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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON BASED ON ACACIA LIGNOCELLULOSIC BIOMASS

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ABSTRACT

The aim of our study is to investigate the correlation between the porous texture, chemical nature, and the sorption capacity of activated carbons based on acacia lignocellulosic biomass. Two samples with different ratios of active carbon and chemical activating agent were examined. For this purpose, a two-stage laboratory technology was used - carbonization and chemical activation with potassium hydroxide.

The data obtained from the conducted analyses show that the adsorbents based on this type of carbon material have a high surface area and good textural characteristics. They can be used in water purification, catalyst carriers, and other applications.

Keywords: activated carbon, chemical activation, water purification, wood biomass.

INTRODUCTION

Activated carbons (ACs) are one of the most used adsorbents in many liquid and gas phase applications due to their good adsorption capacity related to their high porosity and developed surface area. ACs can be obtained from a wide variety of carbon-rich raw materials, including wood, coal, fruit pits, lignocellulosic biomass [1], synthetic polymers [2], etc. The initial material to produce AC often affects the pore distribution and pore surface area. As a result, activated carbons derived from diverse starting materials have different adsorption properties and applications.

ACs are widely used in air and wastewater purification, for industrial applications - purification of liquids in the petrochemical industry, in chemical and pharmaceutical industries, for gas filtration - separation and purification of gasses, gas masks, in medicine, etc. [3].

They can be applied to treat some water pollutants organic and inorganic, directly or in combination with other processes. Their production can be done in two ways, either by physical activation or by chemical activation. Physical activation results in heat treatment and consists of two main processes: carbonization or pyrolysis and activation with carbon dioxide or steam. For chemical activation, various chemicals such as KOH, NaOH, H_3PO_4, and $ZnCl_2$ can be used as activating agents [4 - 7]. The purpose of the activation process is opening of the pores and increasing the surface area. The large pore surface in activated carbon and its adsorption properties make it a multifunctional purifying material.

Among the various natural sources to produce activated carbon, acacia lignocellulosic biomass was chosen as an abundant and low-cost precursor for AC production, with good physic-mechanical and absorption properties [8, 9].

The present study focuses on the production and comparison of the characteristics of AC obtained from acacia lignocellulosic biomass by chemical activation with KOH (ratio 1:1 and 1:2). This work aims to estimate the efficiency of acacia-based activated carbon (from local *Acacia* tree branches) with a view to domestic and industrial wastewater treatment and other applications.

EXPERIMENTAL

Acacia-based activated carbon was initially carbonized for 1 h at 500°C. The obtained carbonized sample was subjected to chemical activation with the chemical agent potassium hydroxide, in a ratio of 1:1 AC:KOH and 1:2 AC:KOH. The samples were denoted ACK1 for the first one with a ratio 1:1 and ACK2 for the sample with a ratio 1:2. Then, mixing was done in a mortar by carefully grinding the carbonized samples and potassium hydroxide until a homogeneous mass was obtained. The activation process was carried out in a tube furnace at a temperature of 500°C under a vacuum for 1 h. The resulting samples after chemical activation were neutralized with 10 % HCl, then repeatedly washed with distilled water until the absence of chlorine ions, and finally subjected to continuous drying for 12 h at 110°C.

Elemental composition analysis

A Euro EA 3000, Italy analyser was used to determine the elemental composition and the weight fraction of the C, H, and N. The oxygen content was calculated as a difference on this basis.

The data obtained from the elemental analysis (Table 1) of the acacia samples show that after the process of carbonization, the carbon content increases and hydrogen content decreases. Oxygen content significantly increases for the sample activated with a higher ratio AC:KOH. They are confirmed by the data from the IR spectra, indicating the formation of significant amounts of oxygen-containing structures on the carbon surface because of the activation process.

Acacia wood has high cellulose (45 - 50 %) and hemicellulose content (15 - 20 %) and lower lignin content (9 - 15 %). The high cellulose content favours the production of activated carbon with highly developed porous structure and high mechanical strength [10].

Table 1. Elemental composition of carbonized acacia sample and the ACs samples.

