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Preparation and Characterization of a Bioadsorbent from Lignocellulosic Waste of Cocoa Pod Husk

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Chocolate is obtained from *Theobroma cacao* L., which is in high demand worldwide. However, industrialization generates quantities of waste ranging from cocoa pods, mucilage, and seed shells. Shells are sources of lignocellulosic residues rich in hemicellulose, cellulose, and lignin. These are useful as feedstock in the production of adsorbents for the removal of pollutants from water. Therefore, the objective of this study was to synthesize and characterize a biosorbent from cocoa shell, evaluating the effect of alkaline treatment on the properties of the material. From cocoa fruits obtained from the “Montes de Maria”, municipality of “Maria La Baja” in the department of Bolivar, Colombia, South America. The raw material was selected, washed, cut and dried in a tray at room temperature. The shells were classified according to their size (< 0.212 mm, 0.150 mm and 0.106 mm). Then, one part was subjected to alkaline treatment by immersing them in a 0.1 M NaOH solution, 60 min, room temperature and another part of the samples was not treated with an alkaline solution. Once the biosorbent was obtained, it was analyzed using scanning electron microscopy and X-ray spectroscopy. The SEM images showed that the samples without alkaline treatment do not have high porosity and have smooth surfaces, which is to be expected since when performing the alkaline treatment, it is expected that the modifications can improve the general adsorption properties of the natural form of the biomaterials; that is, increase the surface area and the number and diversity of functional groups, improve their adsorption capacity, and improve particle size, pore size, pore volume and morphology, stability, others. EDS analysis showed the presence of carbon and oxygen in the samples, and iron, potassium, chlorine, and gold were also found in most of them; and very few samples showed the presence of magnesium, bromine, and calcium. In conclusion, alkaline treatment made it possible to obtain high-porosity bioadsorbents that can be used to remove contaminants from water.

1. Introduction

Theobroma cacao L., also known as cocoa, is a tree that can grow up to 6-8 meters in height. It is a highly valued crop worldwide due to its contribution to the global economy and its use as the raw material for various products, including cocoa liquor, cocoa powder, cocoa butter, chocolate, and other commercially important derivatives (Darmawan and Mutalib, 2024; Jaimez, 2022). It is documented that global production between 2022 and 2023 was about 4.9 million tons (MT). It is noteworthy that most of this is produced in the humid tropics of West and Central Africa, Latin America and Southeast Asia (Tosto et al., 2023).
The growth of this sector has resulted in a significant increase in waste generation. This is due to the fact that the outer shell, cob, and husk of the seed constitute 92% of the product's dry weight and are discarded, while only the seed is of interest to the industry. In other words, only 8% of the fruit is utilized (Díaz, 2015).
The decrease in the use of these residues may be due to producers' limited knowledge of efficient and sustainable production processes, which can help reduce waste and promote the potential of this industry at the national level. The absence of reutilization technologies in the cocoa agroindustry has impeded the exploitation

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of valuable bio-components that could be used to generate high-value bioproducts (Zambrano et al., 2023). It is worth noting that the cocoa pod husk (CPH) has gained attention as a crop residue with potential uses in various industries, yielding excellent results (Bannor et al., 2024). In recent decades, the lignocellulosic composition of CPH has been the focus of scientific and production attention (Porto, 2022). Based on Fedecacao data, 2.1 MT of CPH was discarded in 2021 (Restrepo, 2023).

Colombian cocoa has been recognized for its unique flavor and aroma compared to cocoa from other countries, placing it in a select group of specialty cocoas. The cocoa sector's contribution to economic development and employment generation in the country has been significant. According to the National Federation of Cocoa Growers (Fedecacao), cocoa bean production increased from 37,000 tons in 2011 to over 62,000 tons in 2022. Additionally, the total area harvested for this product was 213,165.32 hectares in 2020 (Statista Agriculture, 2023). Cocoa shells are a promising bio adsorbent due to their high content of dietary fiber, which is formed by lignin and cellulose. This results in the presence of hemicellulose and polysaccharides, making them an attractive alternative for wastewater treatment. The use of bio adsorbents from lignocellulosic waste has gained popularity due to its low cost, high availability, and ease of operation (Akman et al., 2013).

This study aimed to obtain a bioadsorbent from lignocellulosic Cocoa Pod Husk (CPH) residues for the removal of pollutants from wastewater. The powdered CPH samples were divided into two groups, one treated with NaOH and the other left untreated. Chemical and morphological analyses were conducted on the surface of both the untreated and NaOH-treated CPH powdered samples.

