



Research article

Opuntia ficus-indica is an excellent eco-friendly biosorbent for the removal of chromium in leather industry effluents



Juliana Andreza Figueirôa^a, Guilherme Urias Menezes Novaes^b, Hélder de Souza Gomes^b, Vera Lúcia Meira de Moraes Silva^c, Danilo de Moraes Lucena^c, Lígia Maria Ribeiro Lima^c, Seldon Almeida de Souza^d, Lucas Gustavo Ferreira Cordeiro Viana^d, Larissa Araújo Rolim^d, Jackson Roberto Guedes da Silva Almeida^d, Ana Paula de Oliveira^{e,*}, Josivanda Palmeira Gomes^f

^a Federal Institute of Education, Science and Technology of Sertão Pernambucano, Serra Talhada Campus, Pernambuco, Brazil

^b Federal Institute of Education, Science and Technology of Sertão Pernambucano, Forest Campus, Pernambuco, Brazil

^c State University of Paraíba, Campina Grande Campus, Paraíba, Brazil

^d Federal University of San Francisco Valley, Petrolina Campus, Pernambuco, Brazil

^e Federal Institute of Education, Science and Technology of Sertão Pernambucano, Santa Maria da Boa Vista Campus, Pernambuco, Brazil

^f Federal University of Paraíba, Campina Grande Campus, Paraíba, Brazil

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ABSTRACT

In Brazil, the leather industry is an important economic segment moving around US\$ 3 billions of dollars a year. However, high amounts of water are requested to transform skin animals into leather, causing high wastewater amounts to be consequently produced. A major problem is attached to the presence of chromium in the wastewater from the tanning process. Chromium is a heavy metal potentially toxic both to the environment and to the human health. In order to control the levels of chrome dumped into the environment, Brazilian agencies require the treatment of effluents by the generating source. Thus, this study aimed to develop an alternative method to the removal of chromium in wastewater from the leather industry using the *Opuntia ficus-indica* biomass as eco-friendly biosorbent. Crude waste samples were collected in a tannery stabilization pond for chromium quantification and further treatments. The powdered *Opuntia ficus-indica* was obtained from species collected in Pernambuco, Brazil, and its physical parameters and pH_{PZ} were characterized. Adsorption studies and acute toxicity were also carried out. The biomass remaining after the sorption was analyzed through scanning electron microscopy and Fourier-transform infrared spectroscopy. The chromium content was above the limit allowed by the Brazilian regulatory agency. In sorption studies, biomass was able to remove 74.8% and 84.88% of Cr (III) using 2.0 g and 4.0 g of biomass, respectively. The surface of biomass is very favorable to biosorption and the chemical bindings among oxygen atoms present in the chemical components of this biomass and the heavy metal was confirmed through infrared spectrum. This study proved that *Opuntia ficus-indica* is effectively biosorbent to chromium, promising and with low costs for the leather industry, able to reduce its ecotoxicity as proven by chemical and biological assays.

1. Introduction

According to Brazil Tanneries Center, Brazil has nowadays the largest commercial cattle herd and is the third largest producer of leather, moving around US\$ 3 billions of dollars per year (Brasil, 2020). Despite the high economic impact, the leather industry is known also by its high consumption of water during the production process. The literature has

shown that for each ton of skin processed, 30 m³ of water is consumed (Bhattacharya et al., 2016).

In order to permanently alter the skin structure, the leather industry employs a series of steps as soaking, liming, bating, picking, skin degreasing, tanning, neutralization, retanning, dyeing, greasing and finishing. In each process, several chemicals are used and an amount of liquid waste is yielded. In general lines, the leather industrial effluents

* Corresponding author.

E-mail address: paula.oliveira@ifsertao-pe.edu.br (A.P. Oliveira).

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contain organic and inorganic compounds as fats, protein and heavy metals as arsenic and chromium (Bhattacharya et al., 2015; Shanthi et al., 2013; Mella et al., 2015). Because of such process and waste, the tannery industry is one of most polluting ones (Bhattacharya et al., 2015).

