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ENVIRONMENTAL ENGINEERING

Cocoa husk-derived Biochars synthesized at low temperature impregnated with zinc chloride for removal of ibuprofen in different solutions

INGENIERÍA AMBIENTAL

Biochars derivados de cacao sintetizados a baja temperatura impregnados con cloruro de zinc para la eliminación de ibuprofeno en diferentes soluciones

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Abstract

Metabolites and residual compounds from pharmaceutic industry are considered as emerging contaminants and an increasing source of environmental pollution, as they are used by a quantity of people, and due to their physicochemical properties, they are easily transported to hydrological systems and bodies of water. Then, the elimination of this kind of compounds from water by adsorption is one of the most promising techniques. The aim of this research was to study the kinetic and isotherms of ibuprofen adsorption onto low temperature-synthetized activated carbons from cocoa husks (*Theobroma cacao*) and impregnated with a solution of Zinc Chloride ($ZnCl_2$) at impregnations ratios

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biomass:solution of 1:2 (CA1:2) and 1:3 (CA1:3). The material source and activated underwent a chemical and textural characterization by elemental analysis, scanning electron microscopy (SEM) and the Brunauer Emmett Teller method (BET), for knowing their morphology, chemical composition, and surface area. Ibuprofen solutions at 20, 30 and 40 ppm were used to perform adsorption tests. The activation of cocoa husk caused an increase in the porosity and surface area of the charcoals, evidenced in the results of the SEM analysis, with CA1:2 being the one that presented such properties in a greater proportion (297.21 m^2/g); likewise, it was the carbon that eliminated the highest ibuprofen quantity. The maximum amount of ibuprofen adsorbed by CA1:2 and CA1:3 were 68.27 mg/g and 65.75 mg/g, respectively. Results suggest that the charcoals activated from cocoa husk are considered as good adsorbents of ibuprofen, collaborating in the reduction of this pollutant in the aqueous phase, contributing to environmental sanitation.

Keywords*: adsorption, charcoal, emerging contaminants, pharmaceutical compounds.*

Resumen

Los compuestos residuales y sus metabolitos de la industria farmacéutica son considerados contaminantes emergentes y una fuente creciente de contaminación ambiental, ya que son utilizados Por una gran cantidad de personas. Debido a sus propiedades fisicoquímicas, se transportan fácilmente a los sistemas hidrológicos y a cuerpos de agua. Así, la eliminación de este tipo de compuestos del agua mediante adsorción es una de las técnicas más prometedoras. El objetivo de éste investigación fue el estudiar la cinética y las isotermas de adsorción del ibuprofeno sobre carbones activados sintetizados a baja temperatura a partir de cáscaras de cacao (*Theobroma cacao*), e impregnadas con cloruro de zinc ($ZnCl_2$) a relaciones de impregnación 1:2 (CA1: 2) y 1:3 (CA1: 3). Al material de partida y activado se le realizó-una caracterización química y textural mediante análisis elemental, microscopía electrónica de barrido (SEM) y método Brunauer Emmett Teller (BET). para conocer su morfología, composición física y área superficial. Para realizar las pruebas de adsorción se utilizaron soluciones de ibuprofeno a 20, 30 y 40 ppm. La activación de la cáscara de cacao causó un aumento en la porosidad y área superficial de los carbones, como se evidencia en los resultados del análisis SEM, siendo CA1:2 el que presentó dichas propiedades en mayor proporción (297.21 m^2/g), asimismo, fue el carbón que eliminó la mayor cantidad de ibuprofeno. La cantidad máxima de ibuprofeno adsorbida por CA1:2 y CA1:3 fueron de 68.27 mg/g y 65.75 mg/g, respectivamente. Los resultados sugieren que los bio-carbones activados elaborados a partir de cáscara de cacao, son considerados buenos adsorbentes de ibuprofeno, colaborando en la disminución de este contaminante en fase acuosa, contribuyendo al saneamiento ambiental.

