

Adsorption Properties of Activated Biochars Produced from Agro-industrial Residual Biomass

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Abstract— *The use of organic wastes (residual biomasses) is a subject of great importance due to the enormous quantities generated around the world and the undesirable environmental impact caused by the incorrect disposal of this material. In this paper, it will be discussed the use of pyrolysis for some of these residual biomasses (coconut fiber, coffee silver skin and sugarcane bagasse and straw), reducing the volume and producing activated carbon for use in adsorption processes. The produced biochar was chemically activated by using potassium carbonate (K_2CO_3) and applied in the adsorption of copper (II) from aqueous samples. Batch experiments were done to evaluate the influence of contact time and initial metal concentration. The activated carbon produced proved to be an excellent adsorbent for metallic ions (Cu^{2+}) from aqueous solution, mainly due to its superficial area. Using an initial concentration of 500 mg L^{-1} of $Cu(II)$, the uptake of the activated carbon obtained from sugarcane straw was 135.7 mg g^{-1} , which is an excellent value for metal ions removal from water.*

Short conclusion: The produced biochars, after the activation showed a very large surface area that confirms the potential use as a powerful adsorbent to recover polluted waters.

Keywords— *Coconut fiber, silver skin, sugarcane; activated carbon; adsorption; copper.*

I. INTRODUCTION

Biomass is an abundant source of energy and biomaterials and can be originated from agricultural wastes. [1,2]The use of these organic wastes is a subject of great importance due to the enormous quantities generated around the world and their undesirable environmental impact caused by the incorrect disposal. This topic assumes a great importance in Brazil [3,4]due to its intense agricultural activity generating a large amount of agro-industrial residues. The solution of this environmental problem is a challenge for researchers and the aim of the proposed processes must be not only to reduce the amount of residues but also to aggregate value to these materials.

Thermo-degradation is an important tool for reducing waste biomass volumes associated with agro-industrial activities and avoiding their inappropriate discard. In this

paper, it will be discussed the use of pyrolysis for some of these residual biomasses (coconut, coffee and sugarcane), reducing the volume and producing activated biochar for use in adsorption processes. The importance of these residues in the Brazilian economy and environment has been discussed in previous papers of our research group.[5-8]

These residual biomasses can be used in the pyrolysis process to obtain solid (biochar), liquid (bio-oil and water) and gaseous products. Biochar is the solid residue from the pyrolysis of biomass and are normally formed by organic residual carbon and inorganic oxides produced from the original biomass. Some of its uses is in soil management, waste management and water purification in sanitation stations.[9]

The properties of biochar can vary depending on the original biomass and the pyrolytic conditions. These properties are highly influenced by the temperature of pyrolysis, on the extent of carbonization increases with increasing pyrolysis temperature, increasing the carbon content, and decreasing the hydrogen and oxygen content in the resulting biochar. [6]

In general, biochar has low surface area, [10] consequently, it needs to be activated for increasing its surface area, porosity and change the volume and diameter of the pores. Activated carbon is one of the most effective adsorbents for removing a wide range of contaminants from industrial and municipal landfill leachate and contaminated groundwater. [11,12]

Metal ion salts are important contaminants from natural waters [13,14] and one of the ways to reduce this impact, besides the reduction or elimination of the source, is the use of efficient removal techniques, such as adsorption on porous solids. [13,14] The behavior of the metal salts against adsorption on activated carbon can be exemplified with the use of copper salts, since they have a behavior that is already well studied, although they are not among the most toxic in the environment. [15-20] Thus, with relatively simple techniques such as batch adsorption and measurement of residual ions by molecular spectroscopy in the visible region, it is possible to determine the adsorbent quality.

From the above information, the goal of this paper was to produce biochar from the pyrolysis of agro-industrial residues such as coconut fiber, coffee silver skin, bagasse and sugarcane straw. After the production of biochar, it was activated, characterized and tested in the adsorption of copper (II) in aqueous phase. Batch experiments were done to evaluate the influence of contact time and initial metal concentration.