Chromium is a heavy metal very present in leather waste with two oxidation states. Chromium III, at low levels, is an essential nutrient to the human organism because it is involved in glucose, protein and lipid metabolisms. However, chromium IV is very toxic to vegetables, animals and human health, with the likelihood of causing ulcer, respiratory tract irritations, headaches, corneal damage, vomiting, gastrointestinal, hematological, hepatic and renal problems, as well as cancer (Medeiros et al., 2013).

In its Guidelines for drinking water quality, the World Health Organization limits the chromium content to $50 \mu\text{g}\cdot\text{l}^{-1}$ for drinking water (Organization, 2017). Based on this limit, the Brazilian National Environment Council (CONAMA) resolution 430/2011 assigns the generating source the responsibility for treating its effluents before disposal. For chromium, the acceptable limits are up to 0.1 ppm and 1.0 ppm to Cr(VI) and Cr(III), respectively (Brasil, 2011).

Several physical and chemical methods are used to remove heavy metals in effluents, such as precipitation, ionic change, electrochemical treatment and biosorption (Bhattacharya et al., 2016; Dal Magro et al., 2013; Gerola et al., 2013; Mella et al., 2015; Mimura et al., 2010; Medeiros et al., 2013). Among these, the adsorption using a vegetable matrix (biosorption) is highlighted because many species have biomass constituted by compounds, including humic acids, lignin, cellulose, hemicellulose and proteins. All these have adsorptive sites such as carbonyl groups, carboxyls, amines and hydroxyls able to adsorb heavy metals through ion exchange or chelation (Gerola et al., 2013; Mimura et al., 2010). Biosorbents have still low operational costs, easy-to-obtain processes and high efficiency, what makes them an attractive alternative to waste treatments (Barka et al., 2013a; Dal Magro et al., 2013; Gerola et al., 2013).

Opuntia ficus-indica, a plant from the cactus family and known in Brazil as “palma forrageira”, is within the biomass currently used. It is a species native from Mexico and widely grown in the Brazilian north-eastern region for goat breeding feed due to high nutritional value, adaptability, reproducibility and low water request (Almeida, 2012; de Assis et al., 2019).

Opuntia species have, on average, 21% of cellulose (de Assis et al., 2019), 18.8% of mucilage, 14.84% of pectin (Bayar et al., 2018) and 2.9%–6.0% of protein (Frota et al., 2015). This chemical profile has aroused the interest from several authors for the use of this species or its derivatives as sorbent for heavy metals and pollution. In studies performed by Adjeroud et al. (2018) and Fox et al. (2012), the mucilage was extracted and used to copper and arsenic sorption respectively (Fox et al., 2012; Adjeroud et al., 2018). Dried cactus cladodes was used for

cadmium and lead removal (Barka et al., 2013a), while prickly pear was used for dye removal (Barka et al., 2013b). All these studies were carried out with synthetic aqueous solutions.

In light of the adsorption properties of the biomass, of the chemical composition, of the adsorption properties of “palma forrageira” from the Caatinga biome and of governmental concern over the toxicity from industrial waste, this study aimed to assess the potential of *Oputinia ficus-inida* var. orelha de elefante as an eco-friendly biosorbent with low cost, to sorption of chromium in the leather industry effluents.

2. Materials and methods

2.1. Plant material

Cladodes of *Oputinia ficus-inida* var. “Orelha de elefante” were harvested in July of 2019 in the IFERTA0-PE experimental field, located in the rural area of the Floresta city in the state of Pernambuco (Brazil, $8^{\circ}38'15.6''\text{S}$; $38^{\circ}33'27.8''\text{W}$). The plant material was washed, cut into pieces with $3 \times 3 \times 1$ cm dimensions, dried on oven De Leo® AESRSE model at 55°C for 72 hours and powdered in mill Fortinox® STAR FT 50 model using 1 mm sieve. Then, the powdered was stored in a closed and dried container at 25°C until use (de Assis et al., 2019).

2.2. Waste samples

The crude effluent samples were collected in the tannery stabilization pond ($8^{\circ}34'08.2''\text{S}$ $38^{\circ}31'02.6''\text{W}$) using plastic containers in two moments in July of 2019 and stored at 4°C until use (Figure 1) (ABNT, 2014).

