Low-temperature Activated Carbon from Mixed Biomass Oil Palm Residuals (fibrilla and cuesco) for Use in the Treatment of Oily Water

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Abstract : The present research aimed to prepare low temperature activated carbon from cuesco and oil palm fibrilla in a ratio of 50-50 % w w^{-1} with an impregnation ratio of 1:2 and 1:3 zinc chloride ($ZnCl_2$) to be used in the oily substances adsorption in synthetic solutions. The biomass was initially washed, reduced in size and sieved with particle sizes between 2 mm and 1 mm. Afterwards, 10 g of cuesco and 10 g of fibrilla were weighed, mixed, homogenized and impregnated with aqueous $ZnCl_2$ solutions, the impregnated biomass was filtered and heated for 40 min with a ramp of 5°C min^{-1} from 150°C to 350°C and then activated with 0.1 M HCl.The precursor (mixture of cuesco and fibrilla) was characterized by analysis of Fourier Transform Infrared Spectroscopy (FTIR) and synthesized carbons were characterized by Brunauer Emmett Teller (BET), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (DRX) analysis. The presence of cellulose, hemicellulose and pectin, and activated carbon of zinc and chlorine on the surface of both carbons were found in biomass, the almost total deterioration of the bands corresponding to lignin and cellulose, and surface areas of 23.24 m^{2}g^{-1} and 12.38 m^{2}g^{-1}, respectively.Adsorption tests of methylene blue and iodine index showed that carbon 1:2 showed better adsorption capacity. The experimental adsorption data were best adjusted by Elovich's kinetic model and Freundlich's isotherm. Therefore, the use of mixed biomass for the preparation of activated carbon can be used in the adsorption of oil present in water.

Keywords : low temperature, cuesco and palm fiber, BET, DRX, Elovich Model, Freundlich Model, SEM.

1.   Introduction

The African palm oil extraction industry has grown significantly, since Colombia is currently the world's fourth largest producer of palm oil, and it is for this reason that a growing concern has been developing over the final disposal of the various residues that this generates.This process obtains large quantities of organic waste, including cuesco and fibrilla, which come from the stages of nut breaking and defibrillating, as well as

wastewater with traces of oils from washing equipment such as presses and clarifiers [1].Although these residues have been used as fuel for boilers or their mixture between the asphalt components, these measures have not been sufficient because the amounts produced of cuesco and fibrilla annually are exorbitant, and most of these are piled up and become a refuge for pests and a source of unpleasant odours at the time of decomposition [2].

On the other hand, water contaminated with traces of oil is a problem that causes great concern all over the world, which is why several investigations have been led with the objective of evaluating different types of technologies that are capable of removing the oily particles or at least considerably reducing their presence in the effluents so that they can be released without any problem to lakes, rivers and seas, and thus be able to continue with their natural process [3].

In recent years, several research projects have been carried out in order to evaluate the adsorption capacity of certain materials, among which the use of residues from the main agricultural industries has become very important; seeds, stalks, leaves and bark are usually recycled from different types of crops, which can be used as biomass or modified into activated carbon.The main application that is given to this type of materials is in the treatment of wastewater, where it has been tested to remove heavy metals and emerging contaminants such as drug metabolites, in addition to residues of organic compounds, since these are substances that endanger the life not only of human beings but also the subsistence of the environment [4].

Studies have been carried out in which different technologies are implemented together, such as the use of hydrodynamic cavitation as a pre-treatment of oily wastewater and then taken to a final anaerobic digestion treatment with residual activated sludge. The main objective of this study is to produce biogas from the digestion of the oil contained in the water.The results showed that as the oil content in water increased, biogas production rates increased considerably, suggesting that although the main objective was not to clean water, in the future it could be considered to use wastewater with high fatty acid content for biogas production [5].

For this reason, the present study proposes to prepare activated carbon with $ZnCl_2$ synthesized at low temperature from the mixture of agro-industrial residues of palm oil production: of cuesco and oil palm fibrilla for use in the adsorption of oils present in aqueous solution in batch system.

2.   Materials and methods

For the development of the present investigation, African palm residues (cuesco and fibrilla) obtained from a palm oil extractor in the Colombian Caribbean Region were used.They also used an oven, UV-Vis spectrophotometer, microscope, surface area and porosity analyzer and an X-ray disguiser model Thermo Scientific FB-1415M, Spectro UV-2650, JSM 6490 LV, MicroActive TriStar II Plus 2.03 and XPERT-PRO from PANalytical, respectively. In addition, analytical grade reagents mark Merck. For the preparation of activated carbon, the following variables were taken as dependent variables: surface area (m^2g^{-1}), porosity (mm, μm, nm) and chemical composition of the surface of the carbons; as independent the impregnation ratio in % w w^{-1}; and agitation (rpm), impregnation time (min), activation temperature (ºC) and the type of biomass.