II. MATERIAL AND METHODS

2.1. Biomasses

Coconut Fiber (CF) was provided by the Brazilian Agricultural Research Corporation (EMBRAPA) from Sergipe, Brazil. Coffee Silverskin (SS) was provided by a coffee processing company also from Sergipe (Brazil) and were collected directly from the industry production line. Sugarcane (straw and bagasse – SCS and SCB, respectively) were collected in the Taquari Plant, Capela, Brazil.

The ash content of the biomasses was determined according to the procedure adapted from Spanish Standard UNE 32 111 of October 1995. (UNE 1995) The tests were

carried out in a Nabertherm muffle furnace (model L 5/11) with air circulation.

2.2. Pyrolysis of Biomasses

The pyrolytic system used for the four biomasses was detailed reported in a previous work. [6] The conditions for the experimental process of the pyrolysis were as follows: 150 g of each biomass, heating rate of 20 °C min⁻¹ until 700 °C and residence time of about 35 min. The yield of the products obtained was calculated based on the total raw material fed into the reactor and the mass of products obtained (biochar and bio oil). The possible losses of the process were included in the calculation of the non-condensable gases, which were not the object of study of this work. All the experiments were conducted in triplicate. The biochar produced in this step were named as CFB - coconut fiber biochar; SSB - Silverskin biochar; SCSB - sugarcane straw biochar and SCBB - sugarcane bagasse biochar.

2.3. Activated Carbon production

The activated carbon were prepared by physical mixture of biochar (particle size below 0.297 mm) with ground potassium carbonate (K₂CO₃, Aldrich, 99%) in 1:3 weight ratio of biochar/K₂CO₃. The mixtures were activated in a horizontal furnace (Thermolyne mod. 21100) equipped with a ceramic tube, adapted with a stainless steel tube (15 cm in length and 2 cm in diameter) under N₂ flow (5 cm³ s⁻¹). The temperature was raised up to the activation temperature (800 °C) using a heating rate of 10 °C min⁻¹, and kept for 1 h. After cooling, under N₂ flow, the samples were thoroughly washed with distilled water up to pH 7 and dried at 100 °C. The activated carbons were named by adding the term AC (activated carbon) to the corresponding biochar name: CFAC, SSAC, SCSAC and SCBAC. The yield of the activation process was calculated by the difference of biochar mass used in relation to the activated carbon final mass.

2.4. Characterization of the biochar and activated carbon

2.4.1. Ultimate and proximate analyses

The proximate analysis was conducted according to ASTM D 3172-3175 standards, (ASTM 1999) and the results were expressed in terms of volatile matter, ash and fixed carbon contents. CHN analysis was performed in an elemental analyzer (Flash mod. EA 1112).

2.4.2. Nanotextural and Chemical Characterization

The textural characterization of the samples was made by N₂ adsorption isotherms at -196 °C measured in an automatic apparatus Micromeritics ASAP 2010. Before the isotherms acquisition, approximately 50 mg of the samples were out gassed overnight at 120 °C, under vacuum (P

$<10^{-2}$ Pa). From N_2 adsorption data, the apparent surface area, A_{BET} , and micro porosity were evaluated through, respectively, BET equation ($0.05 < p/p^0 < 0.15$) [21] and α_s method, taking as reference the isotherm reported by Rodriguez-Reinoso [22]. The pH at the point of zero charge (pH_{PZC}) was determined (Symphony SP70P pH Meter) by reverse mass titration, as proposed by Noh and Schwarz [23].

2.5. Batch adsorption experiments

The adsorption of copper onto different types of activated carbons was tested using standard metal solutions prepared from copper sulfate ($CuSO_4 \cdot 5H_2O$; CAS: 7758-99-8). An aqueous metal stock solution at 5000 mg L^{-1} were prepared by adding a metal salt to Milli-Q water and work solutions were obtained by diluted to obtain lower concentration solutions. All reagents used were of analytical reagent grade from Merck®. Prior to each experiment, the metal solution (25 mL) and adsorbent material (0.125 g) were mixed together in a specific flask with the initial pH of ~ 5.0 . The effects of the concentration of metal and adsorption time on the adsorption efficiency of copper ions over activated carbon were studied. The experiments were controlled through blank tests in the same conditions developed for the samples. For the study of the initial metal concentration solution at 500, 750 and 1000 mg L^{-1} of copper in water were tested with contact time of 24 h.