Palabras clave: *adsorción, carbón vegetal, compuestos farmacéuticos, contaminantes emergentes.*

1. Introduction

Emerging contaminants include pharmaceutical products, pesticides, personal care products, surfactants, industrial additives and a wide variety of chemical products, which affect the quality of water, and thus the quality of life of aquatic organisms and humans [(1)]. Specifically, the presence of pharmaceutical compounds in water sources, especially non-steroidal anti-inflammatory drugs, is a major concern because they can affect human health, and also produces negative effects on terrestrial and aquatic ecosystems, due to bio-accumulation [(2)]. The emissions of pharmaceutical compounds (PhCs) to the ecosystem are increasing as result of the hospital discharge, self-medication, elimination of expired drugs, and other sources of emission [(3)]. Therefore, the induced pollution by these residues is classified as being one of the major problems requiring a deep study in order find solutions for their elimination [(4)]. Thus, these residues are still residues in the environment are considered treated as "compounds of emerging concern" and their hazardous potential was recently stablished, determining that some environmental effects of pharmaceuticals can be established in the μg/L and ng/L concentration ranges [(5)].

There have been advances who have allowed the identification of many pharmaceutical metabolites in the environment; thus could help to unravel their mobility, fate, possible effects and toxicity as well as methods for their efficient removal from different water sources [(6)]. Pharmaceuticals compounds have ecological and

environmental risks such as inhibition of protein synthesis, nucleic acid (DNA/RNA) synthesis, exert toxic effects on numerous organisms in the environment, abnormal protein and enzyme activities, antibiotic resistance in bacteria, gene expression alterations, , and growth malformations in rats, birds [7]. Likewise, various processes are designed to remove toxic pollutants from wastewater prior to entering rivers, including adsorption [4,8], membrane filtration [9], precipitation, and electrochemical advanced oxidation methods [10], in order to preserving the freshwater sources. Finding that, these technologies have good approach at low initial concentrations of pollutants (0.1 to 6 ppm), reaching efficiencies around 55% [11–13].

The adsorption process is one of the most used techniques for water treatment [14]; which consist in the retention of the pollutant on the surface of a solid by the action of a physical or chemical bond [15]. In this sense, agricultural wastes are substances discarded in the process of agricultural production, and refers to crop stalks and animal manure [16]. Several works have used activated carbon as a low-cost adsorbent in the removal of (PhCs) through adsorption process, due of its great pore diffusion and adsorption kinetics, and developed microporous structure, high specific surface area, and can be easy handled [17]. Different by-products such as date, peach and olive stones [18–20], cocoa pod husk [3], Mung bean husk [21,22], pine residues [23,24], coffee beans [25], and so on, had been valorized and used in the elimination of ibuprofen from aqueous solutions.

The final disposal of agro-industrial waste, represents an environmental problem such as the appearance of unpleasant odors and the deterioration of the landscape; the cocoa industry increased its production in last years, and the husk is taken as a waste while the fruit is harvested, becoming in a problem of final disposal [26]. Cocoa husk has been used for the preparation of activated carbon to remove methylene blue [27], dyes and drugs such as diclofenac and nimesulide [28].

Thus, this study aims to transform cocoa husk into activated carbon with chemical activation with $ZnCl_2$, and to evaluate their characteristics as an Ibuprofen adsorbent compare the behavior of the adsorbents, regarding to the adsorption capacity as well as the kinetic performance, through the development of equilibrium and dynamic adsorption tests. The bio-adsorbent was characterized using a BET analysis. The capacity of ibuprofen removal was determined by UV-Vis.

2. Methodology

2.1. Synthesis of activated charcoal

For the preparation of the raw material, the cocoa shells were initially reduced in size and washed with deionized water, then taken to the oven at a temperature of 105°C for 48 hours. After this time, they could stand until they reached room temperature and were subjected to grinding and sieving to take the particles of size between 1 and 2 mm.

The activated carbon was obtained taking 5g of the prepared biomass, impregnated with a solution of 15 mL of $ZnCl_2$ solution at ratios biomass: solution of 1:2 and 1:3 [29,30], and the mixture was brought to the shaker at 50°C for 3 hours, to ensure the access of $ZnCl_2$ to the interior of the biomass. Then, it was heated to a temperature range from 150 to 350°C in one muffle with a ramp of 5°C/min in Nitrogen atmosphere (110mL/min) [31], leaving the final temperature for 3 hours.

Once the heating was finished, the system was cooled at room temperature, and the product obtained, was washed with a 0.1 M hydrochloric acid solution in order to remove the $ZnCl_2$ residues. For a better removal, the samples were placed in a shaking incubator (Germmy shaker co) at 120 rpm, at 30°C for 2 hours.

2.2. Characterization of biomass and carbons

Physicochemical characteristics of the bio-adsorbents used were studied using the following techniques: Brunauer-Emmett-Teller analysis (BET), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectrometry (EDS) and elemental analysis. These techniques were important to investigate the structure of the materials, bromatological composition and possible interactions with the studied pollutant. Analysis SEM was made by preparing the samples, coating the surface with a gold plating coating in a Denton Vacum Model Desk IV Equipment, this in order to generate a surface that was conductive.

