

DEVELOPMENT AND ANALYSIS OF AN ALTERNATIVE METHOD FOR REMOVING POTENTIALLY TOXIC METALS FROM WATER USING SORBENT MATERIALS**B. B. CANELHAS¹, A. DE CAMPOS, D. C. FERREIRA, V. C. ROCHA, C. POLETO, M. S. DA LUZ, J. C. S. I. GONÇALVES***Universidade Federal do Triângulo Mineiro (UFTM)
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ABSTRACT

The current work presents the use of a sorbent material to develop an alternative method for removing lead and barium from public water supplies. The sorbent material used was coconut fiber, which in addition to mitigating environmental pollution by reusing discarded waste, aids in the treatment of public water supplies by removing potentially toxic ions where conventional methods are not effective. In the alternative method used, we have a system of fixed bed reactors connected in series, with a volume of 0.250 L in each reactor. To characterize the adsorption process, we analyzed the variables pH, contact time, initial metal concentration, concentration of the sorbent material, and flow rate. Analysis of variance (ANOVA), multivariate analysis of variance

(MANOVA), and the T-test were carried out. The parameters initial metal concentration and flow rate were shown to be non-significant for the confidence interval adopted in the conditions of the current work. The removal of Pb²⁺ and Ba²⁺ ions was greater than 60% in all the parameters studied, and in a single pass through the reactors, showing the viability of this procedure. Coconut fiber presented appropriate characteristics for the biosorption of lead and barium ions, constituting a sustainable and promising process to be used together with classical water treatment processes to remove potentially toxic metals.

KEYWORDS: Environment pollution, Alternative sorbent materials, Metals.**DESENVOLVIMENTO E ANÁLISE DE UM MÉTODO ALTERNATIVO PARA REMOÇÃO DE METAIS POTENCIALMENTE TÓXICOS DA ÁGUA EMPREGANDO MATERIAIS SORVENTES****RESUMO**

O presente trabalho apresenta a utilização de material sorvente para o desenvolvimento de um método alternativo para remoção de chumbo e bário das águas de abastecimento público. O material utilizado foi a fibra de coco que além de mitigar a poluição ambiental pela reutilização de resíduos descartados auxiliam o tratamento das águas de abastecimento público pela remoção de íons potencialmente tóxicos. No método utilizado temos um sistema de reatores de leito fixo ligados em série, com volume de 0,250 L em cada reator. Para caracterização do processo de adsorção, foram analisadas as variáveis pH, tempo de contato, concentração inicial do metal, concentração do material

sorvente e vazão. Realizou-se a análise de variância (ANOVA), análise multivariada da variância (MANOVA) e teste-T. Os parâmetros concentração inicial do metal e vazão mostraram-se não significativos para o intervalo de confiança adotado nas condições do trabalho. As remoções dos íons Pb²⁺ e Ba²⁺ foram superiores a 60%, dentro de todos os parâmetros estudados e em uma única passagem pelos reatores, mostrando a viabilidade deste procedimento. A fibra de coco apresentou características apropriadas para o processo de biossorção dos íons chumbo e bário, constituindo como um processo sustentável e promissor para ser empregado juntamente com os processos clássicos de tratamento de água.

Palavras chave: Poluição ambiental, Materiais sorventes alternativos, Metais.

1 INTRODUCTION

The entire world is facing a serious water crisis due to the very rapid growth of the world population and also due to the high consumption of large quantities of this resource by industries, agricultural activities, and for domestic use. Fresh water is of fundamental importance for all living beings, as it is the main source of health, food, and energy generation (EL-AMIER et al., 2021).

Several pollutants are released daily into water resources, leading to widely varying undesirable effects on the environment. Among these pollutants, we can highlight potentially toxic metals, originating from different industrial activities, such as tanning, plastics, paper and cellulose production, textiles, pharmaceuticals, ferrous industries, oil refineries, and battery production, among others, in addition to being the result of disorderly population growth. These potentially toxic metals can be absorbed directly or indirectly by plants, aquatic animals, and humans, having a strong tendency to bioaccumulate, and triggering several harmful effects (DE SÁ COSTA et al., 2021; LAKSHMI et al., 2021).