Adsorption kinetic studies were performed in a 750 mL erlenmeyer flask, using 500 mL of the aqueous metal solution and 2.5 g of the adsorbent. Aliquots (5 mL) were taken after 1 min, 2 min, 5 min, 30 min, 2 h, 8 h and 24 h of reaction. (Runtti et al. 2014) The experiments were done in triplicate and the relative standard deviations were calculated. All samples including the initial samples were filtered through $0.45 \mu\text{m}$ filter paper (Sartorius Stedim Biotech). The stirring was carried out in a chilled incubator

Marconi model MA830/A (at 100 rpm). The amount of copper was determined in the filtrate by UV-Vis in a Spectrophotometer Hach, model DL at 810 nm (maximum absorption wavelength found). The percentage removal of metal (%) from the solution was calculated by the equations follows: [24]

$$\text{Metal removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations in solution (mg L^{-1}).

The uptake q_e (mg g^{-1}) after equilibrium was calculated by using equation 2:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

Where V is the volume of the solution (L) and m is the mass of the adsorbent (g).

III. RESULTS AND DISCUSSION

3.1. Yield of Pyrolysis Products

The results of the experiments are summarized in the **Table 1**. The mass yields varied from 22.1% (SCB sample) to 29.9% (CF sample), and presented coefficient of variation (CV%) of up to 2.7% (for SCB sample). For the liquid fraction (bio-oil + water), the mass yield varied from 31.8% (SCS sample) to 45.4% (SCB sample). Non-condensable gases (NCG) were not measured and were considered as all the produced gases (such as H_2 , CO_2 , CO , CH_4) expelled at the end of the process, in addition to other possible losses generated during the procedure, once they were estimated by difference. The NCG had the lowest value in the coconut fiber sample (CF sample 28.8%) and the highest value for the sugarcane straw sample (CS sample 40.7%).

Table 1: Mass yield of the pyrolytic process and for the activation for the biomasses studied.

Biomass	Yield in the pyrolysis					
	Biochar		Crude Bio-oil(*)		NCG(**)	
	Yield (%)	STD% (***)	Yield (%)	STD%	Yield (%)	STD%
CF	29.9	2.4	41.3	3.2	28.8	4.6
SS	29.4	1.7	35.6	2.7	35.0	1.4
SCS	27.5	1.3	31.8	2.7	40.7	1.4
SCB	22.1	2.7	45.4	3.8	32.5	7.1

(*) Crude Bio-Oil = bio-oil composed by organic and aqueous phase;

(**) NCG = non-condensable gases

(***) STD% = standard deviation

CF= coconut fiber; SS= Silverskin; SCS= sugarcane straw; SCB= sugarcane bagasse.

The mass yield of pyrolysis products are similar to others researches for coconut fiber,[25,26]sugarcane straw [27]and sugarcane bagasse.[25,28]The higher amount of biochar was found in the pyrolysis of silverskin (29.4%) and coconut fiber (29.9%). There are not registers in the literature about pyrolysis of silverskin, the main researches in this area were related to coffee bean pyrolysis, and the result are similar to found in this search.[29]

3.2. Biochar Characterization

In **Table 2** it is presented the results of proximate and elemental analysis of the biochar. These parameters could define the main characteristics of the fuel, and includes the moisture content, volatile matter, ash and fixed carbon, beside the elemental analysis namely the contents of C, H, O and N (wt.%).

Table 2: Proximate and elemental analysis of biomasses, biochar and activated carbons.