Sample	Elemental composition, %			
	Carbon	Hydrogen	Nitrogen	Oxygen
Carbonized Acacia	89.98	4.08	< 0.01	5.94
ACK1	95.29	2.41	< 0.01	2.30
ACK2	76.51	3.32	< 0.01	20.17

Fig. 1. Process of the production of AC based on acacia wood biomass.

Iodine number

The measurement of iodine adsorption was used to estimate the surface area and microporosity of the examined samples. It was done based on the standard test method of determination of iodine number [11]. This test method determines the relative activation level of carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed is given (in mg) per 1 g of active carbon.

The obtained results (Table 2) show that the sample ACK1 has iodine number 519.3 mg g^{-1} versus 761.4 mg g^{-1} for the ACK2. The higher iodine adsorption has the sample ACK2, activated with the higher content of KOH. This indicates that increasing of the activating agent leads to the formation of new meso- and micropores and to the enlargement of the surface area.

Adsorption-textural parameters determined by BET analysis

The functional application of ACs is determined to the greatest extent by its specific surface area and its textural parameters, which were recorded by low-temperature adsorption on nitrogen (N_2, 77 K). The specific surface area, S_{BET}, was determined by using N_2 adsorption in the range of relative pressures up to 1.4×10^{-1} and the linear form of BET equation [12]. The total pore volume, $V_{0.98}$, was determined as the volume of adsorbate, recorded on the desorption branch of the adsorption isotherm at a relative pressure $P_i/P_0 = 0.98$. The micropore volume (V_{micro}) was calculated by using the Dubinin-Radushkevich equation in the region of relative pressure $10^{-4} < P_i/P_0 < 0.1$ [13].

Porous characteristics of the ACs under consideration can be deduced from N_2 adsorption isotherms presented in Fig. 2 and Fig. 3, characterized by a steep rise at relative pressures up to 0.01, a broad knee at relative pressures up to 0.2, and smooth, almost parallel to the abscissa course at medium and high relative pressures. The isotherms can be classified as type I according to IUPAC indicating a predominantly microporous texture, with a narrow pore size distribution within the samples. The part of the isotherms of relatively low pressures and a sharp rise with a tendency to saturation is typical for the microporous adsorbents. The higher adsorption saturation in sample ACK2 shows a more developed microporous structure of the obtained activated carbon.

Table 3 gives the values of the specific surface area and the main textural parameters of the obtained AC samples.

It is evident from the data that ACK2 is characterized by a higher developed specific surface area (S_{BET} = 943 m^2 g^{-1}) compared to S_{BET} = 646 m^2 g^{-1} for ACK1 sample.

Table 2. The iodine number of the samples activated carbons.

Sample	Iodine number, mg g^{-1}
ACK1	519.3
ACK2	761.4

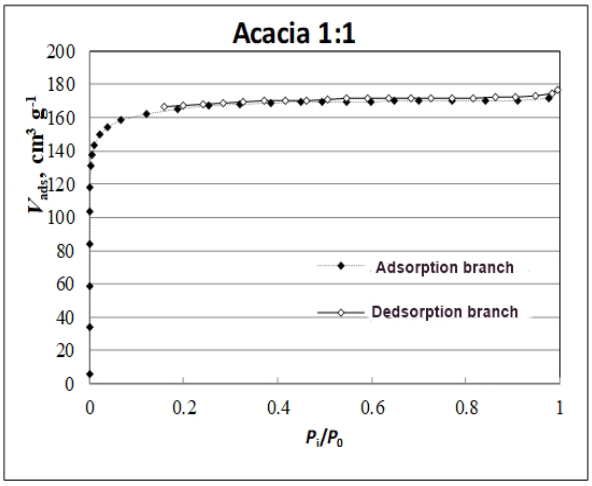

Fig. 2. Low-temperature nitrogen adsorption isotherm at 77.4 K of ACK1.

