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ACTIVATED NANOCARBON SYNTHESIZED BY HEAT TREATMENT (FLUX-N_2) ON LIGNOCELLULOSIC COCOA POD RESIDUES APPLIED IN COCOA PODS REMOVAL.

NANOACTIVATED CARBON SYNTHESIZED BY THERMAL TREATMENT (FLOW-N_2) OVER LIGNOCELLULOSIC WASTES FROM COCOA POD HUSK APPLIED IN REMOVAL

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Abstract - Nanomaterials, i.e. materials at nanometer scale, with dimensions smaller than 100 nm, using lignocellulosic residues (residual biomass) as raw material for synthesis, are a sustainable alternative, which contributes to the principles of green chemistry and circular economy. The synthesis method used is based on a delignification process, promoted by pyrolysis, using a Nabertherm tubular muffle with a quartz tube. The process was carried out at temperatures of 500°C and 700°C for 1 or 2 hours in the presence of N_2flow, using a Proportional Integral Derivative (PID) controller, which generated Activated NanoCarbon (NCA) from Cocoa Husk.

Eutrophicated systems resulting from poor management of domestic wastewater include negative consequences such as human health, destruction of aquatic ecosystems and deterioration of water quality for human consumption. For this reason, we tested our NAC in liquid samples taken from Laguna de las Ilusiones, considered a Natural Protected Area of our State, to demonstrate the capacity of the synthesized bioadsorbent nanomaterials contributing with efficient, modern and low-cost technologies in the elimination of pollutants in real systems.

The adsorption experiments were carried out at 30°C conditions, reaching efficient removal rates of 70% of Total Organic Carbon (TOC). Furthermore, in comparison to the materials treated with chemical agents, these reached 70% of Chemical Oxygen Demand (COD) at more severe conditions of 35°C. Thus, the improvement in process economics was demonstrated with the NCA synthesized by heat treatment.

Key words: bioadsorbent nanomaterials, environmental impact, waste management, removal, aqueous contaminants, lignocellulosic wastes.

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The adsorption experiments were carried out under conditions of 30 °C, reaching an efficient 70% removal. Furthermore, compared to materials treated with chemical agents, these reached 70% but with more severe conditions of 35°C. Therefore, the improvement in the economy of the process was achieved with the NAC synthesized by thermal treatment.

Key words **-** bioadsorbent nanomaterials, environmental impact, waste management, removal, aqueous pollutants, lignocellulosic wastes.

INTRODUCTION

Natural Protected Areas (NPAs) are fundamental pillars in the conservation of biodiversity and the preservation of ecosystems. However, these areas face a growing threat due to anthropogenic pollution from sewage, which can compromise the health of the aquatic and terrestrial ecosystems they host. Laguna de las Ilusiones in Tabasco, Mexico, is no exception, and its ecological and socioeconomic value is threatened by the presence of domestic aqueous pollutants that affect its water quality and the biodiversity that inhabits it [1-3].

It should be taken into account that every year millions of cubic meters of wastewater are discharged into water bodies worldwide, coming from anthropogenic activities derived from municipal, industrial and/or agricultural discharges, either inadequately treated or untreated. For this reason, the proper use of water in the different sectors where it is used should be taken into account, since it is known that water scarcity in recent years has been increasing considerably in Mexico and the world [4-5]. Due to these data, we understand the high concern that the sources of human consumption continue to be preserved for future generations, unfortunately thanks to the enormous amount of domestic wastewater from industry and homes, there is no coverage to process this waste in Wastewater Treatment Plants (WWTP) or that do not have adequate treatments for the removal of certain pollutants that are very difficult to degrade, is that we are endangering the future of this vital resource, to be sufficient for the world's population [4-7].

In fact, there are freshwater bodies in different parts of the world, whether rivers, lakes, and lagoons that have been closed for use as drinking and recreational water, due to the high contamination they present and the adverse health effects for humans and aquatic organisms [8]. In addition to this, currently, there are areas in the world that show water depletion due to water stress, including extreme droughts, due to global warming. High temperatures modify the water cycle, and the amount of water that falls and is stored in freshwater bodies has decreased with respect to previous years [4,9].

One of the main causes of this decrease is due to eutrophication, which refers to the excess supply of organic nutrients from biodegradable organic matter, such as food waste, feces and urine, and due to their microbial decomposition there can be an excess of nutrients, mainly Nitrogen (N) and Phosphorus (P), in an aquatic ecosystem. Another source of excess nitrogen and phosphorus is derived from agricultural fields that are nourished with synthetic fertilizers and that reach freshwater bodies through runoff and slopes [2, 3, 10].

