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Adsorption characteristics of activated carbon obtained from residual hydrolyzed lignin

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Large amounts of technical hydrolyzed lignin are a residual waste of the hydrolysis industry. Hence, there is an interest to investigate its thermal decomposition. The latter applied in this study consists in a preliminary selective thermal treatment with a subsequent activation aiming to increase the specific area and develop the porous structure. The adsorption-structural method is applied to study the behavior of the activated carbon adsorbents obtained. The main parameters of the porous structure are determined on the ground of the experimentally derived isotherms of Brunnauer, Emmett and Teller. The surface thermodynamic characteristics obtained provide a comparative analysis of the samples of the initial hydrolyzed lignin and the activated carbon obtained through pyrolysis as well as through initial hydrolysis and subsequent pyrolysis of the residual hydrolyzed lignin.

Keywords: activated carbon; technical hydrolyzed lignin, BET isotherm

INTRODUCTION

Technical hydrolyzed lignin (THL) is residual waste of the hydrolysis industry. It presents a complex mixture of wood's hydrolytic decomposition including lignin, incomplete hydrolyzable polysaccharides, reducing substances, resins, mineral compounds and monosaccharides. The interest towards studying its thermal decomposition is determined by the large amounts left in the course of production [1]. THL is characterized by its capillary-porous structure determined by its initial wood capillary structure and the lignin production conditions. The porous structure developed determines the sorption properties of THL with respect to organic and inorganic products [2]. It is suitable for production of activated carbon [3] which is predominantly a microporous material with an additionally developed inner surface. Its pore distribution with respect to their dimensions depends on the type of the initial raw material, the process of activation and the conditions of its application [4]. The basic principle of activated carbon production on the ground of a carbonaceous material consists in a preliminary selective thermal treatment and subsequent activation under specific conditions. Thus, the specific surface area of the material is increased and its porous structure is additionally developed. Chemical activators can be used. KOH is one of them. It is experimentally verified that it can split graphite microcrystals thus assuring micro-pore formation. Its application in case of activated carbon production on the ground of carbonaceous materials is also reported [5]. The basic parameters required to properly choose an activated carbon refer to its texture and mechanical parameters as well as the chemical nature of its surface. Different methods are used to study the adsorbents to be used. One finds that the adsorption-structure has the widest application in case of activated carbon adsorbents. It provides the determination of the main parameters of the porous structure only on the ground of experimentally derived adsorption isotherms [5], which is in fact its basic advantage.

The adsorption isotherm of Brunnauer, Emmett and Teller (BET) is often found valid in the case of physical adsorption on highly energetic powder-like materials. The adsorption model of BET has the following characteristics: A) The adsorbent surface behaves as an energetically homogeneous one with adsorption centers of an identical capacity to adsorb; B) The adsorption layers are subsequently deposited, while each new one is identical to that previously formed; C) There are no intermolecular forces of interaction in the adsorbate itself [6, 7]. The classic form of the BET equation connects the amount of the adsorbed substance (Γ) on the surface of a solid adsorbent with the pressure of the adsorbate vapors (p). It refers to polymolecular adsorption in a pressure range from p = 0 to the pressure of the adsorbate saturated vapors p^0:

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$$\Gamma = \frac{\Gamma_m \theta_0 C\left(\frac{p}{p^0}\right)}{\left(1-\left(\frac{p}{p^0}\right)\right)^2} \qquad (1)$$

where Γ_m is the maximum surface concentration of the adsorbate, C is a constant (known as the BET constant C_{BET}) which depends on the temperature, while θ_0 is the accessible surface of the adsorbent. θ_0 is expressed through the following relation:

$$\theta_0 = \frac{1-\left(\frac{p}{p^0}\right)}{1+(C-1)\left(\frac{p}{p^0}\right)} \qquad (2)$$

