

PREPARATION OF EFFICIENT CARBONACEOUS MATERIAL
(ACTIVE CARBON) FROM HYDROLYSED LIGNIN THROUGH DIRECT
ACTIVATION WITH PHOSPHORIC ACID

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The increasing interest in bioethanol production from vegetal raw materials raises the question of utilizing waste hydrolysed lignin containing some quantity of cellulose. One possibility to solve this problem is to clarify the potential of using such residues for obtaining efficient carbonaceous materials through direct activation with phosphoric acid.

It has been established that during the process of preparing active carbon, a decisive influence on the morphology of the prepared samples, as well as on the type of the obtained pores, is exerted by the preliminary wetting conditions of the samples and the chosen lignin:acid ratio. The greatest specific surface area was recorded for the sample treated with H₃PO₄ at a ratio of 1:5, while the largest volume of the micropores – for the sample treated with H₃PO₄ at a ratio of 1:1. In this investigation, active carbon samples possessing very good adsorption-textural parameters have been prepared, with specific surface area varying from 1029 up to 1824 m²/g, volume of the micropores ranging from about 0.320 up to 0.500 m³/g, and volumes of the mesopores varying within wide ranges, depending on the conditions of preparation.

Keywords: active carbon, micropores, mesopores, waste hydrolysed lignin

INTRODUCTION

The growing interest in various bioproducts prepared from lignin can be explained by the fact that there is an unprecedented demand for biofuels obtained from lignocellulosic biomass. Most contemporary biorefineries are directed towards the utilization of hydrolysed waste for the synthesis of new materials for long-lasting application. These are, for example, carbon fibres, polyurethanes, formaldehyde resins, as well as various lignin mixtures with synthetic polymers.

Active carbon is one of the most often applied adsorbents in the process of removing industrial contaminants, organic compounds, heavy metals, herbicides and dyes, as well as many other toxic compounds. These are widely applied in many branches of the industry for separation and purification of liquid and gaseous mixtures. Their flexibility in designing the distribution of pore sizes, as well as in modifying their superficial properties, enables a wide spectrum of applications, such as catalysts, means for preventing contamination and storing liquid and gaseous fuels.

Active carbons are produced in great variety from carbonaceous materials, including agricultural waste products.^{1,2} A review³ has summarized the various activation conditions of different species of wood biomass-derived activated carbons. Chemically impregnated biomass is subjected to heat treatment under an inert atmosphere to obtain activated carbons with porous structure and extended surface area.

There are two types of methods for activation during their production: physical and chemical ones.³ In the case of physical activation, the lignocellulosic raw material or carbonized in advance materials can undergo gasification with water vapor, carbon dioxide or exhaust combustion gases. Chemical activation consists in impregnating the lignocellulosic or some other carbon-containing raw material with chemical reagents, such as alkaline bases (KOH), ZnCl₂ or H₃PO₄, which are then subjected to carbonization or pyrolysis. The application of a gaseous flow stream, such as air or nitrogen, is often used in practice during pyrolysis, generating better

porosity of the material. Activated carbons are highly porous materials with large ($500\text{-}2000\text{ m}^2\text{g}^{-1}$) internal surface areas. These carbon materials have high thermal and chemical stability, and they can be effectively used in a wide range of applications, such as gas separation, catalyst supports, and filtration systems.⁵⁻⁷

Due to the high carbon content and functionalized phenolic structure of lignin, it can be considered as one of the ideal precursors for activated carbons. The properties of activated carbons largely depend on the quantity and nature of the pores present.⁴

In recent years, the use of ZnCl_2 has been decreasing due to its influence upon the environment and phosphoric acid is increasingly preferred as activating reagent.^{7,8}

The physical and the chemical properties of active carbon, prepared from Kraft lignin, commercial xylane and cellulose have been studied upon activation with H_3PO_4 . The results show greater reactivity of the precursor under acidic conditions, more developed porosity and especially, higher volume of the mesopores. This investigation also confirms the fact that the nature of the precursor, its ratio to the activating reagent, and the temperature of activation are substantial factors influencing the properties of the final products.⁹