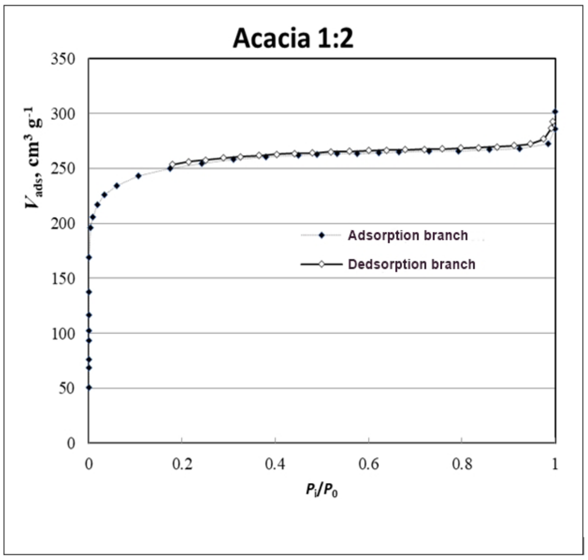

Fig. 3. Low-temperature nitrogen adsorption isotherm at 77.4 K of ACK2.

Table 3. Textural parameters and surface area of the obtained activated carbons.

Sample	S_{BET}, m^2 g^{-1}	V_{micro}, cm^3 g^{-1}	V_{meso}, cm^3 g^{-1}	V_{micro}, %	V_{meso}, %	$V_{0.98}$, cm^3 g^{-1}
ACK1	646	0.2451	0.0218	91.8	8.2	0.2669
ACK2	943	0.3622	0.0591	86.0	14.0	0.4213

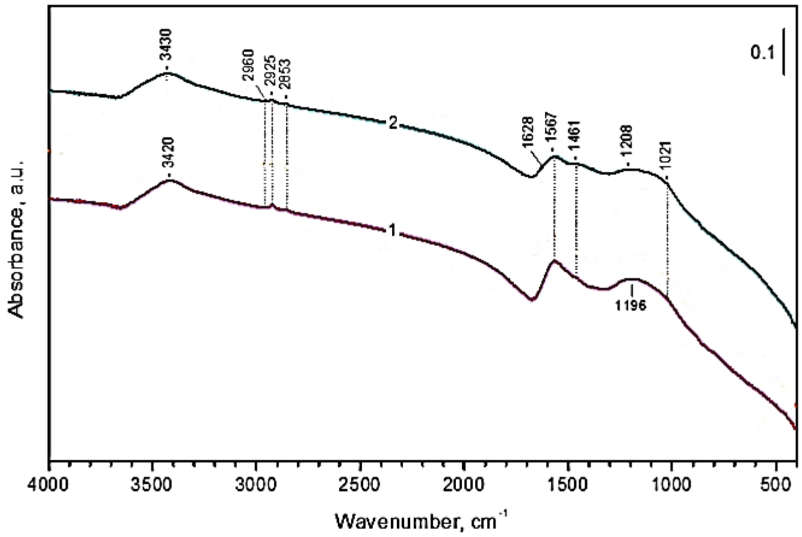

Fig. 4. FT-IR spectra of the activated samples 1 - ACK1, 2 - ACK2.

The volume of mesopores increases from 8.2 for ACK1 to 14.0 for ACK2. The total pore volume $V_{0.98}$ also increases from 0.2669 cm^3 g^{-1} to 0.4213 cm^3 g^{-1} with an increase in the amount of the activating agent.

FT-IR

The infrared spectra of the samples (Fig. 4) were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer, Germany. KBr pellets were used as a matrix. The spectra were recorded in the region 4000 - 500 cm^{-1}.

The absorption peak at 3430 cm^{-1} may be attributed to the stretching vibration 3500 - 3700 cm^{-1} of hydroxyl functional groups.

The peaks at about 1460 cm^{-1} can be associated with oxygen functional groups, such as C=O and C–O. The vibration at 1000 - 1200 is connected to the stretching of the C–O group in alcohol, ether, or ester. The peaks about 1570 and 1630 cm^{-1} can be related to the C=C stretching vibration [14]. The bands around 2950 cm^{-1} are due to aliphatic C–H structures.