The substitution of the latter into Eq. (1) leads to the following expression:

$$\Gamma = \frac{\Gamma_m C\left(\frac{p}{p^0}\right)}{\left(1+(C-1)\left(\frac{p}{p^0}\right)\right)\left(1-\left(\frac{p}{p^0}\right)\right)} \qquad (3)$$

Eq. (3) can be simplified through a rearrangement. This leads to:

$$\frac{1}{\Gamma\left(\left(\frac{p}{p^0}\right)-1\right)} = \frac{1}{\Gamma_m} + \frac{C-1}{\Gamma_m C}\left(\frac{p}{p^0}\right) \qquad (4)$$

One of the forms of the BET equation is obtained through the substitution of Γ with the volume of the adsorbed gas V corresponding to a specific value of $\left(\frac{p}{p^0}\right)$ and that of Γ_m with the maximum volume of the adsorbed gas V_m , i.e.

$$\frac{x}{V(1-x)} = \frac{1}{CV_m} + \frac{C-1}{V_m C}x \qquad (5)$$

where $x = \frac{p}{p^0}$. Eq. (5) is an adequate form of the BET isotherm because the dependence of $\frac{x}{V(1-x)}$ on x is linear and provides the determination of V_m and the constant C_{BET}. The value of V_m can be used to estimate the specific surface of the adsorbent S_{BET}:

$$S_{BET} = \frac{V_m N_A A^o}{V_0} \qquad (6)$$

where N_A is the Avogadro's number, A^o is the van der Waals area of the molecule, while V_0 is the volume of a mole of a gas under normal conditions. The total area of the adsorbent's surface S_{EXT} can be calculated on the ground of:

$$S_{EXT} = S_{BET}.m \qquad (7)$$

where m is the sample's mass. The value of S_{BET} and S_{EXT} are used to estimate the micro-pores area S_{MI}:

$$S_{MI} = S_{BET} - S_{EXT} \qquad (8)$$

The other important characteristic term, the BET constant C_{BET}, is related to the adsorption heat ΔH_1 referring to the first adsorption layer:

$$C_{BET} \approx \exp\left(\frac{\Delta H_1 - \Delta H_{cond}}{RT}\right) \qquad (9)$$

ΔH_{cond} is the heat of condensation of the adsorption layers deposited on the initial one [8, 9].

The aim of the present work is to carry out a comparative thermodynamic analysis of the adsorption characteristics of highly effective carbonaceous materials (activated carbons) obtained from residual hydrolyzed lignin.

EXPERIMENTAL

The investigation was carried out with technical hydrolyzed lignin which is a residual waste obtained in the course of wood hydrolysis carried out in the course of forage yeast production. It is worth noting that it has been kept for more than 20 years on a sole.

HPLS (UltiMate 3000) was used to determine the content of residual polysaccharides with respect to that of glucose, lignin and mineral compounds. The humidity of the hydrolyzed lignin sample was determined using the Kern and Sohn apparatus at 105°C. The pH was read using a pH-meter. The characteristics of the initial material are summarized in Table 1.

Table 1. Characteristics of the initial THL.

Parameters	Values
Content of THL polysaccharides (%)	18.84
Content of mineral compounds (%)	5.18
Content of lignin (%)	65.98
pH of the aqueous suspension	3.30
Easily reduced saccharides (%)	2.00

The pyrolysis was carried out in an aluminum Fischer retort following the standard procedure. It produced semi-coke (at a final temperature of 520°C) used for the subsequent preparation of activated carbon. The liquid product obtained after THL pyrolysis was used to determine the moisture content. This was done at a pH of 5.5 using the Dean-Stark apparatus. The material balance of the pyrolyzed THL and of that subjected to hydrolysis and subsequent pyrolysis is presented in Table 2.

Table 2. Material balance of L1 and L2 samples.