Different techniques have been used to remove pollutants, including potentially toxic ions, from public water supplies. In addition to conventional water treatment, which is not effective for heavy metals, other processes have been investigated, such as biodegradation (enzymatic and microbial), electrochemical processes, advanced oxidation processes, reverse osmosis, chemical precipitation, ultrafiltration, and separation membranes. However, these processes have limited applicability due to their high operational, practical, and economic costs and also due to the incomplete removal of potentially toxic metals and large waste generation (GIRISH et al., 2012; JAAFER et al., 2021).

In this context, biosorption presents itself as a viable method for removing potentially toxic metals from public water supplies due to its effectiveness, availability, and low cost (BABEL; KURNIAWAN, 2004; FAROOQ et al., 2010; Paz et al., 2018; Antunes et al.; SHEIKH, et al., 2021). We can also highlight biosorption as a very promising technique for recovering potentially toxic metals, as it avoids the formation of chemical sludge, mitigating environmental pollution (HEILMANN et al., 2021).

The biosorption process consists of a reversible reaction between an adsorbent material and the adsorbed material (adsorbate), which allows its constant reuse after the desorption process in a sustainable way (SANTOSH et al., 2017). Biosorption is based on the capacity of the most varied materials to adsorb heavy metals, due to their ability to bind to potentially toxic ions through the mechanism of ion exchange, electrostatic force, and microprecipitation (ACHEAMPONG et al., 2015).

Several materials with adsorption capacity are already used industrially, such as activated carbon, but they are considered very expensive to be used on large scales (KRIKA et al., 2021).

Another important point is the need to reduce the environmental impact arising from enormous amounts of waste, and this has led researchers to seek and use other materials for the biosorption process, such as palm seed tegument (RENGARAJ et al., 2002), bamboo (HAMEED et al., 2007), corn cob (TSENG et al., 2005), beet pulp and coconut husk (DURSUN et al., 2005), rice

straw (DAIFULLAH et al., 2007), and coffee and banana peel (GETACHEW et al., 2015), among others. It should be noted that agro-industrial waste, rich in lignocellulosic materials, is also considered a serious environmental problem, as it takes a long time to decompose in landfill sites (GOLVEIA et al., 2021).

Cocos nucifera Linn, popularly known as the coconut tree, coconut palm, coco nult palm, and also as green coconut, is one of the most widespread fruit trees (FERREIRA et al., 2012). Worldwide, more than 90 countries produce around 60 million tons of this fruit per year (GEORGE; TEMBHURKAR, 2019). Taking into account the significant lignocellulosic proportions of *Cocos nucifera* L, it is believed that the fibers obtained from this fruit present good adsorption capacity (DARLA; GARIMELLA, 2019). Other points highlighted are its low cost, high availability for use, and stability, facts that enhance its use as a sorbent material (HYMAVATHI; PRABHAKAR, 2017).

The present work also proposes an alternative and complementary method to conventional water treatments, which are not satisfactory for removing potentially toxic metals, using a system of fixed bed reactors with continuous flow connected in series. This system was duly studied, in relation to several work factors, and was shown to be capable of being used in real conditions of use, after the necessary adjustments.

2 MATERIALS AND METHODS

The adsorbent material used was green coconut fiber, which was fragmented, removing the epicarp (external part or shell), the endocarp (nut), and the albumen (solid). Only the mesocarp remained, from which we obtained the fibers by manual fragmentation (FERREIRA et al., 2012). The coconut fibers were placed to dry in an oven with forced air circulation at a temperature of 60°C, for a period of 24 hours, to reduce the initial humidity (around 85%) to values close to 15% or even constant mass (ROSA et al., 2001). Afterwards, the fibers were treated with Sodium Hydroxide, NaOH (Sigma-Aldrich, 98%) 0.1 mol L⁻¹ solution for a period of 3 hours at room temperature. This procedure aimed to increase the adsorption capacity of the material, as this feature leaves the active sites with negative charges (PINO; TOREM, 2011). After this period, the coconut fibers were washed with distilled water until neutral (pH = 7) and dried in an oven at 60 °C for 24h.

