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CONVERSION OF LIGNOCELLULOSIC AGRICULTURAL WASTES INTO ADSORBENTS FOR PHARMACEUTICAL DRUGS

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Abstract

Lignocellulosic agricultural wastes e.g. corn cobs, straws and corn stalks were converted into carbonaceous adsorbents using a sequence of thermal and chemical activation processes. The derived solids obtained after each type of activation were characterized by determination of fix carbon content, iodine number, Boehm titration and DRIFT spectrometry. The results obtained at the adsorption tests were well correlated to those of the characterization, showing that the most promising adsorbents for amoxicillin removal were those submitted to a thermal treatment followed by a chemical alkaline activation, followed by washing and a secondary thermal treatment. The most promising bio-based adsorbent was the one derived from corn stalks (90.6% adsorption efficiency).

Keywords: *activated carbon, adsorption, antibiotic, carbonization, lignocellulosic agricultural wastes*

Introduction

Antibiotics, the most important part of pharmaceuticals drugs, are produced in large quantities and used all over the world for both human and animals infections treatment caused by Gram-positive or Gram-negative bacteria. The intensive use of antibiotics may produce acute and chronic toxicity as well as multi-resistant bacteria not only in the treated patient's organism but also in the environment due to the fact that significant quantities of the antibiotics ingested by humans and animals are often excreted in the active form, as unmodified parent compound. For example, it has been reported that over 80% of oral administration of amoxicillin in humans is excreted through urine after 2 h of consumption. (Chaba & Nomngongo 2019). For this reason, we chose amoxicillin, as a model pharmaceutical drug for our study since it is a common antibiotic often used and it is not removed by wastewater and sewage treatment plants. (Balarak et al. 2017)

Thus, different methods have been applied in order to solve effectively the antibiotic pollution. Among all the treatment methods, the adsorption process is highly beneficial due to the advantage of not being toxic or having the ability to degrade contaminants. Liquid – solid adsorption of organic pollutants from wastewaters is a relatively inexpensive and very efficient process, simple to design and operate. The efficiency of adsorption processes is highly affected by the type of adsorbent, the adsorbate properties, and the compositions of the waste stream. (Ahmed et al. 2015; Limousy et al. 2016; Tseng et al. 2005) Generally, for many pollutants, the most commonly used

adsorbent is the activated carbon that can be produced from different carbonaceous materials, such as lignocellulosic agricultural wastes. The use of these unnecessary and inexpensive materials makes it possible to obtain activated carbon-like solids with new physicochemical properties, large specific surface area, high volume of pores and to convert them to valuable products.

This research is focused on the obtaining of some activated carbons from common agricultural wastes: i.e. corncobs, corn stalks, wheat straws and the physicochemical characterization of the prepared solids. Different preparation parameters, particularly activation procedures, were examined in order to evaluate the influence of the activation conditions on the textural and acid–base properties of the final products. Finally, the surface properties of the solids were correlated to their performances in amoxicillin removal from aqueous solutions.

Materials and Methods

Activated carbon preparation

The starting materials: corncobs (CB), corn stalks (TB) and wheat straws (PB) were chopped, handpicked, washed with distilled water, in order to remove dust and color, dried at 110°C, for 72 h, ground with a ball mill and sieved to a uniform size in the range of 1–1.5 mm. Next, raw solids were subjected to carbonization for 20 min (CC20, TC20, PC20) and 40 min (CC40, TC40, PC40) under a stream of methane at 650°C.

CC40, TC40, PC40 were chemically activated by treatment with KOH aqueous solution (at 5/1 weight ratio between the KOH solution (2M) and the solid) under magnetic stirring. After 2h, the activated solids were separated by centrifugation and dried at 90°C for 72 h yielding CC40A, TC40A and PC40A samples. The pH of these solids was approximately 12 upH. Therefore, in the next step, the activated solids were washed with distilled water until the washing water became colorless, its pH reached 8 upH and its conductivity was lower than 50 $\mu\text{S}/\text{cm}$. The washed solids were further dried overnight at 90°C yielding the solids denoted CC40AS, TC40AS, and PC40AS. Then, the AS suffixed solids were subjected to a new carbonization step for 20 min (CC40ASC, TC40ASC, PC40ASC) under a stream of methane at 650°C.

