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VALORISATION OF NATURAL FIBRES FROM AFRICAN BAOBAB WASTES BY THE PRODUCTION OF ACTIVATED CARBONS FOR ADSORPTION OF DIURON

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Abstract

In this work we report the use of a natural fibrous biomass, the African Baobab, as precursor to produce activated carbons tailored for the removal of a pollutant frequently found in water streams, the herbicide Diuron. The precursors used were Baobab wastes, namely bark, wood and seeds, collected in Angola. The activated carbons produced by physical activation with carbon dioxide showed an interesting porosity with apparent surface area and pore volume, up to $2130 m^2 g^{-1}$ and $0.99 cm^3 g^{-1}$, respectively. All the activated adsorbents are of microporous nature, with mean pore width between 0.69 and 1.94nm. Selected samples were tested for the adsorption of Diuron from liquid-phase. The maximum adsorption capacity reached $400 mg g^{-1}$ for sample BS-62. This work shows the suitability of using Baobab wastes to produce activated carbons, which can be considered a new route to the valorization of its wastes, with good properties for the adsorption of Diuron.

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1. Introduction

The scientific name for Baobab is *Adansonia Digitata*, as a tribute to the French Explorer and botanist, Michel Adanson (1727-1806), who observed a specimen in 1749 on the island of Sor, Senegal. The African Baobab can reach 30m high and 7m diameter with a lifespan of several hundred years. This tree in also known as the African Tree of Life because during the rainy season it absorbs and stores water, up to $7m^3$, in the trunk with the production of a rich fruit in the dry season. The fruits, flowers, leaves, shoots, roots of seedlings and even the tree roots are

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edible. The inner bark furnishes a fiber that can be made into ropes, twisted into strings for musical instruments, and woven into cloth. The fiber is so strong as to give rise to a common Swahili saying, "as secure as an elephant bound with a baobab rope". This fibrous structure of Baobab is very useful for many applications amongst which we can find medicinal, nutritional, clothing, protection, among others [1, 2]. Nevertheless, in the adsorption field studies or applications are practically non-existent, with only few examples of biosorbents [3-5], and one or two references to the production of activated carbons (ACs) [6, 7].

ACs have been one of the most important materials used all over the world for centuries and they are nowadays one of the most relevant adsorbent materials in our society and in diverse areas of human activity. ACs are used in a wide range of applications performed in gas and liquid medium that include, among others, medicinal uses, gas storage, pollutants removal, gas separations and odours removal [8-11].

The lignocellulosic (LC) materials (comprising wood, coconut shells, peat, agricultural residues, and other plant substances) are the single largest source of precursors for the industrially manufactured ACs with an annual worldwide production of over 175,000 tons/year. The composition of biomass is rather complex, but it is generally accepted that the LC materials are basically composed of three components, namely, polysaccharides (cellulose and hemicellulose), lignin and extraneous matter, namely extractives and ash [12]. In some cases, the fibrous nature of biomass is significant, which opens the door to new applications.

The originality of this work is the use of a novel precursor, namely the bark, wood and seed from the Baobab, containing a high content of natural fibres, in the production of ACs and its application to remove a herbicide with a broad use in agriculture, Diuron (3-(3 4-dichlorophenyl)-1,1-dimethylurea), from aqueous solutions. To the best of our knowledge the use of Baobab for the production of activated carbon (AC) by activation with carbon dioxide was never reported before. Another relevant aspect of the work is the valorisation of agriculture wastes to produce an added value material like ACs. It is noteworthy to mention that the Baobab used in this work was collected after its use by the local population in Benguela Region (Angola).

Angola, like many developing countries, has seen an expansion of agriculture that has lead to the introduction of emerging pollutants into the water streams and soil by the extensive use of pesticides and herbicides, like Diuron that has a significant use in Angola. Concerns regarding Diuron have been frequently reported worldwide. For example, in France, Diuron was found to be one of the most used products commonly found as a contaminant [13]. In Germany, recurring detection of Diuron residues in drinking water supplies has led to prohibition of Diuron usage in confined areas where excess water can flow into drainage pipes and sewer [14]. Diuron is classified as a potential human carcinogen by USEPA [15] and considered as a highly toxic, persistent priority substance by the European Union (EU) [16].