Sample	(wt. %)									
	Moisture	VM(*)	ASH	FC(**)	C	H	N	O(***)	H/C(****)	
Biomass	CF	-	-	3.9±0.03	-	49.6	5.9	0.5	44.0	1.4
	SS	-	-	4.8±0.02	-	44.7	5.4	2.1	47.8	1.5
	SCS	-	-	4.8±0.02	-	46.6	6.5	1.2	45.7	1.7
	SCB	-	-	1.4±0.02	-	43.2	7.3	0.9	48.6	2.0
Biochar	CFB	1.1±0.01	19.3±0.02	5.3±0.01	75.4±0.04	76.4	0.4	1.0	22.2	0.1
	SSB	1.2±0.01	21.9±0.04	11.4±0.02	66.7±0.03	80.4	2.3	1.0	16.3	0.3
	SCSB	2.6±0.01	29.9±0.03	6.9±0.01	63.2±0.04	69.5	3.6	0.4	26.5	0.6
	SCBB	1.4±0.01	29.2±0.03	4.4±0.01	66.4±0.03	71.7	3.6	0.5	24.2	0.6
Activated carbon	CFAC	3.6±0.02	14.1±0.04	8.5±0.02	77.4±0.05	62.8	3.2	0.9	33.1	0.6
	SSAC	3.4±0.01	16.3±0.02	16.1±0.04	67.6±0.06	73.7	1.9	1.7	22.7	0.3
	SCSAC	4.2±0.01	11.7±0.02	11.2±0.03	77.1±0.04	68.4	2.1	0.8	28.7	0.4
	SCBAC	6.0±0.01	8.5±0.02	6.5±0.03	85.0±0.06	74.8	3.0	0.7	21.5	0.5

(*)VM=Volatile matter; (**)FC= Fixed carbon; (***)By difference; (****)Atomic ratio between hydrogen and carbon.

Samples = CF= coconut fiber; SS= silverskin; SCS= sugarcane straw; SCB= sugarcane bagasse; CFB= coconut fiber biochar; SSB= silverskin biochar; SCSB= sugarcane straw biochar; SCBB= sugarcane bagasse biochar; CFCA= coconut fiber activated carbon; SSCA= silverskin activated carbon; SCSCA= sugarcane straw activated carbon; SCBCA= sugarcane bagasse activated carbon;

Based on these data, the nature of biomass have pronounced effects on the development of the volatile matter, ash and fixed carbon, as shown in **Table 2**. The biomass elemental composition reveals that they are composed mainly by carbon, oxygen and hydrogen, as can be expected in most lignocellulosic materials.[30]

The biomasses present low ash content and showed to be suitable for pyrolysis. The ash content and its composition

are important factors for biomass use in thermochemical processing due to its catalytic activity. [31] This biochar could be utilized as a cheap absorbent, carbon coating, solid fuel, direct fuel, household briquette, carbon sequestration and soil improvement. [32]

Elemental analysis results revealed that the carbon content is increased after pyrolysis in all the samples, as it was expected. The values are similar to those previously

reported for coconut fiber [33,34], silverskin [35], sugarcane straw [27] and sugarcane bagasse. [36,37] The high nitrogen content of the silverskin sample was already expected due to the origin of the biomass, which has a high content of this element, mainly due to the presence of caffeine and its homologues.

During the activation step, the action of the oxidant agents produce an increase in oxygen content and a decrease in carbon content as can be observed in **Table 2**, but chemically activated carbons still presented a carbon content (62.8% - 74.8%). The change in the elemental content is in agreement with the concentration of oxygenated functional groups on the surface of the activated biochar.

The H/C ratio gives an idea of the aromaticity of the sample and, as a consequence, their energy power. Very

Table 3: Mass yield, surface area (BET), volume of micro and mesoporous, pH_{PZC} and uptake of activated carbons.

Activated carbon	BET Area ($m^2 g^{-1}$)	VT ($cm^3 g^{-1}$)	Vme ($cm^3 g^{-1}$)	Vmi ($cm^3 g^{-1}$)	Vul ($cm^3 g^{-1}$)	Vsu ($cm^3 g^{-1}$)	pH_{PZC}	q_{max} ($mg g^{-1}$)
CFAC	1130	0.55	0.05	0.50	0.25	0.25	6.3	28.6
SSAC	1308	0.66	0.07	0.59	0.18	0.41	7.6	93.3
SCSAC	1185	0.58	0.08	0.50	0.27	0.23	5.9	135.7
SCBAC	791	0.37	0.03	0.34	0.11	0.23	6.6	16.7

BET Area: total surface area; VT: total volume; Vme: mesoporous volume; Vmi: microporous volume; Vul: ultra-microporous volume; Vsu: super-microporous volume; q_{max} : uptake.

Samples: CFAC= coconut fiber activated carbon; SSAC= silverskin activated carbon; SCSAC= sugarcane straw activated carbon; SCBAC= sugarcane bagasse activated carbon.