Product	Yield, (%)	
	Pyrolyzed THL	Pyrolyzed THL after preliminary hydrolysis
Solid carbonaceous product	49.4	48.7
Total liquid product	29.8	31.1
- water*	67.7	70.9
- tar*	32.3	29.1
Gas and losses**	20.8	20.2

* in % on the ground of the liquid product; ** as a balance difference to 100%

The chemical activation of the samples was carried out with KOH. The samples used consisted of pyrolyzed THL (L1**)** and pyrolyzed THL, but were initially subjected to hydrolysis (L2**)**. A sample of the initial THL (L0) was used as well.

A mixture of a precursor and KOH in the ratio of 1:1.2 was added to the samples described above. Then they were ground to obtain a homogeneous mass. The activation was carried out for 1 hour in a tube oven at 600 °C under vacuum. Then they were washed thoroughly to reach a neutral pH value. The subsequent process of reactivation was carried out for 2 hours in a reactor under vacuum at 300°C.

The determination of the specific surface area and the parameters of the porous structure of the treated samples were carried out using a High-Speed Surface & Pore size Analyzer System, type NOVA 1200 *e* of QUANTACHROME instruments (USA) through low temperature adsorption of nitrogen at 77.4 K.

The morphology of the initial and fabricated lignin samples was investigated by scanning electron microscopy at 20 kV using JEOL JSM 6390 with a INCA x-sight chemical analysis detector from OXFORD INSTRUMENTS.

RESULTS AND DISCUSSION

The adsorption-desorption isotherms of L0, L1 and L2 were determined through adsorption of nitrogen. They are presented in Figs.1, 2 and 3, with the corresponding SEM images.

Fig. 1 shows that the isotherm of the untreated initial THL (L0) refers to type II adsorption isotherms characteristic for nonporous solid substances or for macroporous adsorbents according to the IUPAC classification. The image presented shows that the surface of the initial lignin has a layered structure of a wavy and chaotic character which is in fact typical for most of the natural polymers.

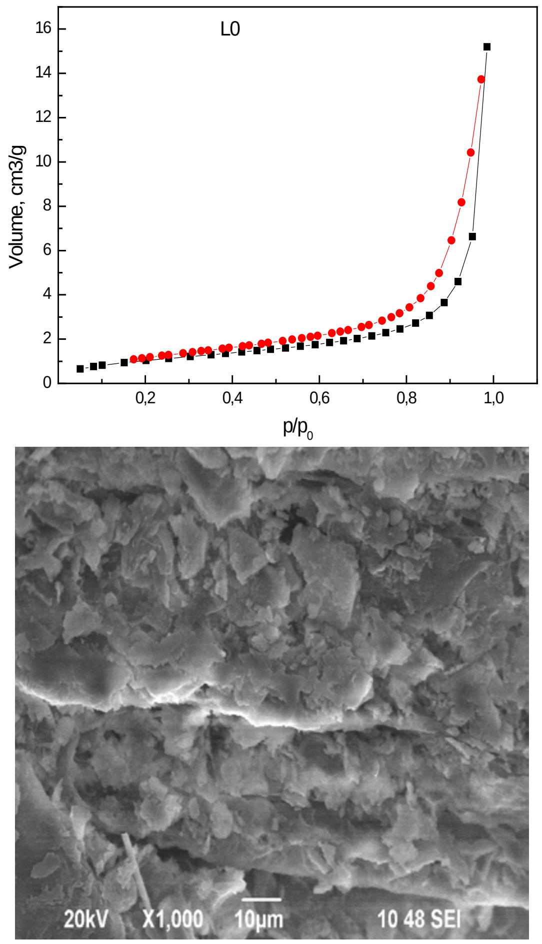

Fig.1. An adsorption-desorption isotherm of the L0 sample and the corresponding SEM image.

Fig. 2 shows that the isotherm of L1 obtained from the initial THL subjected to pyrolysis refers to a type I isotherm relevant to microporous adsorbents. There the width of the pores does not exceed the value of several adsorbate molecule diameters. The force field of the neighboring walls is overlapped by the energy of the adsorbent-adsorbate interaction. The interactions of this type are strong enough to provide complete coverage of the pores at relatively low pressures.