Subsequently, the JEOL Model JSM 6490 LV microscope was inspected in secondary electrons mode (magnifications of 50, 250, 500 and 1000 magnifications were used with 20kV). Analysis EDS: the chemical composition of the samples was evaluated on several points or areas of inspection, by means of the EDS probe of Oxford Instrument Model INCAPentaFETx3. Analysis BET: the measurement of the surface area of charcoals was obtained by the N_2 adsorption isotherm at 77 K using the BET equation [32], the BET analysis was performed by using the Micro Active Tri Star II Plus 2.03 equipment.

2.3. Adsorption tests

To evaluate the adsorbent capacity of the coals, 100 mL of an ibuprofen solution with an initial concentration of 20 ppm was prepared and contacted with 0.4 g of bio-adsorbent at 120 rpm during 24 h; the adsorbent was filtered, and the sample was taken to be analyzed by visible ultraviolet spectrophotometry analysis (UV-VIS). The same procedure was also performed for an initial concentration of 30 ppm and 40 ppm [33,34]. Adsorption efficiency (%E) and capacity (q_t) were determined according to Equations 1 and 2:

$$\%E = \frac{C_i - C_f}{C_i} * 100 \%E = \frac{C_i - C_f}{C_i} * 100 \quad (1)$$

$$q_t = \frac{(C_i - C_f) * V}{m} q_t = \frac{(C_i - C_f) * V}{m} \quad (2)$$

Where C_i and C_f are the initial and final concentration in ppm, V is the volume of solution in L and m the mass of adsorbent in g.

3. Results

3.1. Characterization of biomass and activated carbons

Figure 1 shows the images reported by the SEM analysis for unmodified cocoa husk. In this, a fibrous appearance and little porosity was evidenced in comparison with the morphology of the coals presented in Figures 2 and 3

Figures 2 and 3 shows the SEM images for synthetized biochars; in there, the fibrous appearance of the UHC (Figure 1) disappears, suggesting a disintegration of the original structure of the biomaterial; due to the modification with $ClZn_2$ and carbonization process. The roughness of the coals, greater porosity and appearance of cavities is also evident, indicating that these characteristics were developed by the activating agent [28].

Different types of pores in size and shape are clearly visible, causing the increase in the BET surface area and the micropore volume of the coals. CA1:2 evidenced more pores, while CA1:3 exhibited a more defined pore morphology, this could be attributed to the characteristic impregnation ratio of each carbon; $ZnCl_2$ dehydrates the sample and increases its porosity, as having a 1:2 ratio greater amount of this activating agent results in a material with more pores [35]. In Table 1 is shown the elemental analysis of the bio-adsorbents.

