4. The pH influence on the adsorption of these metal ions dues to the competition between them and H_3O^+ ions for active sites on the biomass surface (CHUBAR; CARVALHO; NEIVA, 2004).

Tuning the parameters influencing the adsorption process. In fact, the pH is an important factor, which can influence the equilibrium of a solution. By simply varying

the pH, we can lead to an adsorption or a chemical precipitation of nickel and lead contents. The Pourbaix (EH-pH) diagram is a plot of electrochemical potential versus pH, which shows the domains of various metals and the nature of this species. According to Pourbaix diagram of Lead and nickel in aqueous matrix, in the pH range used in this work, these metals are in the soluble state such as Pb²⁺ and Ni²⁺, respectively (NIKOLAYCHUK, 2018; HUANG; RONDINELLI, 2017). For that reason, we can say that in our experiments the only possible process is adsorption, which leads to a reduction in the concentration of these ions in the final solution.

Most carboxyl groups, in the biomass particles, are not dissociated at low pH values and it blocks their interaction with the metal ions in the solution, although they can participate in complexation reactions (VOLESKY, 2004).

The pH-dependence of metal ion adsorption techniques based on biomass use can be explained through the association and dissociation of some functional groups found in the matrices used in the treatment. A large number of functional groups (carboxylic acids) present negative charges and can attract positive-charge ions through electrostatic interactions when the pH value increases (CHUBAR; CARVALHO; NEIVA, 2004).

Thus, it was possible seeing that the highest removal of both lead and nickel happened at acid pH. This outcome was already expected, since Pb²⁺ and Ni²⁺ ions at basic pH react to excessive OH⁻ ions and form insoluble bases that are not adsorbed by the coconut fiber (FERREIRA et al., 2012).

The particle size of the coconut shell fiber powder is one of the investigated parameters to be applied to the adsorption of metal ions, since granulometry has strong influence on the number of active adsorption sites on the biosorbent material surface; moreover, several materials present better adsorption capacity when they have larger contact surfaces. Thus, the contact surface between sorbent material and the liquid phase (solvent) also plays a key role in the adsorption process (TARLEY; ARRUDA, 2004).

Table 3 presents the results of Pb²⁺ and Ni²⁺ removal efficiency by the coconut fiber based on granulometry variation.

Granulometry (mesh)	Pb²⁺removal (%)	Ni ²⁺ removal (%)
45	88.15 ± 0.29	85.69 ± 0.16
60	97.42 ± 0.19	95.39 ± 0.23
80	91.21 ± 0.32	93.22 ± 0.33

Table 3- Pb ²⁺ and Ni ²⁺ removal efficience	y based ongranulometry
---	------------------------

Source: authors

Based on the joint analysis applied to the results shown in Table 3, the highest removal of both metal ions took place at 60-mesh granulometry. The Pb²⁺ ion removal was slightly higher than that of Ni²⁺ at the three granulometries analyzed in our study. It happened because these ions have different ionic radius sizes: the ionic radius of Pb²⁺ is larger than that of Ni²⁺; consequently, the potential solvation energy of these ions in aqueous medium is also different, since such energy is inversely proportional to the square of the ionic radius (FERREIRA et al., 2012).Therefore, Ni²⁺ ions present lower ionic mobility - i.e., they are more solvated -under higher solvation energy; consequently, they are less attracted to the active sites of the coconut fiber.

According toVolesky (1994), there is increased adsorption of smaller particles when the metal ion adsorption to a solid adsorbent material is based on the adsorption to the particle surface. On the other hand, when this process is attributed to the mass transfer into sorbent particles, larger spherical-shaped particles overall present higher adsorption.

Table 4 presents the results of Pb²⁺ and Ni²⁺ removal efficiency by the coconut fiber based on biomass concentration variations.