This eutrophication process causes the abundance of algae, water lilies and surface plants, as they feed on the exuberance of biodegradable organic matter, by performing the process of photosynthesis of plants, increase exponentially on the surface of the water body, because they come to be discharged these substances by the lack of capacity of Wastewater Treatment Plants, and to previously remove these substances [11]. What happens next is the decrease in the amount of oxygen dissolved in water, which causes the death of fish, reptiles or species that inhabit that body of fresh water, in addition to the proliferation of anaerobic microorganisms, many of which are pathogenic. This anaerobic environment produces the generation of toxins by the release of these substances through the secretion of pathogenic microorganisms. Animals can in turn act as a biological vector affecting other species and even reaching humans. The anoxic conditions of the bottom give rise to the growth of bacteria that produce lethal toxins for living beings that interact with the body of water, affecting the quality of the water, making it unfit for human consumption. Finally, in aesthetic aspects, the waters acquire a nauseating odor, losing their crystallinity and transparency [2, 3, 10, 11].

The application of innovative and low-cost technologies is becoming a pressing need for the preservation of PNAs in Mexico [12]. One of the most promising emerging technologies is the use of bioadsorbent nanomaterials for contaminant removal in aquatic systems [13-15]. These nanomaterials offer unique adsorption properties and may be an effective and sustainable solution for improving water quality in the Laguna de las Ilusiones. Bioadsorbent nanomaterials, derived from natural or synthetic sources, have a high surface area and a high adsorption capacity for organic and inorganic contaminants present in water. Their application in Laguna de las Ilusiones could contribute significantly to the removal of heavy metals, organic compounds and other domestic aqueous pollutants that threaten the health of this aquatic ecosystem. In addition to their effectiveness in the removal of pollutants, bioadsorbent nanomaterials also present advantages such as biocompatibility, low

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environmental impact, and possibility of regeneration and reuse, which makes them an attractive option for the preservation of ANP such as Laguna de las Ilusiones [16-19].

The objective of this project is to use nanomaterials, which are materials with dimensions of less than 100 nanometers, made from lignocellulosic waste (residual biomass) as raw material for their synthesis. These nanomaterials have adsorbent properties. Depending on the experimental conditions during their synthesis, they can be obtained as activated or partially carbonized carbon, with nanometric properties, called Activated NanoCarbon.

The raw material, cocoa pod (Theobroma Cacao L.) for the synthesis of activated carbon, was selected in this study, as it is a residual product that accumulates daily in the markets and processing plants of the State of Tabasco. The project obtained activated nanocarbon based on lignocellulosic residues of Cocoa Shell (CC), which was washed, dried, crushed, pulverized and followed by calcination in a tubular muffle at a temperature of 500 and 700°C with a flow of N_2. This resulted in a bioadsorbent nanomaterial with the capacity to remove pollutants from contaminated aquifers. In Tabasco, special attention is given to the Laguna de las Ilusiones, since it presents severe environmental damage, and its removal capacity was gratifyingly demonstrated with samples taken in this Natural Protected Area of our State.

DEVELOPMENT

Methodology

A) Synthesis of Nanomaterials

The synthesis method was carried out at the Research Laboratory I, Nanotechnology Area at the National Technological Institute of Mexico, specifically at the Technological Institute of Villahermosa, located at km 3.5 of the Villahermosa-Frontera highway.

Relevant information in the scientific literature was gathered and reviewed to understand the preparation methods and parameters that most significantly affect the structural and textural properties of biomass-based nanoadsorbent materials. There are several techniques, including immersion in acidic and/or alkaline chemical solutions, as well as thermal, ultrasonic, microwave treatments, among others.

For the synthesis of the nanomaterial, we chose residues of agro-industrial products of great economic impact in our State of Tabasco and in the South-Southeast Region, derived from the processing of cocoa beans. For the preparation process, a preliminary step, which included dehydration and pulverization, was performed on the cocoa shell.