Activated carbon characterization

Fixed carbon content determination

The fixed carbon content can be calculated based on the results obtained using the standard method for coals technical analysis which consists in the determination of coal moisture content (U%), ash content (A%), coke (Cx %) and volatile matter content (VM%). The fixed carbon content (FC) is given by the equation (1): $\text{FC \%} = \text{Cx \%} - \text{A \%}$. The surface areas and porosities of the solids were estimated based on the iodine number which is defined as the milligrams of iodine adsorbed by one gram of material and is a widely used parameter for activated carbon testing (Mianowski et al. 2007). For this determination, the solid samples (0.045 g) were placed in Erlenmeyer flasks containing 25 mL of I_2 aqueous solution (0.01 N) and were agitated for 24h (150 rpm, room temperature). The solutions were filtered through a 0.45- μm membrane filter, and the excess of iodine was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ (0.01 N).

The amounts and the distributions of the oxygenated surface groups were determined by Boehm titration. To this aim 0.045 g of solid sample were placed in Erlenmeyer flasks containing 25 mL of 0.01 N of HCl, NaOH, NaHCO_3 , and Na_2CO_3 , respectively. Then, the mixtures were agitated for 24h (150 rpm, room temperature). The solutions were filtered through a 0.45 μm membrane filter, and the excess (base or acid) was titrated

with 0.01 N HCl or 0.01N NaOH, respectively. The amount of acidic groups on the solids was calculated under the assumption that NaOH neutralizes carboxylic, lactones, and phenol groups; Na₂CO₃ neutralizes carboxylic and lactones; NaHCO₃ neutralizes only carboxylic group. The number of surface base sites was calculated from the amount of HCl that reacted with the carbon.

All solids have been characterized by FTIR spectroscopy to identify the superficial functional groups. All the spectra were recorded on a JASCO 4700 FT-IR with DRIFTS accessory. For each spectrum 100 scans were performed at a resolution of 4 cm⁻¹ on the 4000-400 cm⁻¹ domain. Each sample was mixed with KBr in a ratio of 10/90 w/w.

Adsorption tests

Adsorption experiments were performed by the batch method, contacting a known dosage of adsorbent (0.25-0.75g/L) with 9 mL solution of known amoxicillin concentration (100mg/L) under gentle stirring (150-300rpm), at different temperatures (25-40°C) and 2 pH values (5 and 8.5 upH) until the equilibrium was reached (30-480min). At the end of each experiment, the solid was filtered off and the amount of unadsorbed amoxicillin was dosed by UV–visible spectrophotometry.

Results and Discussion

The results obtained after the characterization of the biomass derived-solids by coal technical analysis are displayed in Tables 1a,b. The aim of this analysis is to determine the fixed carbon content (FC), using eq. (1).

Table 1a. Characterization of raw and thermally activated solids

Solids	Cx %	U %	VM %	A %	FC %	IN (mg I₂/g)
PB	37.3	5.6	57.0	0.8	33.1	235
TB	28.1	5.8	66.2	4.3	27.3	255
CB	17.5	6.2	76.3	0.7	16.8	275
PC20	65.5	6.3	28.2	4.3	56.2	470
TC20	57.3	5.6	37.1	12.4	52.9	360
CC20	68.2	4.9	26.9	2.6	65.6	390
PC40	76.8	6.2	16.9	1.4	75.4	600
TC40	67.7	5.9	26.4	2.5	65.2	620
CC40	52.0	5.4	42.6	2.3	50	460