Table 4 - Pb ²⁺ and Ni ²⁺ remova	l by the coconut f	fiber based on biomass	concentration
--	--------------------	------------------------	---------------

Biomass concentration (g L ⁻¹)	Pb ²⁺ removal (%)	Ni ²⁺ removal (%)
10	92.11 ± 0.19	90.17 ± 0.21
25	97.54 ± 0.12	95.20 ± 0.19
40	94.90 ± 0.10	92.89 ± 0.17

Source: authors

Based on results presented in Table 4, the 25 g L⁻¹biosorbent material concentration was sufficient to enable the maximum Pb²⁺ and Ni²⁺ removal under the herein set experimental conditions.

According to VOLESKY (2004), the initial biomass concentration must be evaluated to help determining the minimum amount of necessary adsorbent material to enable the maximum removal of metal ions, since this item has strong influence on the costs with treatments applied to water supply systems.

Experiments were also carried out to evaluate the biomass adsorption potential based on different initial concentrations (10 mg.L⁻¹, 55 mg L⁻¹ and 100 m L⁻¹) of multielement solutions containing Pb²⁺ and Ni²⁺. Results are presented in Table 5.

Table 5 - Pb²⁺and Ni²⁺removal by the coconut fiber based on initial metal concentrations

Initial Pb ²⁺ and Ni ²⁺ concentration (mg L ⁻¹)	Pb²+removal (%)	Ni ²⁺ removal (%)
10.01 ± 0.09	93.91 ± 0.12	92.65 ± 0.11
55.32 ± 0.06	95.14 ± 0.15	94.56 ± 0.12
100.06 ± 0.09	97.10 ± 0.13	96.43 ± 0.15

Source: authors

Based on results in Table 5, there was high proportion between the number of active sites in the biomass and the ions at low initial Pb²⁺ and Ni²⁺concentrations in the solution. The removal efficiency increased as the initial ion concentration also increased because the active sites on the biosorbent surface are not fully saturated.

In addition, the biosorption efficiency of the green coconut shell fiber increased as the initial metal ion concentration in the solution also increased; such efficiency did not decrease due to saturation. This outcome evidences that the maximum metal ion concentration used in the experiment (100 mg L⁻¹) did not saturate the active sites of the coconut fiber under the herein applied experimental conditions.

With respect to variable contact time', absorption efficiency directly depended on stirring time, and indirectly depended on contact time, to find the equilibrium. The remaining adsorbate concentration in the solution decreased with time until it reached a constant value beyond which there was no further adsorbate removal from the solution. From this point on, the ion amount adsorbed by the biosorbent was in dynamic equilibrium with the desorbed amount. The necessary time to reach such state is known as equilibrium time (MONTEIRO; BONIOLO; YAMAURA, 2012). Results are shown in Table 6.

|--|

Contact time (min)	Pb ²⁺ removal (%)	Ni ²⁺ removal (%)
10	70.41 ± 0.18	65.76 ± 0.10
25	97.83 ± 0.16	94.33 ± 0.14
40	96.26 ± 0.17	95.10 ± 0.12

Source: authors

The adsorption equilibrium was hit quickly, since theNi²⁺ and Pb²⁺ ion removal reach close values for contact times of 25 and 40 minutes. Thus, the contact time of 25 minutes would be sufficient to enable efficient metal removal in the order of 95-97%. The shorter mechanical stirring time favored the economic viability of the process due to lower electric power consumption.

3.2.Adsorption isotherms

Variables such as contact time, pH, granulometry, biomass concentration and metal concentration, and their respective values, were applied to the Langmuir and Freundlich models, using their linearized equations - Equations 2 and 4, respectively.

Adjustment was applied to the central points of each variable, namely: contact time (25 minutes), particle size (60 mesh), optimum pH (4), biomass concentration (25 g L⁻¹) and metal concentration (55 mg L⁻¹), since we intended to work with the optimal point of each variable. Table 7 shows Langmuir and Freundlich constants deriving from the isotherms and the correlation coefficients.