Nomenclature

BB	Baobab Bark
BW	Baobab Wood
BS	Baobab Seed
A_{BET} (m^2/g)	Apparent surface area
A_S (m^2/g)	External area determined by the alpha-s method
V_S (cm^3/g)	Pore volume determined by the alpha-s method
V_0 (cm^3/g)	Micropore volume determined by the DR method
L_0 (nm)	Mean pore size determined by the DR method
pzc	Point of zero charge
ACs	Activated carbons
XRD	X-ray diffraction
BET	Brunauer-Emmtt-Teller
α_S	Alpha-S
DR	Dubinin-Radushkevich
FTIR	Fourier Transform Infrared

2. Experimental

2.1. Precursors

The precursors were bark (BB), wood (BW) and seed (BS) from the Baobab tree, all collected in Angola. The precursors were crushed into pieces of size up to 3 mm in one dimension, dried in an oven at 110ºC and then pre-washed with an acid aqueous solution of 20% in H_2SO_4 for 24h. After filtration, the solid material was washed with distilled water, until the pH of the effluent matched the pH of the distilled water, and dried in oven at 110ºC.

2.2. Activated carbon production

The production of the ACs was done in a stationary horizontal tubular furnace using a dual stage process that starts with a carbonisation carried out at 800ºC (for the Baobab wood - BW), and 900ºC, (for Baobab bark - BB and Baobab seed - BS) with a 10ºCmin^{-1} heating rate under a constant N_2 flow of 85cm^{3}min^{-1}. After carbonization the char was activated at 800ºC (for BW) or 900ºC (for BB and BS) for different periods of time, in order to achieve different degree of burn-off, under constant CO_2 flow of 83cm^{3}min^{-1}. The burn-offs of the ACs produced were within the range 26-63%. The sample was then allowed to cool down below 50ºC under N_2 flow before removing. Each sample was identified with a code name indicating the type of Baobab precursor (BP) and the percentage of burn-off (BO), BP - BO. For the carbonised samples the letter C replaces the burn-off, BP - C.

2.3. Materials characterisation

The determination of wood precursors content in cellulose and lignin was made by Agroleico (Porto Salvo, Portugal) using Portuguese Standards NP2029 and ME-414, respectively. Helium density was determined by picnometry in an Accupyc 1330 from Micromeritics.

Nitrogen adsorption isotherms at 77K were determined using a Quantachrome Instruments Quadrasorb *SI* after outgassing the samples at 573 K for a period of 3 h in a Quantachrome Master Prep Unit. The isotherms were analysed using the Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR) and α_s methods. The point of zero charge was determined by mass titrations using three suspensions with 7%(w/v) in carbon material with initial pH of 3, 6, and 11, more details given elsewhere [17]. X-ray diffraction (XRD) patterns were determined on a Bruker AXS D8 Advance diffractometer using CuKα radiation, 40 kV and 30 mA, with a step size of 0.020º between 5.000 and 60.020º. Elemental analysis was carried out for carbon, hydrogen, sulfur and nitrogen using a Eurovector EuroEA elemental analyzer.

The Diuron adsorption from liquid-phase on the samples was carried out at 25ºC under pH slightly acid, pH ~ 6, by using a fixed amount of AC that was added to an aqueous solution of the pesticide, with an initial specific concentrations, on Erlenmeyer flasks hermetically closed, under agitation on a thermostated shaker bath. After the equilibrium time of 24h, the AC suspensions were filtered, and the residual pesticide concentration determined by UV/Visible spectrophotometry, using a PerkinElmer Lambda 850 spectrophotometer, at a wavelength of 248nm. The Diuron (3-(3 4-dichlorophenyl)-1,1-dimethylurea) was purchased from Aldrich with a purity of 98%.

3. Results and Discussion

3.1. Adsorbents characterisation

The precursors were characterized by helium density and the determination of the cellulose, hemicellulose and lignin content. As can be seen in Table 1, the precursors have similar density with a value of 1.45 ± 0.05g/cm^3 that for biomass materials can be considered relatively high. Regarding the composition, we can observe differences among the 3 precursors, namely on cellulose and lignin. BS is the precursor with the lower content on cellulose (21.9%) but with a high content on lignin (20.7%). The precursor with the lowest content on lignin is BW with 7.4%. It seems that the ratio cellulose:lignin is linked with the density of the material as we can observe a

proportionality between these factors. The ratio for BW, BB and BS are 5:1, 2:1 and 1:1, respectively, and the density decreases on the same way (BW>BB<BS). Thus, we can say higher content in cellulose, in comparison with lignin, leads to more dense materials.

Table 1. Characterisation of the precursors.