Table 1b. Characterization of chemically and thermally activated solids

Solids	Cx %	U %	VM %	A %	FC %	IN (mg I₂/g)
PC40A	77.1	6.7	16.2	48.9	28.2	200
TC40A	64.6	6.2	29.3	46.0	18.5	210
CC40A	77.6	5.5	16.9	46.7	30.4	180
PC40AS	76.2	6.6	17.2	1.2	75	740
TC40AS	60.0	7.1	32.9	9.5	50.5	875
CC40AS	56.0	7.6	36.4	10.4	45.6	410

The obtained results indicate that the thermal activation process leads to an increase of the fixed carbon content compared to the corresponding raw materials. The increase of the thermal treatment duration leads to an enhanced fixed carbon content only for the straws- and corn stalks-derived solids (e.g. PC40, TC40), whereas in the case of corncob-derived ones (CC40) a decrease of the fixed carbon content is noticed compared to CC20. For all biomass-derived solids the chemical activation leads to an important decrease of FC content, which is more significant for PC40A and TC40A

samples. After the removal of the KOH excess by washing, the values of FC for PC40AS, TC40AS, CC40AS) are almost restored to those obtained for the thermally activated samples (PC40, TC40, CC40). The FC content decreases in the order PC40 > TC40 > CC40 and the same variation trend is noticed after chemical activation followed by washing: PC40AS > TC40AS > CC40AS.

The iodine numbers (IN) for the biomass-derived adsorbents compared to the starting raw materials are also displayed in Table 1a, 1b. The results indicate that the thermal treatment (samples suffixed C20, C40) leads to the increase of IN compared to the raw materials. Moreover, the increase of the duration of the thermal activation from 20 to 40 minutes leads to a significant modification of IN for the straw- and corn stalks-derived solids whereas a modest increase is noticed for corncobs-derived materials. For the straw- and corn stalks-derived solids the chemical activation followed by washing leads to an increase by ca. 15% of the IN compared to the thermally activated samples. These increases of the IN are related to a specific surface area that is large enough and an adequate porosity to ensure an efficient adsorption.

The results obtained following the determination of surface acid sites concentration are presented in Table 2. The obtained results indicate that the thermal activation leads to the decrease of the concentration of carboxyl groups compared to the raw materials and moreover the extension of the duration of the carbonization process determines the decrease of the total concentration of acid sites. Meanwhile, the application of the chemical activation after the thermal treatment followed by the washing of the obtained solids leads to an increase of the total concentration of acid sites.

Table 2. Concentration of surface acid sites of the investigated solids

Samples	Acid sites (mequiv. NaHCO ₃ /g)	Acid sites (mequiv. Na ₂ CO ₃ /g)	Acid sites (mequiv. NaOH/g)	Total acid sites	Types of acid sites (mequiv./g)		
	C*	C*+L [#]	C*+F ^{&} +L [#]		F ^{&}	C*	L [#]
PB	2.0	3.5	5.2	5.2	1.7	2.0	1.5
PC20	2.5	4.4	6.8	6.8	2.4	2.5	1.9
PC40	0.6	1.3	4.7	4.7	3.3	0.6	0.7
PC40AS	0.8	2.2	4.8	4.8	2.6	0.8	1.4
TB	1.3	2.3	4.6	4.6	2.3	1.3	1.0
TC20	1.6	3.3	5.9	5.9	2.6	1.6	1.7
TC40	1.2	1.3	4.5	4.5	3.2	1.2	0.2
TC40AS	0.8	2.2	5.1	5.1	2.9	0.8	1.4
CB	2.7	3.2	3.9	3.9	0.7	2.7	0.5
CC20	3.0	3.7	4.7	4.7	1.0	3.0	0.7
CC40	0.1	1.1	4.2	4.2	3.1	0.1	1.0
CC40AS	0.3	1.1	4.8	4.8	3.7	0.3	0.8

***C=carboxylic; [#]L=lactonic; [&]F=phenol**

The concentration of surface base sites

The results obtained at the determination of the surface base sites are displayed in figure 1.