2.1.   Preparation and characterization of biomasses

The cuesco and fibrilla were washed repeatedly with water at room temperature until they did not have oily remains, then dried in the sun for two days.Then both the cuesco and the fibrilla were reduced in size, followed by a sieving process where the desired particle sizes were obtained between 2 mm and 1 mm, to ensure that the synthesized carbon was granular and similar to the commercial type.Afterwards, 10 g of cuesco and 10 g of fibrilla were weighed, mixed and then homogenized in the shaker for 5 min. [6].The FTIR analysis was carried out on an IR spectrophotometer in order to determine the predominant functional groups in the mixture that were responsible for the adsorption process. For this purpose, 20g of precursor were weighed with equal amounts of cuesco and African palm fibrilla, then mixed, homogenized and a tablet was formed with the material which was analyzed[6].

2.2.   Synthesis of activated carbon and characterization

Biomass samples were impregnated with aqueous $ZnCl_2$ solutions with 1:2 and 1:3 ratios, with the aim of increasing their surface area, adding 20 g of biomass mixture in 60 mL of the prepared solution, which was

agitated in the shaker at 150 rpm and 60 °C for 3 h.Later, the impregnated biomass was filtered and heated for 40 min with a 5°C min^{-1} ramp from 150°C to 350°C, to let the carbon stand for one h [7]. When the carbon reached 350°C, it was activated with 0.1 M hydrochloric acid solution (HCl) for 3 h. The samples were then cooled to room temperature and washed with hot and cold distilled water, alternating until pH between 6 and 7, finally dried at 110°C for 16 h [7].The synthesized carbons were characterized by Brunauer Emmett Teller (BET), SEM and DRX analyses to determine surface area, surface chemical composition and inorganic composition, respectively[8].

The BET analysis was performed using adsorption isotherms, using nitrogen (N_2) adsorbate at 77 K (-196.15 °C) and the MicroActive TriStar II Plus 2.03 equipment. Subsequently, with the data obtained, the BET method is applied [9]–[11].

For the SEM analysis, the activated carbon sample was adhered to a carbon tape and then surface metallized with gold using a Denton Vacum Desk IV model, in order to generate a conductive surface.Subsequently, the inspection was carried out on a JEOL JSM 6490 LV model microscope in the secondary electron mode (with magnifications of 100 and 250x magnification at 20kV).In addition, the chemical composition of the samples was evaluated on several points or areas of inspection, using the Oxford Instrument Model INCAPentaFETx3 EDS probe [9]–[11]. The DRX analysis was performed on the XPERT-PRO equipment of PANalytical, making them measurements with Cu tube, with a voltage of 45kV and a current of 40mA, the time per step is 215.790s and the size of the step is 0.0197º. The data produced by the team were plotted to obtain diffractograms[12].

2.3. Preparation of oily water

For the preparation of synthetic water, the following consideration was given: if the treated wastewater sample from the palm oil extraction plant exceeded 20 ppm, which is the legal limit for the presence of vegetable oil in the water according to Colombian regulations, solutions of the concentration indicated in the report would be prepared, but if its concentration were lower, solutions of 100 mg L^{-1} would be prepared.To prepare the 100 mg L^{-1} solutions, 0.01g of oil was taken for every 100 mL of distilled water, a pinch of Ariel detergent powder was added to the mixture, then taken to the blender at low speed for 1 minute, and finally the pH of the solution was adjusted to 8.

2.4. Determination of the adsorption capacity of activated carbon

Initially, a calibration curve of methylene blue was made taking into account concentrations of 0 mg L^{-1},5 mg L^{-1} and 10mg L^{-1}; then solutions of 30 mL methylene blue with concentration of 100 mg L^{-1} were prepared.Subsequently, 0.5g of activated carbon was added to each solution with constant shaking at 150 rpm and 30°C for 24 h.These samples were then registred in the UV-VIS with a wavelength of 665 nm, where absorbances were obtained that were interpreted with the calibration curve previously made, and that allowed to know the final concentration of the solution, to determine the adsorption capacity of the activated carbon, using the Equation 1, where C_0 and C_e (mg. L^{-1}) are the initial and final concentration respectively, V (L) the solution volume and W (g) the amount of activated carbon used [11], [13], [14].

$$Q_e = (C_0 - C_e)\frac{V}{W} \quad (1)$$

(1)

1g of activated carbon was contacted with 10 mL of a 5% hydrochloric acid (HCl) solution, heated for 30 s until fully evaporated, then removed from the fire and cooled to room temperature.Then 100mL of a 0.1N iodine solution was added to determine the mg of adsorbed I2, and the mixture was shaken for 30 min at 150 rpm, then the remaining solution was filtered and 50mL was taken and titrated with a 0.1N sodium thiosulfate solution using starch as an indicator. [15], [16].

2.5. Adsorption tests: kinetics and isotherms

They were placed in contact with 0.5 g of best-results carbon presented in the adsorption test of methylene blue with five solutions at 100 mg L^{-1} of oil with a volume of 40 mL in a shaker at 30ºC and 150 rpm.The containers were removed one by one at 3.5h, 8h, 13h, 19h and 24h in order to determine the residual oil concentration over time and saturation point of the material.The experimental data were adjusted to

Freundlich and Langmuir adsorption models by adding 0.5g activated carbon to five solutions at concentrations of 100 mg L^{-1},80 mg L^{-1},60 mg L^{-1},40 mg L^{-1} and 20 mg L^{-1} crude oil of African palm oil with volumes of 40 mL to 150 rpm and 30ºC. The containers were taken out completed the 24h. Subsequently, the samples were filtered and analyzed by gas-mass chromatography to determine the remaining final oil concentrations in the water [2].

