

Application of waste-derived activated carbon as a sorbent for Re ions recovery from acidic aqueous solution

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Activated carbons were prepared based on hydrolyzed lignocellulosic biomass, and were chemically activated with potassium hydroxide and phosphoric acid. The texture parameters of the adsorbents obtained were determined by low-temperature nitrogen adsorption; their thermal stability was studied by DTA/ TG and the surface functional groups - by FTIR spectroscopy. The adsorption properties of the obtained activated carbons toward perrhenate ions from an aqueous solution were investigated at three different pH values. The adsorbent obtained after activation of hydrolyzed lignin with KOH was found to have significantly better adsorption capacity than that obtained after activation with H₃PO₄. The maximum adsorption value of the perrhenate anion – 95.7% was obtained at a concentration of rhenium in the solution 5 mg l⁻¹ and pH 2. Results from this study indicated that waste-derived activated carbon can act as an effective adsorbent for perrhenate ions from acidic wastewater.

Keywords: hydrolyzed lignocellulosic material; activated carbon; chemical activation; adsorption; rhenium

INTRODUCTION

Activated carbons are produced in great variety from carbonaceous materials including agricultural waste products [1, 2]. Various activation methods of the different species of wood biomass-derived carbonized materials have been described in the literature [3]. Two types of methods exist for activation in the production of activated carbons: physical and chemical. The properties of activated carbons largely depend on the quantity and nature of the pores at hand [4]. 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.

In case of physical activation, the lignocellulosic raw material or pre-carbonized materials can undergo gasification with water vapor, carbon dioxide or exhaust combustion gases. The chemical activation consists of impregnation of the lignocellulosic or other carbon-containing raw materials with chemical reagents such as alkali bases (KOH), ZnCl₂ or H₃PO₄, which are later subjected to carbonization or pyrolysis. The application of gaseous flow streams such as air or nitrogen is often met in the practice during the pyrolysis, which generates better development of the porosity of the material. Activated carbons are highly porous materials with large (500-2000 m²g⁻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 energy storage, gas separation, catalyst supports and others [5].

The use of ZnCl₂ has been decreasing in recent years due to its influence upon the environment and the phosphoric acid has been increasingly preferred as an activating reagent [6]. The physical and the chemical properties of activated carbon prepared from Kraft lignin, commercial xylan and cellulose, have been studied upon activation with H₃PO₄. Diao *et al.* [7] reported that the results show higher reactivity of the precursor under acidic conditions, more developed porosity and particularly larger volume of the mesopores. This investigation also confirms the fact that the nature of the precursor, the ratio with respect to activating reagent, as well as the temperature of activation are substantial factors influencing the properties of the final products.

With regard to the porous structure of the activated carbon, Gonzalez-Serrano *et al.* [8] studied the influence of carbonization. It has been established that the maximal specific surface area is achieved at 600°C temperature of activation and upon using ZnCl₂ or H₃PO₄ as activating chemical reagents and the surface areas are as large as those of the trademarks of activated carbon. 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, carbonaceous material was obtained through the chemical activation of technical lignin hydrolyzed with H₃PO₄ [9] and KOH [10].

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The use of activated carbons is well known for cleaning dyes and many other organic and inorganic contaminants - ions and other compounds from aqueous or gaseous media. An important problem is the extraction of metal ions such as rhenium, molybdenum, gold, and more, from the environment.

Rhenium is one of the rarest elements, but it is widely used in high technology as an important component in super alloys for blades in turbine engines. It is a perfect metal for operation at very high temperatures, which makes it suitable for rocket engines. Rhenium is produced as by-product at pyro- and hydrometallurgical processing of molybdenum and copper concentrates. During the treatment processes, it passes into wash acidic solutions as perrhenic acid (HReO_4) in ppm concentrations [11]. Different methods are used for the selective separation and preconcentration of perrhenate ions (ReO_4^-): ion exchange, solvent extraction, adsorption, electrolysis, etc. [12, 13]. Each of them has its advantages and drawbacks [14].

In this aspect, the aim of the present work is to investigate the adsorption capacity towards rhenium ions of activated carbons obtained from technical hydrolyzed lignin after chemical activation with KOH and H_3PO_4 .