2.3. pH and chromium III content

The pH was measured on a pH apparatus previously calibrated (Bel Engineering, PHS3BW model) at 20°C and chromium III content expressed as Cr_2O_3 ($\text{g}\cdot\text{l}^{-1}$) was carried out. For the latter purpose, samples of total effluent or supernatants (after removal of chromium), were submitted to nitric/perchloric acid digestion and then to titration with sodium thiosulfate, according to ABNT NBR ISO 5398-1 (ABNT, 2014).

2.4. Biomass characterization

The *Oputinia ficus-inida* powdered, hereafter called biomass, had the humidity content, sulphated ash, total ash, ethanol extractable substances, moisture test for loss by dissection, foam index and granulometry measured according to the Brazilian pharmacopeia, 5th edition (Bakha et al., 2019; Barka et al., 2013a; BRASIL., 2010; Cavalcante et al., 2014; Pessoa et al., 2013; Silva et al., 2013b).

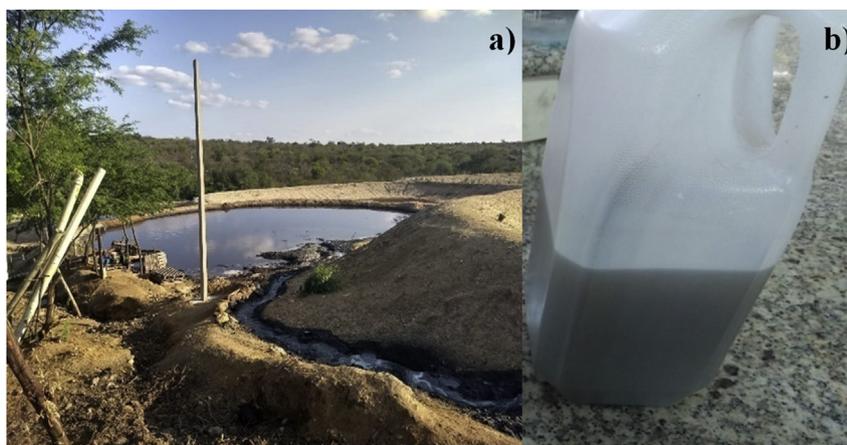


Figure 1. Tannery stabilization pond (a) and crude effluent sample (b).

Table 1. Chromium oxide content in crude effluent samples.

Collection period	Chromium oxide content (g.l ⁻¹)
1 th week of July	1.55 ± 0.150
4 th week of July	1.72 ± 0.173

Samples collected in 2019. Values expressed as Cr₂O₃(g.l⁻¹) average ± standard deviation (n = 3); there was no statistically significant difference when p < 0.05 according to unpaired Student's t-test.

2.5. Zero charge potential (pH_{ZCP})

The zero-charge potential powdered was determined through the mass titration method. Briefly, 100.0 mg of biomass was added to 50.0 ml of NaCl 0.01 M solution range to 0 at 12 pH values (pHmeter, Bel Engineering, PHS3BW model). The mixtures were stirred continuously at 160 rpm and room temperature (30 °C) during 3 hours. Then, the final pH of the solutions was measured and a graphic constructed by pH variation (ΔpH = initial pH - final pH) versus initial pH. The pH_{ZCP} was considered as defined when pH variation equaled zero. All measurements were performed in triplicate (Santos et al., 2008).

2.6. Adsorption kinetics

For the adsorption kinetics study, two assays were performed in duplicate. Therefore, 2.000 g or 4.000 g of biomass, measured on an analytical balance (Mars Scientific, 0.0001g ± 0.001g, ATY224 model) was added to an aliquot of total effluent in a time interval ranging between 5-60 minutes and stirred continuously at 130 rpm on a shaker apparatus (Novatecnica. NT 146 model). Then, each sample was filtrated using a nylon screen with a 0.3 × 0.87 mm opening and the supernatants were collected for later Cr (III) content quantification. The efficiency of chromium adsorption was obtained using Eq. (1) (Ribeiro Lima et al., 2019):

Equation 1. Percentage of adsorbed chromium III.

$$\% \text{ Cr (III) adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i is the initial chromium oxide concentration in the effluent before the biosorption process; C_f is the final chromium oxide concentration in the effluent after the biosorption process.