During chemical activation by K_2CO_3 , the chemical agent is introduced into the precursor, producing physical and chemical changes and modifying the thermal degradation process. The textural parameters reveal that the chemically activated carbons prepared have a well-developed porous structure, enhancing the porosity. The isotherms configuration reveals that the samples have a well-developed microporous structure associated with some mesoporosity, detected by an upward deviation of the curves for higher p/p_0 values. Pore characteristics of all activated carbons are given in **Table 3**. Specific surface areas obtained after activation steps are similar, or slightly superior, to those of activated carbons produced in laboratory scale, ranging between 800 and 1300 $m^2 g^{-1}$. [39]

It may be noted that activated carbons produced from silverskin, coconut fiber and sugarcane straw have a higher specific surface area than those produced from sugarcane bagasse. This may be due to the lignocellulosic composition of the precursors, which influences in the

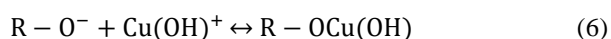
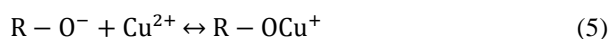
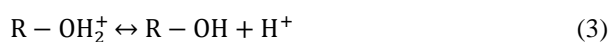
high values indicate low aromaticity, that is, high number of hydrogen atoms related to the carbon ones and lower energy power. The H/C atomic ratios obtained for the bagasse samples were higher than the other biomasses, indicating a lower proportion of condensed structures, besides tending to have a greater energy potential. Studies with lignocellulosic biomass demonstrate similar results both in relation to the elemental analysis and in relation to the atomic fraction H/C. [36,38] In the production of activated carbon, a relatively high yields was obtained for the four samples. The mass yields of activated carbon obtained in this work was 65.3, 44.2, 57.5 and 72.5% for CFAC, SSAC, SCSAC and SCBAC samples respectively, that can be considered satisfactory if the porosity are adequate.

biochar yield and porosity due to the differences in thermal stability of the major components (lignin, cellulose, hemicellulose). [40] All samples generated activated carbons with a high percentage of microporosity (approximately 90%) and a lower mesopores concentration (**Table 3**).

Concerning the surface chemistry, the pH_{PZC} values (**Table 3**) of the materials activated at 800 °C revealed that the chemistry activation produces a material with slightly acidic surface for the coconut fiber, sugarcane straw and bagasse (pH_{PZC} 6.3, 5.9 and 6.6, respectively). However, the activated carbon derived from silverskin presents a basic surface chemistry (pH_{PZC} 7.6). This difference of acidity in the surface indicates different uses for the activated carbons, and for the biochar itself, if it would be applied as a soil corrective.

3.3. Adsorption studies

The pH of the aqueous solution is an important parameter in the adsorption process because it affects the aqueous solution chemistry and the adsorbent surface binding sites. The relation between pH and the efficiency of the adsorption of copper could be interpreted by the pH effects on: (1) the association/dissociation of surface functional groups from the activated carbon; (2) the surface charges; (3) the formation of ion species, and (4) the interactions between functional group and metal ions. Below pH 5, the main species involved in the adsorption process is free ions Cu (II) [41], while at low pHs, the electrical repulsion between Cu (II) ions and positively charged functional groups on the carbon surface are responsible for low Cu adsorption. In addition, at low pHs, the overall surface of the carbon becomes positive and hinders the binding of positively charged metal ions. At pH values higher than 5.0, precipitation of insoluble metal hydroxides occurs which restricts the adsorption studies. This effect can be explained by the interaction and equilibrium of the Cu (II), Cu (OH)⁺ and Cu (OH)₂ species with the surface functional groups on the activated carbon, according to the equations below [42]:



Where:

R represents the active sites on the surface of activated carbon;

R - OH₂⁺, R - OH, R - O⁻ are protonated, neutral, and ionized surface hydroxyl functional groups; and

R - OCu⁺ and R - OCu(OH) are complexes species involving the copper.