EXPERIMENTAL

Materials and methods

The experiments were carried out with technical hydrolyzed lignocellulosic biomass (THLB). Residual waste has been obtained in the course of wood hydrolysis from the forage yeast production. It is worth noting that it has been kept for more than 20 years in a depot.

The lignin first underwent a milling process and then sieve fractioning. Sieve fractions of 0.6-1 mm were used.

The initial material (THLB) was characterized with respect to its chemical composition (content of lignin, cellulose and mineral substances) and elemental composition, determined by automated analyzer EuroEA 3000. DTA analysis was also performed to determine its thermal stability.

The chemical activation was carried out with KOH and H_3PO_4 . The appropriate conditions for activation of THL have been investigated in our previous studies [9].

The method of chemical activation as a typical thermochemical process was conducted in a controlled gaseous medium, by a modified version, under the conditions of continuous vacuum. It is considered that, by this modification, the mass transfer processes will be intensified as the gaseous

products will be easily removed from the reaction zone during the activation process.

Chemical activation of hydrolyzed lignin

Activation with the activating reagent KOH. Technical hydrolyzed lignin contains residual polysaccharides in an amount of 15-35%. For the present study, the starting technical hydrolyzed lignin was further treated with 80% H_2SO_4 at room temperature in order to remove residual polysaccharides [14].

The preliminary pyrolysis of the hydrolyzed lignin was carried out in a standard retort. At 170 °C water was released, which could mean that the product contained a lot of O_2 . At 414 °C, gaseous products were released. The final product obtained at a temperature of 520 °C, was the starting material for the production of activated carbon. The carbonized material thus obtained was mixed with KOH at a ratio of 1: 1.2 (precursor: KOH). The activation was carried out in a tube furnace at 600 °C under vacuum for 1 hour after which the product thus obtained was washed with deionized water until neutral reaction.

Activation with the activating reagent H_3PO_4 . The starting sample (THLB) was activated with phosphoric acid at a ratio of 1:3 (precursor: H_3PO_4). After homogenizing, the samples were treated for 2 hours at 180°C. The actual activation was carried out in the tube furnace under vacuum, at 600°C for 1.5 hours. After cooling, the sample was washed with deionized water until neutral reaction. The reactivation of the sample was carried out at 300°C under vacuum according to Vladov *et al.* [9].

The carbonized samples obtained were labeled as follows:

- sample of activated lignin $\text{L}_{\text{H}_3\text{PO}_4}$, prepared by mixing of THL: H_3PO_4 at a ratio of 1:3;
- sample of activated lignin L_{KOH} , waste hydrolyzed lignin sample, further hydrolyzed to remove polysaccharides prior to pyrolysis in standard retort;
- initial THL denoted as L_0 .

Characterization of activated carbons

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

The following textural parameters of the activated carbons were calculated: specific surface

areas (S_{BET}). based on the equation of Brunauer-Emmet-Teller (BET), for the interval $p/p_0 = 0.05 \div 0.35$; volumes of the micropores (V_{MI}), determined by means of the simplified equation; total pore volume (V_t) according to the rule of Gurvich at $p/p_0 = 0.95$; volumes of the mesopores (V_{MES}) as the difference between the total pore volume and the volumes 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 cylindrical model 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 a ratio between V_t (multiplied by four) and S_{BET} ; size distribution of the micropores by means of the simplified equation, assuming flat-parallel model of the micropores; specific surface area of the micropores $S_{MI} \text{ m}^2/\text{g}$.

FTIR spectra of the activated carbons were obtained on a Nicolet Avatar 360 FTIR Thermo Scientific spectrometer.

The thermal stability of the composites obtained was examined by differential thermal analysis (DTA/TG) with a Setaram Labsys Evo 1600 instrument in the temperature range 25-800 °C at a heating rate of 10 °C /min in air atmosphere.