Table 7 - Ni²⁺ and Pb²⁺ adsorption constants in green coconut fiber powder

Metal	Langmuir			Freundlich		
	q _{max} (mg. g ⁻¹)	K _{ads} (L.mg ⁻	R ²	K _f (L. mg ⁻¹)	n	R ²

		¹)				
Pb	16.429	0.995	0.7996	26.011	6.399	0.9989
Ni	15.886	0.817	0.8498	27.028	5.709	0.9979

Source: authors

Based on values presented in Table 7, the application of experimental data about metal species (lead and nickel) to Langmuir and Freundlich adsorption models showed more satisfactory results in the Freundlich model, whose coefficient of determination (R²)recorded values higher than 0.99.

Constant n was the Freundlich parameter associated with the biomass adsorption surface or the constant indirectly associated with the material type. Values close to n recorded for the two isotherm models can be explained by the use of coconut fiber as biosorbent material in both cases.

With respect to the Freundlich isotherms, high Kf values recorded for both metal species showed that the metals were easily physically adsorbed by the coconut fiber (PINO, 2005).

Coefficients Kf and n are the best descriptive parameters to be applied when there is no consistent evidence on the nature of the adsorption mechanisms, (BUCHTER et al., 1989). Variations in the n values of the Freundlich isotherm show that the elements were adsorbed at different energy levels (BUCHTER et al., 1989; SOARES; SOUZA; CAVALHEIRO, 2004).

3.3.Coconut fiber application to treat water from public supply systems

In order to verify the efficiency of the optimized process (biomass concentration = 25 g L⁻¹, granulometry = 60 mesh, pH = 4 and contact time = 25 minutes) for metals removal in public water, coconut fiber was used to purify two samples: one of tap water and another groundwater, city from Uberaba, Brazil. The Table 8 shows the metal ions content in the samples without treatment and after the adsorption process using coconut fibers.

Table 8 -Metal removal from water samples collected in the CODAU network and in the UFTM well, based on the use of coconut fiber under optimized experimental conditions

Metals	Concentration in CODAU water (mg L ⁻¹)	Metal removal (%)	Concentration in the underground water (mg L ⁻¹)	Metal removal (%)
Fe	5.23 ± 0.07	92.31± 0.19	2.35± 0.06	83.71± 0.13
Ca	10.42± 0.09	84.18± 0.19	110.19± 0.04	91.13± 0.15
Mg	47.55± 0.05	85.14± 0.16	90.36± 0.06	87.33± 0.17
Pb	0.71± 0.07	91.75± 0.15	0.51± 0.05	93.52± 0.15
Zn	0.04± 0.04	90.35± 0.14	0.13± 0.07	85.39± 0.14
Ni	0.13± 0.06	90.31± 0.16	0.11± 0.07	91.51± 0.19

Source: authors

According to data presented in Table 8, the lead and nickel removal in the two analyzed water samples was higher than 90%. However, this value was lower than the Pb²⁺ and Ni²⁺ ion removal values recorded in previous experiments (univariate optimization). It happened due to competition between several ions found in these water samples for the active sites of the coconut fiber (FERREIRA et al., 2012).

Our results are corroborated by YU et al. (2014), who recently reported that tree leaf remnants presented relative selectivity as adsorbents in the presence of multielement solution. Based on their results, modified leaf remnants presentediondependent selectivity: $Cu^{2+} > Cd^{2+} > Zn^{2+}$.

Moreover, Qi and Picler (2016) reported selectivity when a solution containing both Sb (III) and Sb (V) ions was exposed to adsorbent material such as hydrated (Fe(OH)O) iron (III) oxide. The occurrence of Sb (V) did not influence Sb (III) adsorption. However, Sb (V) adsorption was significantly inhibited by Sb (III) at pH=4.

We could not determine the order of selectivity in our experiments, but we can say that coconut fiber satisfactorily removed several ions, simultaneously, found at trace concentrations in the water from the public supply system.