From this and considering the literature for copper (II) adsorption, the pH selected for all experiments was 5. [43-45]

3.4. Effect of contact time

The adsorption of Cu (II) on four activated carbon produced was studied as a function of adsorption time from 1 min to 24 h. Corresponding results are showed in **Figure 1**. In all cases, the rate of percent metal removal was rapid during the initial stage. This is due to the high concentration gradient in the beginning, which exhibited a high driving force for the migration of copper ions from solution to the surface of activated carbons; in addition, there was a larger surface area of the adsorbent being available for the adsorption of Cu (II) in the process beginning. Thereafter the rate of adsorption was lower and finally approached equilibrium, reaching a plateau (mainly for the SSAC and SCSAC activated carbons) after 480 min of contact time between the two phases. For the all activated carbons, the maximum uptake is not achieved during adsorption experiment (24 h). SCSAC was the sample that most approached the maximum adsorption reaching, in 24 hours, 76% of removal (**Figure 1**).

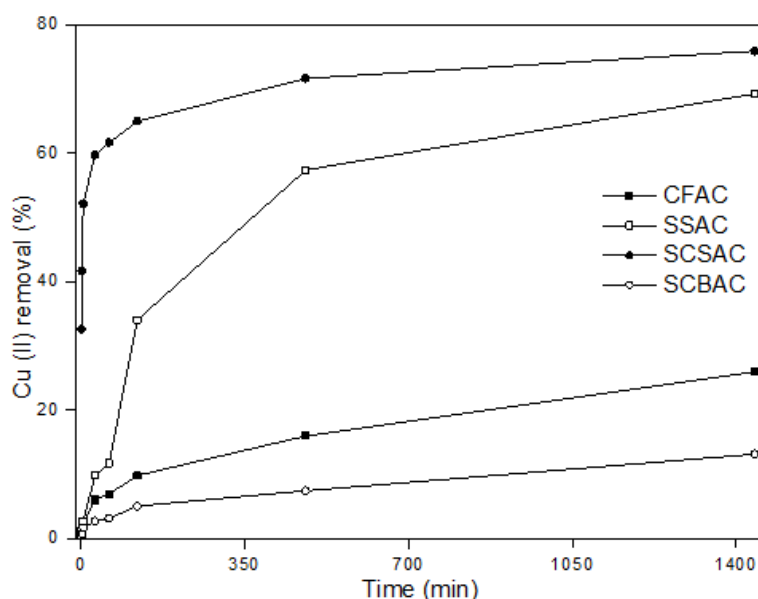


Fig.1: Effect of contact time on the removal efficiency (%) on the different samples.

Legend: CFAC= coconut fiber activated carbon; SSAC= silverskin activated carbon; SCSAC= sugarcane straw activated carbon; SCBAC= sugarcane bagasse activated carbon;

3.5. Effect of initial metal ion concentration

Experimental results for the removal of copper on the four tested activated carbon in the metal concentration range from 500 to 1000 mg L⁻¹ using 0.125 g/ 25 mL activated carbon are shown in Table 03. Different Cu (II) concentration resulted in different uptake. The amount of metal ions adsorbed on the activated carbon varied from 20.0 to 28.6 mg g⁻¹ (for CFAC); 64.8 to 93.3 mg g⁻¹ (for SSAC); 76.7 to 135.7 mg g⁻¹ (for SCSAC); 13.3 to 16.7 mg g⁻¹ (for SCBAC) (Figure 2a). In all of the samples (except CFAC), the q value increased with increase of the concentration, that is, the maximum sorption capacities of

SSAC, SCSAC and SCBAC was get in the concentration 1000 mg L⁻¹. The increase in uptake may be because the high concentration of metal ions provides greater driving force for the transfer process to overcome the mass transfer resistance. Thus, the driving force to overcome all the mass transfer resistances of the metal ions from the aqueous phase to the solid phase provided higher probability of collision between metallic ions and the active sites of the activated carbon. [46] Considering the percentage of copper adsorbed, the optimum initial metal concentration for all the samples was 500 mg L⁻¹ (Figure 2b).