Scanning electron microscopy

The surface morphology of the samples was characterized by SEM (Philips, Germany). A small amount of AC sample was placed on the conductive tape and fixed on a holder and then by JFC-1100 sputter coater thin film platinum coating was obtained. The measurement was done in mode 10 kV, 0^o and 0.1 mm scan spacing.

The micrograph images of the obtained adsorbents are presented in Fig. 5.

During the process of carbonization (KOH melting point is around 360^{o}C), melted at high-temperature potassium removes from the sites of the contact of precursor, thus the oxygen cross-linking of the carbon atoms is made. At the activation temperature, potassium hydroxide reacts mainly with peripheral and amorphous carbon, resulting in K_2CO_3, K_2O (decomposition product), and water vapor. The water vapor participates in the removal of amorphous carbon, in the form of CO, leading to the formation of pores [15]. These reactions contribute to the porous texture formation in the carbon precursors.

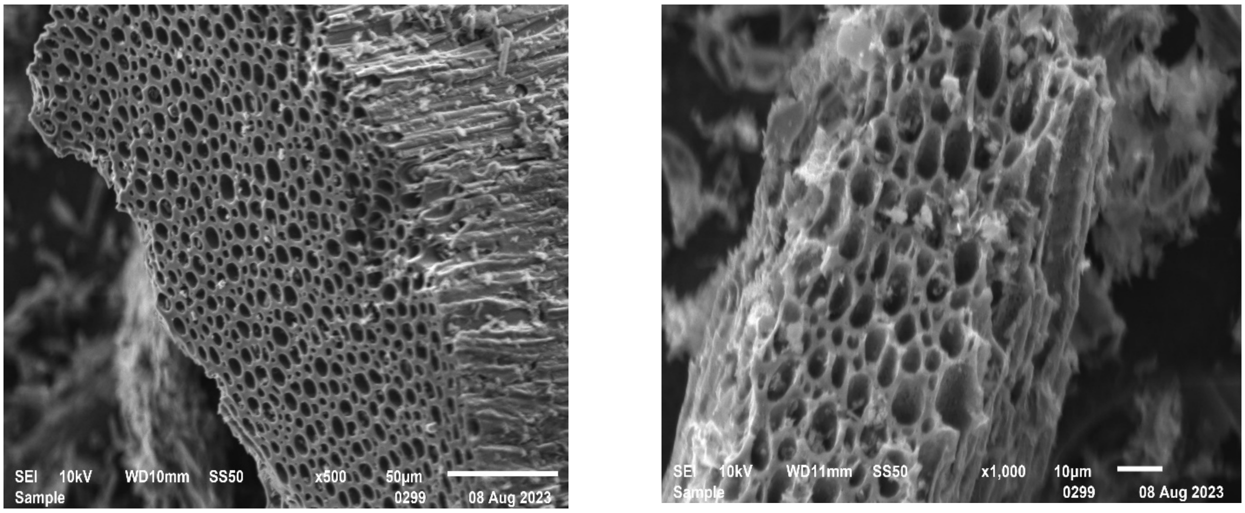

Fig. 5. SEM images of the obtained ACK2 sample.

CONCLUSIONS

Activated carbons having high surface area have been produced from abundant and cheap precursor acacia lignocellulosic biomass. They were chemically activated using KOH as an activated agent (ratio 1:1 and 1:2). It is evident from the conducted analysis that the adsorbents based on this type of carbon have high surface area and good textural parameters.

The analysis of the nitrogen adsorption data shows that the samples possess a developed porous structure and high specific surface area S_{BET} 646 $m^2 g^{-1}$ for ACK1 and 943 $m^2 g^{-1}$ for the sample ACK2. It was found that increasing the potassium hydroxide concentration leads to the increasing of the surface area for a sample activated in a ratio of 1:2 AC:KOH.

The obtained ACs with highly porous specific surface area and good textural parameters can be used as adsorbents in liquid and gas phases, in water purification and other applications.

Authors' contribution: *K.R. Investigation, Experimental work, Writing - original draft, Editing of the manuscript, Conaceptualization; L.M.: Investigation, Experimental work, Review, Editing of the mauscript, Conaceptualization; L.G.: BET analysis.*

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