2.7. Adsorption isotherm

2.000 g of biomass was added to solutions containing water/effluent in several proportions ranging between 0 and 100% v/v of waste. Then, each mixture was stirred continuously at 130 rpm on a shaker apparatus for 60 minutes (Novatecnica. NT 146 model). All experiments were performed in triplicate (Ribeiro Lima et al., 2019).

2.8. Scanning electron microscopy (SEM)

Biomass before and after adsorption processes was analyzed through SEM in Tescan scanning electron microscope Vega3 model. Therefore, the samples were fixed on carbon strips in aluminum stubs and metalized with gold powder for 30 s. The images were obtained at 10 kVA and elementary composition of the samples was carried out by energy dispersive spectroscopy (EDS) on the same apparatus (Oliveira et al., 2019).

2.9. Fourier-transform infrared spectroscopy (FTIR) analysis

Biomass before and after 5 minutes of adsorption processes was analyzed on a Shimadzu IRTracer-100 FTIR spectrophotometer. Initially, pellets were prepared for each sample using KBr salt. Then, the analysis

was carried out with 400–4 000 cm⁻¹ spectral widows and 4 cm of resolution (Oliveira et al., 2019).

2.10. Artemia salina toxicity assay

The acute toxicity test for effluent was carried out with the *Artemia salina* assay using ABNT NBR 16530/2016 standard. Commercial cysts were purchased for hatching and the nauplii submitted to the assays after 24 h of life. The degree of toxicity expressed as CL₅₀, the concentration that causes lethality in 50% of the population of the organisms tested, was calculated by means of non-linear regression using the software *Graph Pad Prism* version 7.0.

3. Results and discussion

3.1. pH and chromium content

The neutral character of samples, pH of wastewater, was 7.25 and the chromium content expressed as Cr₂O₃ (g.l⁻¹) was quantified in crude effluent samples. In both moments of collection, the chromium content was above the allowed limit allowed by the Brazilian National Environment Council (CONAMA) in its resolution 430/2011 (Table 1).

The results obtained showed the urgent necessity of treatments in this wastewater. However, although above the allowed limit, the stability in chromium content can be understood as a positive point for future treatments using the biomass studied in this paper.

3.2. Biomass characterization

In this study, the biomass showed low dried weight (7.0%) content and consequently, high water content. Table 2 presents the values obtained for physicochemical characterization. Our results are similar to those obtained by Silva et al. (2013) (Silva et al., 2013b), Cavalcante et al. (2014) (Cavalcante et al., 2014) and Pessoa et al. (2013) (Pessoa et al., 2013), where low amounts of dried weight were also verified. It is known that *Opuntia ficus-indica* is rich in mineral compounds - especially calcium, potassium and magnesium (Teles et al., 2004; Wanderley et al., 2002). In this study, the high mineral content was confirmed through the high total ash content (20.423%).

In Table 3, we present the meshes used with their appropriate openings and the mass fraction of the adsorbent particles retained in each of the sieves. Through Eq. (2), the average diameter of the particles in each sieve was calculated through arithmetic means between the sieves in which the particle was retained and the sieve through which the particle passed.

Equation 2. Average diameter of particles of palm biomass.

$$\bar{d}_p = \frac{d_i + d_{i-1}}{2} \quad (2)$$

Where d_i is the mesh diameter of the particle passed (mm) and d_{i-1} is the mesh diameter of the particle retained (mm).

According to physicochemical principles, small particles promote high contact surfaces (Barka et al., 2013a) (Barka et al., 2013b). This

Table 2. Palm biomass (*Opuntia ficus-indica*) characterization.

Parameters	% Average
Moisture	6.164 ± 0.078
Total ash	20.423 ± 0.206
Sulphated ash	24.310 ± 0.132
Ethanol extractable substances	1.823 ± 0.025
Foam index	<100

Values expressed as average percentage ± standard deviation of all replicates. (n = 3).

Table 3. Distribution of the size of palm biomass (*Opuntia ficus-indica*) particle.