In another similar study, it was established that in the case of activation of cotton plant stems with phosphoric acid in nitrogen medium, the temperature interval for obtaining the final product is $500\text{-}800\text{ }^\circ\text{C}$. The pyrolysis is carried out in a thermo-gravimetric analyser, and the complete degradation of the raw material was observed to occur at $740\text{ }^\circ\text{C}$. The relationship between the impregnation and the temperature of activation exerts a strong effect on the yield and on the porous structure of the prepared active carbon. The obtained material is of high quality with well-developed meso- and micro-porous texture, while its total pore volume reaches values up to $1.23\text{ cm}^3\text{ g}^{-1}$.^{8,10}

The influence of carbonization has been studied with regard to the porous structure of active carbon. It has been established that the maximal specific surface area is achieved at $600\text{ }^\circ\text{C}$ temperature of activation and upon using ZnCl_2 or H_3PO_4 as activating chemical reagent, while the surface areas are as great as those of the trademarks of active carbon.¹¹

Active carbon is considered to be an expensive material because of the high consumption of

energy during its physical and chemical treatment, as well as because of the low yield of the final product.

A purification process has been optimized for eucalyptus and sugarcane lignins in order to meet the specification requirements for obtaining high-quality carbon materials free of contaminants.¹²

The use of a suitable activating reagent is aimed at increasing the rate of activation in order to improve the quality of the material, as well as to reduce the production expenses. In our previous investigations, a carbonaceous material was obtained through the chemical activation of technical hydrolysis lignin with KOH .¹³

The aim of the present work has been to obtain an efficient carbonaceous material from hydrolysed lignin, through direct activation with phosphoric acid, with potential for various applications.

EXPERIMENTAL

Chemical activation, as a typical thermochemical process, is carried out in controlled gaseous medium. In this study, chemical activation was carried out by a modified method, under the conditions of continuous vacuum. It was assumed that by this modification the mass transfer processes would be facilitated and various products formed by the gases/vapours would be easily removed from the reaction zone.

The investigation was carried out with technical hydrolysed lignin (THL), a residual waste obtained during wood hydrolysis carried out in fodder yeast production. It is worth noting that it had been kept for more than 20 years in a depot.

The lignin underwent first a milling process and then fractionation by sieves. We used the sieve fraction of $0.6\text{-}1\text{ mm}$.

The hydrolysed lignin was characterized with respect to its chemical composition (content of lignin, cellulose and mineral substances) and elemental composition, determined by a EuroEA 3000 automated analyser.

The conditions for the pretreatment of the samples for their activation were determined by investigating the conditions of wetting with phosphoric acid. Thus, the treated lignin samples were first mixed with the activating reagent H_3PO_4 and then ground carefully in a mortar until a homogeneous mass was obtained. After homogenizing, the samples were treated for 2 hours at $180\text{ }^\circ\text{C}$. The actual activation was carried out in a tube furnace under vacuum, at $600\text{ }^\circ\text{C}$ during 1.5 hours. After cooling down, the sample was washed until a neutral reaction with distilled water was reached. The reactivation of the sample was carried out at $300\text{ }^\circ\text{C}$ under vacuum.

The lignin samples were denoted in the following way:

- sample of activated lignin L1, prepared by mixing THL and H₃PO₄ in a ratio of 1:0.5;
- sample of activated lignin L2, prepared by mixing THL and H₃PO₄ in a ratio of 1:1;
- sample of activated lignin L3, prepared by mixing THL and H₃PO₄ in a ratio of 1:3;
- sample of activated lignin L4, prepared by mixing THL and H₃PO₄ in a ratio of 1:5;
- initial THL is denoted as L0.

The characterization of the specific surface area and the parameters of the porous texture of the prepared samples was carried out using a sorption apparatus – High-Speed Surface & Pore Size Analyzer System, model NOVA 1200, manufactured by QUANTACHROME Instruments (USA) applying low temperature adsorption of nitrogen (77 K).