4 CONCLUSIONS

Coconut fiber can be applied under optimized experimental conditions to remove potentially toxic metals from supply water. The Freundlich model presented the best fit to the experimental data; adsorption can be characterized as physical. Based on the mentioned above, we can say that the green coconut shell powder is an effective adsorbent with potential to adsorb metals - such as nickel and lead - found in the water from supply systems. The use of this biosorbent material to remove metal species found at trace concentrations in public water supply systems is a method that corroborates environmental and economic sustainability strategies, since coconut fiber is a low-cost and nationally-abundant renewable material sometimes discarded as waste.

ACKNOWLEDGEMENT

The authors would like to thank the Brazilian funding agencies: FAPEMIG, CAPES and CNPq for partial financial support.

REFERENCES

BRASIL; Ministério da Saúde. Portaria Nº 2914/11 - **Dispõe sobre os procedimentos de controle e de vigilância da qualidade da água para consumo humano e seu padrão de potabilidade.** Brasília (Brasil): Ministério da Saúde; 2011.

BUCHTER B, DAVIDOFF B, AMACHER M.C, HINZ C, ISKANDAR IK., SELIM HM. Correlation of Freundlich Kd and n retention parameters with soils and elements. Soil Sci. 1989;148 (5):370-379.

CARRIJO O A, LIZ RS, MAKISHIMA N. **Fibra da casca do coco verde como substrato agrícola.** Horticultura Brasileira. 2002; 20 (4):533-535.

CETESB [Internet]. **São Paulo: Companhia Ambiental do Estado de São Paulo (BR)** [cited 20 mar 2018]. Ficha de informação toxicológica:chumbo. 2012. Available from: https://cetesb.sp.gov.br/laboratorios/wpcontent/uploads/sites/24/2013/11/Chumbo.pdf

CHUBAR N, CARVALHO J, CORREIA MJN. **Heavy metals biosorption on cork biomass: effect of the pre-treatment.** Colloids Surf A Physicochem Eng Asp. 2004; 238(1-3):51-58.

DI BERNARDO L, DANTAS A D B. **Métodos e técnicas de tratamento de água.** 2st ed.. São Carlos: Rima, 2005.

FERREIRA D C, SILVA NA, LIMA AF, BEGNINI ML. **Biossorção de chumbo e níquel pelas fibras do** *Cocos Nucifera* **L.** Fazu em Revista. 2012; 18(9):64-68.

FRANCISCHETTI J. **Remoção de Metais Pesados em Efluentes Líquidos Através da Filtração Adsortiva, em Florianópolis/SC** [dissertation]. Florianópolis: Universidade Federal de Santa Catarina/UFSC; 2004. 91 p.

HUANG LF, RONDINELLI JM. Electrochemical phase diagrams of Ni from ab initio simulations: role of exchange interactions on accuracy. J. Phys. Condens. Matter. 2017; 29: 1-12.

JALALI R, GHAFOURIAN H, ASEF Y, DAVARPANAH SJ, SEPEHR S. **Removal and recovery of lead using nonliving biomass of marine algae.** J. Hazard. Mater. 2002; B92: 253-262.

MAGRO C D, DEON MC,THOMÉ A, PICCIN JS, COLLA LM. **Biossorção passiva de Cromo (IV) através da microalga** *Spirulinaplatensis***.** Quím. Nova. 2013; 32 (8): 1-7.

MONTEIRO R A. **Avaliação do potencial de adsorção de U, Th, PB, Zn Ni pelas fibras do coco, em São Paulo/SP** [dissetation]. São Paulo: Instituto de Pesquisas Energéticas e Nucleares/ Área de Tecnologia Nuclear - materiais; 2009. 86 p.