The adsorption properties of the obtained activated carbons - $L_{H_3PO_4}$ and L_{KOH} toward perrhenate ions (ReO_4^-) from an aqueous medium were investigated. The experiments were carried out in the batch mode in plugged polypropylene test tubes containing 10 ml of Re (VII) aqueous solution and 50 mg of sorbent at $20 \pm 1^\circ \text{C}$. The effect of the following parameters on the adsorption was studied: i) pH of the solution (2-7), ii) initial rhenium concentration (5-100 mg l^{-1}), iii) contact time between solution and sorbent (5-180 min). Working solutions with different Re concentrations were obtained by diluting the stock solution of KReO_4 with $C_{\text{Re}} = 1000 \text{ mg l}^{-1}$ with distilled water. The pH of the starting solutions was adjusted by dropwise adding 0.1 N HNO_3 and 0.1 N NaOH . The samples were shaken on a rotary shaker at 150 rpm until

equilibrium was reached, then filtered through a blue-ribbon filter. The content of Re in the filtrate was determined spectrophotometrically (UV-vis Thermo Evolution 160) by the highly selective catalytic method with N, N-dimethyldithioamide [15]. The adsorption was calculated as follows:

$$A (\%) = \frac{(C_0 - C_e)100}{C_0},$$

where C_0 and C_e are the initial and equilibrium concentration of rhenium (mg l^{-1}) in the solution.

RESULTS AND DISCUSSION

Physicochemical characteristics

The initial THLB (L_0) contains 78 % lignin, 12.8 % cellulose and 9.1 % mineral substances. Actually, THL contains a quantity 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 when stored in the open air space. Table 1 presents the data from the elemental analysis of the activated samples.

Table 1. Elemental analysis of the initial THL and the THL activated with H_3PO_4 and KOH using the automated analyzer EuroEA 3000

Sample	Element, %			
	N	C	H	S
L_0	-	50.21	5.00	0.60
L_{KOH}	0.40	78.90	4.78	<0.01
$L_{H_3PO_4}$	0.33	58.50	4.60	<0.01

The above data show that the activated carbon obtained after activation of hydrolyzed lignin with KOH has a higher carbon content - 78.90% compared to that treated with H_3PO_4 - 58.50%, which shows that the treatment process hydrolyzed most of the residual polysaccharides.

Table 2 shows 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 [9, 10].

Table 2. Basic adsorption-textural parameters of the initial THL and the samples of activated carbons

Sample	$S_{BET}, \text{ m}^2/\text{g}$	$V_t, \text{ cm}^3/\text{g}$	$V_{MI}, \text{ cm}^3/\text{g}$	$V_{MES}, \text{ cm}^3/\text{g}$	$D_{AV}, \text{ nm}$	$S_{MI}, \text{ m}^2/\text{g}$	$S_{EXT}, \text{ m}^2/\text{g}$
L_0	4	0.020	-	0.020	20.0	-	-
L_{KOH}	1428	0.700	0.515	0.185	2.0	1259	169
$L_{H_3PO_4}$	1497	0.790	0.320	0.471	2.1	741	756

The activated carbons obtained by both methods have almost the same surface area, S_{BET} - 1428 - 1497 m^2g^{-1} , but the activated carbon obtained after activation of hydrolyzed lignin with KOH, has a larger surface area and micropore volume - 1259 m^2g^{-1} and 0.515 m^3g^{-1} , respectively, compared to that treated with H_3PO_4 - 741 m^2g^{-1} and 0.32 m^3g^{-1} , indicating that the activated carbon obtained by activation with KOH is characterized by a much more developed microporous texture (more than 1.6 times in terms of micropore volume and almost twice in terms of specific micropore surface) compared to activated carbon obtained by phosphoric acid activation.

FTIR analysis

To identify the functional groups present on the surface of the initial sample, L_{KOH} and $L_{H_3PO_4}$, FTIR spectra were recorded, shown in Figs. 1 and 2.