Mesh	Mesh opening (mm)	$\overline{d_p}$ (mm)	Retained weight(g)	Particle size fraction (%)
(10; 12)	2.00	1.85	-	0.00
[12; 20)	1.70	0.892	-	0.00
[20; 28)	0.085	0.072	-	0.00
[28; 40)	0.06	0.051	-	0.00
[40; 48)	0.042	0.036	-	0.00
[48; bottom)	0.03	0.015	95.42	1
Total			95.42	1

capacity is a desirable feature in materials intended for adsorption processes because high contact surfaces promote higher interactions sites. In our study, the biomass showed characteristics of an extremely fine powder with size particles averaging 15 μm , which is lower than that found by Barka et al. (2013) for the same species. In this study, the decrease in the size of particles increased the adsorption potential. Thus, it was expected a higher chromium adsorption potential was expected with our biomass.

3.3. Zero charge potential (pHZCP)

According to results, the biomass has a zero charge potential when the system pH is at 5.4, a value slightly higher than that obtained by Barka et al. (2013) when *Opuntia ficus-indica* was used to remove dye in aqueous solutions (Barka et al., 2013b). Adsorption is one of the most effective techniques for treating chemical separations. It is characterized as a unit solid-fluid mass transfer operation in which the ability of certain solids to concentrate substances present in liquid or gaseous solutions on their surface is exploited to separate them from the other components of these solutions. The migration of these components from one phase to another is driven by affinity between the fluid and the surface of the adsorbent.

pH has a direct influence in the adsorption capacity of the biosorbents. For example, systems that contain pH value greater than pHZCP are favorable for the adsorption of cationic compounds as Cr^{3+} , since greater interaction between the matrix of the biosorbent and the metal occurs at its surface through electrostatic attraction. In palm biomass, the high content of OH groups present in its proteins, cellulose, pectin and mucilage is deprotonated when the pH of the reaction medium is higher than 5.4, i.e., greater than the pHZCP. Above this value, the adsorbent presents negatives charges, making the system favorable to cationic compound adsorptions through electrostatic interactions (Nascimento et al., 2014). Thus, the pH of samples (7.25) makes the system favorable to interactions between metal Cr (III) and biomass.

3.4. Adsorption studies

The time contact and ratio between biomass-effluent amounts were the variables studied to verify the adsorptive capacity of biomass. The assays were carried out at room temperature and after the end of the process, the chromium oxide content in each remaining material was measured to verify the process efficiency.

In the kinetics study, the time range was 5–60 minutes whereas the biomass amount 2.0 g and 4.0 g were used resulting in biomass-effluent solutions at 5% and 10 % (w/v), respectively (Figure 2). The results showed that the biomass was able to remove 74.8% and 84.88% in assays using 2.0 g and 4.0, respectively, in the first 5 minutes (Figure 1). The effluent samples used in this study had in average $1.635 \pm 0.120 \text{ g.l}^{-1}$ or 1,635 ppm of Cr(III). Converting the results found in mg of Cr (III) removed by g of biomass, it can be seen that 611.49 mg and 346.947 mg of heavy metal was removed for each g of biomass, in assays using 2.0 g and 4.0 g respectively. These results showed that the lower weight used presents more efficiency in the removal of Cr (III).

In a study developed by Fox et al. (2012) (Fox et al., 2012), the mucilage extracted from *Opuntia ficus-indica* was used for arsenic (As) biosorption with synthetic heavy metal solutions. The authors observed a sorption capacity range of 0.14–2.8 mg As/g of biomaterial tested and according to them, the mucilage aggregation can have hindered the interactions between metal and biomass resulting in a low sorption. In another study developed by Barka et al. (2013) (Barka et al., 2013a), also with *Opuntia ficus-indica*, in lead and cadmium removal, 34.12% of Cd (II) removal was observed at 4.0 g.l^{-1} and 78.84% Pb (II) removal at 10.0 g.l^{-1} , efficiencies of removal also lower than that found in the present study.