The preliminary step for the cocoa shell included removing the pericarp and endocarp to keep only the mesocarp and exocarp. With this process, the cocoa husk was exposed from its pod; these residues were obtained from a local producer, who retails dry beans for the preparation of pozol in the municipality of Nacajuca, Tabasco. The cocoa pod shells were reduced in size by cutting them into pieces for efficient washing and that, at the time of drying, the heat transfer is as homogeneous as possible. The washing was done in three stages, the first with purified water, the second with distilled water, and the third with deionized water at 40°C. After washing, it was dried by forced convection to remove surface water from the pod. After removing the surface water, the sample was weighed and dried in an oven at 100°C for a period of 24 hours.

The delignification process for the synthesis of nanomaterials was carried out with the heat treatment synthesis method. The finely generated cocoa shell powder previously washed and dehydrated in the same way as the previous treatment was placed in a Nabertherm tubular flask in a quartz tube with gas inlet and outlet(N_2) . The dry sample was calcined at a temperature of 500 and 700 °C for 1 hour occupying a heating rate of 10°C/min and a volumetric flow rate of 75 ml/min (1.25 ml/s). With this thermal method of synthesis, a dark colored powder was generated, characteristic of activated carbon, with nanoporous structure and nanocrystals, attributing characteristics of Activated NanoCarbon, from the characterizations by EIR and SEM.

Details of the synthesis experiments carried out are given in Table 1 (the alkaline treatment, reported elsewhere, is included).

Table 1. *Experimental conditions used in the thermal and alkaline treatment.*

Method	Experimental conditions occupied
Alkaline -Cocoa	White
	Treated with 0.1 M NaOH
	Treated with 5M NaOH
N_2-Cocoa	White
	500°C for 2 hours, 10 °C/min, 1.25 ml/s of $N_{(2)}$ (with gradual cooling).
	500°C for 1 hour, 10 °C/min,1.25 ml/s of $N_{(2)}$ (without gradual cooling).
	500°C for 1 hour, 10 °C/min, 1.25 ml/s of $N_{(2)}$ (replicate, no gradual cooling).
	500°C for 1 hour, 10 °C/min, 1.25 ml/s of $N_{(2)}$ (replicate, with gradual cooling).
	700°C for 1 hour, 10 °C/min, 1.25 ml/s of $N_{(2)}$ (replicate, no gradual cooling).
	700°C for 1 hour, 10 °C/min, 1.25 ml/s of $N_{(2)}$ (replicate, with gradual cooling).

B) Characterization of the synthesized nanomaterials by Scanning Electron Microscopy and Infrared Spectrophotometry.

Scanning Electron Microscopy (SEM) is an imaging technique widely used in materials research due to its high resolution and capabilities to analyze morphological, structural and chemical characteristics of the samples under study. SEM studies were carried out using a Scanning Electron Microscope (Hitachi S-3000N model) at an electron accelerating voltage of 20 kV. This analysis was carried out by the Centro de Investigación de Ciencia y Tecnología Aplicada de Tabasco of the División Académica de Ciencias Básicas of the Universidad Juárez Autónoma de Tabasco, as well as the collaboration of Benemérita Universidad Autónoma de Puebla (BUAP), in the Chemical Sciences faculty at the Laboratorio de Pruebas Analíticas no destructivas, with the support of Dr. Gerardo Enrique Córdova Pérez.

The Infrared Spectrophotometry method, also known as IR, was selected. It is based on the interaction of infrared radiation with matter by absorption, emission or reflection. Thus, infrared (IR) spectrophotometers are widely used to identify chemicals with specific functional groups. This analysis was carried out in the specialized laboratory of process engineering, located in the Academic Division of Agricultural Sciences of the UJAT, with the collaboration of Dr. Pedro García Alamilla.

C) Contaminant removal experiments in liquid samples taken at Laguna de las Ilusiones

The ideal site for sampling was identified, in this case Vaso Cencali, since it is considered the most contaminated area of the Laguna de las Ilusiones. The sampling procedure was based on Standard NMX-AA-003-1980 Wastewater-Sampling. For the sampling process, nitrile gloves, mouth covers and a clean gown were used. The sampling container was rinsed 10 times before sampling, the rinsing was done by completely filling the container and submerging it completely.

The sampling container was attached to a PVC tube, which provided a sampling depth of 30 cm, the sampling was performed with gloves on each hand and mouth covers, approximately 1 liter was extracted. The sample was labeled to be correctly identified at any time, and was placed in a cooler at 277K (4°C) for transport to the site of the adsorption or contaminant removal experiments.