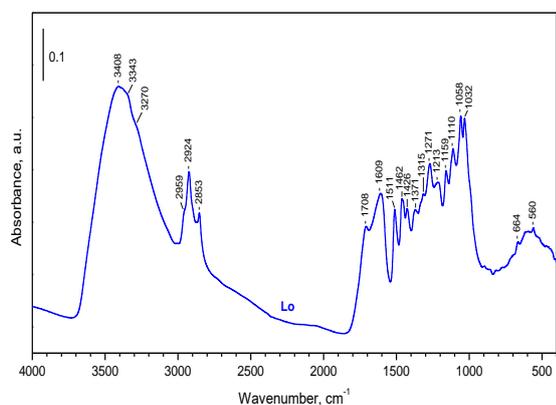


Fig.1. FTIR spectra of initial THL

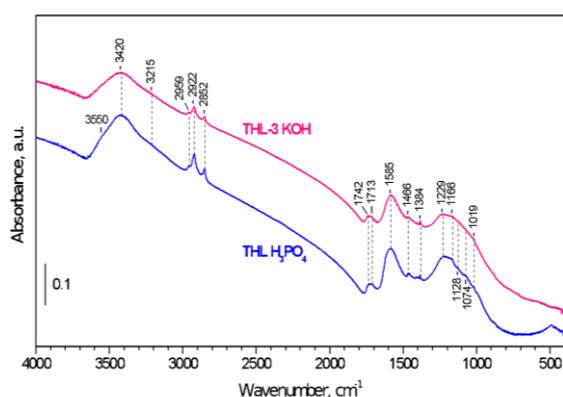


Fig. 2. FTIR spectra of activated carbons L_{KOH} and $L_{H_3PO_4}$

An intense broad band in the 3300-3500 cm^{-1} region is observed in the feedstock spectrum (Fig. 1) due to the valence vibrations of the alcohol and phenolic hydroxyl groups in lignin [16]. In the spectra of activated carbons, the bands in this region

exist but are with lower intensity. The peak of activated carbon obtained by activation with phosphoric acid is more intense than that of $L_{H_3PO_4}$ due to the greater amount of hardly hydrolysable polysaccharides (which have not been previously separated by THP).

The signals at 2924 and 2852 cm^{-1} are ascribed to the aliphatic $-CH_3$ and $-CH_2$ stretching vibrations. The bands in the range 1700 - 1600 cm^{-1} indicate the $C=O$ group from the carboxyl groups. The signals at 1585 cm^{-1} (Fig. 2) are attributed to the $C=C$ vibration in aromatic rings and the bands at 1229 cm^{-1} are due to the $C-O$ stretching vibration of the phenol group. After activation, in the FTIR spectra (Fig. 2) of activated carbons, some of the peaks have disappeared or weakened [17].

Phenolic and carboxylic functional groups could transform into $-COOH^{2+}$, $-OH^{2+}$ or $=C=OH^+$ by reaction with H^+ in the solution. The more of these cations existed on the sorbent surface, the better was the recovery of perrhenate anion *via* adsorption from aqueous solution. In accordance with the conclusions of Hu *et al.* [18], the phenolic and carboxylic groups contributed to the Re (VII) adsorption on the examined sample.

Thermal analysis

The thermal characteristics of THL and activated carbon samples were determined using DTA/TG, and the thermogravimetric curves are shown in Figures 3-6.

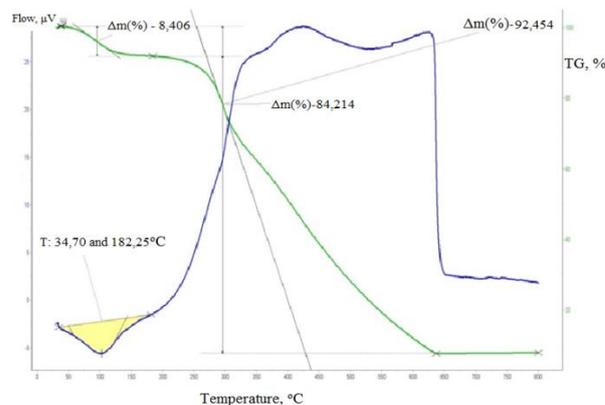


Fig. 3. DTA/TG curves of THL

As can be seen from Fig. 3, between 50 and 140°C, endothermic reactions occur that result from the separation of the adsorbed water on the surface of the lignin and the water bound in its structure. The wide exothermic effect in the 230-650 °C range may be due to the destruction of both weak and stable bonds in the lignin molecules, resulting in the destruction of lignin [19, 20]. Weight loss was about

84%. Total weight loss was 92.5% at the end of the process.

