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Removal of Pb^{2+} from industrial wastewater using activated carbon from *Persea americana* seed

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ABSTRACT

Activated carbon is a material that has various environmental applications, such as the adsorption of metallic lead ions (Pb^{2+}). It can be obtained from different plant species. In this research, the seed of *Persea americana* (Avocado- HASS variety) was obtained from local markets in the city of Cartagena to be used in the removal of Pb^{2+} from wastewater from the fishing industry. To obtain activated carbon, the seed was carbonized in a Terrigeno-brand clay oven, Model DB 1200. Orthophosphoric acid at 21% w/v was used as an activating agent. The residual water was characterized following the APHA specifications. The turbidity was determined by nephelometry in a Turbiquant 300 IR turbidimeter. The Pb^{2+} concentration was determined by atomic absorption spectroscopy in a Thermo Scientific iCE 3300 equipment. The chemical surface of the material was performed by Fourier transform infrared spectroscopy (FTIR). The carbons were morphologically characterized using a scanning electron microscope SEM (Jeol 5910LV), visualized at 15kV. A yield of 20.38% by mass of coal is achieved. The pores are of irregular size, ranging from 16.2 to 55.98 μm. 65% of Pb^{2+}, turbidity (57.6%), color (57%), total solids (50.2%), as well as BOD (53.12%) and COD (36%) are removed, finding statistically significant differences in values at the 95% level of significance. The seed of *Persea americana* (HASS avocado) can serve as plant material to obtain an adsorbent material (activated carbon) and be used in the removal of Pb^{2+} from wastewater.

Keywords: activated carbon, adsorption, avocado seeds (HASS variety), Pb^{2+}, removal.

Remoção de Pb^{2+} de efluentes industriais utilizando carvão ativado de semente de *Persea americana*

RESUMO

O carvão ativado é um material que possui diversas aplicações ambientais, como a adsorção de íons de chumbo metálico (Pb^{2+}). Pode ser obtido a partir de diferentes espécies de plantas. Nesta pesquisa, foi utilizada a semente de *Persea americana* (variedade abacate-HASS), proveniente de mercados locais da cidade de Cartagena, para ser usado na remoção de Pb^{2+} de águas residuais da indústria pesqueira. Para obtenção do carvão ativado, a semente foi carbonizada em forno de barro da marca Terrigeno, modelo DB 1200. Foi utilizado ácido ortofosfórico a 21% p/v como agente ativador. A água residual foi caracterizada seguindo as especificações da APHA. A turbidez foi determinada por nefelometria em um turbidímetro Turbiquant 300 IR. A concentração de Pb2+ foi determinada por espectroscopia de absorção atômica em um equipamento Thermo Scientific iCE 3300. A superfície química do material foi realizada por espectroscopia no infravermelho com transformada de Fourier (FTIR). Os carbonos foram caracterizados morfologicamente usando um microscópio eletrônico de varredura SEM (Jeol 5910LV), visualizado a 15kV. Obtém-se um rendimento de 20,38% em massa de carvão. Os poros são de tamanho irregular, variando de 16,2 a 55,98 µm. 65% de Pb2+, turbidez (57,6%), cor (57%), sólidos totais (50,2%), bem como DBO (53,12%) e DQO (36%) são removidos, encontrando diferenças estatisticamente significativas nos valores a 95 % Nível de significância. A semente de *Persea americana* (abacate HASS) pode servir como material vegetal para obter um material adsorvente (carvão ativado) e ser utilizado na remoção de metais pesados de águas residuais.

Palavras-chave: adsorção, carvão ativado, Pb^{2+}, remoção, sementes de abacate (variedade HASS).