The mono- and multi-elemental solutions of metal ions used in the aforementioned work (Pb²⁺ and Ba²⁺) were prepared using the salts of lead II acetate, Pb (H₃CCOO)₂ (MERCK, 99%) and barium nitrate, Ba(NO₃)₂ (MERCK, 99%). All solutions prepared used distilled water, with conductivity less than 3.0 μS cm⁻¹.

To optimize the removal of potentially toxic metals, an experimental system was developed, consisting of fixed-bed reactors with continuous flow and a circular section, made of acrylic. The reactors have a height of 14.50 cm and an internal diameter of 4.70 cm, with an internal volume of approximately 250 mL (0.250 L). The system was installed on a wooden support with clamps. This configuration allows the installation of reactors in series to optimize results in the adsorption process.

Figure 1a presents the aforementioned fixed bed reactor and Figure 1b presents the system of fixed bed reactors connected in series in operation.

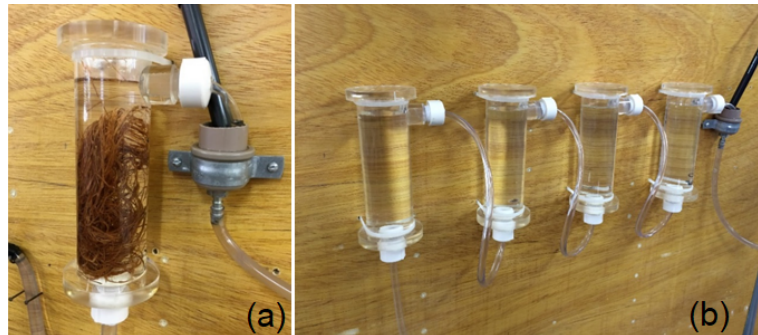


Fig. 1. a) Fixed bed reactor with continuous flow with coconut fiber. b) Fixed bed reactor system with continuous flow in series.

The reactors were fed with solutions containing the metals Pb^{2+} and Ba^{2+} using a Grundfos DDA dosing pump.

The experiments were carried out in a fixed bed reactor with continuous flow (Figure 1), following the univariate method, which involves the estimation of one variable at a time. The variables studied were: pH, contact time (min.), concentration of the sorbent material ($g L^{-1}$), initial metal concentration ($mg L^{-1}$), and flow rate ($L \cdot h^{-1}$) for the metal ions lead (Pb) and barium (Ba). Regarding univariate analyses, the fixed values used in each parameter were chosen according to data obtained in the literature (FERREIRA et al., 2012).

The values used in each parameter are described in Table 1.

Table 1: Values of the parameters used in the experiments.

Parameters	Values Applied					
pH	0.5	1.0	2.0	3.0	5.0	5.5
Contact time (min.)	5.0	10.0	30.0	50.0	60.0	-
Concentration ($g L^{-1}$)	2.0	8.0	12.0	16.0	24.0	32.0
Metal concentration ($mg L^{-1}$)	2.5	5.0	45.0	85.0	100.0	-
Flow rate ($L h^{-1}$)	2.0	3.0	4.0	6.0	10.0	12.0

The volume of solution used in all experiments was 400 mL, as this volume provides the greatest agitation allowed in the system. All experiments and all parameters were carried out in triplicate, therefore the results presented correspond to the means obtained with their respective standard deviations. For each parameter analyzed, the system was cleaned so that there was no contamination of subsequent samples.