For the adsorption or removal experiments, we carried out a 3-factor experimental design with 2 levels and one replicate for the adsorption of contaminants in samples taken in Laguna de las Ilusiones, a 2^3. The factors to be controlled in the experiments were: 1) temperature of the medium (30°C and 50 °C), 2) adsorbent loading (2 g/l and 4 g/l; 0.300 g and 0.600 g of nanoadsorbent material) and 3) pH of the medium (2 and 6). Table 2 details the conditions of the 8 experiments generated occupied a 2^3, which were subsequently carried out randomly.

Table 2. *Experimental design of 3 factors with 2 levels and one replication for the adsorption of contaminants in samples collected in Laguna de las Ilusiones ($2^{3)}$.*

Experiment	Factor A Medium temperature (°C)	Factor B Adsorbent load (g)	Factor C pH of the medium
1	30	0.300	2
2	50	0.300	2
3	30	0.600	2
4	50	0.600	2
5	30	0.300	6
6	50	0.300	6
7	30	0.600	6
8	50	0.600	6

In a 250 mL beaker, 0.3 or 0.6 g of bioadsorbent nanomaterial synthesized with Cocoa Husk biomass was added using heat treatment at 500 °C and 150 mL of the problem solution regulated at pH 6 or pH 2 using hydrochloric acid dripping, over a heating grill with magnetic stirring, regulating the stirring speed at 600 rpm

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and the temperature at 30 or 50°C. The process time was 180 min. Samples were taken every half hour and at zero time. Prior analysis these will be filtered to avoid the presence of bionanoadsorbent residues and then deposited in eppendorf tubes, wrapped with light insulating paper and stored in refrigerator, for later analysis. Then to measure the Chemical Oxygen Demand, using Hanna vials with a medium range of 0 to 1500 mg/L, 2 ml of sample were taken to be digested at 150°C for 2 h and then measured with a compatible spectrophotometer, the Hanna iris visible spectrophotometer model HI801-01 of 115 V, at 600 nm.

Another analysis involved was the Total Organic Carbon (TOC). The determination of TOC values of the initial and final solution treated with the nanoadsorbents synthesized by thermal treatment was performed with a Shimadzu equipment. In this (differential) method, Total Carbon (TC) and Inorganic Carbon (IC) are determined separately, and TOC can be calculated by subtracting IC from TC.

DISCUSSION AND ANALYSIS OF RESULTS

A) Characterization of the synthesized nanomaterials by Scanning Electron Microscopy and Infrared Spectrophotometry.

The morphological and textural properties of cocoa pod shell biomass occupying heat treatments with Nitrogen Flux at 500 and 700°C respectively, with a process time of 1 and 2 hours respectively, were investigated by Scanning Electron Microscopy (SEM), as well as the comparison with the blank, are presented in Figure 1-3.

After the dehydration and pulverization process, the samples lost approximately 70% moisture by weight. In addition, after the heat treatment, in which 20 g of the dehydrated samples were taken, there was a weight loss of approximately 60%.

Figure 2 shows the SEM micrographs of an area of the sample taken randomly from the Cocoa Husk, dehydrated and pulverized with heat treatment with nitrogen flow at 500°C, in a process time of 1 hour with slow cooling. The lignocellulosic structure shows amorphous crystals even after treatment, possibly due to the presence of hemicellulose, pectin and lignin [20]. However, it still shows a greater number of three-dimensional crystals in hemispherical form and in the form of rods;

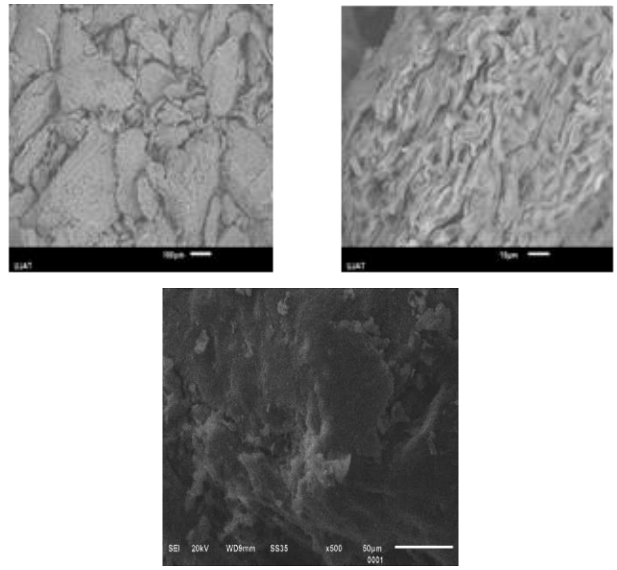


Figure 1. *Micrographs of dehydrated and powdered Cocoa Shell (CC) without heat treatment.*