1. INTRODUCTION

The amount of industrial and domestic waste dumped into the environment has increased the contamination of aquatic reservoirs and water resources (Prado *et al.*, 2014). Due to this, regulations are increasingly strict regarding the elimination of pollutants from effluents (Jiménez *et al.*, 2017). The presence of heavy metals stands out among the contaminants of greatest interest due to their toxicity to biota, since they do not degrade to less harmful species (Mohammadi *et al.*, 2010). Leena and Selvaraj (2019) report the presence of dyes (350 Hazen) and heavy metals (Pb^{2+} 0.2 mg/L) in wastewater from the textile industry while Kadam *et al.* (2018). report 0.40 mg/L for Pb^{2+} for the same type of raw wastewater.

The quality of wastewater is determined in terms of physical, chemical, and biological parameters and its monitoring is of the utmost importance since it is known that the consumption of contaminated water accelerates the appearance of health problems (Naghipour *et al.*, 2018; Mirzabeygi *et al.*, 2017; Soleimani *et al.*, 2018). High concentrations of heavy metals such as Pb^{2+}, organic compounds and suspended particles in the water increase turbidity, serving as a means of transmission of pathogenic organisms; therefore, the removal of metals, the reduction of turbidity and contaminants is an important process in water treatment (Mandal *et al.*, 2021; Hameed *et al.*, 2018). To remove these contaminants, different materials and methods have been used, among which is active carbon from plant species (Khairiah, 2020).

Activated carbon production from agricultural by-products has potential economic and environmental impacts, as it converts unwanted agricultural waste into useful, high-value adsorbents. Chemically modified activated carbons show a high adsorption capacity for dyes and heavy metals, which is why they are increasingly used in water treatment to remove organic chemicals and metals of environmental and/or economic interest. Activated carbon is one of the most versatile and common adsorbents due to its large surface area and pore size (Lojero *et al.*, 2019). Activated carbon (CA) is considered a carbonaceous material, with structure and properties like pure carbon, such as graphite and diamond; it is strong, and permeable and is classified as basic carbon, due to the lack of contaminants and an oxygenated surface (Shekhar, 2015).

The main features of activated carbon are the organic groups on its surface, which are generated by oxidation; and the property to adsorb, due to its high surface area, where the surface of a solid (adsorbent) retains molecules (adsorbates) contained in a liquid or gas.

The structure and arrangement of activated carbon (AC) atoms depend on the type of activation; thermal/physical or chemical activation. Both activation types generate a porous surface. Chemical activation has two stages: first, an impregnation of a chemical must be carried out on the raw material; subsequently, the material must be carbonized at high temperatures to obtain the porous structure (Agrowaster, 2013).

This research aims to obtain carbon from the seed of *Persea americana* (avocado-Hass variety) and subsequently activate and characterize it, for its application in the removal of Pb^{2+} in wastewater.

2. MATERIALS AND METHODS

2.1. *Vegetal material*

In this research, the seeds of *Persea americana*, a product of fruit pulping, from local markets in the city of Cartagena de Indias, Colombia, were used to obtain AC. Initially they were dried in a conventional oven at 105ºC/4h, to eliminate moisture, and then mechanically crushed to facilitate the carbonization process.

2.2. *Physicochemical characterization of wastewater*

The wastewater used comes from a fishing industry to which the physicochemical characterization was carried out, following the methodology proposed by APHA*et al.* (2012) for this type of water. Turbidity was determined by the nephelometric method (method 2130B), using a Turbiquant 300 IR turbidimeter, with formalin polymer as standard solution, expressing turbidity in nephelometric turbidity units (NTU) (Table 1).

Table 1. Physicochemical characterization of wastewater**.**

Parameters	Valor*	Units
Pb^{2+}	0.80 ± 0.02	mgL^{-1}
Turbidity	99.45 ± 0.95	NTU
DBO_5	256 ± 2.23	mgL^{-1}
DQO	310.2 ± 1.93	mgL^{-1}
Color	196.4 ± 0.97	UPC
Total solids	806.0 ± 4.28	mgL^{-1}

*The values represent the average of three determinations.