The quantification of potentially toxic metal ions in all experiments carried out was performed by microwave-induced plasma atomic emission spectrometry (MP-AES 4200 Agilent) with a plasma gas flow of $20 L \cdot min^{-1}$ and an auxiliary gas flow of $1.5 L \cdot min^{-1}$. The nebulizer gas flow is controlled by a computer through precise mass flow control in the range of $0.3 - 1.0 L \cdot min^{-1}$. All readings were performed in triplicate. To analyze the Pb^{2+} ion, we performed measurements in $\lambda = 283.305 nm$ while for the Ba^{2+} ion we carried out measurements in $\lambda = 553.548 nm$.

3 RESULTS AND DISCUSSION

Table 2 presents the final concentrations (C_f) and removal percentages (%) for Ba^{2+} and Pb^{2+} ions with the variation in the pH parameter. To carry out this experiment, the initial concentration of metals was set at 45 mg L⁻¹, contact time was 30 min, the concentration of the sorbent material was 12 g L⁻¹, and the flow rate in the system was 3 L h⁻¹.

Table 2: Final concentrations and removal percentages of Ba^{2+} and Pb^{2+} ions in the analysis of the pH parameter.

pH	Ba^{2+} (553.548 nm)		Pb^{2+} (283.305 nm)	
	C_f (mg L ⁻¹)	%	C_f (mg L ⁻¹)	%
0.5	33.44 ± 0.14	25.70	31.82 ± 0.14	29.30
1.0	35.69 ± 0.03	20.70	30.42 ± 0.05	32.41
2.0	33.40 ± 0.55	25.78	25.75 ± 0.73	42.78
3.0	11.20 ± 0.33	75.11	18.40 ± 2.04	59.11
5.0	10.45 ± 0.51	76.78	18.85 ± 2.72	58.11
5.5	9.92 ± 0.18	77.97	13.01 ± 0.46	70.92

The data obtained from Table 2 present the best removal percentage results at higher pH values for the Ba^{2+} and Pb^{2+} ions. At low pH values, several functional groups, in coconut fiber highlighting the carboxyl and hydroxyl groups, are not ionized, that is, they do not present a negative charge in their active sites and consequently their attraction to the positive charges of metal ions is reduced. Increases in pH lead to an increase in functional groups with a negative charge and a consequent increase in the attraction of positive charges from metal ions (SELATNIA et al., 2004). It has been found that pH values between 3 and 5 proved to be more satisfactory in removing toxic ions.

Final concentrations (mg L⁻¹) and the removal percentages (%) for the Ba^{2+} and Pb^{2+} ions in the variation of the contact time parameter (min) are presented in Table 3. To carry out this experiment, the initial concentration of metals was set at 45 mg L⁻¹; pH = 3.0 (optimal situation for this parameter), the concentration of the sorbent material was 12 g L⁻¹, and the flow rate in the system was 3 L h⁻¹.

Table 3: Final concentrations and removal percentages of Ba^{2+} and Pb^{2+} ions in the analysis of the contact time parameter.

Contact Time (min)	Ba^{2+} (553.548 nm)		Pb^{2+} (283.305 nm)	
	C_f (mg L ⁻¹)	%	C_f (mg L ⁻¹)	%
5.0	18.25 ± 0.20	59.44	23.05 ± 0.08	48.78
10.0	20.75 ± 0.91	53.88	25.65 ± 0.16	43.00
30.0	11.20 ± 0.33	75.11	18.40 ± 2.04	59.11
50.0	8.90 ± 0.32	80.22	17.40 ± 0.46	61.33
60.0	6.34 ± 0.11	85.92	9.89 ± 0.35	78.04

It can be observed that the longer the contact time of the sorbent material, the greater the percentage of metal ion removal. It should be noted that other factors influence the removal efficiency, including particle size, ion concentration in the solution, and the properties of the adsorbent material (OLIVEIRA, 2011).

Times longer than those used in the current work would result in a high energy demand, which would make its practical use in real situations unfeasible, since reductions in the energy used is, without a doubt, one of the main factors for energy efficiency (GASPAR, 2004).