Precursor	Density (g/cm^{-3})	Cellulose (*wt%*)	Hemicellulose (*wt%*)	Lignin (*wt%*)
Baobab wood – BW	1.5076	36.9	9.2	7.4
Baobab bark – BB	1.4305	41.2	17.1	21.0
Baobab seed – BS	1.4118	21.9	17.1	20.7

The nitrogen adsorption/desorption isotherms of representative samples can be seen on Fig. 1. All isotherms are of type I according to the IUPAC classification [18], which indicates that all carbons are of microporous nature. The lack of hysteresis and the well-defined plateau, almost parallel to abscissa axis, reveals that all ACs have small external area and insignificant mesoporous volume. According IUPAC, micropores are pores that have diameter less than 2 nm and mesopores diameter between 2 and 50nm.
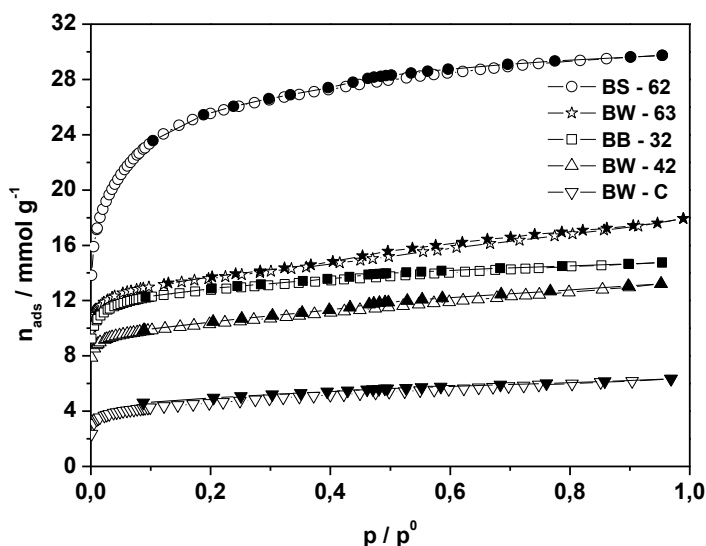

Fig. 1. Nitrogen adsorption/desorption isotherms at 77K (open symbols represent adsorption, closed symbols represent desorption).

The nitrogen isotherms were analyzed by suitable methods, namely Brunauer-Emmtt-Teller (BET), alpha-S (α_S) and Dubinin-Radushkevich (DR) in order to characterize the porous development of each sample. The results exposed on Table 2 show that the African Baobab is an excellent precursor for the production of ACs, it was possible to produce materials with apparent surface area and pore volume up to $2130 m^2/g$ and $0.99 cm^3/g$, respectively. As expected from the isotherms shape, all samples have low external areas, always less than $65 m^2/g$ and mean pore width within the range 0.69 and 3.52nm. All the carbonised samples, not submitted to activation with CO_2, present a relatively high specific surface area for a carbonized material, in the range $302 – 382 m^2 g^{-1}$, and pore volume between 0.14 and 0.19 $cm^3 g^{-1}$. A particular reference to the increment of process yield (BW<BB<BS) that is inversely proportional to the cellulose:lignin ratio, meaning that higher content in lignin will favor the process yield. The yield obtained for BS (~30%) can be considered relatively high for this type of process and for natural renewable biomass resources.

Table 2. Textural characterisation of the carbon materials.

Sample	Yield (%)	Burn-off (%)	A_{BET} (m^2/g)	A_S (m^2/g)	V_S (cm^3/g)	V_0 (cm^3/g)	L_0 (nm)
BW – C	20.7	-	382	22	0.19	0.15	1.69
BW – 42	-	42	875	44	0.40	0.34	0.74
BW – 63	-	63	1147	64	0.52	0.45	0.87
BB – C	23.9	-	302	22	0.14	0.12	2.33
BB – 26	-	26	741	30	0.33	0.29	0.78
BB – 32	-	32	1100	19	0.48	0.44	1.08
BS – C	28.2	-	319	18	0.15	0.13	3.52
BS – 29	-	29	1214	13	0.51	0.48	0.69
BS - 62	-	62	2130	33	0.99	0.79	1.94

(Burn-off - percentage of mass loss due to the activation step; A_{BET} – apparent surface area, A_S - external area determined by the alpha-s method V_0- micropore volume determined by the DR method; V_0 – micropore volume determined by the DR method; L_0 - mean pore width).

The ACs produced are all of basic character with pH of the point of zero charge (pzc) up to 10.40, this is coherent with the oxygen content of the samples. The basic properties of the carbons are the result of the delocalized π electrons in the basal planes, acting as Lewis base, and of the surface chemistry. Regarding the elemental composition it is noteworthy the absence of sulphur and the low content in nitrogen.

Table 3. Elemental composition and point of zero charge of the carbon materials.