The turbidity removal percentage is determined by Equation 1.

$$Turbidity\ removal\ percentage = \frac{T_o - T_f}{T_o} * 100 \tag{1}$$

Where, T_0 is the value of the initial turbidity and T_f the value of the turbidity after the treatment with the adsorbent. The same procedure is followed for the other physicochemical parameters. The concentration of Pb^{2+} was determined by atomic absorption spectroscopy (AA) using the graphite furnace method, in a Thermo Scientific iCE 3300 equipment.

2.2.1. *Pb^{2+} adsorption on activated carbon*

Approximately 0.2 grams of activated carbon was added to 50 mL of wastewater from the local industry. It was continuously stirred at room temperature for 18 hours. Subsequently, it was filtered, and the lead (Pb^{2+}) present was determined by atomic absorption spectroscopy. The results of the Pb^{2+} concentration are referred to a calibration curve from a 1000 mg/L lead concentration standard (Merck) certified and prepared at different concentrations.

2.3. ***Obtaining charcoal***

103.4 grams of the starting plant material was divided into fractions of 34.46 grams, which were carbonized at a heating rate of 10ºC/min up to 350 ± 5ºC in a Terrigeno brand clay oven, Model DB 1200. The Obtained charcoal was sieved on a standard Tyler sieve using a # 40 mesh (0.425 µm).

2.4. ***Chemical activation of carbon***

Each charred fraction was impregnated with 21% w/v orthophosphoric acid with magnetic stirring for five (5) hours, then dried at 110°C for 24 hours. Subsequently, the charred material was heated under a nitrogen atmosphere (flow of 110 mL/min) at a heating rate of 10ºC/min, until reaching a final treatment temperature of 400 ± 5ºC. The samples were washed with hot and cold water until the conductivity of the wash water was between 0.5 and 5 µS/cm.

2.5. ***Activated carbon characterization***

2.5.1. ***Chemical Surface Study***

The study of the chemical surface of the material was performed by Fourier transform infrared spectroscopy (FTIR) in a Nicolet iS50 FTIR unit. For the acquisition of each spectrum, these were obtained using the KBr pellet method. Before the FTIR analysis, the activated (AC) and non-activated (CNA) carbon were placed for a week at 60°C in an oven to ensure that the moisture completely evaporated, then the KBr pellet was made, for the determination of the spectra of each sample.

2.5.2. ***Scanning Electron Microscopy (SEM) morphology***

The morphological characterization of activated and unactivated carbon was carried out using a SEM scanning electron microscope (Jeol 5910LV), visualized at a voltage of 15kV. Before being observed by SEM, the samples were subjected to vacuum and covered with a fine gold layer to have the ability to reflect the electrons that distribute the intensity of the signals in the observation.

2.6. ***Statistical analysis***

The MINITAB computer program was used, through a paired T-test, the existence or not of statistical differences in the values of the physicochemical parameters, before and after treatment with the adsorbent, was analyzed.

3. RESULTS AND DISCUSSION

3.1. ***Carbonization-activation yield***

The wet *Persea americana* seeds initially had a weight of 103.4 grams after carbonization and activation, the samples were weighed again to determine the mass lost in the process. After drying at the end of the activation, the weight of the CA sample was 21.08 grams, with a yield of 20.38%. This result corresponds to that reported by Lojero *et al.* (2019). A possible cause for obtaining these relatively low values in carbon yield lies in the carbonization temperature and the heating rate, the increase of these two variables decreases the organic carbon yield (Yahya *et al.*, 2020).

3.2. ***Estudio de la superficie química del carbón activado y no activado (FTIR)***

Figures 1 and 2 show the FTIR spectra of the activated and unactivated adsorbent material. Figure 2 shows a band between approximately 3450 and 3200 cm–1, corresponding to the stretching vibration of the hydroxyl (OH) bond (Huang *et al.*, 2015, Muhammad and Al-Swaidan, 2015).