Fig. 4 shows the thermal stability of activated carbon from THL obtained after activation of lignin with KOH. In the range 25-210 °C, 8.38% of the carbon weight is lost, which may be due to the separation of water and low-molecular weight fractions of residual polysaccharides in the lignin composition. In the interval from 411°C to the end of the process at 810 °C, the total weight loss was 49.35%.

Fig. 5 shows the thermal stability of activated carbon obtained after activation of lignin with phosphoric acid.

In the temperature range 50 – 244 °C, 14.3% of water was released and some of the lower-molecular weight residual polysaccharide components in lignin were destroyed. Mass weight loss from the sample was observed in the temperature range 500-740 °C, 51.2%, respectively. The ultimate weight loss was 84.7%. Compared to DTA/TG, the analysis of Fig. 3 of the initial THL shows that after treatment with H₃PO₄, it becomes more resistant to thermal treatment.

Investigation of ReO₄⁻ adsorption

A quite important single parameter affecting the adsorption process, is pH of the solution [14]. The adsorption properties of the samples L_{H₃PO₄} and L_{KOH} were tested at four different pH values: 2, 3, 5 and 7 at an initial Re concentration C_{Re}= 5 mg l⁻¹.

Experiments were performed at a contact time of 3 hours. The results are shown in Fig. 6.

It can be seen that, at all tested pH values, the adsorption capacity of the carbon activated with KOH is significantly better than that of the H₃PO₄-activated sorbent. Data show that ReO₄⁻ adsorption on the two obtained activated carbons is affected by the acidity of the initial solution. In both sorbents, the adsorption efficiency for rhenium is higher at lower pH values of the solution. The optimum pH value was found to be at pH 2.

The effect of initial Re concentration on the adsorption of ReO₄⁻ by the two sorbents was tested at pH 2. Fig. 7 shows that the maximum adsorption of 95.7% is achieved at C_{Re}=5 mg l⁻¹ using KOH-activated carbon. The adsorption capacity of the H₃PO₄- activated sorbent under the same conditions is about two times lower. This tendency is also observed at higher concentrations of rhenium in the solution.

In order to optimize the contact time for the ReO₄⁻ adsorption, kinetic experiments were performed in the interval of 5 min - 3 hours. Solutions with initial Re concentrations of 50 mg l⁻¹ were used for this aim.

As can be seen from Fig. 8, maximum adsorption of rhenium on both activated carbons was achieved within the first 15 min of contact between the solution and the sorbent. The rapid adsorption process indicates a good interaction between the adsorbent and the perrhenate ions.