The pyrolysis of the initial THL does not affect the wavy character of the surface but brings about a multilayered tubular structure (Fig.2). The latter corresponds to the structure of plant cells with easily discerned pores.

Fig. 3 shows that the isotherm of L2 obtained from initial THL subjected to hydrolysis and subsequent pyrolysis refers to the mixed type (I and IV) isotherm observed in case of microporous adsorbents with a presence of mesopores. The deviation from type I behavior is observed only in the high pressure range.

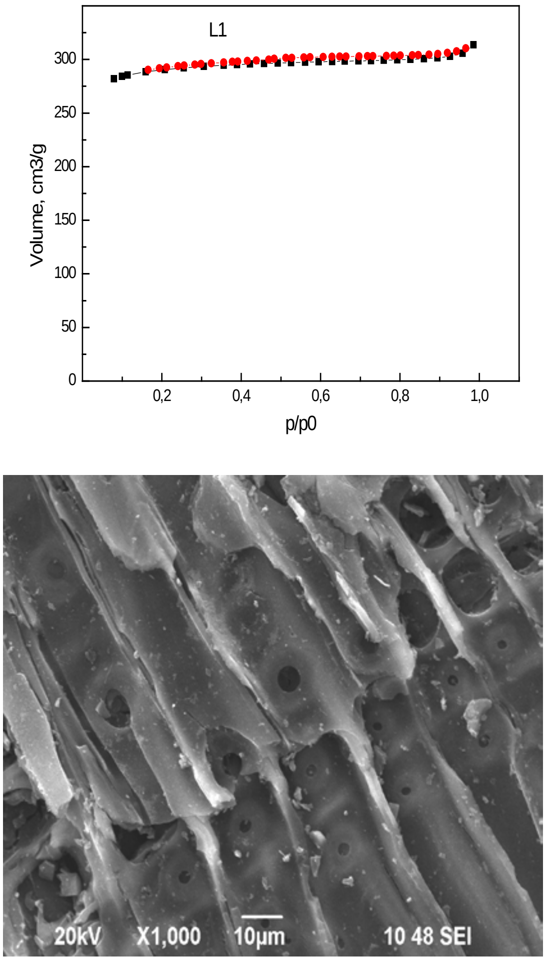

Fig.2. An adsorption-desorption isotherm of the L1 sample and the corresponding SEM image.

The surface of the L2 sample as seen in Fig. 3 is wavy with well expressed micro-pore formation. Its juxtaposition to the structure presented shows that the multilayered tubular structure is in fact preserved but the corresponding tube-like elements are sharply outlined. That is most probably due to the preliminary removal of the residual hardly hydrolysable polysaccharides.

The BET isotherm is applied to the adsorption equilibrium attained in the first monolayer. Eq. (5) is applied in the range from $0.05\left(\frac{p}{p^0}\right)$ to $0.35\left(\frac{p}{p^0}\right)$. The linear dependences obtained in $\frac{x}{V(1-x)}$ vs. x have a slope of ($B=\frac{C-1}{V_mC}$) and an intercept of ($A=\frac{1}{CV_m}$), i.e. they provide for the determination of C_{BET} and the maximum volume of the adsorbed gas V_m of the samples. The values obtained are summarized in Table 3. The latter shows also the values of the specific area of the adsorbent S_{BET}, the total area of the surface S_{EXT} and the specific area of the micropores, S_{MI}, calculated with the application of Eqns. (6), (7) and (8).