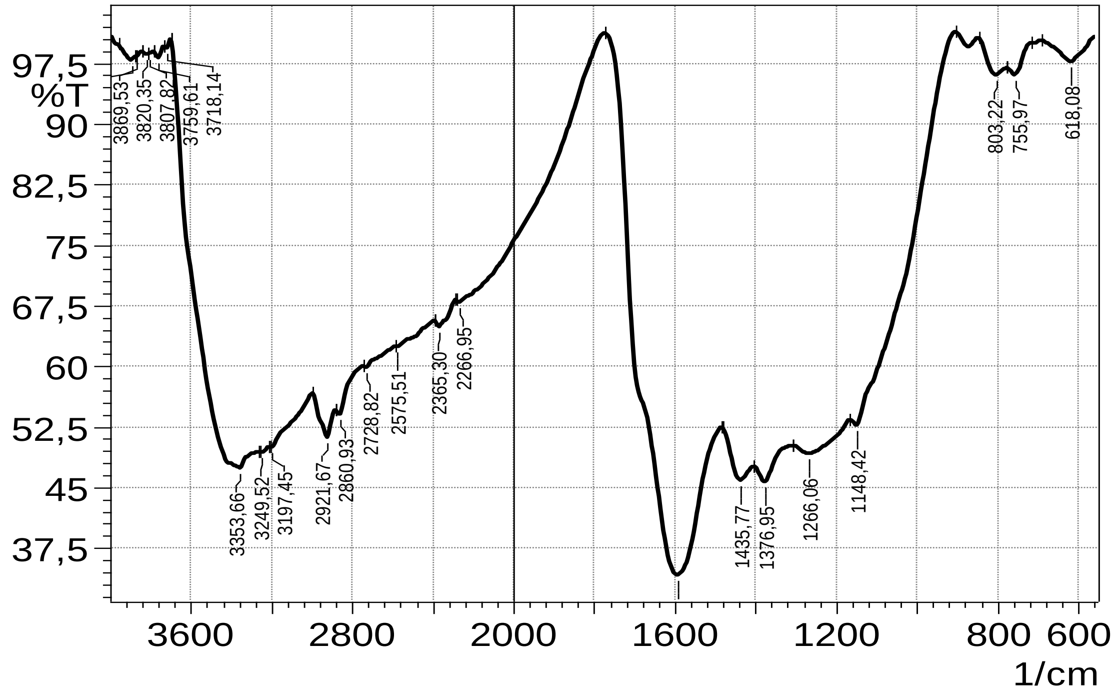


Figure 1. *FTIR spectrum of non-activated carbon from Persea americana seed.*

At 3400 cm^{-1} a broad band attributed to the presence of hydroxyl groups (OH-) is observed; the band presented around 1659 cm-1 corresponds to the presence of carbonyl groups (C=O), this band is not observed in the CNA that presents a signal at 1592 cm^{-1} that corresponds to the C=C signal. This could have undergone an oxidation process when activating the carbon.