3.   Results and discussions

3.1.   Biomass and activated carbon characterisation

Biomass was subjected to FTIR analysis to determine the predominant functional groups, while synthesized activated carbons were subjected to SEM, DRX and BET characterization tests, in which it was sought to know their chemical composition, inorganic, and their apparent surface areas, respectively.The FTIR spectrum of Figure 1 shows peaks between 3000-3500 cm^{-1} corresponding to the OH vibration of carboxylic acids, esters and alcohols present in lignin, hemicellulose, cellulose and pectin; among the peaks 1000-1250 cm^{-1} predominates the presence of alkyl halides such as bronchial alkanes, iodine alkanes and chlorine alkanes, while the signal of carbonyl groups (C=O) is among the peaks of 1700-1500 cm^{-1}, where there are also traces of aromatic groups in lignin.
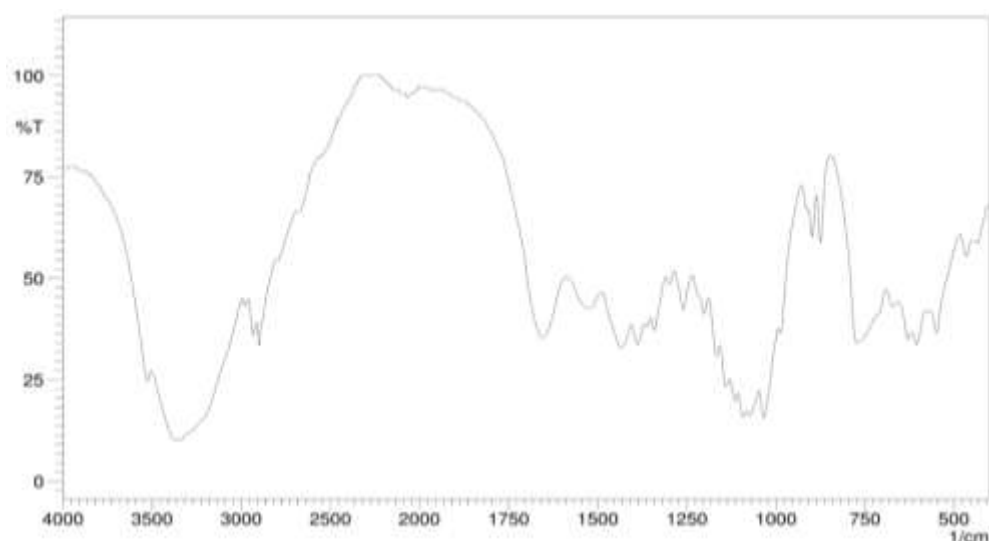

Figure 1.Infrared spectroscopy (FTIR) of mixed biomass of cuesco and palm fibrillation.

After an analysis, the information in Figure 1, in which the functional group with the respective peak number is shown, was organized in Table 1:

Table 1. Functional groups of mixed biomass

Functional group	Peaks
Amides and ammonium salts	3340
Alcohols and phenols	3340
Carbonilo	2932
Alkanes	2932
Halide alkyls C-F	1034
C=CH_2	2979
Aromatics and vinyl	1201

According to reported by Tejada-Tovar *et al.*, [6] in the palm bagasse spectrum, adsorption peaks between 3500 and 3000 cm^{-1} and between 1660 and 1770 cm^{-1} are reported to be atrubutable to the presence of

carboxylic acids and C=H bonds present in lignin.Vibration was also observed around 1450 to 1540 cm^{-1} could be attributed to the aliphatic and aromatic groups, and to the deformation of the methyl, methyl and methoxy groups, which are very similar to those of the spectre of mixed biomass, with, however, more pronounced peaks, which can be attributed to the mixture of the two precursors (cuesco and fibrilla).The presence of these functional groups in the biomass structure guarantees the presence of active sites on the adsorbent surface, thus favouring the process of removal of metal ions as reported by Mahamadi & Nharingo[17], Hossain *et al.*, [18]. Figures 2a and 2b show the results of the SEM analysis for carbons with an impregnation ratio of 1:2 and 1:3, respectively. On the surface a carbon presence of 55.13 and 57.71 was obtained for carbon 1:2 and 1:3, respectively; Cl and Zn presence of 5.38 and 13.36 in carbon 1:2 and 1.21 and 9.69 in 1:3, consequently.
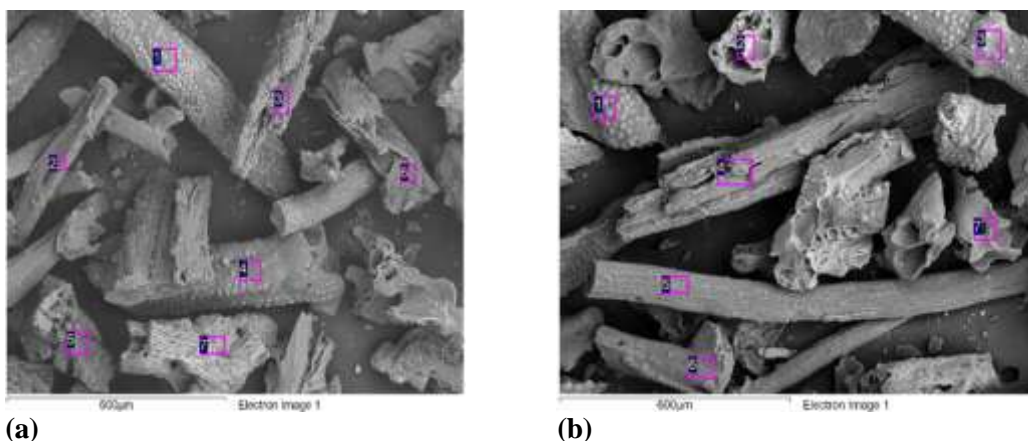