As it can be seen in Figure 2, a decrease in efficiency was observed for both experiments over time and this decrease can be explained by the total effluent complexity. A similar result was found by Lima et al. (2019) (Ribeiro Lima et al., 2019) for gasoline removal in bodies of water using *Opuntia tuna* Mill. In this study, the biomass showed a fast kinetics adsorption also in the first minutes and a decrease over time. Vinodhini and Das (2010) (Vinodhini and Das, 2010) performed Cr(VI) adsorption using *Azadirachta indica* powdered leaves and observed also a decrease in sorption for leather industry crude effluents when compared to the synthetic $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

In addition to chromium, leather industry effluents have other ions from the various stages of skin treatment. Chemical inputs such as CaO , Na_2S , NaCl , surfactants and H_2SO_4 , for example, are added in the skin treatment processes and consequently their ions are present in the effluent. These species compete by binding sites with chromium and thus decrease the sorption of this heavy metal (Vinodhini and Das, 2010). In several studies, the authors run mathematical models in their data to understand the sorption process (Barka et al., 2013a, 2013b; Dal Magro et al., 2013; Gerola et al., 2013; Mimura et al., 2010). However, these

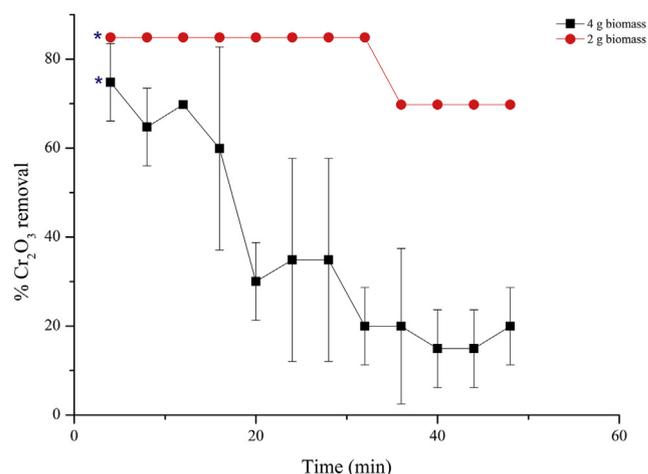


Figure 2. Adsorption kinetics curve in the time interval of 5–60 minutes for 2 and 4 g biomass: Values expressed as average percentage of chromium removal \pm standard deviation; assay performed in triplicate for each time and biomass amount. (*) Marked data do not show statistically significant difference when $p < 0.05$ according to unpaired Student's t-test.

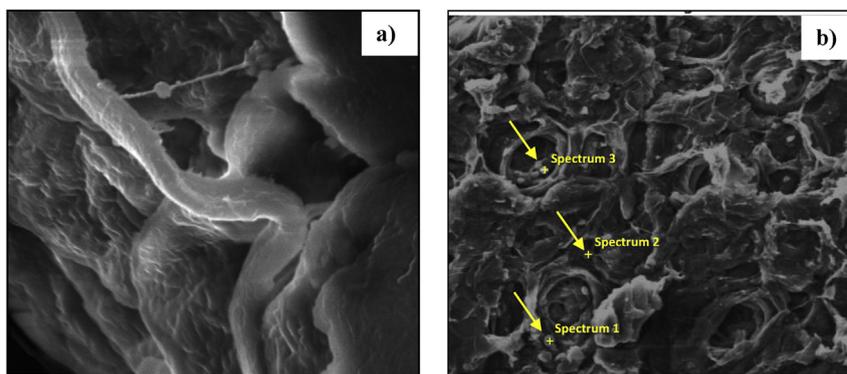


Figure 3. Scanning electron microscopy for *Opuntia ficus-indica*. Biomass before (a) and after 5 minutes of biosorption process; Corpuscles within the porous biomass structures (b).

studies are carried out using metal synthetic solutions. In view of the sample complexity of crude effluent used in this paper, a deeper kinetics study was unworkable.

It's common also in literature, The practice of chemical modifications in bio-organic matrix is also common in literature to increase the adsorption potential and to minimize the competitive effect of ions (Fox et al., 2012) (Silva et al., 2013a). We, however, believe that these modifications can bring additional costs and are even subject to the production of other industrial wastes.

3.5. Scanning electron microscopy (SEM)

SEM was performed to know the morphology of the biosorbent. Figure 3 shows the images obtained before and after the Cr (III) biosorption process. A heterogeneous and fibrous morphology, characteristic of lignocellulosic materials, was observed. One can view also, elongated and interconnected structures forming arrangements with smooth roughness along the fiber, which is characteristic of cellulose. According to literature, these characteristics are very favorable to adsorption processes (Gerola et al., 2013; Rocker et al., 2019).

