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The use of cedar bark as an adsorbent to remove hexavalent chromium from liquid effluents

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Abstract

Hexavalent chromium, Cr (VI), is a heavy metal found in liquid effluents due to its disposal from industry, as it is a common byproduct of metallurgical and automotive processes, for example. However, hexavalent chromium is extremely toxic to life and the environment. In this manner, a study was conducted using pyrolyzed cedar bark to test its ability to adsorb chromium from aqueous solutions, presenting a cheap and viable alternative for removing this toxic compound from aqueous media. The material was pyrolyzed at 500 ºC and characterized by XRD, SEM, FTIR and N_2 adsorption/desorption. Bench tests were conducted using chromium solutions with concentrations of 25 ppm, 50 ppm, 75 ppm, 100 ppm, 150 ppm, and 200 ppm to evaluate the potential of the studied adsorbent. The results were very satisfactory, showing more than 80% removal in all tested samples, demonstrating the high adsorption capacity of cedar bark. This indicates that further investment in studying this promising and low-cost alternative is warranted to achieve less polluted liquid effluents with fewer harmful compounds for humans, plants, and animals.

Keywords: cedar bark; adsorption; hexavalent chromium; pyrolysis; biosorbent.

1. Introduction

Nowadays, the number of studies on the development of biomass-based adsorbents is increasing, mainly involving thermal processes, such as pyrolysis. Although the number of studies is growing, it is still necessary to invest in research so that it is possible to place these materials on larger scales, go beyond the bench scale and exploit the potential of low-value-added biomass, such as agro-industrial waste.

Cedar (*Cedrela fissilis*), a large-sized tree species that can reach up to 30 meters in height and has a preference for moist and deep soils [1], occurs naturally in Costa Rica, Panama, Uruguay, Argentina, Bolivia [2], Colombia, Ecuador, Peru, Paraguay and Venezuela [3]. The wood found in its trunk is considered noble, similar to mahogany (Swietenia macrophylla), and is used in the manufacture of luxury furniture and carving works.

In this context, an adsorbent from cedar bark via the pyrolysis process was used to test its potential adsorption capacity on the removal of hexavalent chromium detected in liquid effluents, a heavy metal industrial waste that is considered carcinogenic and toxic to fauna and flora. This study is characterized as an exploratory study for the application of this material as an adsorbent in the removal of inorganic pollutants from liquid effluents.

2. Methods

2.1 Adsorbent preparation and characterization

The reactor used for the pyrolysis experiments is a tubular reactor (Sanchis, Brazil) which operates in batch sys (Figure 1). It is a furnace that has a quartz reactor coupled internally. The reactor has the following dimensions: 98.1 cm length, 49 mm outside diameter and 43 mm internal diameter. The reactor is heated electrically by two resistors, each one with a 1900 W. Two type K thermocouples are positioned inside the reactor. The experiments were conducted at 5 $\circ$C.min^{-1} heating rate and at 150 L.min^{-1} N_2 flow. A 30 minutes isotherm was used after the final temperature (500

◦C) was reached. The experiments were carried out with an initial biomass of 130 g (previously dried at 105 °C). The pyrolysis vapors condensation was conducted in accordance with CEN standard (adapted) [4], and ten bubblers were used (CEN BT/TF 143 2004). In each experiment 100 mL of isopropyl alcohol was added in each bubbler, except for the first and the last (empty). All the bubblers were kept in a cold box (ice bath, salt and isopropyl alcohol). The aim was to keep the bath bubblers at low temperature (around −10 ℃). The bio–oil and biochar were collected and their masses determined for yield computation. The sample was ground with a mortar and pestle, sieved and stored in plastic containers to be used for characterization and successive adsorption experiments.

In Table 1, the percentage yields of biochar, pyrolytic liquid and uncondensed gases were determined.

Table 1 - Percentage yields of the study.

Percentage yields			
Parameter	Equation	Unit	Eq
Biochar yield	$(m_{biochar}/m_{BMB}) \cdot 100$	%	(1)
Liquid yield	$(m_{liquid}/m_{BMB}) \cdot 100$	%	(2)
Gas yield	$100 - Biochar\ yield - Liquid\ yield$	%	(3)

Where m_{BMB} (g) is the mass of precursor material inserted into the reactor, $m_{biochar}$ (g) is the mass of solid in the reactor after the pyrolysis process and m_{liquid} (g) is the mass of liquid that was stored in the collector of the reaction system after the pyrolysis process.

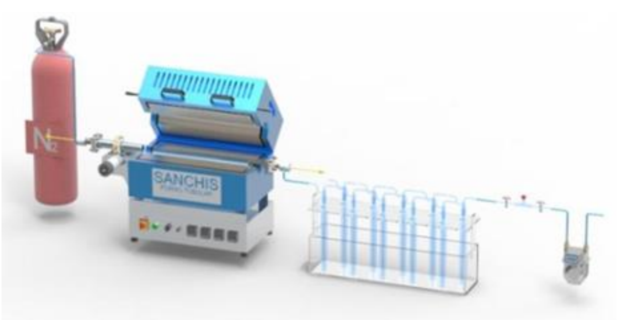

Figure 1 - Equipment used on the pyrolysis process.