(a)   (b)

Figure 2. Microscopy and composition of x100 magnified activated carbon for carbon with ZnCl$_2$ impregnation ratio (a) 1:2 and (b) 1:3

In the activation process, ZnCl$_2$ acts as a dehydrating agent that penetrates into the material, thus favouring the breaking down of compounds present in biomass such as hemicellulose and lignin.In addition, the use of ZnCl$_2$ inhibits the formation of tar and volatile material, which favours carbon performance and the formation of porous structures, which have a direct relationship with the surface area of the same. Table 2 shows the chemical composition of carbons 1:2 and 1:3 with x100 magnification:

Table 2.Surface chemical composition of synthetic carbons.

Area	Carbon 1:2					Carbon 1:3				
	C	O	Si	Cl	Zn	C	O	Si	Cl	Zn
1	38.90	37.91	16.19	1.73	5.27	45.90	37.31	13.62		3.17
2		22.06		20.03	57.91	57.67	38.58	0.80		2.96
3	47.05	27.50	6.09	5.01	14.35	61.55	34.60	0.46		3.40
4	55.30	25.49	0.98	3.19	15.04	59.88	32.41	1.75	0.60	5.36
5	50.97	24.10	2.56	3.76	18.62	61.88	23.18	2.08	1.19	11.67
6	56.80	32.80		2.32	8.08	63.45	30.69	1.75	0.62	3.49
7	55.13	26.13		5.38	13.36	57.71	28.02	3.37	1.21	9.69

Figures 2a and 2b show the influence of zinc and chlorine on the surface of the carbons, which is a result of the impregnation with ZnCl$_2$ in the precursor after carbonization.The greater concentration of this compound was found on the surface of carbon with a dilution factor of 1:2, a result that is consistent with the relationships with which the carbons were impregnated. As shown in Figure 2 and Table 2, carbons have a high content of carbon and oxygen, due to the carbonization of the lignocellulosic material. Also, there are appreciable varieties of pores and cracks present on the surface of the carbons, which are extremely important because in them the encapsulation of pollutants is carried out, being the amount of pores on the surface of the carbon proportional to the characteristics of the adsorbent; for this reason it is considered that the carbons observed in the SEM analyses presented have the desired structure of an activated carbon consistent with that reported by Varriano[19]. The diffractograms obtained from the DRX analysis of carbons 1:2 and 1:3 are presented in Figure 3.
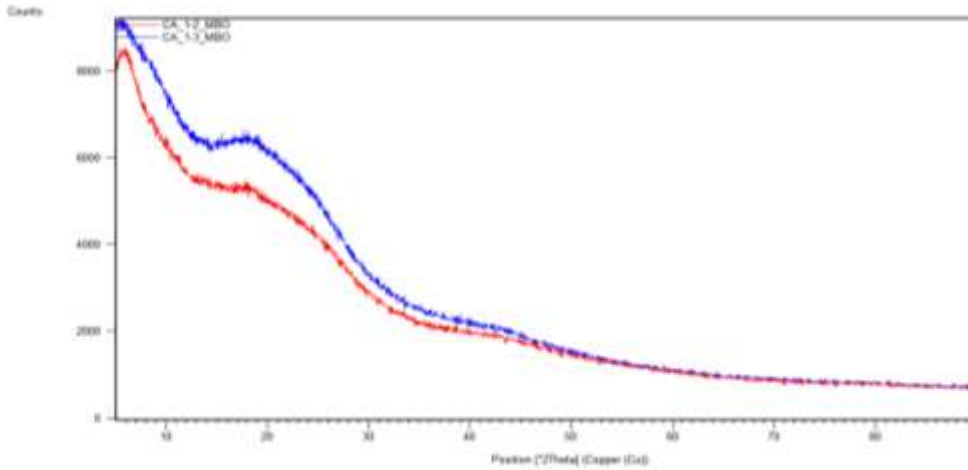
Figure 3. Activated carbons diffractogram 1:2 and 1:3