2. Methodology

2.1. Pretreatment of Cocoa Hulls

The cocoa fruits were obtained from the crops of the Montes de María sub-region, specifically in the municipality of María La Baja in the department of Bolívar, located on the northern coast of Colombia (see Figure 1a). The raw material underwent a washing process with MilliQ water to eliminate dirt. Afterwards, the fruit was cut to separate the seeds from the pod shell (see Figure 1b). The pieces were then dried in trays at room temperature (see Figure 1c). The CPH was ground and sieved using an ASTM No. 100 stainless steel mesh to decrease the particle size to 0.212 mm, 0.150 mm, and 0.106 mm. Finally, it was oven dried at 65 °C for 30 minutes.

The baked samples were then sorted and half of them were subjected to alkaline treatment by immersing them in a 0.1 M NaOH solution (solid-liquid ratio of 50 g/L) without stirring for 60 minutes at room temperature (Pua et al., 2013). Finally, the samples were filtered, washed with distilled water until neutralized (pH 7.0), and dried in an oven at 65 °C for 2 hours. They were then stored in a desiccator until further use. Another portion of the samples was not treated with an alkaline solution.

The total weight loss of CPH after treatment with NaOH can be calculated using the following formula (Statista Agriculture, 2023).

$$\%\,Weigth\ loss = \frac{(W_0 - W_f)}{W_0} * 100$$

Where W_0 is the weigth of CPH before treatment and W_f is the weight of the CPH after NaOH treatment.

Figure 1 shows: a) cocoa fruit, b) pulped cocoa, and c) cocoa shells that have been cut and dried at room temperature.

2.2. Characterization of Cocoa Powder Hulls

SEM (Scanning Electron Microscopy) and EDS (Energy-dispersive X-ray spectroscopy) tests were performed to characterize the bioabsorbent.

2.2.1. Scanning Electron Microscopy (SEM)

The morphology of both untreated and NaOH pre-treated cocoa shell powder samples were analyzed using a Scanning Electron Microscope (Carl Zeiss model evo hd ma 15) at different magnifications. To ensure adequate conductivity, all samples were coated with a gold layer prior to observation.

2.2.2 Analysis EDS (Energy- disperse X ray-spectroscopy)

The elemental composition of both untreated and pretreated cocoa shell powder samples were analyzed using an Energy Dispersive X-Ray Spectrometer (Carl Zeiss model evo hd ma 15).

3. Results

Figure 2 shows electron micrographs of untreated and NaOH-treated CPH samples at different magnifications obtained from SEM analysis. The surface morphology and structure of untreated and NaOH-treated CPH are significantly different. The untreated CPHs have a smoother surface, while the NaOH-treated CPHs have a more porous structure and rougher surface, resulting in an increase in surface area. The weight loss of the HPCs after NaOH treatment indicates the removal of impurities from the HPCs during alkaline NaOH pre-treatment and corroborates Pua (2013), who found a 26.6% weight loss after NaOH treatment. These results demonstrate, as reported by Jimat (2020), who extracted CPH using an alkaline and minimal concentration of sulphuric acid and ultrasonic disintegration. Obtaining the isolation of microcrystalline alpha-cellulose, by pretreatment with 2% w/v NaOH, bleaching, hydrolysis and 12% w/v NaOH at 80 °C and 1% v/v sulfuric acid (H_2SO_4) at 80 °C. In addition, studies published in Colombia show that alkaline treatment associated with pressure is more effective when isolating cellulose microfibers from cocoa husks, allowing its evaluation in the manufacture of composite materials in order to add value to these wastes in the future (Hozman-Manrique, 2023). On the other hand, studies conducted by Ouattara (2023), have exposed the usefulness of performing acid hydrolysis of CPH, obtained from delignification with KOH. Providing advantages in the acid hydrolysis of polysaccharides, under conditions of low combined severity factors. Which is of great importance since the decrease in the recalcitrance of the material facilitates the accessibility of cellulosic compounds during subsequent acid hydrolysis.

Figures 3 (a-c) and 4 (a-c) display the EDS results, indicating the presence and quantity of elements in the sample. The untreated samples show the presence of carbon, oxygen, and potassium, while the NaOH-treated samples reveal the presence of magnesium, sodium, potassium, calcium, carbon, and oxygen.