2.1 Adsorbent assays

Initially, a 500ppm stock solution of chromium (VI) was prepared from potassium dichromate, $K_2Cr_2O_7$. The prepare of the solution was made in a 500 mL volumetric flask, which was after transferred to an amber bottle.

There was also the production of a diphenylcarbazide solution through the addition of 0.125 g of 1,5-diphenylcarbazide, $C_{13}H_{14}N_4O$, in 25 mL of acetone. The material was made in a 25 mL volumetric flask and then transferred to a small amber vial to store in a refrigerated environment.

From the stock solution of potassium dichromate, 100 mL solutions of 25 ppm, 50 ppm, 75 ppm, 100 ppm, 150 ppm and 200 ppm were prepared and the pH was adjusted to 2,5.

Finally, for the bench tests, 0.1 g of pyrolyzed cedar bark was weighted and added to 50 mL of dichromate solution. This process was carried out for all 6 solutions, which were left stirring in a magnetic stirrer for 30 minutes with the cedar.

After that, 5 mL of the solutions were mixed with 5 mL of deionized water and 0.1 mL of diphenylcarbazide solution. Then, to determine the concentration of Cr (VI) in each aliquot, the mixed solutions were analyzed by a spectrophotometer (BEL photonics, SP 1105), λ = 540 nm. Then, the values read, which means the absorbance of Cr (VI) by the cedar, were gathered and a calibration curve was made. After that, the percentage removal of Cr (VI) was found using the equation (4), where C_i and C_f means initial and final concentration after the equilibrium, respectively.

$$R\,(\%) = [(C_i - C_f)/C_i] \cdot 100 \qquad (4)$$

The adsorbent prepared in this work was characterized by the techniques described as follows. X-ray diffraction pattern was obtained using a Rigaku Miniflex 300 diffractometer. The X-ray source was Cu Kα radiation, powered at 30 kV and 10 mA. Data were collected over the 2θ range of 5°–100° with a step size of 0.03° and a count time of 0.9 s per step. The BET surface area was obtained from nitrogen adsorption–desorption isotherm measurements at 77 K, carried out on an analyzer (Quantachrome, New Win 2, USA) at relative pressure (P/P0) ranging from 0 to 0.99. Samples were degassed under vacuum at 120 ºC for 20 h. The morphology was examined by a scanning electron microscope (SEM, MIRA 3 TESCAN). Fourier transform infrared (FTIR) spectrum was recorded on a Shimadzu IR Prestige-21 spectrophotometer in the range of 4000-400 cm.

3. Results and discussion

3.1 Adsorbent and characterization

From pyrolysis processes the yield obtained (%) was 49.06, 45.27 and 33.97 for solid, liquid and gases, respectively. Biochar was produced from Brewer's spent grain using the pyrolysis process and yield (%) values of 31.28, 47.57 and 21.15 for biochar, liquid and gases, respectively, were obtained [5].

The X-ray diffraction patterns was measured to investigate the type of structure of this sample. XRD diffraction patterns are shown in Figure 2. The sample showed an amorphous structure. The amorphous structure is in general adequate for dye adsorption purposes. An amorphous adsorbent has a more disorganized structure, with more empty spaces. This type of structure allows the accommodation of the large pollutant molecules into the adsorbent surface [6].

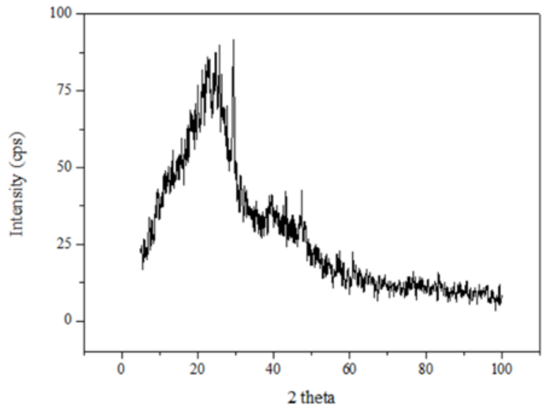

Figure 2 - XRD spectrum.

The FTIR vibrational spectra of cedar bark and cedar bark pyrolyzed are reported in Figure 3. The main intense bands in Fig. 3 were found at 3426 cm-1, 2935 cm-1, 1600 cm-1, and 1050 cm-1 for cedar bark. The band at 3426 cm-1 can be assigned to the O-H stretching vibrations of carboxylic acids, phenols, alcohols, or water and the band at 2935 cm-1 was assigned to C-H, at 1600 cm-1 the C=C stretching of aromatic rings can be verified. Finally, at 1050 cm-1 might represent the C-O-C of an ether group. After the pyrolysis process, the volatile matter was removed from the cedar bark and only the bands at 3426 and 1600 remained, but at a lower intensity. This trend confirms that the volatile matter was removed, corroborating the solid yield, and probably increasing the surface area of this material. This material presented a surface area 66.3 m²g-1, average pore size 3.5 nm and total pore volume 0.058 cm³g-1. It is to corroborate with the SEM images in Figure 4. With SEM images it was possible to observe that the elimination of light hydrocarbons shows an irregular surface formed from the cedar bark with the presence of pores.