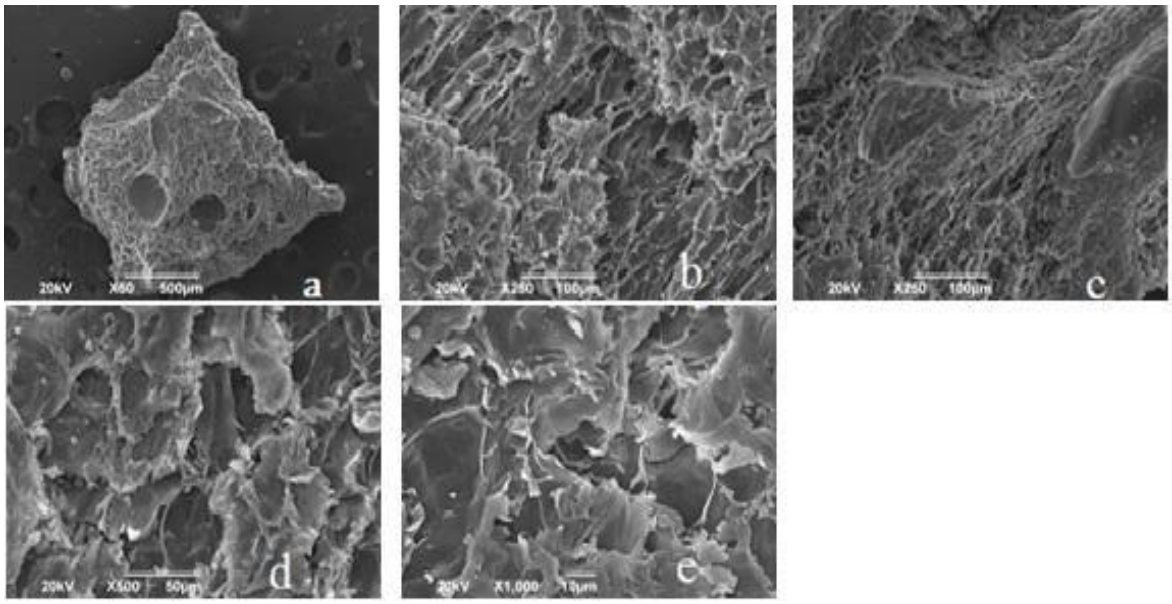

Figure 1. *I mages of the biomass (cocoa husk) shown by the SEM analysis with an approach of: a. * 50, b. * 250, c. * 250, d. * 500, e. 1000. Source: own elaboration*

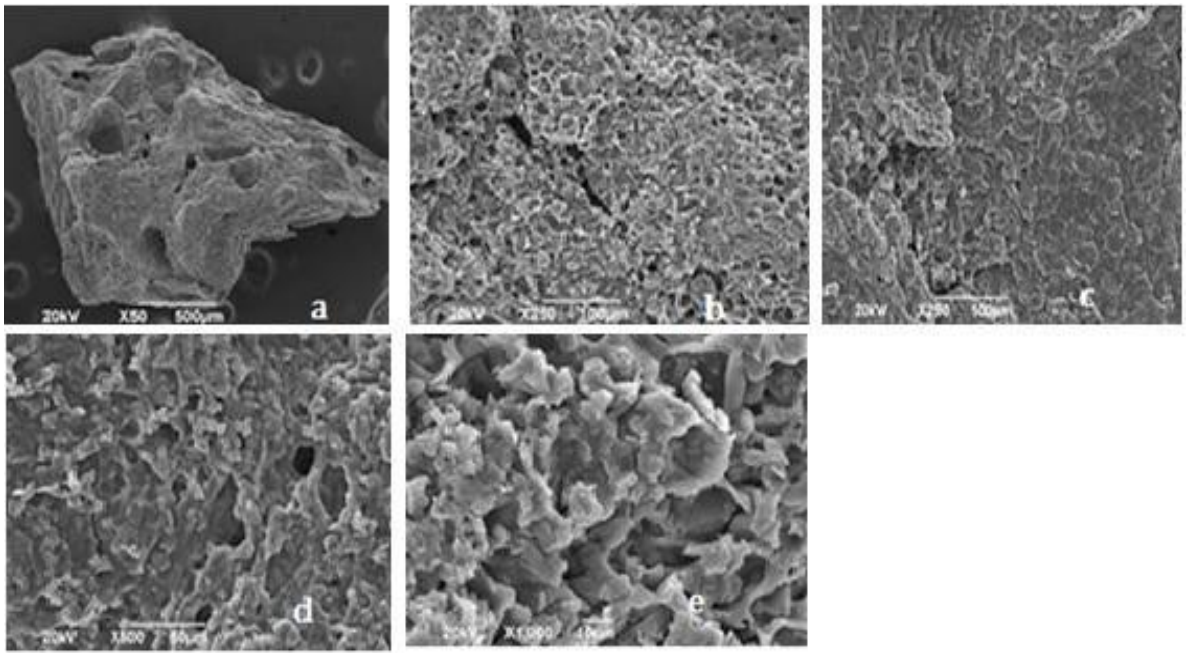

Figure 2. *Images of CA1: 2 shown by the SEM analysis with an approach of a. * 50, b. * 250, c. * 25,. d. * 500, e. 1000. CA1: 2= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution. Source: own elaboration*