In Figure 3 (b), corpuscles within the porous biomass structures were verified. In order to know the compositions of the corpuscles, an energy dispersive spectroscopy analysis was carried out on the same apparatus (Figure 4).

According to Figure 3, the chromium adsorption into three distinct points of biomass pores was proven through other techniques.

3.6. Fourier-transform infrared spectroscopy (FTIR) analysis

Infrared spectra of biomass before and after the adsorption process were acquired so that we could better understand the interaction mode between chromium (III) and our biomass (Figure 5). It is known that sorption processes can be physical or chemical, where the first are characterized by weak bonds while the latter are characterized by strong bonds between electron pair donor groups and metals (Dal Magro et al., 2013). Infrared spectroscopy is very useful to identify interactions

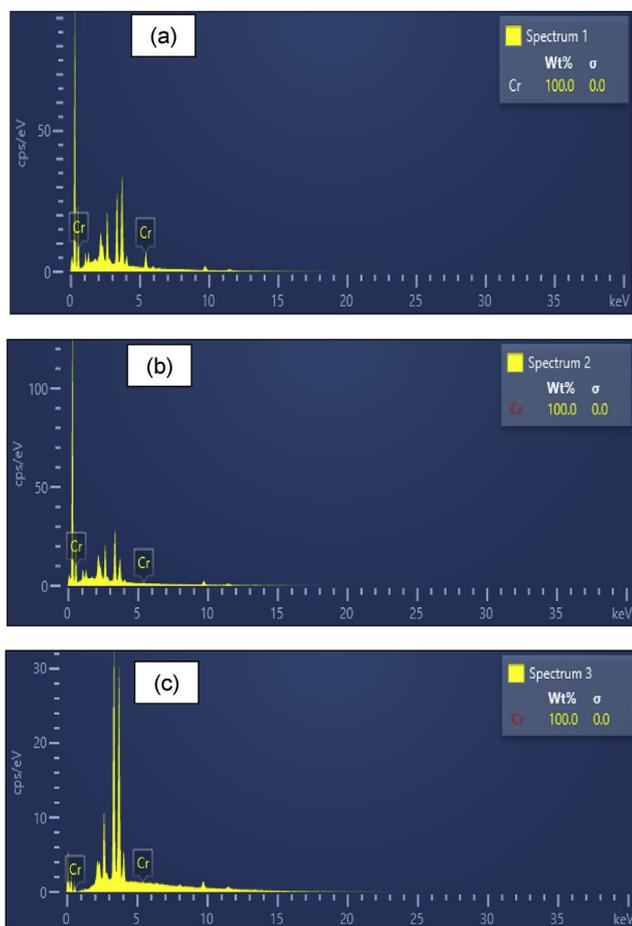


Figure 4. Energy dispersive spectroscopy analysis of corpuscles found in SEM. a) spectrum 1; b) spectrum 2 and c) spectrum 3.

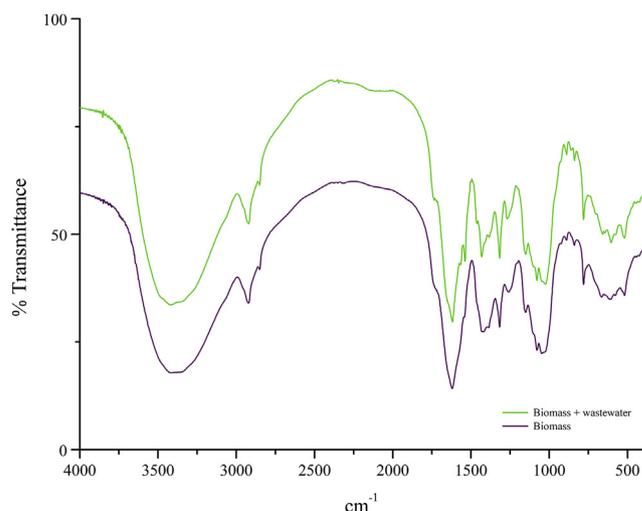


Figure 5. Infrared spectrum of *Opuntia* sp. biomass before and after chromium (III) sorption.

Table 4. Percentage of living organisms after 24 and 48 h of exposure to the total effluent.