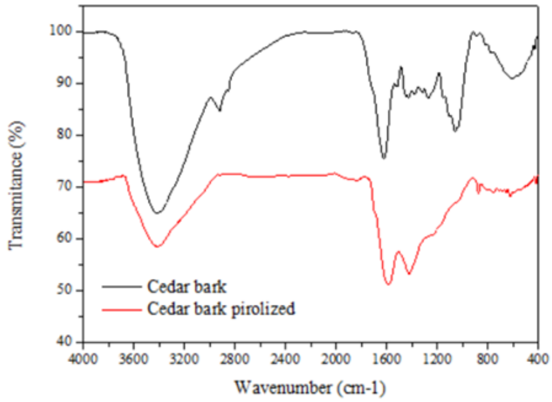

Figure 3 - FTIR spectra of cedar bark and cedar bark pyrolyzed.

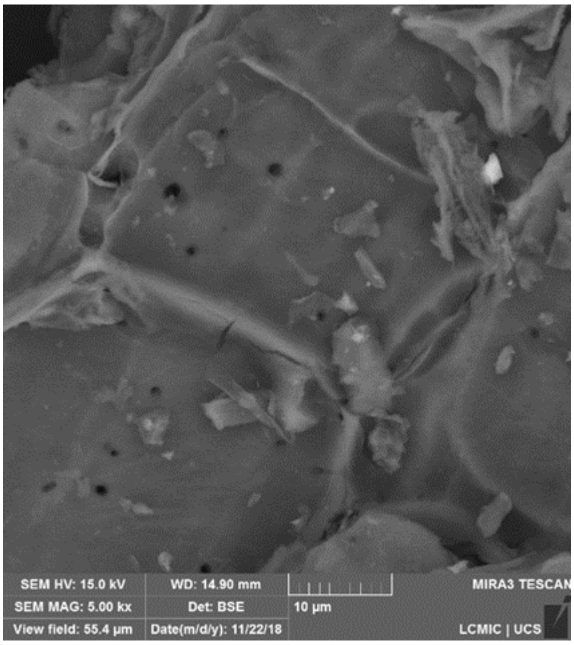

Figure 4 - Scanning electron microscope (SEM) micrographs of cedar bark adsorbent.

3.2 Adsorbent study

The equilibrium of the solutions was reached in 30 minutes. The results are shown in Figure 5, where it is possible to see the high removal capacity of cedar bark, almost 100 %.

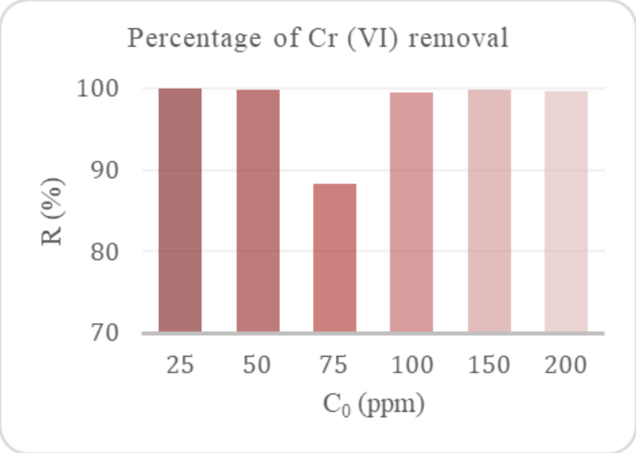

Figure 5 - Removal of hexavalent chromium.

It can be observed all concentration evaluated the adsorbent showed high potential for this pollutant. This behavior can be attributed to the surface area of the material produced from cedar bark. [7] suggests that adsorption of Cr (VI) onto biochar was probably controlled by chemisorption and the biochar was probably covered by the surface layer of the Cr (VI). [8] state that electrostatic interaction and ion exchange dominate the Cr (VI) adsorption onto the biochar materials in acidic pH media. Given these comparisons with the literature, it can be stated that pyrolyzed cedar bark has excellent potential for removing chromium VI and further studies are being carried out to fully study the behavior of this process.

4. Conclusion

The study on the adsorption properties of cedar bark for the removal of hexavalent chromium, Cr (VI), a toxic and carcinogenic heavy metal, from liquid effluents yielded highly promising results. The experiments demonstrated that cedar bark could achieve over 80% removal of chromium from contaminated samples. This significant finding underscores the potential of cedar bark as an effective, low-cost adsorbent for treating industrial wastewater.

This highlights the importance of further research into this and other bioadsorbents. They are not only cost-effective but also environmentally friendly, reducing the reliance on synthetic chemicals and complex treatment processes.

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