The following textural parameters of the active carbons were calculated:

- specific surface areas (S_{BET}), based on the equation of Brunauer-Emmett-Teller, for the interval $p/p_0 = 0.05 \div 0.35$;
- volume of the micropores (V_{MI}), determined by means of the simplified equation;¹³
- total pore volume (V_t), in accordance with the rule of Gurvich, at $p/p_0 = 0.95$;
- volume of the mesopores (V_{MES}) as the difference between the total pore volume and the volume of micropores (V_{MI}) of the respective samples;
- size distribution of the mesopores, on the basis of the adsorption branch of the nitrogen isotherm,

assuming a cylindrical shape of the mesopores, by the method of Piers, within the interval $3 \leq D_{AV}, \text{ nm} \leq 10$;

- average pore diameter (D_{AV}), as the ratio between V_t (multiplied by four) and S_{BET} ;
- size distribution of the micropores by means of the simplified equation, assuming flat parallel micropores;
- specific surface area of the micropores, $S_{MI} \text{ m}^2/\text{g}$.

Microscopic photographs (micrographs) were made using a JEOL JSM 6390 scanning electron microscope from Oxford Instruments, at 20 kV.

RESULTS AND DISCUSSION

It can be seen from the data in Table 1 that THL contains an amount of hardly hydrolysable polysaccharides, determined as cellulose, within the admissible limits. The content of mineral substances is high, probably due to contamination of the lignin during storage.

Table 2 presents the data from the elemental analyses of the activated samples. The data listed for the initial THL and the THL after activation with H₃PO₄ indicate that, after activation (600 °C) and reactivation after washing at 300 °C in vacuum, the samples are richer in carbon, which comes as a result of the additional hydrolysis and removal of the residuals of hardly hydrolysable polysaccharides, resins and other admixtures, including the removal of oxygen-containing surface functional groups.

Table 1
Chemical composition of initial hydrolyzed lignin

| Initial hydrolyzed lignin | | |
|---------------------------|-----------------------|------|
| Chemical composition | Mineral substances, % | 9.1 |
| | Cellulose, % | 12.8 |
| | Lignin, % | 78.0 |

Table 2
Elemental analysis of initial THL and H₃PO₄ activated THL, in various ratios, using a EuroEA 3000 automated analyser

| Sample | Ratio | Element, % | | | |
|--------|-------------|------------|------|-----|-------|
| | | N | C | H | S |
| L0 | Initial THL | - | 50.2 | 5.0 | 0.60 |
| L1 | 1:0.5 | 0.4 | 58.9 | 2.2 | <0.01 |
| L2 | 1:1 | 0.5 | 58.6 | 2.4 | <0.01 |
| L3 | 1:3 | 0.5 | 65.5 | 2.1 | <0.01 |
| L4 | 1:5 | 0.5 | 62.5 | 2.4 | <0.01 |

Table 3 lists data on the specific surface areas and the main parameters of the porous texture of the initial THL material and the samples obtained from it. It may be noted from the data in the table

that the samples are characterized by considerable specific surface area, which is growing proportionally with the increase in the quantity of the activating reagent – H₃PO₄. It should be noted

that even in the case of the ratio $\text{THL}:\text{H}_3\text{PO}_4 = 1:0.5$, the specific surface area exceeds $1000 \text{ m}^2/\text{g}$ probably as a result of the fact that the conditions of the treatment with acid led to hydrolysis of the residual hardly hydrolysable polysaccharides.

Taking into account the fact that, usually, the active carbons that find practical application possess a specific surface area of about $1200 \text{ m}^2/\text{g}$, it can be suggested that the method of activation with H_3PO_4 , besides enabling the possibility to control the values of the specific surface area, also ensures the basis for applying the synthesized active carbons in sensor technologies, electrochemical, medical, biocatalytic technologies and for other specific needs.

Similarly to the increase in the specific surface areas upon increasing the quantity of the activating reagent (H_3PO_4), the values of the total pore volume also rose, while in the case of L3 ($\text{THL}:\text{H}_3\text{PO}_4 = 1:3$), the value of V_t was about 40 times higher than that of initial THL, reaching $0.79 \text{ cm}^3/\text{g}$.

The relation between the volumes of the micropores of the samples and the quantity of the activating reagent (H_3PO_4) remained unclear. With the exception of sample L2 ($\text{THL}:\text{H}_3\text{PO}_4 = 1:1$), which had a micropore volume considerably greater than those of samples L1, L3 and L4, it could be noted that the micropore volumes were comparatively similar in value, which is probably related to the anatomical structure of the initial THL.