Sample	C (%)	H (%)	N (%)	S (%)	O* (%)	pzc
BW – C	86.36	0.37	0.33	-	12.94	8.28
BW – 42	79.04	0.67	0.37	-	19.92	8.33
BW – 63	75.97	0.83	0.35	-	22.85	8.07
BB – C	87.92	0.81	0.23	-	11.04	7.51
BB – 26	79.84	0.83	0.27	-	19.06	8.56
BB – 32	84.80	0.78	0.25	-	14.17	9.13
BS – C	92.03	0.03	1.14	-	6.80	6.68
BS – 29	87.99	0.02	0.84	-	11.24	9.33
BS – 62	93.54	0.01	0.88	-	5.57	10.40

* Estimated by difference.

The chemical characterization was done also by Fourier Transform infrared spectroscopy (FTIR). The analysis of the spectra obtained, see Fig. 2, indicates that all samples have more or less the same absorption bands but with different intensities, which indicates that the nature of the surface functional groups are similar amongst the ACs produced from the 3 precursors but the relative concentration varies.

The bands situated at wavenumbers higher than 3500cm^{-1} are attributed to the presence of hydroxyl group (ν(O-H)). Functional groups with carbonyl bonds are clearly visible in all spectra by the presence of several bands in the ν(C=O) characteristic region 1700-1900cm^{-1}, namely quinones and lactones. Absorption bands at 1565 and 1556cm^{-1} can be attributed to ν(C=C) vibrations in aromatic rings while the bands at 1450-1420cm^{-1} are related to the presence of pyrone groups [19]. The broad and adjacent bands between 990 and 1060cm^{-1} are due to ν(C-O) vibrations in hydroxyl groups and/or ether-type structures. The existence of several bands in this region suggests the presence of different groups and structures containing C-O bonds, such as pyrones [20].
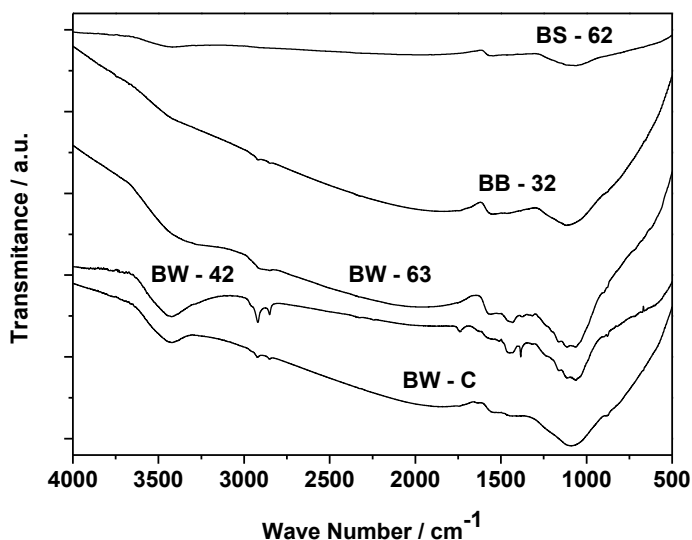
Fig. 2. FTIR spectra of representative samples.

The X-ray diffraction reveals the two typical broad bands from the turbostratic structure of carbon materials, related to reflections from (002) and (10l), around 2θ, 23-24º and 43º, respectively. X-ray diffraction patterns of representative samples are shown in Fig. 3. It is noteworthy to mention the absence of other peaks usually assigned to the presence of inorganic oxides, very common in carbon adsorbents resulting from biomass wastes. Probably this absence is the outcome of the acid pre-washing of the precursors with H_2SO_4 that has leached the inorganic impurities.
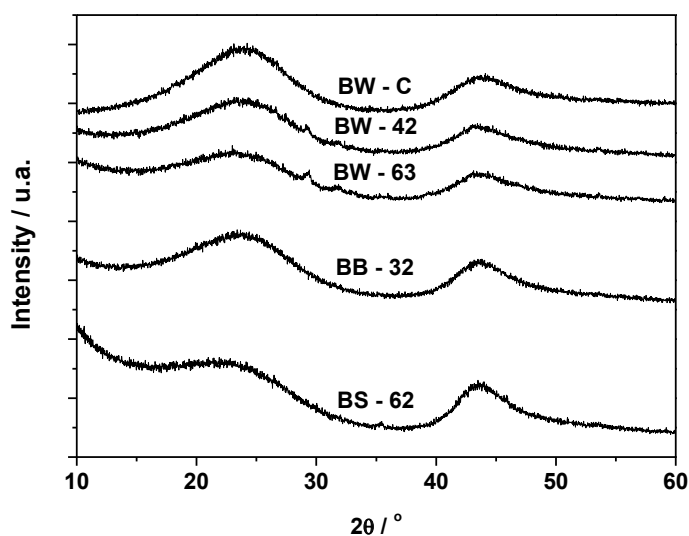

Fig. 3. X-ray diffraction patterns of representative samples.