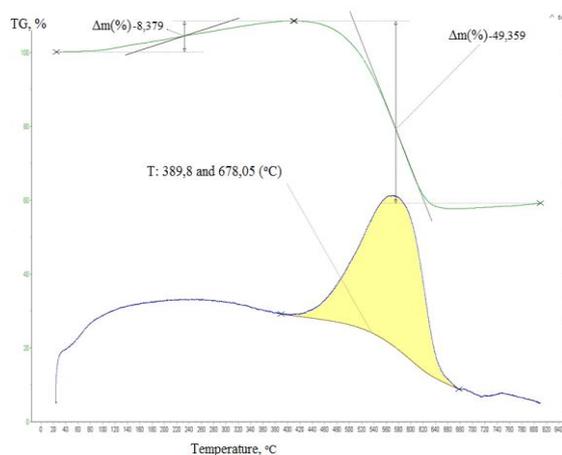


Fig. 4. DTA/TG curves of L_{KOH}

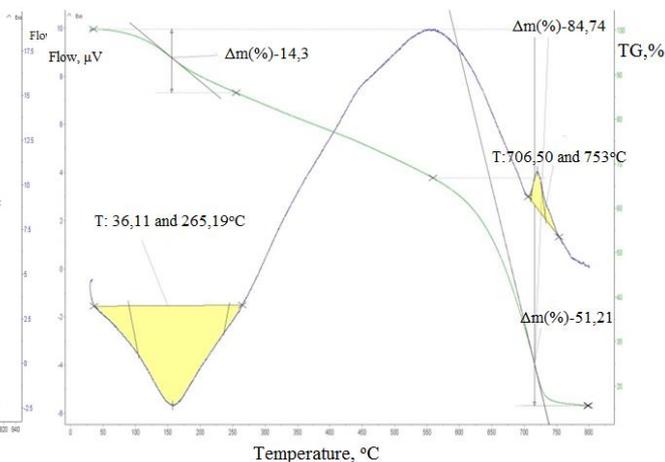


Fig. 5. DTA/TG curves of L_{H₃PO₄}

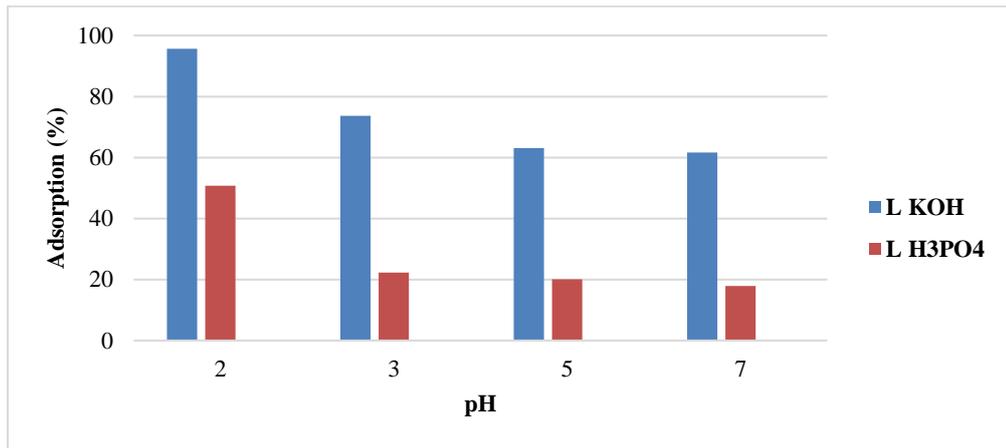


Fig. 6. Effect of pH of the solution with initial $C_{Re} = 5 \text{ mg l}^{-1}$ on adsorption of ReO_4^- by activated carbons $L_{H_3PO_4}$ and L_{KOH}

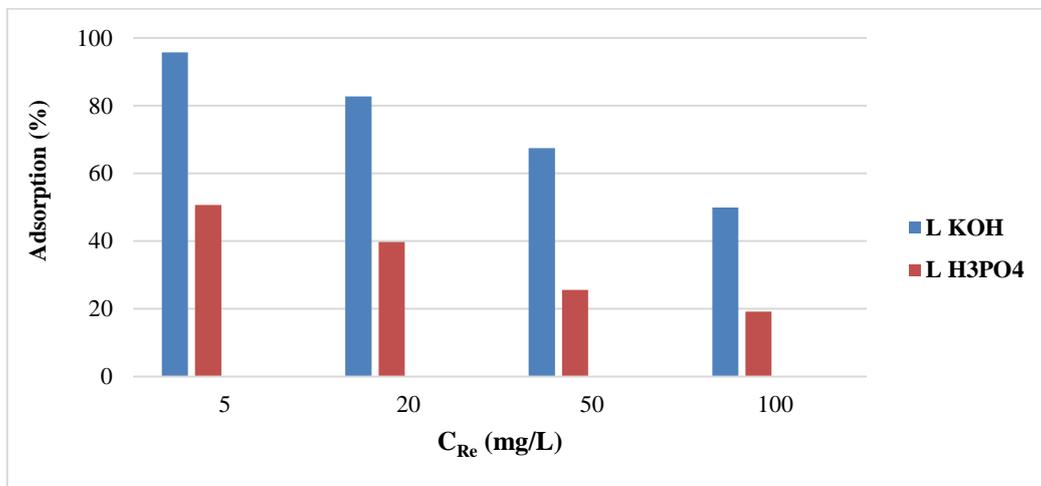


Fig. 7. Effect of initial Re concentration on ReO_4^- adsorption by activated carbons $L_{H_3PO_4}$ and L_{KOH} at pH 2.