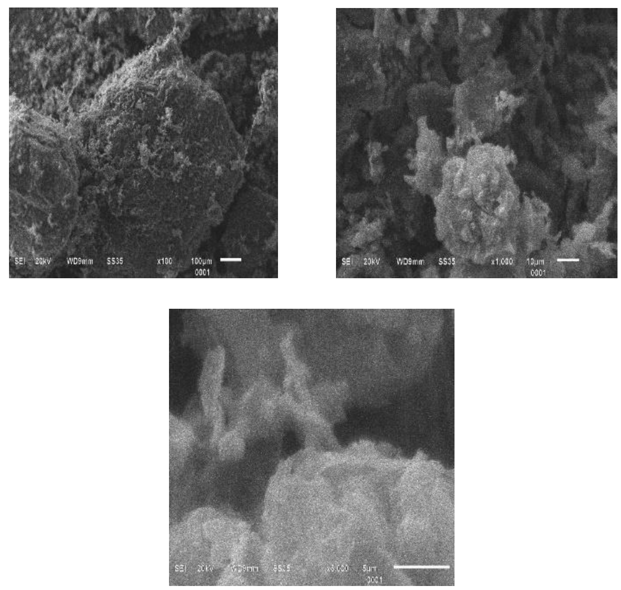


Figure 2. *Micrographs of Cocoa Shell (CC) treated with Nitrogen Flux at 500 °C for 1 hour, with slow cooling.*

The surface is rougher, therefore, more porous, due to a greater number of dark cavities, compared to the white material. In particular, these individual elongated rod-like structures stand out in the nanocrystals that can be seen. This material can be considered polycrystalline. This indicates that this concentration promotes a partial hydrolysis in the residual cocoa biomass [21].

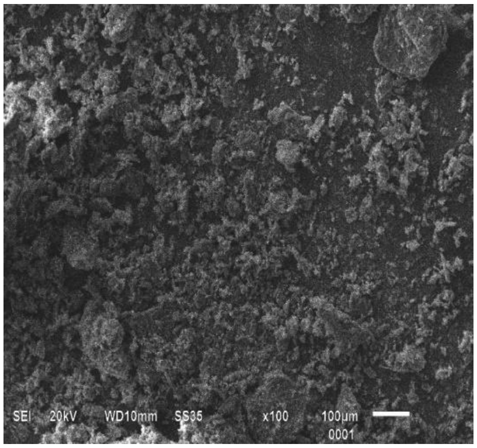


Figure 3. *Micrograph of Cocoa Shell (CC) treated with Nitrogen Flux at 500 °C for 2 hours, with slow cooling.*

Figure 3 shows the SEM micrograph of an area of the sample taken randomly from the Cocoa Husk, dehydrated and pulverized with heat treatment with nitrogen flow at 500°C, in a process time of 2 hours with slow cooling. The image is presented with a magnification of X100, if we compare it with the same magnification in Figure 2, it allows us to qualitatively infer that it has smaller crystal sizes, the longer the calcination time.

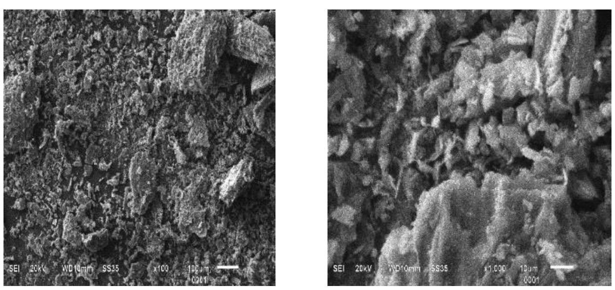
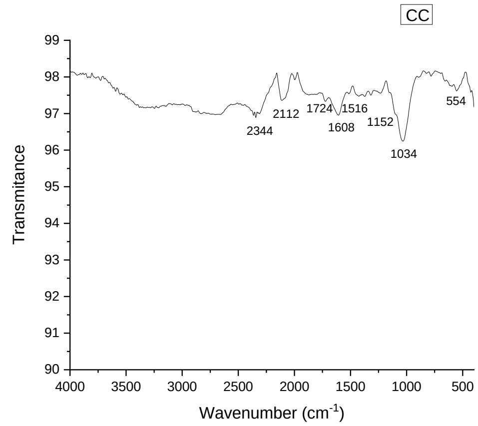


Figure 4. *Micrograph of Cocoa Shell (CC) treated with Nitrogen Flux at 700 °C for 1 hour, with slow cooling.*

Figure 4 shows the SEM micrograph of an area of the sample taken randomly from the Cocoa Husk, dehydrated and pulverized with heat treatment with Nitrogen Flux at 700°C, in a process time of 1 hour with slow cooling. The images are presented
with an enlargement of X100 and X1000.