Toxicity degree	Values
CL ₅₀ of standard substance (24 h)	0.086% ± 0.02 ppm
CL ₅₀ of standard substance (48 h)	0.018% ± 0.00 ppm
Sample CL ₅₀ (24 h)	6.431% ± 0.08%
Sample CL ₅₀ (48 h)	Undetermined

between materials because the vibrational modes of functional groups change when interactions happen and the differences in vibrational modes are reflected in spectra through the appearance or disappearance of bands, as well as changes in the areas of these bands (Gerola et al., 2013; Medeiros et al., 2013; Oliveira et al., 2019).

Both infrared spectra showed axial deformations at 3700–3084 cm⁻¹ attributed to O–H and overlapping N–H, 3008–2856 cm⁻¹ C–H_{sp3}, 1620 for C=O as also angular deformation and folding out of plane for the bands at 1400–400 cm⁻¹ (Figure 5) (Pavia et al., 2010; Tonhi and Plepis, 2002).

However, for biomass spectrum after sorption, an increase in the area of bands was verified at 3700–3084 cm⁻¹, 1620 cm⁻¹, 1316 cm⁻¹ (axial deformation C–O of carboxylic acids) and 1024 cm⁻¹ (axial deformation C–O of primary alcohols). Also, a decrease was verified in areas at 1079 and 1049 cm⁻¹ attributed to angular deformations of C–O groups present in lignocellulosic components contained in biomass (de Assis et al., 2019).

Wastewater samples used in this study had as one of its constituents chromium (VI). Nowadays, its strong oxidative potential is known. The increase in carbonyl band suggests a primary and secondary alcohol oxidation of lignocellulosic structure to its corresponding aldehydes and ketones and reducing of remaining chromium (VI) to chromium (III). In post adsorption spectrum, the higher changes were observed in bands related to C–O bonds. These spectral changes allow us to state that a chemical sorption process occurs between biomass and chromium (III) through the electron pair donation by oxygen atoms from C–O groups (Medeiros et al., 2013).

3.7. *Artemia salina* toxicity assay

The *Artemia salina* toxicity assay was performed in two independent assays, following the standards recommended by ABNT 12713/2016 with organisms after 24 h of cysts hatching. The results were statistically analyzed by the non-linear regression method and from these the LC₅₀ of the total effluent sample could not be determined due to the absence of living organisms in the two replicates performed 24 h after the beginning of the tests, as it can be seen in Table 4.

Artemia salina toxicity assay has been used for years because it is fast, simple and efficient for several types of samples and does not require the use of expensive equipment and large quantities of sample. In Brazil, the environmental control agencies require this type of method to ensure the safety of the effluent before it is discharged into a receiving body (Brasil, 2011). As it can be seen in our results, the treatment with biomass drastically decreases the toxicity of the effluent, proving the efficiency of our treatment also in living organisms.

4. Conclusion

The biosorption with *Opuntia ficus-indica* biomass was shown to be efficient and promising to improve chemical and biological properties of the effluent. In kinetics assays, the equilibrium was achieved in a short time and with high chromium (III) removal rate. Nowadays, the leather industries use in the treatment of their effluents only the chromium precipitation, a methodology that requests considerable amounts of sodium hydroxide. This practice can be replaced by the sustainable process showed in this study, in order to reduce operational costs and

environmental impacts of wastewater treatment and even posterior use of adsorbed chromium in biomass as soil fertilizer (Pavia et al., 2010). Besides the low cost, our results proved the reduction of the chromium content in the effluent provided using forage palm as biosorbent in tannery effluents. Our results also prove the high capacity to reduce the environmental impacts through the reduction of toxicity.

Declarations

Author contribution statement

Juliana Andreza Figueirôa, Ana Paula de Oliveira: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Guilherme Urias Menezes Novaes, Hélder de Souza Gomes, Danilo de Moraes Lucena, Lucas Gustavo Ferreira Cordeiro Viana: Performed the experiments; Analyzed and interpreted the data.

Vera Lúcia Meira de Moraes Silva, Seldon Almeida de Souza: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Lígia Maria Ribeiro Lima: Contributed reagents, materials, analysis tools or data.

Larissa Araújo Rolim, Jackson Roberto Guedes da Silva Almeida, Josivanda Palmeira Gomes: Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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