The mesopore volumes of the samples also showed proportional dependence on the quantity of the activating reagent (with some deviation from the tendency in the case of sample L4). Most typically, the role of the activating reagent is visible in the case of sample L1 ($\text{THL}:\text{H}_3\text{PO}_4 = 1:0.5$), for which V_{MES} is only 2.6 times higher than that of initial THL, but at the same time it is 3.5 times smaller, upon doubling the quantity of the activating reagent in the case of sample L2 (Figs. 1-3).

The higher mesopore volume of sample L3, by some 13%, compared to sample L4, is compensated by its lower volume of the micropores (by approximately 36% compared to sample L2, for example).

Judging from the size distribution curves of the micropores (Figs. 2b, 3b, 4b, 5b), one can conclude that for the four samples (L1, L2, L3 and L4), the characteristic dimensions of the micropores are close in value. The size

distribution curves of the mesopores show that the mesoporous texture of the samples is characterized by polydispersion, which rises with the increase in the volume of the mesopores, thus, in the case of sample L3 and especially, sample L4, there is a considerably enhanced quantity of mesopores with average diameters larger than 4.0 nm.

Figures 1a, 2a, 3a, 4a and 5a illustrate the adsorption-desorption isotherms of initial THL (L0) and the other samples prepared on its basis: L1, L2, L3 and L4. One can observe from the isotherms of samples L1, L2, L3 and L4 that, by the activation using H_3PO_4 , the texture observed for THL (sample L0) changed, *i.e.* type II isotherm, according to the classification put forward by Brunauer, Deming, Deming, Teller,¹⁴ which is characteristic for non-porous and macroporous materials.

Figures 1b, 2c, 3c, 4c and 5c represent the distribution curves of mesopores in the activated lignin samples, while Figures 2b, 3b, 4b and 5b illustrate the distribution of micropores in the activated lignin samples.

The increase in the $\text{THL}:\text{H}_3\text{PO}_4$ ratio, respectively, in the quantity of the activating reagent (H_3PO_4) from 0.5 up to 5 with respect to the mass of THL, leads to changes in the type of the porous texture, and respectively, the type of the isotherm, starting from type I (samples L1 and L2), characteristic of microporous textures, and reaching type IV isotherms (samples L3 and L4), *i.e.* upon increasing the ratio $\text{THL}:\text{H}_3\text{PO}_4 = 1:3$ ($\text{THL}:\text{H}_3\text{PO}_4 = 1:5$), the predominant microporous texture was transformed into a micro-mesoporous type of texture.

The comparatively narrow hysteresis loops of type H4 (in the case of samples L1 and L2) gives evidence for the availability of micropores, characterized by the narrow distribution of the characteristic size (half-width, considering the flat-parallel type of the pore model).¹⁴

The hysteresis loops in the case of samples L3 and L4 have been attributed to type H3, in accordance with the classification put forward by IUPAC,¹⁵ where the wider hysteresis loops are associated with more strongly developed mesoporosity, also including the external surface area (Table 3).

In our previous studies,⁸ the adsorption parameters of a carbonaceous material obtained from TLH after activation with KOH have been investigated.

Table 3
Basic adsorption-textural parameters of initial THL and activated carbon samples

| Sample | $S_{\text{BET}}, \text{m}^2/\text{g}$ | $V_t, \text{cm}^3/\text{g}$ | $V_{\text{MI}}, \text{cm}^3/\text{g}$ | $V_{\text{MES}}, \text{cm}^3/\text{g}$ | D_{AV}, nm | $S_{\text{MI}}, \text{m}^2/\text{g}$ | $S_{\text{EXT}}, \text{m}^2/\text{g}$ |
|--------|---------------------------------------|-----------------------------|---------------------------------------|--|----------------------------|--------------------------------------|---------------------------------------|
| L0 | 4 | 0.020 | - | 0.020 | 20 | - | - |
| L1 | 1029 | 0.430 | 0.38 | 0.053 | 1.7 | 923 | 106 |
| L2 | 1318 | 0.680 | 0.50 | 0.185 | 2.1 | 1174 | 144 |
| L3 | 1497 | 0.790 | 0.32 | 0.471 | 2.1 | 741 | 756 |
| L4 | 1824 | 0.750 | 0.34 | 0.411 | 1.6 | 810 | 1014 |

