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Influence of Activating Reagents on the Porous Structure of Activated Carbon

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Biomass has recently caught considerable interest as a low-cost renewable and sustainable raw material bringing another point of view for worldwide alternatively energy and material production. This study was intended to evaluate the effects of activating reagents on product and the porous structure of activated carbons obtained from biomass processing via conventional pyrolysis. Activation reagents as KOH, NaOH, HCl, $ZnCl_2$ and $MgCO_3$ were used for pyrolysis activation in conventional reactor. The effect of the activating reagents, the influence of activation ratio and the difference for one or two step activation were studied.

1. Introduction

The rapid development of modern society over the second half of the last century encouraged a faster growth in the production and utilization of activated carbon due to stricter environmental regulations regarding water resources, air quality control, energy conversion and economic recovery of valued chemicals. The exploration of an alternative use for several agro industrial wastes, besides the replacement of petroleum-derived products, has suggested the use of waste biomass for the production of activated carbon. It is well known that wood and coconut shells are the most common precursors for the large scale synthesis of activated carbon, yielding to a global production of more than 300,000 t/y (Mourão et al., 2011). However, this would not cover the worldwide demand of 12,804,000 t of activated carbon consumed just in 2015 (Gonzáles-García, 2018).

Lignocellulosics precursors and biomass sources have become important materials to produce activated carbon with many benefits, mainly from the economic and environmental point of view. Nowadays, it is possible to find numerous research papers devoted to the synthesis characterization and applications of novel precursors to produce activated carbon. Therefore, special attention must be paid to the connection between the selected precursor characteristics, the final microstructure and properties of carbon. Pyrolysis is evidently an original form of application technique linked to waste that converts less valuable material to higher value outputs (Hocking, 1994). Activated carbons are substances with the required surface characteristics (Kaouah et al., 2013), which are widely used in various fields of purification and industrial processes (Ceyhan et al., 2013).

Invention methods and the use of low-priced raw materials have been considered (Budinova et al., 2006). Conventional heating is one of the most appropriate methods used for preparation. Traditionally, thermal heating during activated carbon production is carried out by using an electric furnace. In contrast to the former heating technique, microwave provides energy to entire samples via a dielectric heating, whereby heat is transferred from the central part (Lin and Chen, 2015). Hesas et al. (2013) focused on the comparison between conventional heating and microwave heating on $ZnCl_2$ impregnated raw palm shell. They found that both surface area and total pore volume are remarkably higher in term of the conventional furnace heating.

Principally, physical activation and chemical activation are used to obtain activated carbons. Physical activation includes a carbonization and activation stage. For activation steam and carbon dioxide are the most common elements, noticeably stimulating the porosity of the resulting material (Bae et al., 2014). Much more interest in research is shown in chemical activation, and it is due to several benefits. Chemical activation is a single-stage process that includes an impregnation step prior to heat treatment in an inert atmosphere; lower temperatures for process could be used with extremely high surface area. Process corrosiveness and necessity of a washing phase should be pointed out as the main weaknesses of this procedure. The chemicals applied as potential

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activators include alkali (potassium hydroxide and sodium hydroxide); acidic group (phosphoric acid and sulphuric acid); and alkali earth metal salts (aluminium chloride and zinc chloride). Each chemical reacts differently with the precursors and influences adsorption behavior. KOH and $ZnCl_2$ are among the most frequently used compounds for the production of sorbents (Özdemir et al., 2014). Although not common, H_2O_2, K_2CO_3, $CaCl_2$ and formamide have also been used as activating agents (Gonzáles-García, 2018).

Selection of the precursor for the development of low-cost activated carbons depends on a number of factors. The precursor should be freely available, inexpensive, and environmental friendly. The chemically activated carbons have developed surface areas ranging up to 3,708 m^2/g (Gonzáles-García, 2018). According to collected data it is possible to note that activation with alkaline agents produces the highest surface area values: 3,708 m^2/g for corncob activated with KOH (Liu et al., 2014) and 3,167 m^2/g for eucalyptus wood activated with NaOH (Lillo-Ródenas et al., 2007). Secondly, treatment with acids and acid salts also supplies high surface areas; for instance, impregnation of Chinese fir using H_3PO_4 yields to 2,518 m^2/g (Zuo et al., 2009), impregnation of lignin with H_2SO_4 produces 1,946 m^2/g (Babeł and Jurewicz, 2008), the use of $FePO_4$ on peach stone provides 2,160 m^2/g (Ramírez-Montoya et al., 2015), and the use of K_2CO_3 on used tea yields 1,722 m^2/g (Gurten et al., 2012). Lastly, activation of coconut shells with $ZnCl_2$ (Hu et al., 2001) yields to 2,450 m^2/g.

To our knowledge, there are many available reports on the activated carbon preparation with the use of the most frequently used compounds such as KOH. On the other hand, there are only few reports with the use of $MgCO_3$. The objective of this study is to increase knowledge of less used as well as commonly used activating agents. In this study prepared activated materials in the conventional pyrolysis apparatus at the maximum temperature of 850 °C with the 2 h delay at this temperature. KOH, NaOH, HCl, $MgCO_3$ and $ZnCl_2$ were used as the activating agents. After cooling, the activated samples were neutralized, filtered and finally washed. Final characterization of prepared sorbents was made by physisorption of nitrogen at 77 K.