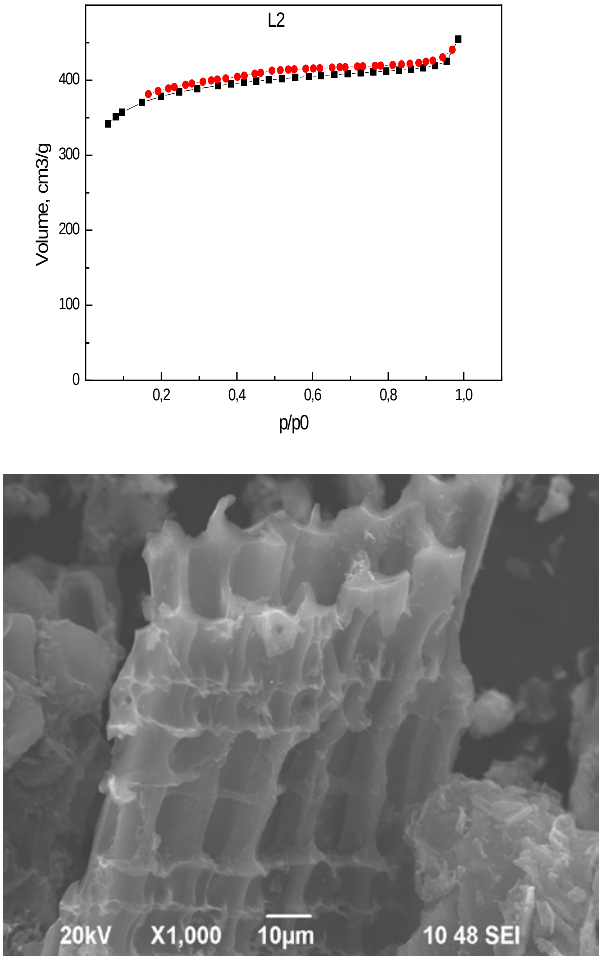

Fig.3. An adsorption-desorption isotherm of the L2 sample and the corresponding SEM image.

Table 3. Basic adsorption parameters of the initial THL and the activated carbon samples.

Sample	S_{BET}, (m^2/g)	S_{MI}, (m^2/g)	S_{EXT}, (m^2/g)	C_{BET}	V_{m}, (cm^3/g)	ΔH_1, (J/mol)
L0	4	-	-	54.4	0.919	- 5361.6
L1	1300	781	519	290	302.6	- 6438.5
L2	1428	1259	169	527	328.3	- 6822.9

As seen from Table 3 the activated carbons obtained (L1 and L2) are characterized by a large specific area S_{BET} and high values of the maximum volumes which refer to the carbonaceous materials suitable for gas adsorption. The preliminary hydrolysis and the subsequent pyrolysis and chemical activation in the case of L2 provide a dominant development of the microporous structure illustrated by the S_{MI} values obtained.

The constant C_{BET} can be used, in accordance with Eq. (9), to determine the adsorption heat (

$-\Delta H_1$) characteristic for the specific interaction of the adsorbate and the adsorbent molecules within the first adsorption layer. The Reference data shows that:

$$-\Delta H_{condN_2} = 2.79(kJ/mol).$$

The process is exothermic, while the relatively low value of the enthalpy change is an indication of the proceeding physical adsorption. But it is worth noting that the energy of the adsorbate-adsorbent interaction is greater than that of the adsorbate-adsorbate, which in turn provides polymolecular adsorption.

The values of the entropy and Gibbs function change for the first adsorption layer, ΔS and ΔG, can be evaluated with the application of Eqns. (10) and (11):

$$\Delta G = RT \ln\left(\frac{p}{p^0}\right) \tag{10}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{11}$$

Table 4 presents the values obtained for the L2 sample.

Table 4. Values of the entropy and Gibbs function change at $\left(\frac{p}{p^0}\right) = const$.