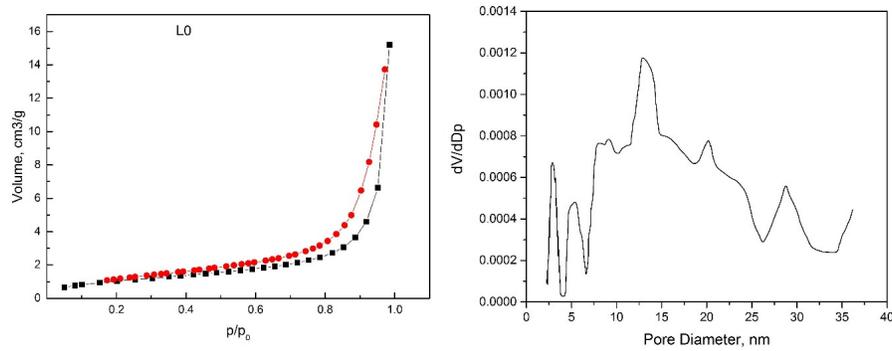


Figure 1: Sample L0 – initial THL; a) Adsorption-desorption isotherm of nitrogen (at 77.4 K); b) Distribution of mesopores by size, calculated from the adsorption-desorption isotherm

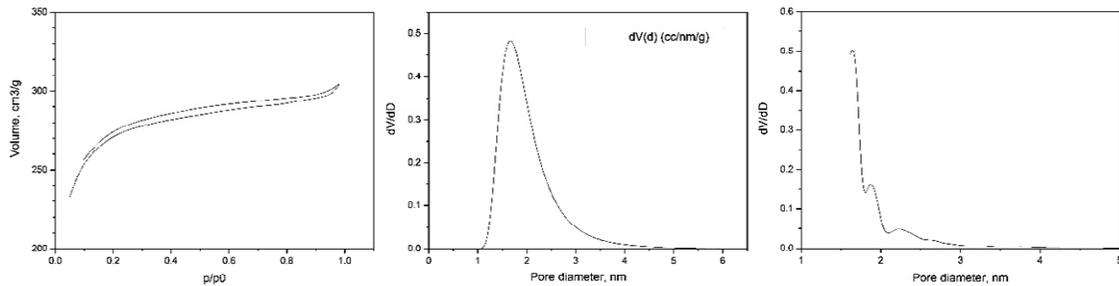


Figure 2: Sample L1 (THL:H₃PO₄ = 1:0.5); a) Adsorption-desorption isotherm of nitrogen (at 77.4 K); b) Distribution of micropores by size; c) Distribution of mesopores by size, calculated from the adsorption-desorption isotherm

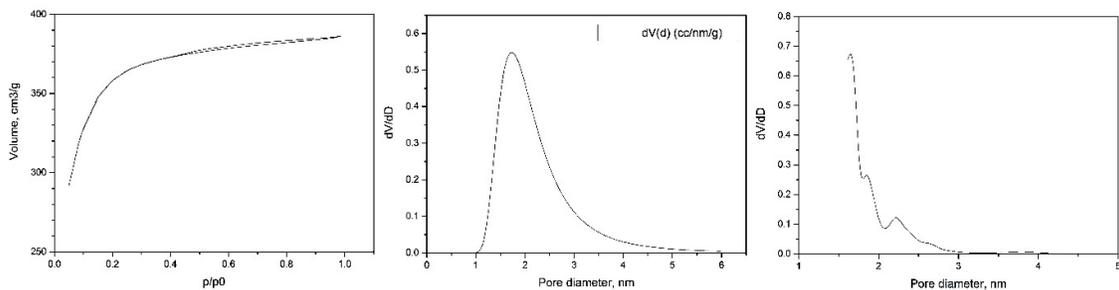


Figure 3: Sample L2 (THL:H₃PO₄ = 1:1); a) Adsorption-desorption isotherm of nitrogen (at 77.4 K); b) Distribution of micropores by size; c) Distribution of mesopores by size, calculated from the adsorption-desorption isotherm