Table 4 presents the final concentrations (mg L^{-1}) and removal percentages (%) for the Ba^{2+} and Pb^{2+} ions in the variation of the initial metal concentration parameter (mg L^{-1}). For this experiment, $\text{pH} = 3.0$ was used, a contact time of 30 min, the concentration of the sorbent material was 12 g L^{-1} , and the flow rate in the system was 3 L h^{-1} .

Table 4: Final concentrations and removal percentages of Ba^{2+} and Pb^{2+} ions in the analysis of the initial metal concentration parameter.

Initial Concentration (mg L^{-1})	Ba^{2+} (553.548 nm)		Pb^{2+} (283.305 nm)	
	C_f (mg L^{-1})	%	C_f (mg L^{-1})	%
2.5	0.67 ± 0.08	73.40	0.85 ± 0.08	66.0
5.0	1.87 ± 0.16	62.70	3.12 ± 0.012	37.70
45.0	11.20 ± 0.33	75.11	18.40 ± 2.04	59.11
85.0	26.10 ± 0.53	69.30	42.85 ± 0.59	49.59
100.0	25.75 ± 0.32	74.25	36.59 ± 0.33	63.42

The analysis of the data obtained suggests that other factors are influencing the removal percentage of potentially toxic ions, since it was not possible to establish a direct relationship between changes in the initial concentrations of metals and their removal percentage or even that the change in this factor does not result in significant changes in working conditions. In solutions with lower concentrations of ions, it is expected that the time for saturation of active sites and consequent formation of equilibrium to occur will be shorter, increasing the removal percentage (ARPA et al., 2000).

Final concentrations (mg L^{-1}) and the removal percentages (%) for ions Ba^{2+} and Pb^{2+} in the variation of the concentration parameter of the sorbent material (g L^{-1}), with $\text{pH} = 3.0$, initial concentration of metals was set at 45 mg L^{-1} ; the contact time was 30 min, and the flow rate in the system was 3 L h^{-1} , as presented in Table 5. It is observed that the increase in the concentration of the sorbent material resulted in higher removal percentages for the analyzed ions. It should be noted that the adsorption capacity is related to the contact area present in the material and, consequently, to the characteristics of the sorbent material itself (AHMARUZZAMAN, 2011).

Table 5: Final concentrations and removal percentages of Ba^{2+} and Pb^{2+} ions in the analysis of the concentration parameter of the sorbent material.

Material Sorbent Concentration (g L^{-1})	Ba^{2+} (553.548 nm)		Pb^{2+} (283.305 nm)	
	C_f (mg L^{-1})	%	C_f (mg L^{-1})	%
2.0	31.00 ± 0.29	31.11	31.30 ± 0.30	30.44
8.0	18.20 ± 0.53	59.56	18.05 ± 0.52	59.89
12.0	11.20 ± 0.33	75.11	18.40 ± 2.04	59.11
16.0	8.85 ± 0.41	80.33	13.80 ± 0.48	69.33
24.0	7.25 ± 0.27	83.89	13.40 ± 0.46	70.22
32.0	7.68 ± 0.56	82.93	$8,99 \pm 0.45$	80.33

Final concentrations (mg L^{-1}) and removal percentages (%) for Ba^{2+} and Pb^{2+} ions when varying the flow rate parameter (L h^{-1}), $\text{pH} = 3.0$ (see Table 6; the initial concentration of metals

was set at 45 mg L⁻¹, the contact time was 30 min, and the concentration of the sorbent material was 12 g L⁻¹) suggest that other factors are influencing the removal percentage of potentially toxic ions, since it was not possible to establish a direct relationship between the change in flow rate and a significant change in the removal percentage under working conditions or even that the change in this factor does not result in significant changes in working conditions.

Flow rate values much lower than those used in the aforementioned work can lead to the process being too slow, making its practical application impossible, while values higher than those also used in these analyses lead to a sharp drop in the retention of these ions, due to the failure to establish the adsorption equilibrium in the reactor (LIMA et al., 2008). Guinesi et al, 2007 observed an increase in flow rate favoring the adsorption of Cu²⁺ ions against chitosan, as the flow supplied the system with a high amount of ions, keeping the active sites saturated. Therefore, the increase in flow rate, in quantitative terms, favored the metal removal capacity of chitosan (GUINESI et al., 2007).