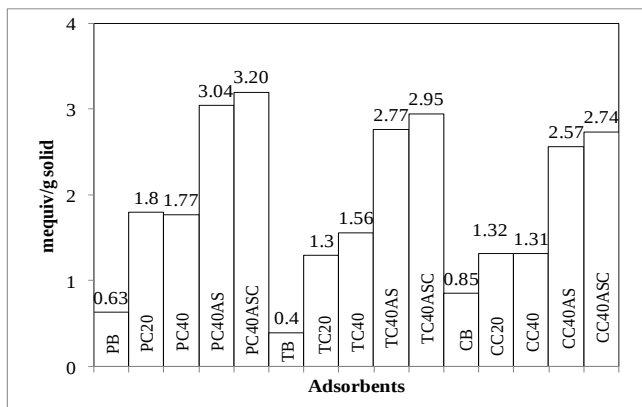


Figure 1. Concentration of surface base sites on the investigated solids

The obtained results showed that the thermal treatment leads to an increase of the base sites concentration compared to the raw materials. However, the extension of the thermal activation duration does not bring significant changes. Meanwhile, the chemical activation followed by washing leads to almost a double fold concentration of surface base sites. The amount of base sites in AS-suffixed samples varies in the following order: PC40AS > TC40AS > CC40AS

DRIFT spectra of all investigated samples are displayed in Figure 2.

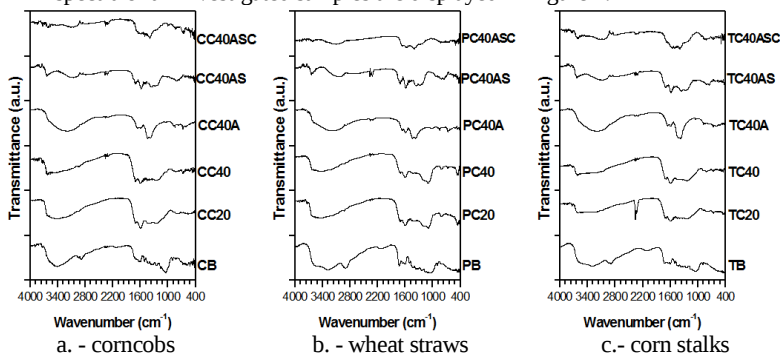


Figure 2. DRIFT spectra of the investigated solids

All the spectra of the raw materials have a broad band in the region attributed to O-H stretching at 3415 cm^{-1} (CB), 3307 cm^{-1} (TB) and 3279 cm^{-1} (PB). The intensity of this band decreases in the order $\text{TB} > \text{PB} > \text{CB}$, suggesting that CB have the lower amount of hydroxyl groups. This band is accompanied by a shoulder at $\text{ca. } 2900\text{ cm}^{-1}$ (C-H stretch) and its intensity variation follows the same trend. The intensity of these bands decreases sharply after carbonization, increases significantly after the alkali treatment (A suffixed samples), and decreases again after the washing of the solids (AS suffixed samples) and the second carbonization process (ASC suffixed samples). However, for all the washed

solids (AS suffixed samples), the occurrence of a new band at ca. 3500-3600 cm^{-1} ascribed to OH free groups was noticed and its intensity was similar irrespective to the raw material. PB and TB spectra show also a band around 2152 cm^{-1} ($\nu_{\text{C}=\text{C}}$) which is not noticed in any other spectra. Two bands corresponding to the stretching of aliphatic and aromatic $\text{C}=\text{O}$ bonds, characteristic to lignin compounds, are noticed in all spectra in the region 1730-1670 cm^{-1} . (Isahak et al. 2013)

For CB and TB samples their intensity is similar, while for PB the band at 1730 cm^{-1} is more intense suggesting the prevalence of aliphatic carbonyl compounds. After the thermal treatment the band around 1670 cm^{-1} increases its intensity revealing an enhancement of the aromatic character. (Wang et al. 2018) All spectra show also a band at 1600-1590 cm^{-1} related to the stretching vibrations of conjugated $\text{C}=\text{C}$ bond. This band has the highest intensity in the spectra of the carbonized samples (CC20, CC40, TC20, TC40) and the second intensity in the spectra of PC20, PC40, revealing a lower aromaticity of the PB-derived adsorbents. The duration of the carbonization process has not an important effect for TB and PB (the spectra of the pairs TC20-TC40, and PC20-PC40 are almost identical), whereas in the case of CB a longer duration leads to a significant alteration of the structure (the bands of the spectrum in the mid infrared region overlap).