The results of Fourier Transform Infrared Spectroscopy Analysis for Cocoa Husk samples dehydrated and heat treated with Nitrogen Flux at 500°C, at a process time of 1 hour with slow cooling, respectively, are presented in Figures 5-6.



Fourier Transform Infrared Spectrum of dehydrated and pulverized Cocoa Shell (CC) without heat treatment.

Figure 5, a band at 1724 $cm^{-1}$is observed which is attributed to the stretching vibration of the acetyl and uronic ester groups in pectin, while the carboxylic acids of hemicelluloses or the ester bond of the carboxylic group of ferulic and p-coumaric acids of lignin, is associated 1516 cm^{-1}.

The band at 1318 cm^{-1}in Figure 5 is attributed to aromatic vibrations in the -C=C- plane of the lignin bond, in conjunction with the out-of-plane bending peaks = CH at 874 and 830 cm^{-1}.

The 1258cm^{-1}band in the spectrum in Figure 6, of dehydrated and pulverized Cocoa Husk heat treated at 500°C is attributed to C=C in planar aromatic vibrations due to the presence of lignin and C-O-C ether extending from the ether bond found in the lignin.

The band at 1724 cm^{-1}that is present in Figure 5, after heat treatment disappeared (Figure 6), which showed that all the ester bonds of hemicelluloses were cleaved by the treatment. However , this treatment does not affect the ether bonds between lignin and hemicelluloses [20].

The disappearance of this band, according to Outtara et al [2023] [22] justifies the cleavage of all ester bonds of hemicelluloses after heat treatment, the changes in this region are attributed to the C = O stretching vibration with the benzene ring (lignin) and the carbonyl and acetyl groups in the xylan component of hemicelluloses.

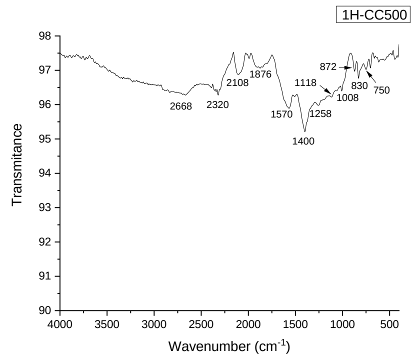


Figure 6. *Fourier Transform Infrared Spectrum of DC treated with nitrogen flux at 500 °C for 1 hour.*

The results of Fourier Transform Infrared Spectroscopy Analysis for Cocoa Husk samples heat treated with Nitrogen Flux at 700°C, at a process time of 1h with and without gradual cooling, respectively, are presented in Figures 7-8.

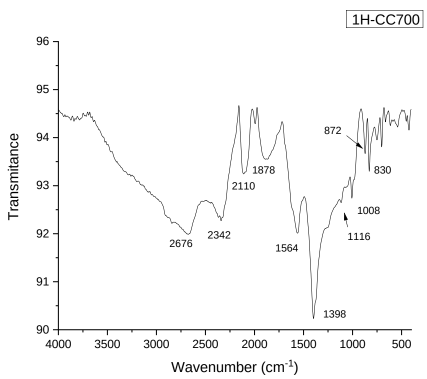
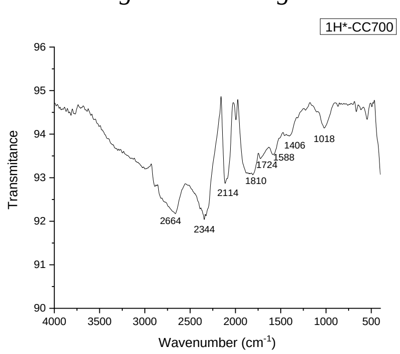


Figure 7. *Fourier Transform Infrared Spectrum of DC treated with Nitrogen flow at 700 °C for 1 hour, without gradual cooling.*



Fourier Transform Infrared Spectrum of DC treated with nitrogen flux at 700 °C for 1 hour, with gradual cooling.