According to the DRX analysis, both carbons present a structure of amorphous nature, which is normal for an activated carbon, which is due to the presence of two graphical planes (d100 and d002) located in the bands 44° and 18° respectively. On the other hand, cellulose and lignin reveal their presence in the bands 18° and 22 according to reported by Hincapie et al.[20], which in the carbons 1:2 and 1:3 are deteriorated.This ratifies that there was an almost complete transformation of the vegetal structure to a graphical structure with pores, characteristic that is attributed to activated carbons.However, it can also be seen that the presence of cellulose and lignin is higher in 1:3 carbon, having a more pronounced peak in the area of 18° and 22°, implying that its transformation is lower than in 1:2, still showing some biomass characteristics that are not perceptible in the latter according to [8], [21], [22]. After applying the BET method, the adsorption isotherm for biomass was obtained and presented in Figure 4.
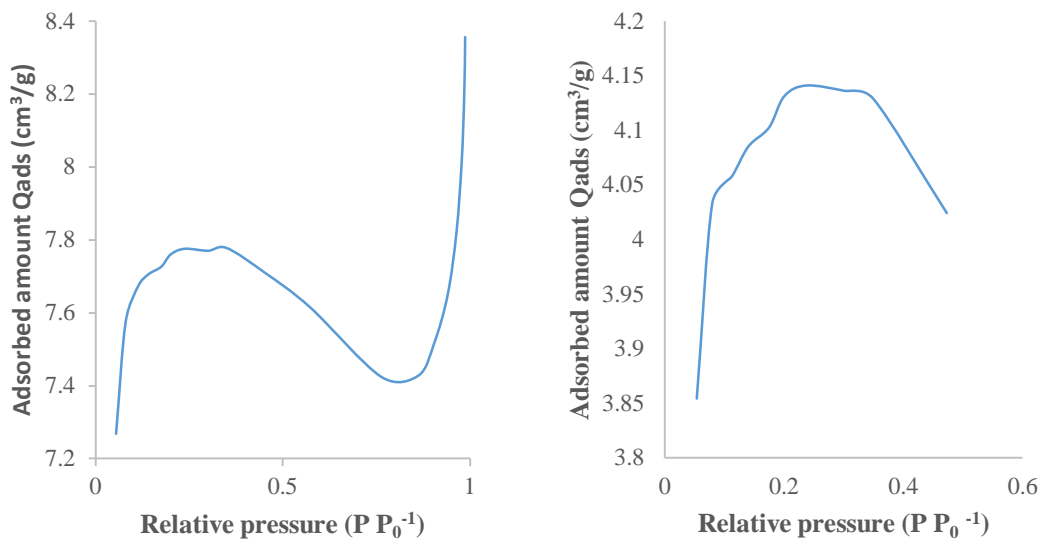
(a)   **(b)**
Figure 4. Adsorption isotherm for carbon (a) 1:2 and (b) 1:3

Looking at the graphs in Figures 3a and 3b, a greater adsorption by activated carbon 1:2 is observed, achieving adsorption of 9.9155 cm^3 of nitrogen per gram of material (P P_0^{-1}=1), while carbon 1:3 was only able to adsorb 4.1412 cm^3 of nitrogen per gram of material (PP$_0^{-1}$ =1).After applying the BET method, the surface areas were calculated and the values of 23.24 m^2g^{-1} and 12.38 m^2g^{-1} were obtained for activated carbons with an impregnation ratio of 1:2 and 1:3, respectively.For carbon 1:2 its surface area is divided into 19.8328 m^2g^{-1} corresponding to the micropores and 3.4041 m^2g^{-1} belonging to the external surface area, while for carbon 1:3 it is 10.6115 m^2g^{-1} corresponding to the micropores and 1.7702 m^2g^{-1} to the external surface area.

Table 3. Different types of carbon and its surface areas

Precursor	AI	T (°C)	RI	BET (m^2g^{-1})	Reference
Soybean Bean Sleeve	$ZnCl_2$	500	1:3	1526.54	Zhong& Dan, [23]
Tomato seeds	$ZnCl_2$	600	1:6	1093	Sayğılı & Güzel, [24]
Cocoa shell	$ZnCl_2$	350	1:3	287.5	Tejada-Tovar et al. [8]
Cocoa shell	$ZnCl_2$	350	1:4	205.4	Tejada-Tovar et al. [8]
Marañón shell	$ZnCl_2$	500	1:3	1478	Spagnoli et al., [25]
Cuesco and palm fiber (50/50)	$ZnCl_2$	350	1:2	23.24	This research
Cuesco and palm fiber (50/50)	$ZnCl_2$	350	1:3	12.38	This research

Where RI is the impregnation ratio and AA is the agent used in carbon impregnation.

Comparing the results obtained with the information reported in Table 3, it can be inferred that 1:2 had a greater surface area, almost double that of 1:3 carbon. Therefore, it can be said that 1:2 carbon has better characteristics and could present a better performance in adsorption tests.However, compared to carbons previously reported in studies that also used $ZnCl_2$ as an activation agent and similar impregnation ratios, those obtained in this study have a very low surface area; this leads us to consider that besides the influence exerted by the impregnation ratio, the temperature at which the material is carbonized is also a key variable in the process, since those that obtained greater surface areas were carbonized at temperatures much higher than 350°C.