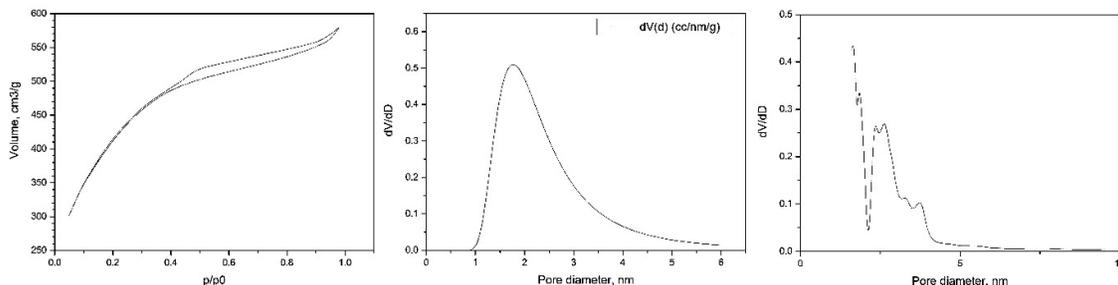


Figure 4: Sample L3 (THL:H₃PO₄ = 1:3); a) Adsorption-desorption isotherm of nitrogen (at 77.4 K); b) Distribution of micropores by size; c) Distribution of mesopores by size, calculated from the adsorption-desorption isotherm

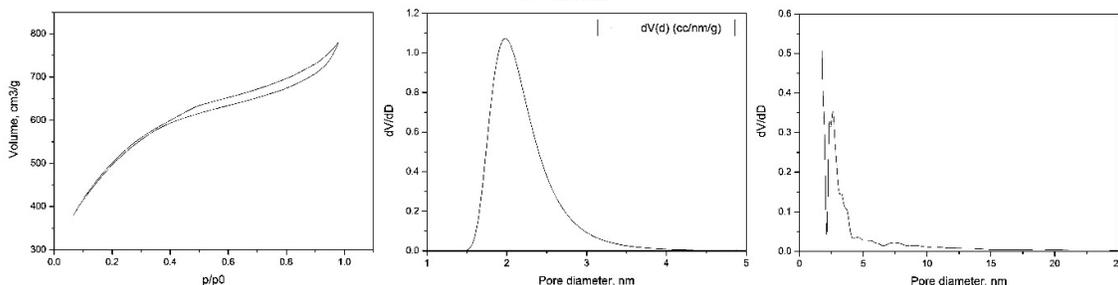


Figure 5: Sample L4 (THL:H₃PO₄ = 1:5); a) Adsorption-desorption isotherm of nitrogen (at 77.4 K); b) Distribution of micropores by size; c) Distribution of mesopores by size, calculated from the adsorption-desorption isotherm

The results achieved showed that the activation with H₃PO₄ produces activated carbon with better texture parameters.

Figures 6-9 illustrate SEM micrographs of the investigated samples. These micrographs demonstrate that the hydrolyzed lignin preserves the anatomic structure of the plant raw material

after undergoing the treatment, which is the object of the present investigation.

The SEM micrographs reveal a typical modified lignin multilayer tubular structure corresponding to the structure of plant cells. Also, well-defined cell wall pores are clearly observed.

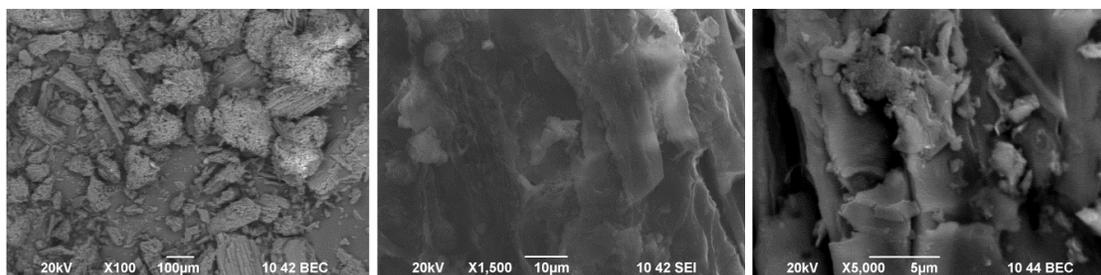


Figure 6: SEM micrographs of sample L0 (initial THL)