MONTEIRO R A, BONIOLO M. R, YAMAURA M. **Uso das Fibras de Coco na Biossorção de Chumbo em Águas Residuárias Industriais.** São Paulo: Instituto de Pesquisas Energéticas e Nucleares - Ipen, 2012. 15 p.

MOREIRA DR. Desenvolvimento de adsorventes naturais para tratamento de efluentes de galvanoplastia, em Porto Alegre/RS [dissertation].Porto Alegre: PontíficaUniversidade Católica do Rio Grande do Sul/PUCRS; 2010. 79p.

NIKOLAYCHUK PA. **The revised-pH diagram for Pb-H₂O system.** Ovid.University Annals of Chemistry. 2018; 29 (2): 55-67.

PINO GAH. **Biossorção de metais pesados utilizando pó da casca de coco verde** (**Cocos nucífera**), **em Rio de Janeiro/RJ** [dissertation]. Rio de Janeiro: Pontífica Universidade Católica do Rio de Janeiro/PUC-Rio; 2005. 128 p.

QI P, PICHLER T. Sequential and simultaneous adsorption of Sb(III) and Sb(V) on ferrihydrite: Implications for oxidation and competition. Chemosphere. 2016; 145: 55-60.

ROSA M F, SANTOS FJS, MONTENEGRO AAT, ABREU FAP, CORREIA D, ARAÚJO FBS, NOROES ERV. **Caracterização do pó da casca de coco verde usado como substrato agrícola.** Fortaleza: Embrapa Agroindústria Tropical, 2001. 6 p.

SEKHAR KC, KAMALA CT, CHARY N, SASTRY ARK, NAGESWARA R, VAIRAMANI M. **Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass.** J. Hazard Mater. 2004;B108:111-117.

SCHIFER T S, BOGUSZ S J, MONTANO M A E. **Aspectos toxicológicos do chumbo.** Infarma, 2005; 17:67-71.

SHUMAN LM. Effect of organic matter on the distribution of manganese, copper, iron, and zinc in soil fractions. Soil Sci. 1988; 146: 192-198.

SOARES JP, SOUZA JA, CAVALHEIRO ETG. Caracterização das amostras comerciais de vermicomposto de esterco bovino e avaliação da influência do pH e do tempo na adsorção de Co (II), Zn (II) e Cu (II). Quím. Nova. 2004; 27(1): 5-9.

SUKSABYE P, THIRAVETYAN P, NAKBANPOTE W. Column study of chromium (VI) adsorption from electroplating industry by coconut coir pith. J. Hazard Mater.2008;160 (1): 56-62.

TARLEY CR, ARRUDA MA. **Biosorption of heavy metals using rice milling byproducts.** Characterization and application for removal of metals from aqueous effluents, Chemosphere. 2004; 54: 987 -995.

LABORATÓRIO VIRTUAL DE QUÍMICA [Internet]. **São Paulo: Universidade Estadual Paulista (BR)** [cited 03 mar 2018]. Publicações. 2017. Available from: https://cti.feb.unesp.br/#!/pesquisa-extensao/publicacoes/

VOLESKY B. Advances in biosorption of metals: selection of biomass types. Microbiology Reviews. 1994; 14: 291 -302.

VOLESKY B. **Detoxification of metal-bearing effluents: biosorption for the next century.** Hydrometallurgy. 2001; 59(2-3): 203-216.

WELZ B. Atomic Absorption Spectrometry, Second Completely Revised Edition, VCH Verlagsgesellschaft mbH, Weinheim 1986: 506p. Seiten, Preis: DM 160—

WHO - WORLD HEALTH ORGANIZATION. **Guidelines for drinking-water quality.** (3. ed.). Geneva. 2006;1: 536p.

YU JX, FENG L Y, CAI XL, WANG LY, CHI RA. **Adsorption of Cu²⁺, Cd²⁺ and Zn²⁺ in a modified leaf fixed-bed column: competition and kinetics.** Environ Earth Sci. 2014;73:1789–1798.