3.2. Determination of adsorption capacity

The methylene blue test was performed to determine the adsorption capacity of the synthesized carbons. Fig. 5 shows the methylene adsorption calibration curve, from which the equation of the line was obtained: x = (y - 0.0257)/0.155 which was used to calculate the final concentration in each case.
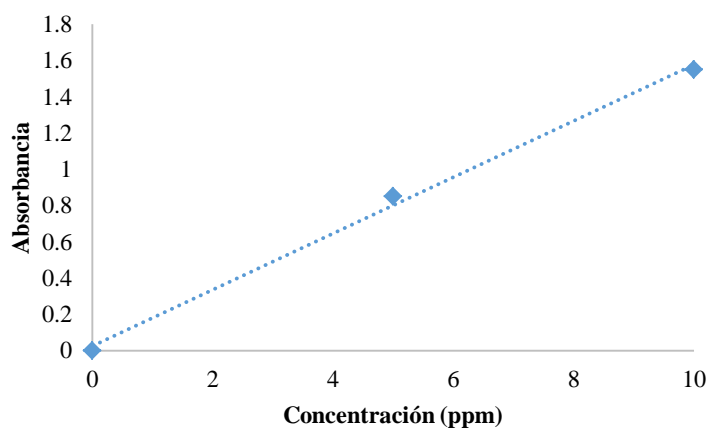

Figure 5. Calibration curve of methylene blue

Table 4 shows the results obtained in each methylene blue test performed with its respective replica. Subsequently, the initial and final concentrations, solution volume and activated carbon mass were used to determine the adsorption capacity of methylene blue (Qe), being 6.0 and 5.9mg/g for 1:2 and 1:3 carbons, respectively.Being the carbon 1:2 the one that presented greater capacity of removal of methylene blue.From Figure 5 it can be noted that the capacity of methylene blue adsorption, increased as the concentration of the $ZnCl_2$ solution with which the biomass was impregnated increased, which is attributed to the capacity of $ZnCl_2$ to promote pore and crack formation in the carbon structure.In turn, as the porosity of the larger material increases, its surface area will be greater, contributing to the easy encapsulation of methylene blue molecules on the surface of the material.On the other hand, for carbon 1:2 the average pore diameter was 2.1 nm, which influences the contaminant's retention capacity since the pores with diameters between 1:1.6-2 nm have a

particle size similar to the particle size of methylene blue molecules, which facilitates removal and thus considerably improves the adsorption capacity consistent with that reported by Spagnoli et al. [25].

Table 4. Data obtained for methylene blue test

Carbon	Volume (ml)	Concentration (ppm)	Replica (ppm)	Adsorption (%)
1:3	30	0.6923	0.7697	99.23
1:2	30	0.0019	0.0081	99.95

It is well known that iodine number is a common indicator used to determine the porosity of activated carbon, but it does not necessarily give an idea of whether or not it is suitable for removing other contaminants.This method has been used as an approximation to measure the surface area, however, it is not possible to generalize that there is a relationship between the two, although they are factors that depend on porosity which at the same time varies according to the material from which the carbon is made and the conditions of the process. Other variables that also affect the measurement of iodine number are the presence of water, sulphur and adsorbed volatile material. Calculation of the iodine number (IN) was carried out under the ASTM D4607 standard. An iodine removal rate of 25 and 16 mg g^{-1} was obtained using carbons with an impregnation ratio of 1:2 and 1:3, respectively.The results obtained for the carbons synthesised in this investigation are considerably low compared to those obtained from the 1101 banana stem reported by AbGhani *et al*. [16], the latter being very similar to commercial carbon.These results are consistent with those obtained from BET surface area and methylene blue adsorption capacity, which indicates that the porosity is considerably lower than other carbons synthesized with the same activating agent.

In addition, by allowing this method to obtain an approximation of the BET surface area, it is possible to observe that the values obtained by the two tests are similar to each other, which makes it possible to observe that they are related, and despite variations between the values obtained by both methods, they continue to demonstrate that carbon 1:2 can adsorb almost twice as much iodine as 1:3, which is equivalent to its surface areas.

3.3. Modelling of adsorption kinetics

The adsorption kinetics is controlled by different stages, including the transfer from the surface to intraparticular active sites, the transfer of solute to the surface of the sorbent and the retention in these active sites by sorption, complexing or precipitation phenomena.The kinetic study of the adsorption of oil in solution on activated carbon at low temperature was carried out from mixed biomass of palm bagasse (quartz and fibrilla) with ZnCl$_2$ impregnation ratio. We reviewed the pseudofirst-order, pseudo-second-order, Elovich and intraparticular diffusion kinetic models shown in table 5 to adjust experimental data.The pseudo-first model assumes that each metal ion is assigned an adsorbent material adsorption site and, therefore, the mechanism and adsorption rate will depend on several factors such as: the presence of another ion in the solution, the selectivity, type and, in general, characteristics of the adsorbent and is symbolized in Equation 1 [26].

Table 5. Kinetic adsorption models

Model	Ecuación	Definición
Pseudo-FirstOrder	$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$	Where q_e and q_t are the adsorption capacities in equilibrium at a given time in (mg/g), and k_1 is the pseudo constant of the first order (min^{-1})
Pseudo-Second Order	$$q_t = \frac{t}{\left(\frac{1}{K_2 q_e^2}\right) + (t/q_e)} \quad (2)$$	Where k_2 is the second order adsorption constant (g^{-1} min^{-1})
Elovich	$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (3)$$	Whereα andβ are the constants of Elovich
Intraparticular Diffusion	$$q_t = k\sqrt{t} \quad (4)$$	Where k is the constant of intraparticular diffusion