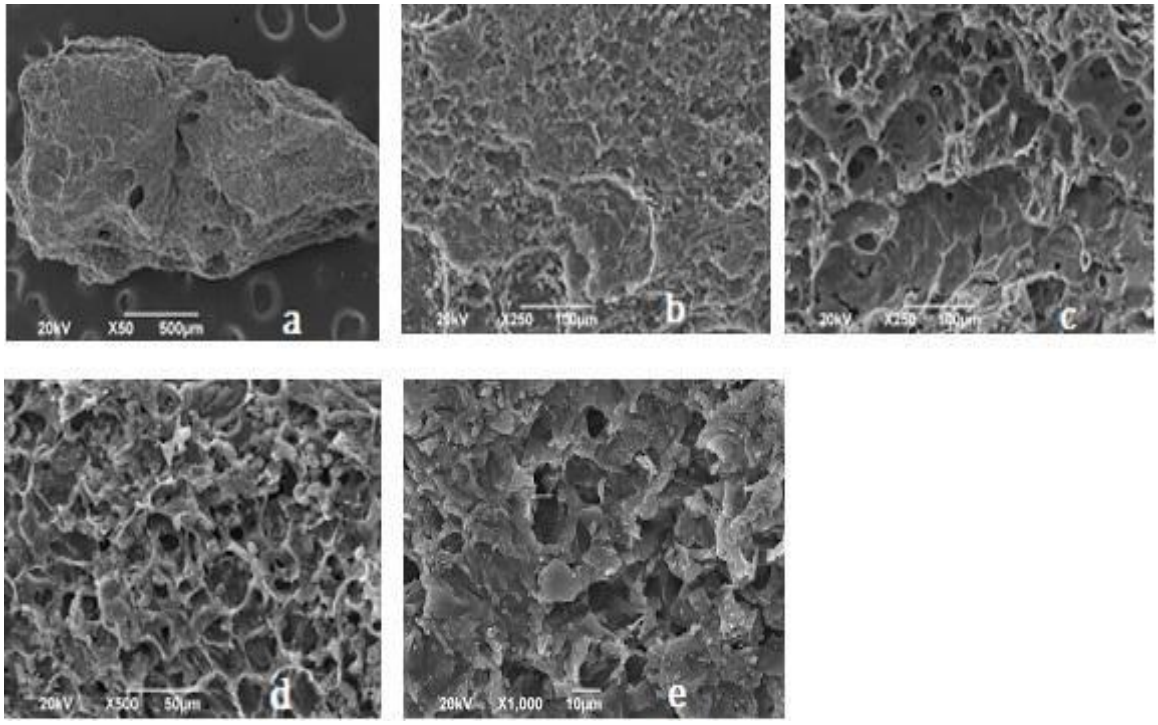

Figure 3. *Images of CA1: 3 shown by the SEM analysis with an approach of a. * 50, b. * 250, c. * 250, d. * 500, e. 1000. CA1: 3= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution. Source: own elaboration*

Table 1. *Elemental Analysis of the biomass*

Bio-adsorbent	Elemental Analysis (% p/p)				
	C	O	K	Cl	Zn
Cacao husk	45.01	43.78	11.21	--	--
CA 1:2	61.73	21.24	--	1.01	16.77
CA 1:3	63.04	22.72	--	1.46	12.78

CA1: 2= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution; CA1: 3= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution. Source: own elaboration

According to the elemental analyses (Table 1), the carbons obtained CA1:2 and CA1: 3 exhibited higher carbon content (68.41% - 64.64%) than cocoa husk (51.43%), while the oxygen content decreased after chemical activation, this may be due to the elimination of some groups that contained oxygen from the surface of the material; during the chemical modification the $ZnCL_2$ causes dehydration reactions in the UHC (unmodified cocoa husk) structure occur, and catalyzes dehydration during carbonization; for this reason, the hydrogen and oxygen atoms were released in the form of water to form a porous structure that affect the amount of oxygen groups in the carbonaceous matrix, causing a decrease in oxygen, as observed in the elemental analysis of the carbons obtained and coincides with that reported by Wang et al. [36], it indicates that more O-containing functional groups were lost in biochar. In other studies, similar amounts of carbon and oxygen have been found in prepared carbons, presenting the same tendency after activation (increase in carbon and decrease in oxygen) [37,38]. Also, loss of moisture or volatile

components, due of this reactions of dehydration [35,38]. The biomass presented potassium content, which disappeared once the modification has been made, which is related with the presence of chlorine and zinc in the bioachars, this could be due to the replacement and exchange of K ions for Cl and Zn for electrostatic forces as reported by Liu, Ji and Wang [39]. As observed in the elemental analysis the biomaterial changed remarkably after the activation process, and the biochars presented similar elementary compositions. After applying the BET method, the information presented in Table 2 was obtained.