Table 6: Final concentrations and removal percentages of Ba²⁺ and Pb²⁺ ions in the analysis of the flow parameter.

Flow rate (L h ⁻¹)	Ba ²⁺ (553.548 nm)		Pb ²⁺ (283.305 nm)	
	C _f (mg L ⁻¹)	%	C _f (mg L ⁻¹)	%
2.0	17.05 ± 0.06	62.11	17.89 ± 0.38	60.25
3.0	11.20 ± 0.33	75.11	18.40 ± 2.04	59.11
4.0	13.93 ± 0.37	69.06	18.15 ± 0.09	59.67
6.0	11.20 ± 0.28	75.11	18.90 ± 0.51	58.00
10.0	11.25 ± 0.45	75.00	16.70 ± 0.99	62.89
12.0	11.95 ± 0.33	73.44	14.90 ± 0.18	66.89

For the studied parameters, the Kolmogorov-Smirnov test of adherence to normality (KS test) was carried out and then an analysis of variance (ANOVA) to verify the significance of the parameters in the aforementioned study.

The main statistical tests assume the normality of the data used, a fact previously verified by the KS test. Normal distribution is required to carry out various statistical inferences, such as the Student's t-test, which are classified as parametric tests, that is, they require a specific probability distribution for the random variable, in this case normal distribution (TORMAN et al., 2012).

The Kolmogorov-Smirnov test, as well as other adherence verification tests, have in common the verification of the hypotheses: the null hypothesis is that the analyzed variable adheres to the normal distribution and the alternative hypothesis that the analyzed variable does not adhere to the normal distribution. This verification is carried out by observing the p-value and comparing it with the adopted significance level. If the p-value of the aforementioned test is lower than the significance level, the normality hypothesis is rejected (THODE, 2002).

After performing the Kolmogorov test, we concluded that the null hypothesis cannot be rejected and that the samples approximate a normal distribution (p-value > α). The use of data that do not adhere to normality generates high and unreliable measures of dispersion, which do not help the evaluation of the analyses (LOPES et al., 2013). Table 7 presents the results obtained in the analysis of variance (ANOVA) for Ba²⁺ and Pb²⁺ ions in the analyzed parameters.

Table 7: Analysis of variance (ANOVA) for Ba²⁺ and Pb²⁺ ions.

Parameters	Ba ²⁺			Pb ²⁺		
	F	Value - p	F critical	F	Value - p	F critical
pH	166.9314	1.167x10 ⁻¹⁰	3.1058	3.4579	0.0363	3.1058
Contact time	20.0177	9.18x10 ⁻⁵	3.4780	4.8503	0.0195	3.4780
Metal concentration	0.6842	0.618791	3.4780	2.4577	0.1134	3.4780
Biomass concentration	71.7308	1.62x10 ⁻⁸	3.1058	14.7542	0.00009	3.1058
Flow rate	9.0037	0.000946	3.1058	0.6279	0.6821	3.1058

Analysis of variance (ANOVA) is used to compare 2 or more factors or samples, to demonstrate the significance of the parameter within the set of samples analyzed, indicating, in an adopted confidence interval of 95%, the influence of the variable in removing the metal ion. Therefore, the null hypothesis represents that the average of all treatments are equal, that is, the analyzed parameter has no significant effect, showing that for different treatments the same statistical average of the response variable would be obtained. The alternative hypothesis represents that the average of all treatments would not be equal, that is, there is a significant effect on the analyzed parameter that leads to the averages of the response variables compared to a difference statistically placed for a value of α equal to 0.05 (ITO, 1980).

According to the results found in Table 7, we can observe the acceptance of the null hypothesis for the metal concentration parameter, which did not show significance for the removal of Ba²⁺ and Pb²⁺ in the 95% significance interval. This indicates that the values studied within the metal concentration parameter did not show statistically different removal values for the two metal ions.