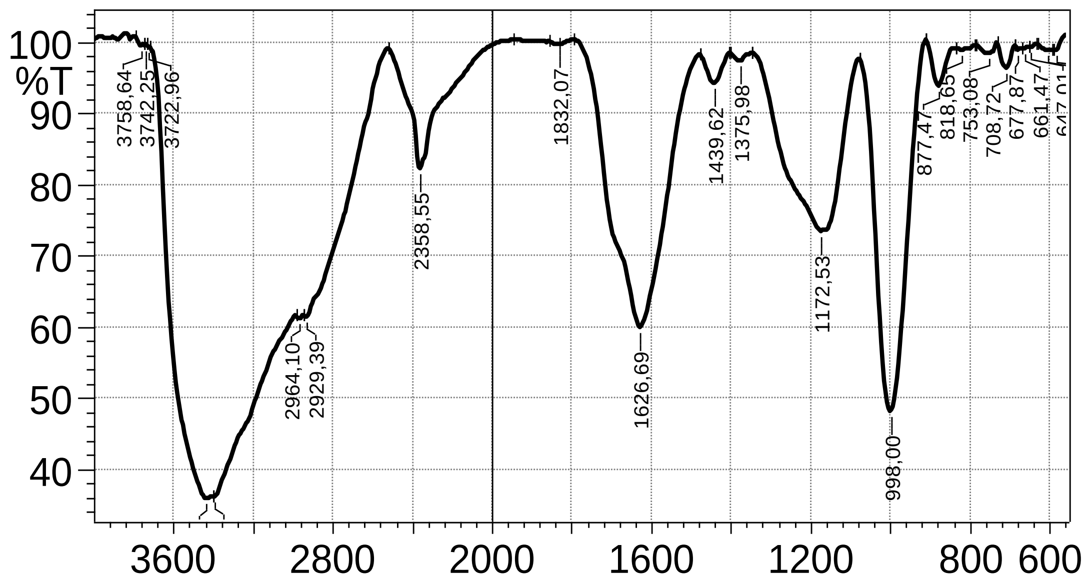


Figure 2. *FTIR spectrum of activated carbon from Persea americana seed.*

Absorption near 1100-1000 cm-1 indicates the existence of C-O bonds, which give the adsorbent material acidic surface characteristics. Bonds of type P=O, and P-O-C are also presented. These observed links are caused by impregnation with orthophosphoric acid (Rincón *et al.*, 2014; Guo and Rockstraw, 2007). FTIR characterization of activated carbon showed that activation with orthophosphoric acid has a very strong effect on surface modification (Figure 3).

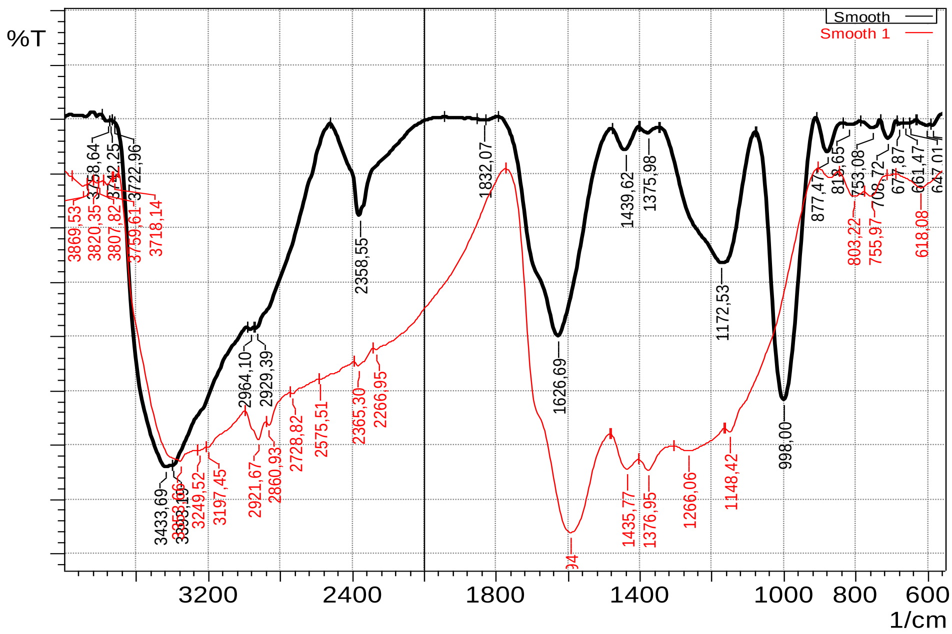


Figure 3. *FTIR spectrum of activated and non-activated (red color spectrum) carbon from Persea americana seed.*

3.3. *Morfología por microscopia electrónica de barrido (SEM)*

Figures 4 and 5 show the electron microscopy micrographs with different magnifications of the activated and non-activated carbon, obtained from the seed of *Persea americana* (HASS avocado), in which the morphology of both carbons is observed.