The pseudo-second order model assumes that adsorbate is adsorbed in two active biomass sites, therefore, the control mechanism of the phenomenon is the adsorption velocity of the metal ion in the adsorbent and not the mass transfer and is represented in Equation 2 [27].The Elovich model assumes that the bioadsorbent active sites are heterogeneous and therefore exhibit different activation energies, based on a second-order reaction mechanism, for a heterogeneous reaction process; it is symbolized in Equation 3 [26].For its part, the intraparticular diffusion model establishes a process controlled by pore adsorption, in which: the initial velocity is directly proportional to the concentration of the solute, is characterized by the dependence between the specific adsorption and the square root of time, the slope being the velocity of diffusion and is represented in Equation 4 [28].
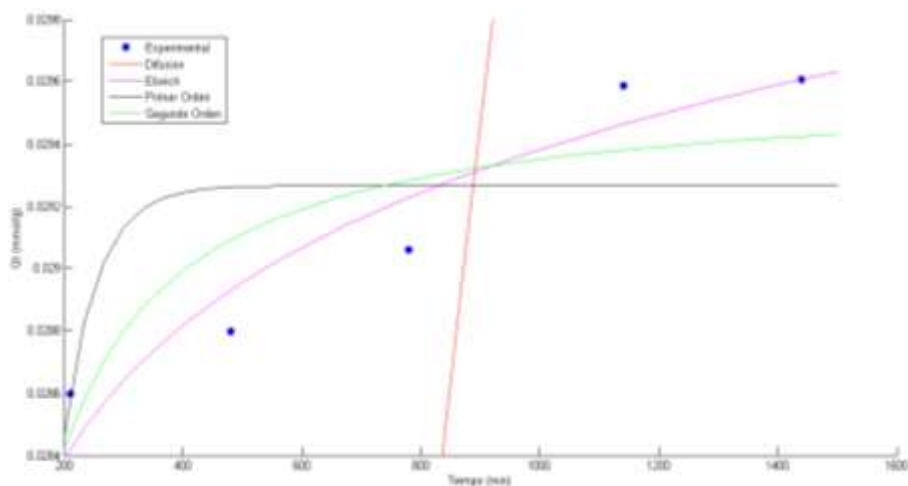

Figure 6.Modelling of the adsorption kinetics of oil adsorption on activated carbon from mixed biomass of palm bagasse (cuesco and fibrilla) with impregnation ratio 1:2 of ZnCl$_2$.

The parameter values of the above models and the corresponding R2 are given in Table 6 and the graphs are shown in Fig. 6.

Table 6. Parameters of pseudo-primer order, pseudo-second order, Elovich and intraparticular diffusion kinetic models for the adsorption of oil in solution using activated carbon from palm bagasse mixed biomass (quartz and fibrilla) with ZnCl2 impregnation ratio 1:2.

Model	Parámeter	Value
Firstorder	K_e	0.0293
	q_e	0.0180
	R^2	0.428
Secondorder	K_e	0.0296
	q_e	4.0772
	R^2	0.725
Elovich	A	2.4627
	B	0.0002
	R^2	0.888
IntraparticularDiffusion	K	0.0098
	R^2	0.215

According to Fig. 6 it can be observed that the experimental data are better suited to the Elovich model with R^2=0.88, and have a very low affinity with the others, which indicates that between activated carbon 1:2 and African palm oil there is a process of chemadsorption, which benefits the encapsulation of the pollutant and prevents desorption.In addition, the active sites are heterogeneous and have different activation energies, using as a basis a second-order reaction mechanism in a heterogeneous reaction consistent with that reported by Nadeem *et al*., [26].The kinetic of the removal of residual oil from a palm oil plant was studied using quitosane obtaining that the pseudo-primer order and pseudo-second order model, with R2 of 0.88 and 0.88 and 0.99

respectively, better match experimental data to the intraparticular diffusion model, which could be explained by the heterogeneous nature of adsorbent and the diversity of active sites according to Ahmad *et al.,* [29].

3.4. Isothermal modeling

The Freundlich and Langmuir (Table 7) models were subjected to the experimental oil adsorption equilibrium data on low temperature synthesized activated carbon from cuesco and African palm fibrilla with $ZnCl_2$ impregnation ratio 1:2.

Model	Equation	Definition
Freundlich	$$q_e = k_f C_e^{1/n} \quad (5)$$	Where k_f is the constant of Freundlich, n is the intensity of adsorption, which is the amount of contaminant adsorbed in the equilibrium, and C_e is the residual concentration in solution.
Langmuir	$$q_e = q_{max} \frac{bC_e}{1 + bC_e} \quad (6)$$	Where what is the concentration of the adsorbed contaminant, C_e is the residual concentration in the solution, q_{max} is the maximum adsorption corresponding to the saturation sites and b is the ratio between adsorption/disposition rates.