Table 2. *Characteristics of CH, CA 1:2. CA 1:3. shown by the BET analysis*

Sample	S_{BET} (m^2/g)	$S_{Langmiur}$ (m^2/g)	V_{Total} (cm^3/g)	D_{BET} (nm)	%E
UCH	0.0208	0.0675	0.000159	1.0940	----
CA1:2	297.2066	460.4968	0.123115	1.0566	75.96
CA1:3	287.5375	441.4094	0.117930	1.0634	65.75

CH= unmodified cocoa husk; CA1: 2= activated carbon with relation 1:2 biomass: $ZnCl_2$ solution; CA1: 3= activated carbon with relation 1:2 biomass: $ZnCl_2$ solution. Source: . own elaboration

In Table 2 is observed that an increasing in surface area is proportionally related with the adsorption efficiency of remotion. The UCH textural properties in regard to activated carbons, showed that chemical impregnation produces materials with better characteristics for the adsorption of pharmaceutical compounds [28]. It was also evidenced the increased in the surface area with after modification with $ZnCl_2$. About this, CA 1:2 has a greater surface area (297.2066m^2/g) than CA 1:3, which is attributed to the impregnation ratio 1: 2 allows better interaction between the chemical agent and the surface of the carbonized solid material, favoring the detachment of the carbonaceous particles that are part of the cellulosic material. With this, the alternative hypothesis is verified in which it is affirmed that the carbon surface area depends on the zinc chloride ratio used.

On the other hand, interactions between the hydroxyl groups of the cellulosic material with the Cl and Zn dissolved in the solution, generated complex reactions producing changes in the carbonaceous matrix, which is evidenced by the formation of the pores [40]. It is important to highlight that, activated carbons prepared by chemical activation from lignocellulosic materials, results in microporous materials which is related with volume of micro-pores (Table 2) [31]. In addition, when the diameter is less than 2 nm, it is indicated the presence of micropores [41]. The area presented by the Langmuir isotherm showed that the adsorption in the monolayer on the surface of the adsorbent at low pressures, directly influences the surface area, which is greater than the BET area; it can be assumed that the process is controlled by physisorption, due to the formation of multilayers on the external surface of the adsorbent [42].

Figure 4 shows a partial isotherm of adsorption of CO_2, used to define the porosity for the unmodified cocoa husk (UCH). Initially the unmodified biomass was subjected to N_2 adsorption without obtaining adsorption data, since the N_2 did not manage to enter due to the lack of porosity of the material.

From Figure 4 is evidenced that the relative pressure increases, this means there is no relationship that shows a considerable adsorption value between the gas adsorbed in the pores of the material and the relative pressure, due there are no inflection points that show this behavior [43]. The almost zero adsorption of the material, is evident when noticing the values of the axis of the ordinates. Figure 5 shows the Nitrogen adsorption and desorption of the synthesized carbon-type bio-adsorbents.

Considering Figure 5, it can be seen that the isotherm is Type I, and is according to the IUPAC classification, therefore CA 1:2 and CA 1:3 are mostly microporous, which is consistent with the results of the BET analysis, in which the most of the area is represented by micropores, which allows initially, N_2 adsorption to increase rapidly to $p/p_o < 0.2 p/p_o < 0.2$ due to the filling of micropores present in the monolayer, between $p/p_o = 0.2 p/p_o = 0.2$ y $p/p_o = 0.9 p/p_o = 0.9$ some of the available pores continue to be covered and at the same time multilayers begin to be developed [44,45].

Between $p/p_o = 0.9 p/p_o = 0.9$ y $p/p_o = 1$ $p/p_o = 1$ there is a greater inclination, because there is no adsorption on the pores of the material, producing a saturation or condensation of N_2 molecules (desorption). It is important to note that for chemically activated lignocellulosic materials, the BET equation gives an adequate description of a relative pressure range, normally between 0.05 and 0.3, in which, for this figure, the behavior of Type I isotherm is more than evident [46]. In addition, can see that in the initial stage, the adsorbed amount of N_2 increases rapidly at low relative pressures, which is due to the microporous structure of the carbon as reported for Arampatzidou and Deliyanni [47], and thus, the curve has a behavior analogous to the characteristic curve of CA 1:2.

3.2. Adsorption essays

Figures 6 and 7 show a high decrease in the concentration of IBP (Ibuprofen) during the initial stage, for both carbons.

The adsorption experiments were carried out at 20, 30 and 40 ppm as initial concentration and results are shown in Table 3. It was evidenced that CA 1:2 has higher IBP removal percentages than the CA1:3. This, could be attributed to the difference in surface areas and volume of pores (Table 2). Nevertheless, in both biochars were observed removal percentages above 60%, due to the presence of micropores which facilitates the removal of ibuprofen [48].