The band at 1724 cm^{-1}that is present in Figure 8, CC heat-treated at 700°C, with gradual cooling, disappeared in Figure 7, with the same conditions, only that the material was drastically cooled after the end of the heat treatment, which showed that all the ester bonds of the hemicelluloses were cleaved by the treatment, for this material. However, this treatment does not affect the ether bonds between lignin and hemicelluloses [20].

B) Contaminant removal experiments in liquid samples taken at Laguna de las Ilusiones

The parameters Chemical Oxygen Demand and Total Organic Carbon were used in this study to determine the efficiency in the removal treatments of contaminants present in a complex matrix of liquid sample taken from Laguna de las Ilusiones, in the Cencali Vessel, in the city of Villahermosa, Tabasco, Mexico.

In order to make a broader process discussion, we first tested the adsorbent nanomaterials synthesized with alkaline treated Cocoa Husk to make a comparative study of the efficiency with thermally synthesized nanomaterials and those treated with chemical agents.

The Laguna de las Ilusiones shows great variability in its initial content of pollutants, measured by $COD_0$and TOC_0, these effects are attributed to periods of drought and the rainy season, which cause a natural dilution of pollutants. The initial characterization of Chemical Oxygen Demand, taken on March 20, 2024, generated a $COD_0$of 1100 mg/l with a pH of 5. On August 21, 2024, it gave us $COD_0$of 87 mg/l with pH 6-7. For the month of September it gave us $COD_0$of 30 and 80 mg/l, respectively with pH 6-7.

In the TOC and COD results, the parameters of temperature, pH and adsorbent load were controlled for the removal of pollutants in the Laguna de las Ilusiones. The TOC and COD results showed that the complex matrix of pollutants present in the Laguna de las Ilusiones was not effectively removed, but we consider, based on the previous preliminary results, that there were indications that what was affecting the results was due to method factors. In addition, the crystallinity and transparency of the water improved after the removal process, as shown in Figure 42. Therefore, water quality was improved since transparency is associated with the amount of suspended particles. Quantitatively, it can be measured through Turbidity analysis and determination of Total Suspended Solids.

Table 3. *TOC and COD results of an experimental design 2^3, whose parameters to be controlled were temperature, pH and adsorbent loading for the removal of pollutants in the Laguna de las Ilusiones.*

Sample	COD (mg/l)	TOC (ppm)

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$E_{(2)\ TO}$	220	4.66
$E_{(2)\ T150}$	239	-
$E_{(2)\ T180}$	259	24.10
$E_{(8)\ TO}$	78	7.10
$E_{(8)\ T150}$	76	-
$E_{(8)\ T180}$	94	124.6
$E_{(5)\ TO}$	28	7.90
$E_{(5)\ T150}$	50	-
$E_{(5)\ T180}$	78	48.21
$E_{(7)\ TO}$	5	7.38
$E_{(7)\ T150}$	54	-
$E_{(7)\ T180}$	52	74.59

In the TOC and COD results, the parameters of temperature, pH and adsorbent loading were controlled for the removal of pollutants in the Laguna de las Ilusiones. The TOC and COD results showed that the complex matrix of pollutants present in the Laguna de las Ilusiones was not effectively removed using thermally synthesized nanomaterials.

Although we considered, from previous preliminary results, that there were indications that what was affecting the results was COD and TOC measurement method factors. In particular, at a slightly acidic pH 6 during the adsorption experiments, the acid-treated pineapple crown showed more than outstanding values of 100% COD removal. The alkaline-treated cocoa pod achieved 70 to 75% after 180 min of adsorption. In addition, it should be noted that at 90 min the pineapple crown had already reached its mass balance, improving the process times, as it was left in less time. Although in both cases, the results of transparency and crystallinity were not achieved with the naked eye.

In addition, the crystallinity and transparency of the water was improved after the pollutant removal process using the heat-treated nanomaterials was qualitatively demonstrated, as shown in Figure 9 and 10. Quantitatively, it can be measured through Turbidity analysis and determination of Total Suspended Solids.