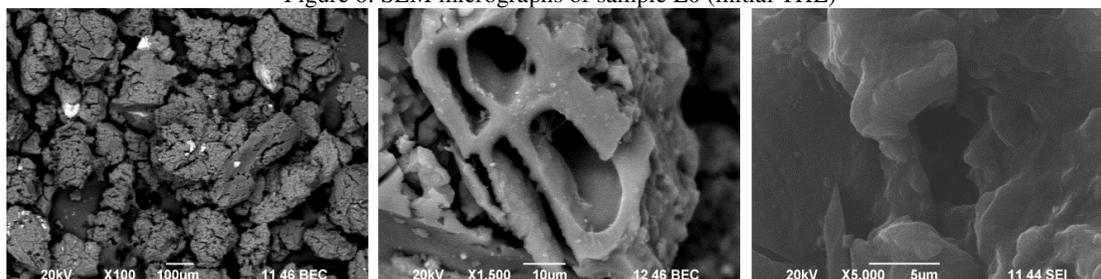


Figure 7: SEM micrographs of sample L2 (THL:H₃PO₄ = 1:1)

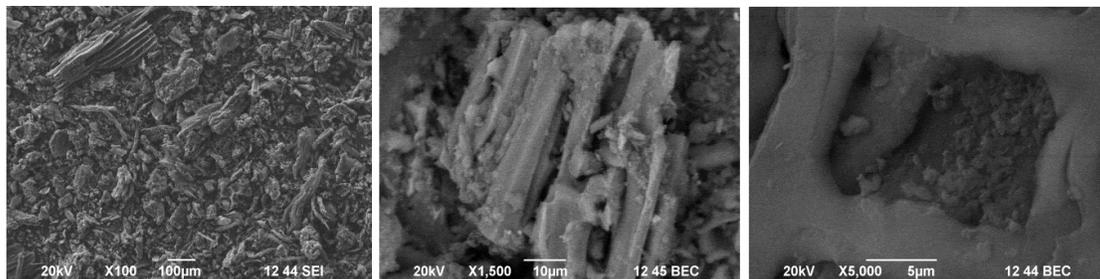


Figure 8: SEM micrographs of sample L3 (THL:H₃PO₄ = 1:3)

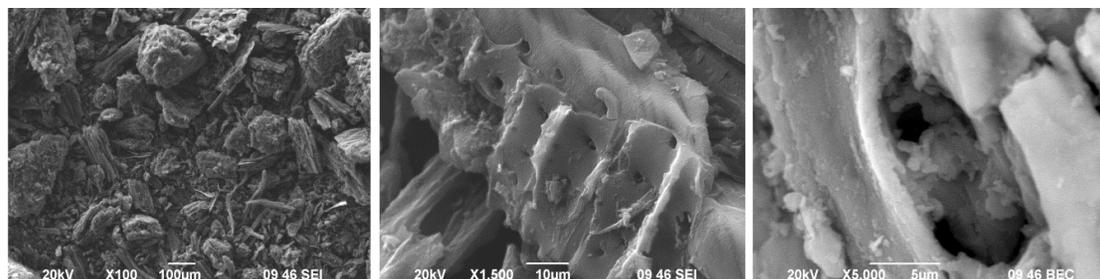


Figure 9: SEM micrographs of sample L4 (THL:H₃PO₄ = 1:5)

After the treatment using H₃PO₄ and heating to the temperature of 600 °C, there occurs the hydrolysis of the residual polysaccharide fraction in the hydrolyzed lignin, which leads to revealing some additional pores within the structure of the lignin and increases its internal surface area. Upon increasing the quantity of H₃PO₄ for the treatment, the internal surface area of the lignin is also enhanced.

CONCLUSION

The possibility to prepare an efficient carbonaceous material (active carbon), starting from waste biomass – technical hydrolyzed lignin, by means of chemical activation using H₃PO₄, has been investigated. Some micro-mesoporous active carbon samples have been prepared possessing very good adsorption-textural parameters: specific surface area varying from 1029 up to 1824 m²/g, volume of the micropores varying from about 0.320 up to 0.500 m³/g, as well as volume of the mesopores varying within wide ranges, depending on the conditions of preparation.