For all raw materials, the alkaline activation has a similar effect. All the spectra of the samples activated with potassium hydroxide CC40A, PC40A, TC40A show as most intense bands the doublet characteristic for carbonate vibrations in the region 1440-1380 cm^{-1} , most probably due to the carbonation of KOH solution utilized in the treatment. The highest intensity of these bands is mostly due to the fact that they overlap the bands characteristic to δ_{CH_3} and δ_{CH_2} vibrations which appear in the same region. After the washing treatment, the intensity of these bands decreases significantly, indicating the removal of the potassium carbonate. In the spectra of CC40AS, PC40AS and TC40AS a band corresponding to $\nu_{\text{as C-O-C}}$ in esters is noticed in the region 1270-1260 cm^{-1} . The band at ca 1038 cm^{-1} corresponding to the stretching vibration of C-O bonds in secondary cyclic alcohols appears in the spectra of all raw materials (CB, PB, TB), but its intensity diminishes significantly along with the successive thermal and chemical treatments. For CB and PB this band is more intense than for TB, suggesting an enhanced concentration of cellulose in these raw materials. In all spectra, a series of bands of low intensity corresponding to out-of-plane deformation of $\text{C}=\text{C}$ bond are also noticed in the region 809-897 cm^{-1} .

In the spectra of all ASC suffixed samples, the most intense band is the one centered at ca. 1400 cm^{-1} ($\delta_{\text{C-H}}$ in $-\text{CH}_2$ groups), while the second most intense band appears in the region 1700-1650 cm^{-1} characteristic for aromatic carbonyl compounds. The absence of the band characteristic to cyclic alcohols suggests that the secondary carbonization treatment enhances even more the aromatic character of the derived adsorbent.

Adsorption tests

The results of the adsorption tests presented in Table 3 reveal that under similar operating conditions corn stalks-derived materials show better adsorption capacity than straws- or corn cob-derived materials, irrespective to the activation procedure applied. The lowest adsorption capacity is recorded for the chemically activated samples (CC40A, PC40A and TC40A), which have the lowest FC content, small specific surface area as indicated by IN (see Table1b) and enhanced basicity (12 upH).

Table 3. Results of the adsorption tests (duration 4 h, adsorbent dosage of 0.25 g/L, 200 rot/min, initial concentration of amoxicillin 100 mg/L).

Sample	Adsorption (%)		Sample	Adsorption (%)		Sample	Adsorption (%)	
	25°C	40°C		25°C	40°C		25°C	40°C
T			T			T		
CB	5.0	3.2	PB	5.2	3.5	TB	7.0	4.2
CC20	7.1	5.4	PC20	10.4	6.5	TC20	9.9	6.1
CC40	35.2	20.1	PC40	31.5	16.3	TC40	41.7	25.3
CC40A	4.2	2.2	PC40A	5.0	2.8	TC40A	7.1	4.5
CC40AS	56.3	44.5	PC40AS	62.5	50.4	TC40AS	71.6	62.3
CC40ASC	64.5	52.3	PC40ASC	72.5	64.5	TC40ASC	80.6	68.5

The highest adsorption capacity was exhibited by corn stalks-derived materials (TC40ASC) which had larger IN than the corresponding samples obtained from straws (PC40ASC). For all materials the adsorption of amoxicillin decreased as the temperature increased from 25°C to 40°C, indicating the exothermic nature of the process.