The SEM images indicate that samples lacking alkaline treatment have low porosity and smooth surfaces. This outcome is expected since alkaline treatment is known to enhance the adsorption properties of natural biomaterials by increasing surface area, functional group diversity and number, adsorption capacity, particle size, pore size, pore volume, morphology, and stability (Wang, J and Wang, S, 2019).

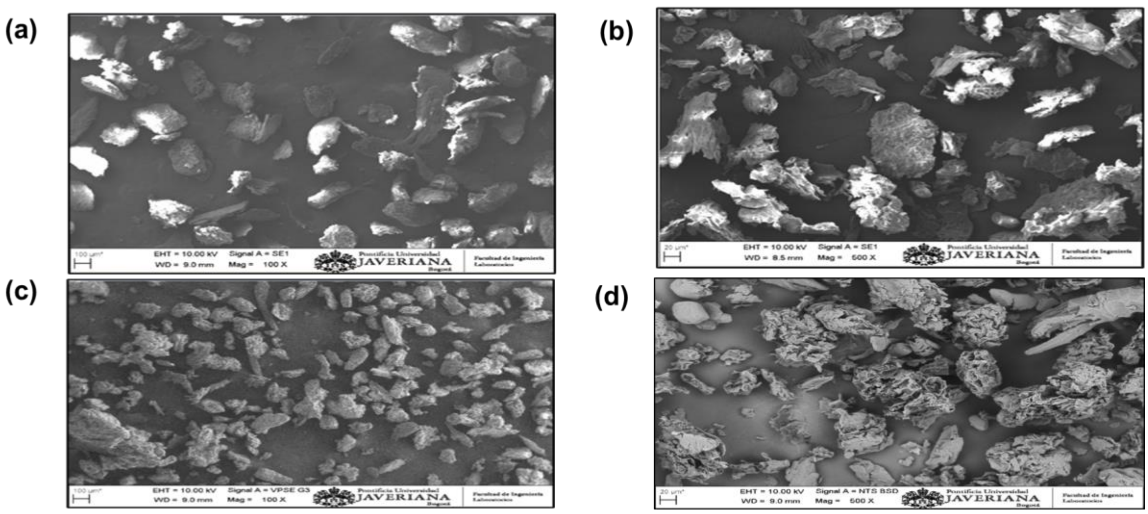

Figure 2 shows: SEM images of the sample before and after NaOH treatment. Panels (a) and (b) show the untreated sample at 100X and 500X magnification, respectively. Panels (c) and (d) show the sample after NaOH treatment at 100X and 500X magnification, respectively.

The EDS analysis revealed the presence of carbon and oxygen in all samples, with iron, potassium, chlorine, and gold also being detected in the majority of samples. Only a small number of samples showed the presence of magnesium, bromine, and calcium (Tony, 2022). Currently, inadequate waste management practices mean that CPH waste is not used in the production chain. This study presents an opportunity for the valorization of CPH in the industrial and academic sectors (Zambrano et al., 2023).