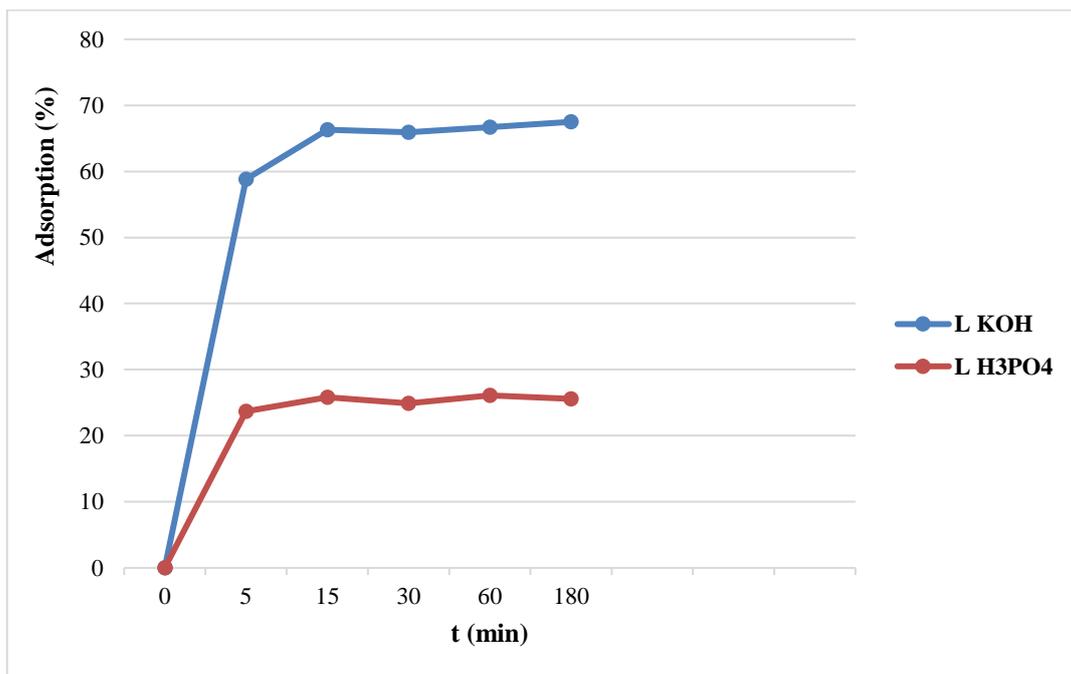


Fig. 8. Effect of contact time on ReO_4^- adsorption on $L_{H_3PO_4}$ and L_{KOH} sorbents at $C_{Re} = 50 \text{ mg l}^{-1}$ and pH 2

CONCLUSIONS

Activated carbons were obtained after activation of technical hydrolyzed lignocellulosic material with KOH and H₃PO₄. The sample obtained after treatment with KOH has a higher carbon content - 78.90% compared to that activated with H₃PO₄ - 58.5%, indicating that, in the first case, after lignin pretreatment with H₂SO₄, most of the residual polysaccharides were hydrolyzed.

- The activated carbons obtained by both methods have almost the same surface area, S_{BET} 1420 - 1497 m² g⁻¹, but the activated carbon obtained after activation of the hydrolytic lignin with KOH has a larger surface area and volume of micropores - 1259 m²g⁻¹ and 0.515 m³g⁻¹, respectively, compared to that treated with H₃PO₄ - 741 m²g⁻¹ and 0.32 m³g⁻¹, indicating that the first type of activated carbon has a more developed internal surface on the micropore level.

- DTA analysis showed that activated carbon obtained after treating THL with KOH, is more thermally resistant than that obtained after treating THL with phosphoric acid, which is probably due to the higher carbon content of the former sample. At a final temperature of 810 °C, the degradation of the starting lignin was 92.5%, of KOH-activated - 49.3% and of H₃PO₄-activated - 84.7%

- The activated carbon obtained after activation of hydrolyzed lignocellulosic material with KOH, has a better adsorption capacity for rhenium than that obtained after activation with H₃PO₄. At initial Re concentration C_{Re}=5 mg l⁻¹ and pH 2 of the tested solution, 95.7 % of ReO₄⁻ are adsorbed. The adsorption process is fast and equilibrium is reached within 15 min, which is promising for the practical application of the sorbent.

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