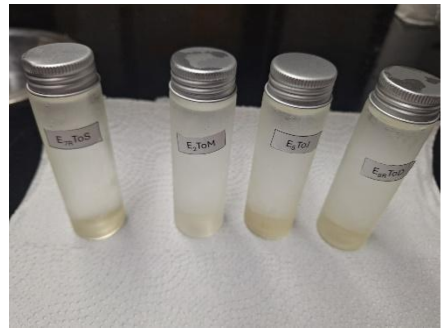
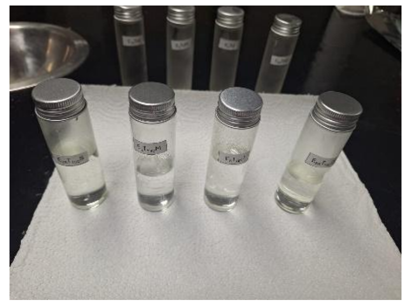


Figure 9. Physical appearance of samples for TOC and COD before the contaminant removal process.



Physical appearance of samples for TOC and COD after the contaminant removal process.

Experiment 7 was repeated, together with its replicate, to take corrective measures. From the previous experiments, the COD and TOC results are presented in Table 4.

The analysis made by our research group allows us to infer that a factor that may have contributed to the lack of improvement in COD removal is that the pH had to be regulated with an acid that did not
will cause the leaching of the activated carbon, that is, its particle size is reduced even more, since both in TOC and COD, the content increased with respect to time, but qualitatively, it is observed that the turbidity was improved, so adjustments will be made to find an acid that does not cause alterations in the activated nanocarbon, in the particle size, since we use filters with a sieve of 0.42 µm, the option is to buy filters with a 0.20 µm sieve, and even dilute the pH control, as was done in the previous study with materials treated with chemical agents, since this effect did not occur there.

Table 4. TOC and COD results of an experimental design 2^3, repetition of experiment 7 for the removal of pollutants in the Laguna de las Ilusiones.

Sample	COD (mg/l)	TOC (ppm)
$E_{(7)\ TO}$	35	29.82

$E_{(7)\ T180}$	54	9.08
$E_{(7)\ TO}$	33	8.20
$E_{(7)\ T180}$	50	44.66

Another decisive factor in the veracity of the results is that activated nanochar, being a biodegradable residue, contributes to TOC and COD, if it is not effectively removed, so that, although it removes pollutants from the liquid medium, to verify how much it removes, it must be effectively removed from the samples to be analyzed. Tests can be done to measure turbidity with turbidimeters and total suspended solids to corroborate the improvements in future projects, since the ultimate goal is to improve water quality, and the activated nanocarbon, being biodegradable, is not adding toxicity to the domestic effluent, but it does effectively remove pollutants from the complex matrix of the lagoon. Another factor to improve is that the addition of HCl to regulate the pH can affect the COD analysis, since the presence of chlorides contributes to oxidation in the HANNA vials. Another cause, the use of clean and dry filters, sufficient for removal of the bioadsorbent nanocarbon, since they did not have enough, by not cleaning the ones they used a day before, to have more available, when the filter was saturated with the activated nanocarbon, it was very difficult to take the volume of the liquid. Even the centrifuge was used, but being very small, with a maximum range of 4000 rev/min, it could not be effective to remove 100% of the nanocarbon. In one of the successful experiments, it was observed that the proper use of clean and dry filters was determinant for the positive result.

CONCLUSIONS

Heat treatment of cocoa husk at 500 and 700 °C under nitrogen flow improved its adsorption capacity by modifying its structure and composition, increasing carbon content and reducing oxygen, as confirmed by EIR and EDX analysis. This optimized the properties of the bioadsorbent by removing hemicellulose, favoring its application in the removal of pollutants in the Laguna de las Ilusiones. The tests showed improvements in water transparency and a partial reduction of COD and TOC, reaching up to 70% removal in certain experiments. However, complete contaminant removal was not achieved due to factors such as the type of acid used to adjust pH and filter saturation.

Equipment limitations, such as the availability of clean filters and centrifuge efficiency, affected the measurement of COD and TOC, highlighting the need for improvements in instrumentation for a more accurate assessment. In addition, the use of HCl to regulate pH could be altering the results due to the presence of chlorides, so it is recommended to explore other acids or dilution methods. In general, the use of bioadsorbent nanomaterials for wastewater treatment represents an advance in environmental protection, requiring specialized personnel to optimize their application and contribute to the improvement of water quality in impacted environments.

Future research from this work could focus on optimizing synthesis of the activated nanocarbon to improve its adsorption capacity by modifications with transition metals.

Also, to study its regeneration and reuse to assess its long-term viability in wastewater treatment.

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