The Langmuir model symbolizes a quantitative description of a large layer of molecules deposited on the surface (pores) of the absorbent by a function of the concentration of the adsorbed material in the liquid with which it is in contact, this isothermal can be determined by Equation 5.The Freundlich isotherm relates the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact at a given temperature. This isotherm is empirical and is determined by Equation 6.
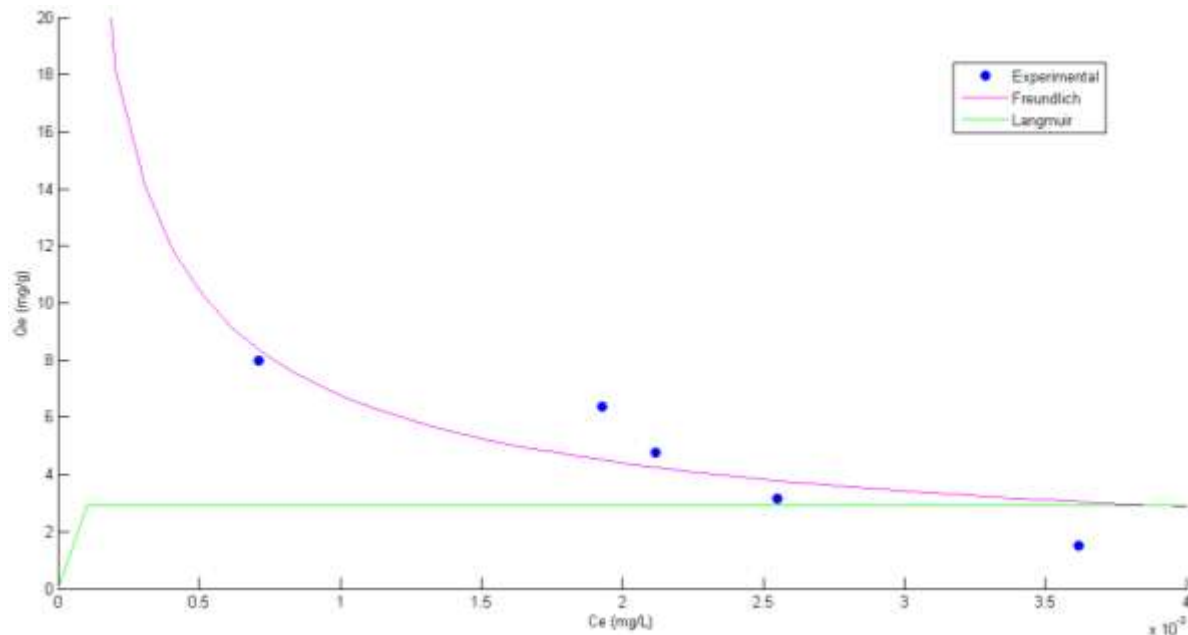

Figure 7. Activated carbon adsorption isotherms 1:2 for Freundlich and Langmuir

Figure 7 shows that the palm oil adsorption presented by activated carbon 1:2 is similar to the Freundlich model with $R^2=0.77$, indicating that it is a non-ideal, heterogeneous, multi-layer adsorption with non-uniform energy distribution, without adsorption affinity on the heterogeneous and reversible surface. The adjustment parameters of the models are reported in table 8.

Table 8.Adjustment parameters of the Langmuir and Freundlich isothermal models for the adsorption of oil in solution on activated carbon from cuesco and palm bagasse fibrilla with ZnCl$_2$ impregnation 1:2.

Model	Parameter	Value
Freundlich	K_f	0.0924
	N	0.6218
	R^2	0.775
Langmuir	B	2.9311
	$q_{máx}$	14
	R^2	0.134

For studies on the adsorption of dibutyl phthalate from an aqueous solution and wastewater from an oil refinery, although both have a higher R^2 factor.But it differs, as the Langmuir model is predominant in situations such as the adsorption of methylene blue; it is established that the type of isotherm is directly related to the pollutant to be treated, the Freundlich model being predominant in the case of oil adsorption [2], [30], [31]. Oil adsorption studies on materials such as chitosan dust and pearls [29], commercial activated carbon [32] have also shown that the Freundlich isotherm best describes adsorption, reaching removal rates of up to 98%.

4.   Conclusions

Activated carbon with low temperature synthesized ZnCl2 was prepared from mixed biomass of cuesco and oil palm fibrilla for use in the removal of oils in aqueous solution.The SEM analysis showed that the structure of the material was slightly porous and cracked by zinc chloride and that the carbon 1:2 concentration of Cl- and Zn+ ions was higher than the carbon 1:3, which is consistent with what was found in the literature.From the DRX it was found that carbons were amorphous in nature and with the presence of graphical planes d002 and d100, for 1:3 carbon it was found to have a slightly pronounced peak between the 18° and 22° bands indicating the presence of cellulose and lignin in its structure.From the application of the BET method, it was found that the surface area of the carbons was 23.24 m^2g^{-1} and 12.38 m^2g^{-1} for carbon 1:2 and 1:3, respectively. A removal percentage of 99.2% and 99.95 was obtained for carbons with an impregnation ratio of 1:3 and 1:2, consequently.With respect to carbon adsorption capacity for methylene blue and iodine index tests, carbon 1:2 had values of 6 mg g^{-1} and 25 mg g^{-1} respectively, while carbon 1:3 had values of 5.9 mg g^{-1} and 16 mg g^{-1}, indicating that carbon 1:2 was the best.The models that best adjusted the experimental adsorption data were Elovich's kinetic model and Freundlich's isothermic model, which implies that the process is controlled by chemo-sorption and that the superficial active sites are heterogeneous and have different activation energies, proving the complex nature of biomass.The preparation of low temperature synthesized ZnCl$_2$ activated carbons from mixed African palm biomass was found to be an option for the treatment of oily water.

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