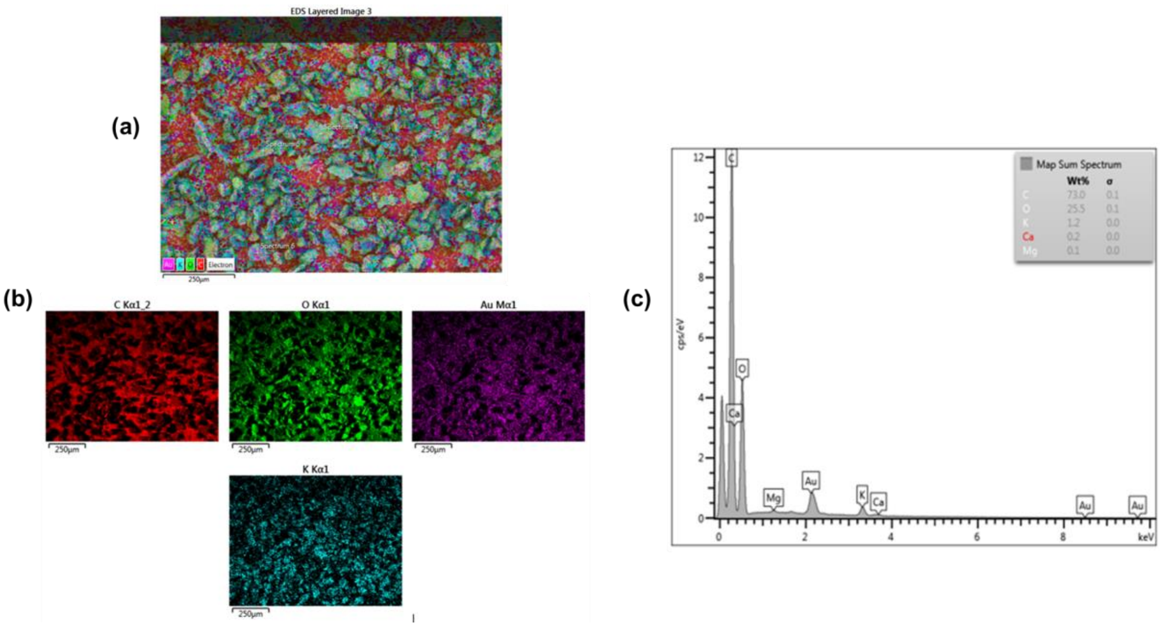

Figure 3: 3a and 3b shows the EDS images for the sample without alkaline treatment. 3c shows the elements found in the EDS analysis of the sample without alkaline treatment, along with their respective weight percentages.

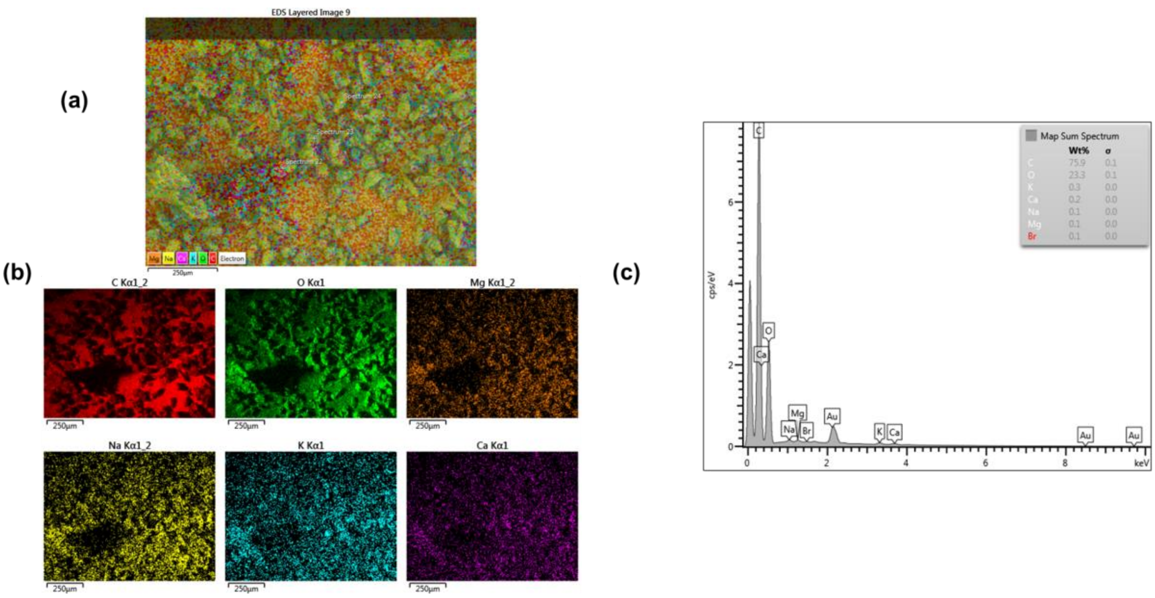

Figure 4: 4a and 4b, shows the EDS images for the sample treated with NaOH. Figure 4c shows the elements found with their weight percentages in EDS for a sample treated with NaOH.

4. Conclusions

Lignocellulosic-based adsorbents have gained widespread attention in recent years due to their renewability, low cost, biodegradability, high availability, and environmental friendliness. These biomaterials offer economically viable solutions to environmental pollution and the removal of undesirable compounds in various industrial applications.

SEM images confirm the change in CPH after treatment with NaOH, as evidenced by the increased porosity of the material. This could potentially make it useful as a bioadsorbent due to the increased surface area. The utilization of cocoa waste aids in decreasing the amount of waste produced in the industry, thereby reducing the environmental impact associated with improper waste disposal. This also helps in preventing soil and water contamination while promoting the development of sustainable bioeconomy strategies for generating value-added products. Such measures have a positive impact on the cocoa sector at the national level.

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