3.2. Adsorption from liquid-phase

The results of the adsorption of Diuron onto the carbon materials produced, see Fig. 4, show that the amount adsorbed increase from the carbonized samples to the activated samples, what can be explained at a first glance by the development of the porous structure of those adsorbents. The adsorption obtained for the BW samples series indicates a direct correlation between the adsorption capacity and the surface area, we can see an increment of the Qads value from 21 to 326mgg^{-1}, with the augment of the specific surface area from 382 to 1147m^{2}g^{-1}. The same trend is also observed for samples BB-32 and BS-62. The shape of the experimental isotherms of BS-62 and BB-32 shows that the plateau was not yet reached, so we can expect that for these samples a higher adsorption capacity can be achieved. Another particular aspect of the BS-62 and BB-32 isotherms is the curvature for Ceq less than 7.5mgL^{-1}. Samples BW-63 and BB-32 have similar apparent surface area, A$_{BET}$, but different mean pore width, respectively 0.87 and 1.08nm, indicating that a minor pore size, within certain limits, can promote a faster adsorption in the low range of concentrations. This is accordance with the literature, the higher A$_{BET}$ value and superior pore volume explain the greater adsorbed amount of Diuron by BS-62 [21, 22].

Furthermore, the basic chemical nature of the samples contributes also to a favorable adsorption process of Diuron. The adsorption capacity increases with the pzc value, for instance for samples BW-42, BB-32 and BS-62 the pzc value is 8.33, 9.13 and 10.40 and the adsorption capacity 177, 275 and 400mgg^{-1}, respectively. Most probably both aspects, porosity and chemical nature, contributes to the adsorption mechanism.
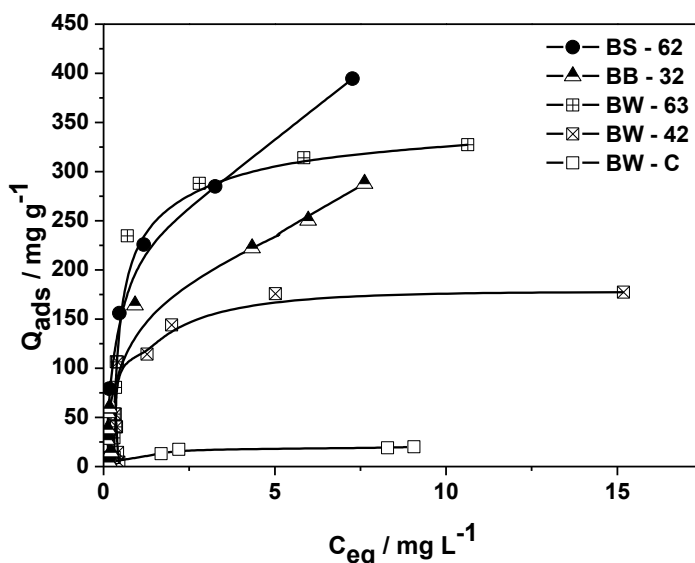

Fig. 4. Adsorption isotherms of Diuron from aqueous solutions, obtained at 25ºC on representative samples.

4. Conclusions

The production of activated carbons from wastes of different components of a natural fibrous biomass, the African Baobab, namely the bark, wood and seed of the tree, is reported. The results show that the materials tested are good precursors with the production of activated carbon by activation with carbon dioxide with a very well developed porous structure. The activated carbon samples reached apparent surface area and pore volume up to 2130m^{2}g^{-1} and 0.99cm^{3}g^{-1}, respectively, and a mean pore width between 0.69 and 1.94nm. All samples, with exception of sample BS - C, present a basic nature with pzc in the range 8.07 to 10.40, that can be explained by the delocalized π electrons in the basal planes, acting as Lewis base, and of the surface chemistry. This combination of characteristics is essential to explain the interesting adsorption capacity for the removal of Diuron from aqueous

medium. The maximum adsorption capacity reached 400mgg^{-1} for sample BS - 62. The analysis of the results obtained for the BW series indicates that the structural characteristics, namely the specific surface area and pore volume, have a major role on the adsorption process from liquid-phase, which is complemented by the chemical nature of the samples, as the basic nature favours the Diuron adsorption. This work shows the suitability of using Baobab wastes to produce activated carbons, which can be considered a new route to the valorization of its wastes, with good properties for the adsorption of Diuron.

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