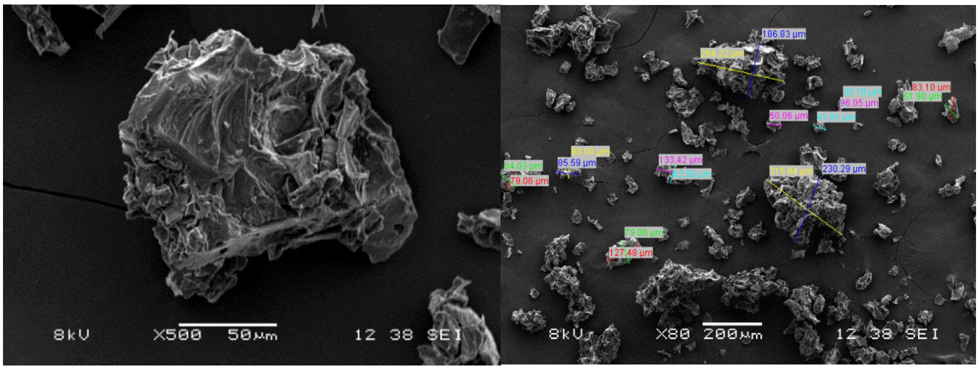


Figure 4. SEM images at different magnifications of unactivated *Persea americana* seed carbon.

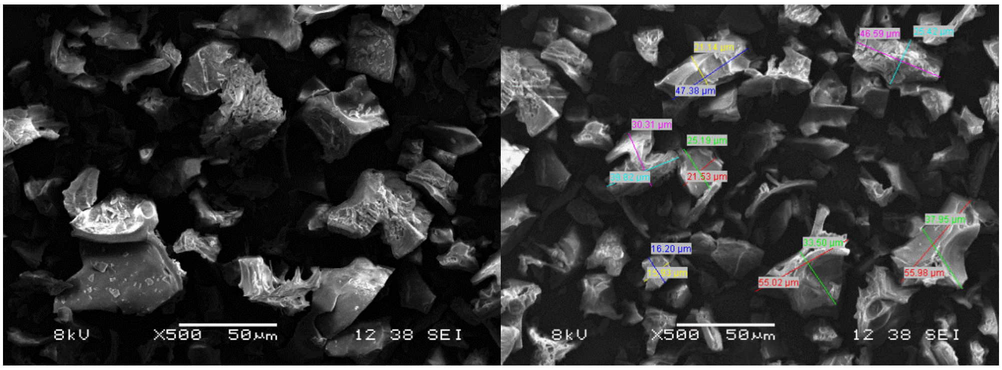


Figure 5. SEM images at different magnifications of *Persea americana* seed charcoal activated with orthophosphoric acid.

The micrograph of Figure 5, corresponding to chemically activated carbon, presents an amorphous structure, very heterogeneous, making its porosity evident due to the irregularity of its particles, a more porous structure than that of non-activated carbon can be clearly seen (Figure 4), which is consistent with the specific surface area values for CA and CNA (Section 3.2 of this manuscript) (Ospina *et al.*, 2014)