The removal percentage caused by the adsorption process is proportional to the concentration of the adsorbate, until saturation of the active sites occurs, however, the change in the amount of metal ion in the work in question did not result in statistically different and significant responses at this removal rate.

Related studies show that the increase in metal concentration in the adsorption equilibrium causes an increase in the biosorption capacity (ratio of metal mass per mass of biomass), causing a decrease in biosorption efficiency, a fact that may be associated with the non-significance of the metal concentration parameter in the work in question (SANDAU et al., 1996; DA SILVA et al., 2014).

Still in Table 7, the flow parameter in the Pb²⁺ ion removal in the study proved to be non-significant, indicating that the variation in flow between 2 and 12 L h⁻¹ did not lead to different removal averages for the lead solution. The flow parameter is closely related to the HDT of the fixed bed reactor and its value directly affects its commercial application, however, its relationship with the removal percentage of Ba²⁺ and Pb²⁺ ions showed significance for the removal of Ba²⁺ with no significance for the removal of Pb²⁺.

This difference results between Ba²⁺ and Pb²⁺ ions can be explained by atomic differences between these metals, such as coordination number, atomic radius, and radius of the solvated ion, among others (FARQUHAR et al., 1997). Larger ions can fit better into an active site on the sorbent material that has two distant functional groups (HE; CHEN, 2014). Some potentially toxic metal ions

have better affinity with biosorbent materials than others and this situation defines the selectivity potential of the functional group (ABDOLALI et al., 2014).

The parameters pH, contact time, and concentration of the sorbent material, for the 95% confidence interval, are significant, as they all presented calculated F values greater than the tabulated F values and significance p-levels within the adopted interval. These parameters show that a variation in their work levels leads to significant changes in the removal responses of both Ba^{2+} and Pb^{2+} metal ions. Studies carried out in the area demonstrate that pH is one of the most important factors in the process of removing potentially toxic ions, as the charge of the active sites present in sorbent materials changes with the change in pH value (PINO et al., 2006; SILVA et al., 2013).

Studies found in the literature demonstrate the influence of the contact time of the sorbent material with the metal ions present in the analyzed solution. This removal rate increases until the system reaches saturation of active sites (MELLIS; RODELLA, 2008). In studies carried out on the effects of the concentration of the adsorbent material on the removal percentage, the removal of potentially toxic ions from the solution was also directly related to the increase in biomass concentration (MONTEIRO, 2009).

After applying ANOVA, multivariate analysis of variance (MANOVA) was carried out, which is used to simultaneously analyze the multiple parameters of each ion in the solutions, followed by the Student's t-test to reject or not a null hypothesis, showing how significant each parameter is in the sample. MANOVA is an extension of ANOVA analysis, and is used whenever it is necessary to make comparisons of means between two different populations. The difference between the tests is that in MANOVA, a certain parameter or factor is compared for two or more populations. In the case of the current study, the populations are represented by solutions of Ba^{2+} and Pb^{2+} ions.

The MANOVA analysis showed whether or not the changes in the parameter values differ in the different groups of ions (Ba^{2+} and Pb^{2+}) and thus showed whether or not the parameter simultaneously explains a statistically significant amount of variation in the removal percentage (JOHNSON; WICHERN, 1999). In MANOVA, the null hypotheses were maintained, which indicate the equality of the removal means of Ba^{2+} and Pb^{2+} ions, and the difference hypothesis, in which there must be at least two treatments that return different mean removal variables between treatments. Table 8 presents the results obtained in the MANOVA analysis for Ba^{2+} and Pb^{2+} ions in the analyzed parameters.

After analyzing Table 8, it can be seen that the calculated F value was lower than the critical F value (tabled) only for the pH parameter, as well as a p value higher than the confidence interval adopted for the study, 95%, for interactions between samples. Thus, the recommendation points to the non-rejection of the null hypothesis, that could be interpreted as a non-significant effect on the pH values within the Ba^{2+} and Pb^{2+} populations, which would not lead to significant differences in removal within these two species. Therefore, it can be considered that the means of the sampled populations, in this case, the removal of barium and lead did not show a significant difference within the barium population and within the lead population, therefore for the same pH range studied, different removal intervals were not observed for each of the Ba^{2+} and Pb^{2+} populations.