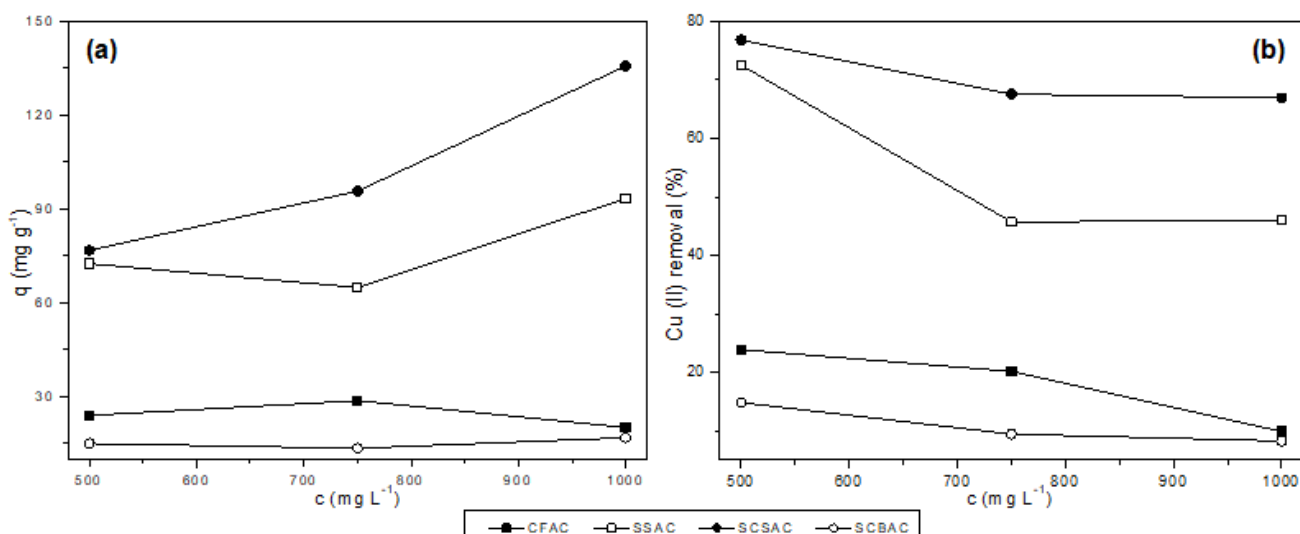


Fig.2: Effect of initial metal ion concentration on the efficiency of the processes: (a) amount of copper adsorbed per gram of adsorbent (q) and (b) percentage of removal of the copper ions by the different sorbents

Legend: CFAC= coconut fiber activated carbon; SSAC= silverskin activated carbon; SCSAC= sugarcane straw activated carbon; SCBAC= sugarcane bagasse activated carbon;

The uptake of SSAC (93.3 mg g⁻¹) and SCSAC (135.7 mg g⁻¹) indicate that the activated carbons, derived from silverskin and sugarcane straw, have extraordinary uptake for Cu (II). These values are almost an order of magnitude higher compared to adsorption capacities of activated carbon obtained from other biomass. [43,44,47]

This can be explained by the surface chemistry of the studied materials in addition to their microporosity characteristics. These data show the importance of the type of the starting material on the efficiency of adsorption of metallic ions. These both samples (SSAC and SCSAC samples) are those that presented greater superficial areas in relation to the others activated carbons studied (Table 2).

IV. CONCLUSIONS

These results showed that it is possible to produce high quality activated carbon from agro-industrial residues as those studied here. The advantage is not only in the cost of the raw material, adding value to an environmental waste not adequately used, but also in the quality of the product, that achieves similar surface areas and, sometimes superiors, to activated carbons produced in laboratory scale.

The activated carbon produced proves to be an excellent adsorbent for metallic ions (Cu²⁺) from aqueous solution, mainly due to the surface chemistry and their microporosity characteristics. Using an initial concentration of 500 mg L⁻¹ of Cu(II), the uptake of the activated carbon obtained from sugarcane straw was 135.7 mg g⁻¹, which is an excellent value for metal ions removal from water. Beside this, the sample achieved a maximum

adsorption in 24 hours, with 76% of removal of Cu(II) from the aqueous matrix.

In previous works, we have already demonstrated that another important product from pyrolysis of agro-industrial residues (bio-oil) can be obtained.[7,48-50]The results achieved in this paper demonstrated that is possible to propose a total exploitation of these residual materials, including the use of biochar beside bio-oil. In that sense, it is possible to think in a bio-refinery based on these wastes.

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