Numerous applications have been reported in the use of activated carbons from biomass. In Table 4, some representative studies of this type are presented, disclosing the precursor material and the activation process used, BET surface area and specific application. As can be seen, the objective is to remove emerging contaminants, and the activating agent that leads to greater surface areas is $ZnCl_2$.

The carbons obtained in the mentioned investigations presented N_2 Type I adsorption-desorption isotherms, reflecting microporosity as the main characteristic, which is also seen in the coals obtained in this project as shown in Table 4 below. It is observed that, although the carbon obtained in the present study has a lower surface area, compared to some previously obtained at high temperatures, like the one prepared by cocoa shell microwave-assisted (619 m^2/g) and *Artemisia vulgaris* modified with H_2SO_4 and N_2 (358.2 m^2/g), obtained an adsorption capacity over those; which shows that activated carbon from cocoa treated with $ZnCl_2$ and synthesized at low temperature, is a good option for its implementation in the removal of contaminants dissolved in aqueous solution and pharmaceutical metabolites.

4. Conclusions

The activation of the cocoa husk caused an increase in its surface area and porosity, which was evidenced in the results of the SEM and BET analyzes, carried out to characterize the biomass and the activated carbons, being the CA1: 2 the one that presented such properties in greater proportion, whose percentage of removal of ibuprofen was 75.96% while for CA1: 3 was 65.75%, CA1: 2 being the most suitable for adsorption.

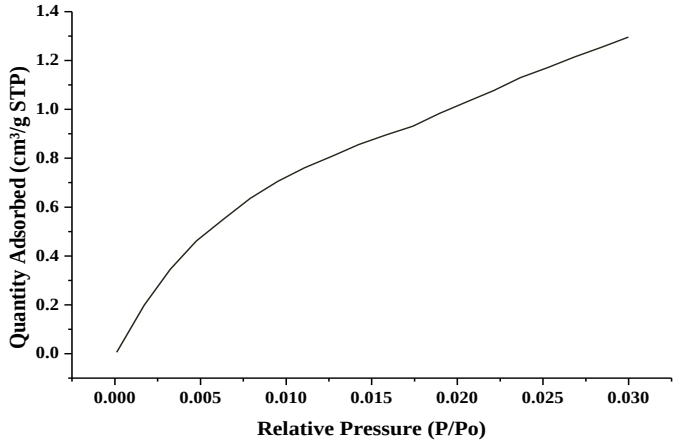

Figure 4. *Adsorption analysis with CO_2 for UCH. Source: own elaboration*

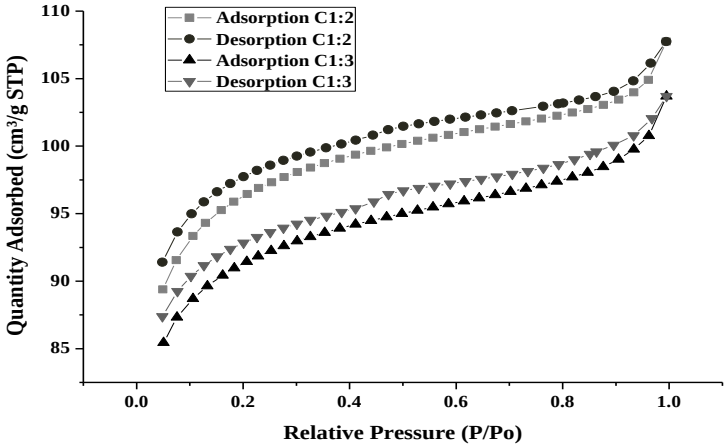

Figure 5. *BET analysis of CA 1:2 and CA 1:3; nitrogen adsorption and desorption. CA1: 2= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution; CA1: 3= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution. Source: own elaboration*