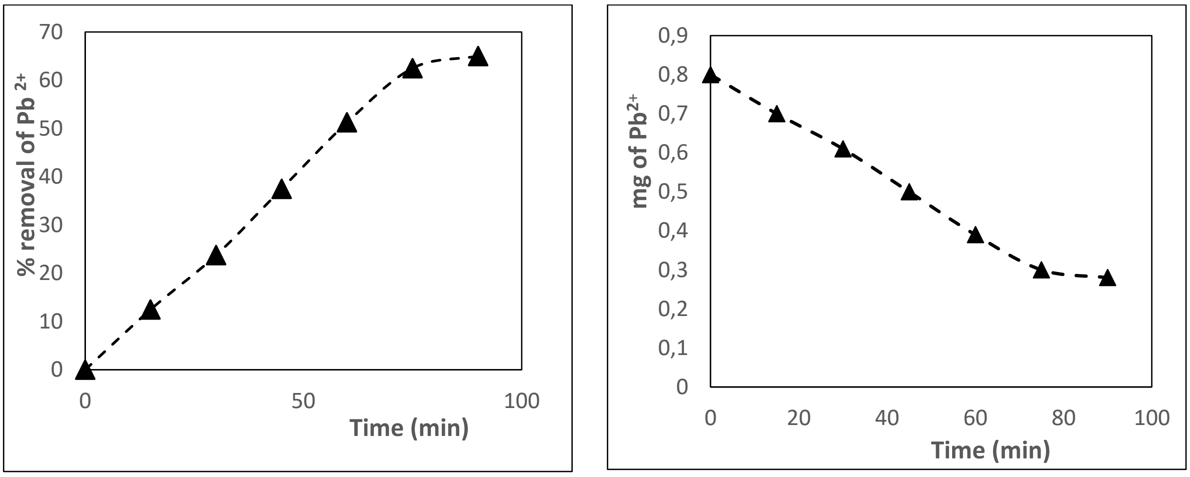
The cavities or pores of irregular sizes are in the range of 16.2 and 55.98 μm, while for the micrograph corresponding to non-activated carbon, the structure is not very porous, with a larger dispersion of sizes that are between 30 .1 and 83.10 μm, the results are comparable to those reported by Cruz *et al.* (2016), for activated carbons obtained from corn (Cruz *et al.*, 2016).

Activated carbon granules are highly variegated in shape and possibly highly porous, with pores of various shapes from hexagonal to irregular (Figure 5). Some solid structures are observed that are not part of the activated carbon walls, which have a size in the order of micrometers.

These structures could be related to the activating chemical agent, or to small pieces of the same carbons that are produced during the crushing of *Persea americana* seeds. Activated carbon (CA) and non-activated carbon (CNA) present grains of various sizes and shapes, showing the intertwining with the cellulose fibers (Figures 4 and 5).

3.4. *Pb^{2+} removal*

Figure 6 shows the % removal of Pb^{2+} from industrial wastewater (Figure 6a) and the amount of Pb^{2+} removed (Figure 6b.).



a b

Figure 6. Levels of Pb^{2+} removal in wastewater (0.2g of activated carbon/50mL).

The adsorbent material removes 65% of Pb^{2+} from the residual water in a time of 90 minutes, at longer times, the adsorbent does not show an increase in its removal capacity. In the interval between 20 and 75 minutes, the activated carbon manages to remove around 0.5 mg of Pb^{2+}, equivalent to 62.5% of the lead present in the wastewater. The lead values found after treatment with the adsorbent material are within the permissible limits by current Colombian regulations. These removal percentages are below those found by Jiménez *et al.* (2017).

Table 2 shows the values of the physicochemical parameters after treatment with activated carbon, it is possible to remove turbidity (57.6%), color (57%), total solids (50.2%), as well as BOD (53.12%) and COD (36%), finding significant statistical differences in the values at a significance level of 95%; the results correspond to those found by Tarón *et al.* (2021).

Table 2. Physicochemical characterization after treatment with activated carbon.

Parameter	Valor	Unids
Pb^{2+}	0.28 ± 0.31	mgL^{-1}
Turbidity	52.15 ± 1.2	NTU
DBO_5	120.0 ± 2.0	mgL^{-1}
DQO	198 ± 1.87	mgL^{-1}
Color	84.0 ± 1,15	UPC
Total solids	402 ± 2.30	mgL^{-1}

*Values represent the mean of three determinations.

4. CONCLUSIONS

The seed of *Persea americana* (HASS avocado) can serve as plant material to obtain an adsorbent material (activated carbon) and be used in the removal of heavy metals from wastewater. Activation with orthophosphoric acid increases the specific area, obtaining coal with a specific area of 203.2 m^2/kg. The FTIR study determined the presence of the important OH group in the adsorption of metal ions. Activation with orthophosphoric acid has a very strong effect on surface modification. Activated carbon from *Persea americana* can remove Pb^{2+} ions from wastewater, as well as reducing those of turbidity, color, total solids, BOD_5 and COD.

5. ACKNOWLEDGMENT

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