The influence of the adsorbent concentration and stirring on the adsorption capacity was investigated for the sample TC40ASC and the results are displayed in Table 4.

Table 4. Influence of adsorbent dosage, duration of the adsorption process and stirring for TC40ASC sample (initial concentration of amoxicillin 100 mg/L)

Time (h)	Adsorbent dosage (g/L)	Stirring (rpm)	Adsorption efficiency (%)
1	0.25	200	40.2
2	0.25	200	60.5
4	0.25	200	80.6
4	0.25	300	72.5
4	0.5	200	90.6
4	0.5	300	83.5
4	0.75	200	75.2
6	0.5	200	93
8	0.5	200	95

From these results it may be seen that the highest adsorption rate is recorded in the first two hours of the process when the adsorption efficiency reaches 60.5%, whereas in the next two hours the increase is only 20%. The increase of the adsorbent dosage from 0.25 g/L to 0.5 g/L leads to an increase of the adsorption efficiency with 10%. However, a further increase of the amount of adsorbent to 0.75 g/L decreases the adsorption efficiency from 90.6% to 75.2% probably due to the agglomeration of the solid particles which hinders the access to the adsorption sites. The extension of the duration of the adsorption process to 6 or 8 hours brings long an increase of only 3-5% of the adsorption efficiency. The increase of the agitation from 200 rpm to 300 rpm has also a negative effect on the adsorption efficiency since it limits the contact time between the amoxicillin and the active sites for adsorption.

Conclusions

Common vegetal wastes such as corn stalks, corncob and straws, were successfully converted into adsorbents following a sequence of thermal and chemical activation procedures. The most active adsorbent for amoxicillin was the one derived from corn stalks (TC40ASC) which allowed reaching an adsorption efficiency of 90.6% after 4 hours with an adsorbent dosage of 0.5 g/L. The variation of the adsorption efficiencies of the bio-based adsorbents under similar adsorption conditions could be well correlated to their physical-chemical properties (fixed carbon content, iodine number, aromatic character).

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References

- Ahmed, MB, Zhou, JL, Ngo, HH & Guo, W 2015, 'Adsorptive removal of antibiotics from water and wastewater: Progress and challenges', *Science of the Total Environment*, vol. 532, pp. 112–126.
- Balarak, D, Mostafapour, FK, Akbari, H & Joghtaei, A 2017, 'Adsorption of Amoxicillin Antibiotic from Pharmaceutical Wastewater by Activated Carbon Prepared from *Azolla filiculoides*', *Journal of Pharmaceutical Research International*, vol. 18, no. 3, pp. 1-13.
- Chaba, JM & Nomngongo, PN 2019, 'Effective adsorptive removal of amoxicillin from aqueous solutions and wastewater samples using zinc oxide coated carbon nanofiber composite', *Emerging Contaminants*, vol. 5, pp. 143-149.
- Isahak, WNRW, Hisham, MWM & Yarmo, MA 2013, 'Highly Porous Carbon Materials from Biomass by Chemical and Carbonization Method: A Comparison Study', *Journal of Chemistry Volume*, vol. 2013, pp. 1-6.
- Limousy, L, Ghouma, I, Ouederni, A & Jeguirim, M 2017, 'Amoxicillin removal from aqueous solution using activated carbon prepared by chemical activation of olive stone', *Environmental Science and Pollution Research*, vol. 24, no. 11, pp. 9993-10004.
- Mianowski, A, Owczarek, M & Marecka, A 2007, 'Surface Area of Activated Carbon Determined by the Iodine Adsorption Number', *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 29, no. 9, pp. 839-850.
- Tseng, RL & Tseng, SK 2005, 'Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob', *Journal of Colloid and Interface Science*, vol. 287, no. 2, pp. 428-437.
- Wang, T, Zhai, Y, Zhu, Y, Li, C & Zeng, G 2018, 'A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties', *Renewable and Sustainable Energy Reviews*, vol. 90, pp. 223–247.