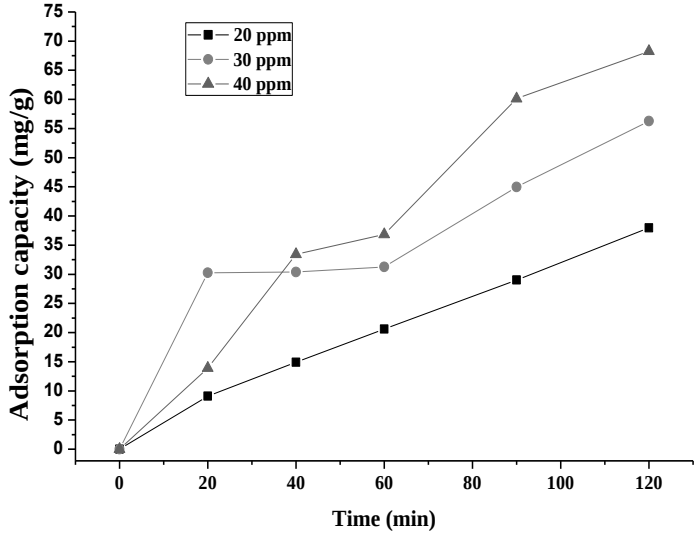

Figure 6. *Removal of IBP with CA1:2 in the solution of 20, 30 and 40 ppm. Source: own elaboration*

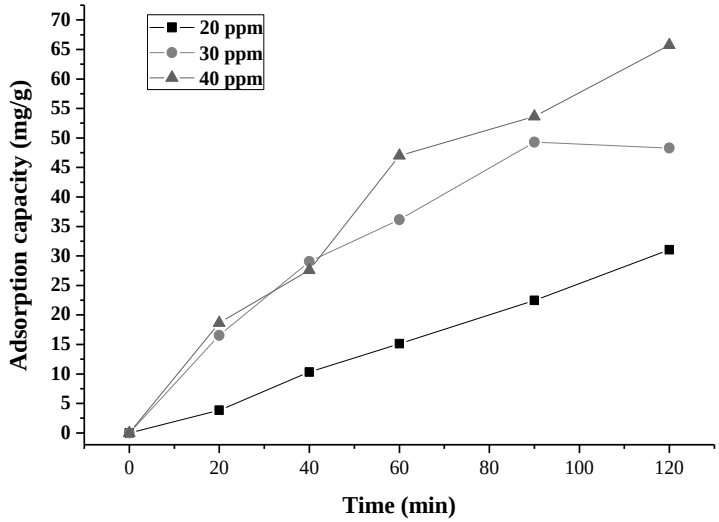

Figure 7. *Removal of IBP with CA1:3 in the solution of 20, 30 and 40 ppm CA1: 2= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution; CA1: 3= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution. Source: own elaboration*

Table 3. *Removal percentage obtained with CA1: 2 and CA1: 3*

Type of Carbon	Initial concentration (ppm)	Final concentration (ppm)	% E	q_t (mg/g)
CA1:2	20	4.809	75.96	37.98
	30	7.486	75.05	56.28
	40	12.69	68.28	68.27
CA1:3	20	7.587	62.07	31.03
	30	10.52	64.93	48.7
	40	13.7	65.75	65.75

CA1: 2= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution; CA1: 3= activated carbon with relation 1:2 biomass:$ZnCl_2$ solution; %E= Adsorption efficiency. Source: own elaboration

Table 4. *Comparison of activated carbons from agricultural waste with different types of activation*

Biomass	Treatment	S_{BET} (m^2/g)	Pollutant	q_t (mg/g)	References
Cocoa Husks	Physical, CO_2	85.09	Blue methylene dye	212.77	(49)
Cocoa Husks	Physical, CO_2	248.75	4-nitrophenol	166.67	(50)
Cocoa Husks	Physical, CO_2	558.25	----	----	(51)
Seeds of Elaeagmus angustifolia	Chemical, $ZnCl_2$	697	Iodine	1009	(41)
Cocoa Husks	Chemical, assisted by microwaves	619	Diclofenac Nimesulide	63.47 74.81	(28)
Pineapple	Chemical, $ZnCl_2$	914.67	Blue methylene dye	288.34	(35)
Artemisia vulgaris	Physicochemical, H_2SO_4 y N_2	358.2	Ibuprofen	16.945	(52)
Cocoa Husks	Chemical, $ZnCl_2$	205.4	Amoxicillin Ibuprofen	3.096 5.462	(53)
Cocoa Husks	Chemical, $ZnCl_2$	CA1: 2= 297.21 CA1: 3= 287.54	Ibuprofen	68.27 65.75	Present study

Source: own elaboration

The coals in general, turned out to be good materials for the removal of the drug, with a maximum adsorption capacity of 68.27 mg/g and 65.75 mg/g respectively. The potential of the cocoa husk as a precursor for the generation of activated carbons was demonstrated, which represents a valuable contribution to the research lines related to the use of agro-industrial waste. The use of the low temperature method has the potential to improve the production of activated carbons in economic aspects, which differs from the conventional known method (high temperature).

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