It has been established that, during the process of preparation of the active carbon samples, a decisive influence on the morphology of the prepared samples and on the type of the obtained pores is exerted by the conditions of the preliminary wetting of the samples and the chosen ratio of lignin to acid. The greatest specific

surface area is displayed by the sample treated with H₃PO₄ at a ratio of 1:5. The largest volume of the micropores is manifested by the sample treated with H₃PO₄ at the ratio of 1:1.

REFERENCES

- ¹ N. Supanchaiyamat, K. Jetsrisuparb, J. T. N. Knijnenburg, D. C. W. Tsang and A. J. Hunt, *Bioresour. Technol.*, **272**, 570 (2019), <https://doi.org/10.1016/j.biortech.2018.09.139>
- ² T. Vernersson, P. R. Bonelli, E. G. Cerrella and A. L. Cukierman, *Bioresour. Technol.*, **83**, 95 (2002), [https://doi.org/10.1016/S0960-8524\(01\)00205-X](https://doi.org/10.1016/S0960-8524(01)00205-X)
- ³ M. Danish and T. Ahmad, *Renew. Sust. Energ. Rev.*, **87**, 1 (2018), <https://doi.org/10.1016/j.rser.2018.02.003>
- ⁴ S. Chatterjee and T. Saito, *ChemSusChem*, **8**, 3941 (2015), <https://doi.org/10.1002/cssc.201500692>
- ⁵ P. Suhas, J. M. Carrott and M. M. L. Ribeiro Carrott, *Bioresour. Technol.*, **98**, 2301 (2007), <https://doi.org/10.1016/j.biortech.2006.08.008>
- ⁶ S. Chatterjee, T. Saito, O. Rios and A. Johs, “Lignin Based Carbon Materials for Energy Storage Applications, Green Technologies for the Environment”, ACS Symposium Series, Vol. 1186, 2014, Chapter 11, pp. 203-218, <https://doi.org/10.1021/bk-2014-1186.ch011>
- ⁷ J. I. Hayashi, K. Muroyama, V. G. Gomes and A. P. Watkinson, *Carbon*, **40**, 630 (2002), [https://doi.org/10.1016/S0008-6223\(02\)00017-9](https://doi.org/10.1016/S0008-6223(02)00017-9)

⁸ H. Teng, T. S. Yeh and L. Y. Hsu, *Carbon*, **36**, 1387 (1998), [https://doi.org/10.1016/S0008-6223\(98\)00127-4](https://doi.org/10.1016/S0008-6223(98)00127-4)

⁹ Y. Diao, W. P. Walawender and L. P. Fan, *Bioresour. Technol.*, **81**, 45 (2002), [https://doi.org/10.1016/S0960-8524\(01\)00100-6](https://doi.org/10.1016/S0960-8524(01)00100-6)

¹⁰ S. Sircar, T. C. Golden and M. B. Rao, *Carbon*, **34**, 1 (1996), [https://doi.org/10.1016/0008-6223\(95\)00128-X](https://doi.org/10.1016/0008-6223(95)00128-X)

¹¹ E. Gonzalez-Serrano, T. Cordero, J. Rodriguez-Mirasol, L. Cotoruelo and J. J. Rodriguez, *Water Res.*, **38**, 3043 (2004), <http://www.biblioteca.uma.es/bbl/doc/articulos/16494611.pdf>

¹² K. Santos Damacena Nunes and L. C. Pardini, *Cellulose Chem. Technol.*, **53**, 227 (2019), [http://www.cellulosechemtechnol.ro/pdf/CCT3-4\(2019\)/p.227-242.pdf](http://www.cellulosechemtechnol.ro/pdf/CCT3-4(2019)/p.227-242.pdf)

¹³ L. Raicheva, G. Radeva, S. Nenkova and R. Nikolov, *Bulg. Chem. Commun.*, **49**, 139 (2017), http://www.bcc.bas.bg/BCC_Volumes/Volume_49_Number_1_2017/49-1-2017-4083-Radeva-139-144.pdf

¹⁴ S. J. Gregg and K. S. W. Sing, "Adsorption, Surface Area and Porosity", second edition, Academic Press, London, 1982, <https://www.scribd.com/doc/48553301/Adsorption-surface-area-and-porosity>

¹⁵ IUPAC Recommendations, *Pure Appl. Chem.*, **57**, 603 (1985), <http://publications.iupac.org/pac/pdf/1985/pdf/5704x0603.pdf>