Studies report that high pH values can lead to complexation and precipitation of some potentially toxic metals, while very low pH values reduce the adsorption of metals through protonation of the material, a fact that drives the determination of an optimal pH value to be used in the analyses (NAJA; VOLESKY, 2006).

Table 8: Multivariate analysis of variance (MANOVA) for Ba²⁺ and Pb²⁺ ions.

Parameters		Ba ²⁺ e Pb ²⁺		
		F	Value - p	F critical
pH	Sample	0.394176	0.536041	4.259677
	Columns	23.24081	1.77x10 ⁻⁸	2.620654
	Interactions	2.062938	0.105585	2.620654
Contact time (min)	Sample	17.40004	0.000471	4.351243
	Columns	15.09214	7.75x10 ⁻⁶	2.866082
	Interactions	0.502085	0.734576	2.866082
Metal Concentration (mg L ⁻¹)	Sample	13.24332	0.001633	4.351244
	Columns	2.92363	0.0466947	2.866082
	Interactions	0.520037	0.72202	2.866082
Biomass concentration (g L ⁻¹)	Sample	6.563033	0.017115	4.259677
	Columns	54.44363	2.58x10 ⁻¹²	2.620654
	Interactions	1.660874	0.182458	2.620654
Flow rate (L h ⁻¹)	Sample	8.458363	0.007708	4.259677
	Columns	2.685629	0.045896	2.620654
	Interactions	2.05948	0.106081	2.620654

In strongly acidic media, electrostatic repulsion occurs between the ions and the surface of the adsorbent material, accentuating the competitive effect. On the other hand, in strongly alkaline media, increasing the concentration of hydroxyls increases the number of active adsorption sites due to the organic groups present on the surface of the adsorbent material, favoring interaction with the metal (SALVADOR; LAUS; FÁVERE, 2009; MUHAMAD; DOAN; LOHI, 2010).

The F values for the interactions line also allow us to state that the calculated values, for all parameters, are lower than the critical F values (tabled F), which is completely in line with what was carried out in practice, as the analysis was performed in uni-element solutions, that is, there are no interactions and interferences between the barium and lead samples, indicated by the non-significant interaction between the Ba²⁺ and Pb²⁺ ions. The calculated F values are greater than the critical F values when interference occurs or when multi-element solutions are use.

From Table 8 it can also be observed that the p values in the column index in the metal concentration and flow parameters were very close to the α value of 0.05 and the values of F and critical F were found to be outside the 95% confidence interval. The concentration result corroborates that observed in the ANOVA for each of the species, indicating that the variation in this parameter did not show statistically different removal values for the two populations. The flow rate result, which in the ANOVA analysis was significant for Ba²⁺ ions, but not for Pb²⁺ ions, in the MANOVA analysis showed F and critical F values outside the 95% confidence interval, so for the analysis together of Ba²⁺ and Pb²⁺ ions, the flow parameter did not show significance.

With the data available, the Student's t-test was used to compare the two means and the variations related to the hypotheses tested, showing how significant each parameter value is for the average removal within the sample. It was concluded that the initial metal concentration and flow parameters were not significant for the confidence interval adopted in the work conditions.

4 CONCLUSION

Green coconut fiber was used as a biosorbent material to remove Ba²⁺ and Pb²⁺ ions. This alternative method is promising for adsorbing Ba²⁺ and Pb²⁺ ions, in trace concentrations, from public water supply systems. The proposed methodology, in addition to mitigating damage to public health, also corroborates environmental and economic sustainability, since coconut fiber is a renewable, low-cost, and nationally abundant material, in addition to constituting a more environmentally appropriate form of final destination for the coconut, which is a bulky solid waste that reduces the useful life of landfill sites.

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