$\left(\frac{p}{p^0}\right)$	ΔG, (J/mol)	L1		L2	
		V, (cm^3/g)	ΔS, (J/K.mol)	V, (cm^3/g)	ΔS, (J/K.mol)
0,1	-1480.5	284.6	-102.3	361.0	-107.3
0,15	-1220.8	287.0	-98.9	371.3	-103.9
0,20	-1035.6	291.8	-96.5	385.0	-101.5
0,25	-892.1	292.0	-94.7	389.5	-99.7
0,30	-774.7	293.3	-93.2	394.1	-98.2
0,35	-675.5	294.4	-91.9	394.2	-96.9

As expected on the ground of the exothermic character of the process the values of ΔG and ΔS are negative. Furthermore they decrease with the increase of the gas adsorbed because the number of the degrees of freedom of the adsorbed species decreases with the simultaneous decrease of the forces of interaction determining the proceeding adsorption. It is worth adding that the tendency observed in the case of L2 is also followed in L1 although the corresponding values cannot be directly juxtaposed at $V = const$.

CONCLUSION

The surface thermodynamic characteristics of the activated carbon obtained from the technical hydrolyzed lignin and of that produced from the same residual waste but through pyrolysis as well as by initial hydrolysis and subsequent pyrolysis are derived on the ground of the corresponding BET adsorption isotherms. The comparative analysis carried out shows that the additionally treated samples have a large specific area and a microporous texture. The preliminary removal of the residual non-hydrolyzable polysaccharides is a prerequisite for obtaining well outlined multilayered structures. The adsorbents' surface is energetically homogeneous and favors polymolecular adsorption. The process is a spontaneous one.

REFERENCES

1. R. J. A. Gosselink, E. de Jong, B. Guran and A. Abächerli, *Ind. Crop. Prod.*, **20**, 121 (2004).
2. C. Vasile, R. J. A. Gosselink, P. Quintus, E. G.Koukios, D.P. Koullas, E. Avgerinos, D. A. Abacherli, *Cellulose Chem. Technol.*, **40**, 421 (2006).
3. C. Hörnell, Thermochemical and Catalytic Upgrading in a Fuel Context: Peat, Biomass and Alkenes, Dissertation, Royal Institute of Technology, Department of Chemical Engineering and Technology, Stockholm, 2001.
4. G. Krüger, ,*Chemie in unserer Zeit*, 10, 21, (1976).
5. M. Smisek, S. Cerny, Active carbon, Elsevier Publ. Co., New York, 1970.
6. J.S. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, (second ed.), Academic Press, London, (1982).
7. F. Rouquerol, J. Rouquerol, K.S.W. Sing, Adsoprtion by Powders and Porous Solids: Priciples, Methodology and Applications, Academic Press, London, (1999).
8. A. K. Ladavos, A. P. Katsoulidis, A. Iosifidis, K. S. Triantafylidis, T. J. Pinnavaia, P. J. Pomonis, *Micropor. Mesopor. Mater.*, **151**, 126, (2012).
9. K. Nakai, Y. Nakada, M. Hakuman, M. Yoshida, Y. Senda, Y. Tateishi, J. Sonda, H. Naono, *J. Coll. Int. Sci.*, **367** (1), 383, (2012).

АДСОРБЦИОННИ ХАРАКТЕРИСТИКИ НА АКТИВЕН ВЪГЛЕН ПОЛУЧЕН ОТ ОТПАДЪЧЕН ТЕХНИЧЕСКИ ХИДРОЛИЗИРАН ЛИГНИН

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(Резюме)

Големите количества отпадъчен хидролизен лигнин предизвикват силен интерес към проучванията за неговото термично разлагане. Основният принцип за получаване на активен въглен от въглеродсъдържащ материал се състои в предварителна селективна термична обработка, с последваща активация с цел увеличаване на специфичната повърхност и на порестата структура. Изследването на получените въглеродни адсорбенти е направено чрез адсорбционно-структурния метод. Главните параметри на порестата текстура са определени въз основа на опитно построените изотерми на Брунауер, Емет и Телер. На базата на получените термодинамични характеристики на повърхността е направен сравнителен термодинамичен анализ на проби от изходен хидролизен лигнин и активен въглен от пиролизиран и предварително хидролизиран и пиролизиран технически хидролизен лигнин.