2. Materials and methods

2.1 Material

Raw sawdust (RS) and carbonized sawdust (CS) were used as materials for preparation of activated carbons. The carbonized sawdust was prepared by carbonization in a tube reactor at 850 °C for 2 h with heating rate 10 °C/min. Proximate and ultimate analyses were carried out. For the determination of moisture content W, ash A and volatiles matter V thermogravimetric analyser TGA - 601 was used according to the standards ČSN 44 1377, CSN ISO 562 and ČSN ISO 1171. Elemental analysis was performed with the use of the unit LECO CHSN628. The HHV was determined according to ISO 1928 with the use of the unit LECO AC - 350.

2.2 Laboratory devices

The laboratory apparatus was composed of the tubular electric furnace (length of the reactor 65 cm, length of the heated zone 30 cm, inner diameter of the heating zone 5 cm), the reactor was placed in (it is possible pyrolysed batch about 200 g). Nitrogen was used as an inert medium.

2.3 Activation

Activation was done in a tubular electric furnace. Approx. 10 g of carbonized sawdust was activated with KOH, NaOH and HCl. The exact amount of KOH and NaOH was dissolved in 100 mL distilled water. The activation ratio for KOH and NaOH was 0.25:1 and 2:1 (KOH:carbonized sawdust). Activation with HCl was done similarly. 10 g of carbonized sawdust was activated in 100 ml of 0.5 M and 2 M HCl solution. Activation with $ZnCl_2$ and $MgCO_3$ was done with raw sawdust and with carbonized sawdust. Again 10 g of raw or carbonized sawdust was activated in 100 mL of 1 M $ZnCl_2$ and $MgCO_3$ solution. Then the mixture was thermal treated in an inert atmosphere of nitrogen at 850 °C for 2 h. After cooling, the samples activated with NaOH and KOH were neutralized with hydrochloric acid and finally all the samples were washed. After drying on temperature 110 °C by 24 h, the activated samples were ready for subsequent surface analysis.

2.4 Characterization of solid residues

Final characterization of solid residues of pyrolyzed samples was done by physisorption of N_2 at 77 K. Nitrogen physisorption measurement was carried out on the 3Flex Surface Characterization Analyser (Micromeritics). Ahead of the nitrogen physisorption measurements, the activated samples were degassed at 300 °C for 24 h under vacuum less than 1 Pa. The specific surface area of the samples, S_{BET}, was evaluated using BET method and micropore volume and mesopore (external) surface areas were determined based on the t-plot method (using STSA Carbon black standard isotherm). The mesopore-macropore-size distribution was determined by using BJH method, assuming cylindrical pore geometry and using STSA standard isotherm. The micropore-size distribution was determined using Horvath-Kawazoe method, assuming slit pore geometry of pores. Samples were also subjected to true (skeletal) density analysis. The density was measured by the Thermo Scientific Pycnomatic ATC semiautomatic pycnometer by using helium as a carrier gas.

3. Results and Discussion

3.1 Evaluation of input materials

As an input material for activation the carbonized sawdust was used. For the sample proximate and ultimate analyses were carried out (Table 1 and Table 2).

Table 1: Proximate analysis of raw and carbonized sawdust

Sample	RS	CS
Moisture (wt.%)	17.3	1.2
Volatile (wt.%)	77.5	7.2
Fixed Carbon (wt.%)	21.9	89.3
Ash (wt.%)	0.6	2.4

Table 2: Ultimate analysis of raw and carbonized sawdust

Sample	RS	CS
Carbon (wt.%)	51.8	90.7
Hydrogen (wt.%)	6.1	1.1
Nitrogen (wt.%)	1.0	0.8
Oxygen (wt.%)	40.6	5.1

3.2 Evaluation of activated carbons

Ten activations were carried out. Carbon yield was calculated according to weight of activated carbon and carbonized sawdust.

$$\text{Activation yield (\%)} = \frac{\text{activated carbon (g)}}{\text{carbonized sawdust (g)}}$$

Table 3: Activation yields

Sample	KOH-1	KOH-2	NaOH-1	NaOH-2
Activation ratio	0.25:1	2:1	0.25:1	2:1
Activation yield (wt.%)	58	52	50	54
Activation yield (wt.%) counted for raw sawdust	12	10	11	10

Sample	HCl-1	HCl-2	$ZnCl_2$-RS	$ZnCl_2$-CS	$MgCO_3$-RS	$MgCO_3$-CS
Activation concentration	0,5 M	2 M	1 M	1 M	1 M	1 M
Activation yield (wt.%)	58	64		45		42
Activation yield (wt.%) counted for raw sawdust	12	13	7	9	5	8

The activation yield from carbonized sawdust varies from 42 to 64 % (Table 3). The highest activation yield had sample activated with HCl. The activation of raw sawdust gave lower activation yields then the activation of carbonized sawdust.

The textural properties such as the specific surface area, micropore volume, mesopore (external) surface area, total pore volume and micropore width are summarized in Table 4. These properties were evaluated from measured nitrogen adsorption-desorption isotherms shown in Figure 1a and b. The micropore-size distributions of samples are evaluated as well and are shown in Figure 2a and b. From Figure 1a and b it is evident that all samples are microporous solids (according to IUPAC classification) with some amount of mesopore-macropores.

The evaluated data in Table 4 reveal that the activation with KOH gives the best results concerning the volume of micropores which is positively reflected to the highest total pore volumes of prepared activated carbons. These facts are visible from Figure 1a. However, while the increasing activation ratio with KOH leads to increased volume of micropores but decreased mesopore (external) surface area, the increasing activation ratio with NaOH and HCl leads to increasing of volume of micropores as well as mesopore (external) surface area. With respect to biggest effect of the activation agent on all textural properties, it is observed for activation with NaOH. The positive effect of activation with ZnCl2 as well as MgCO3 on micropore volume and external surface area is more significant for activation of raw sawdust (RS) then carbonized sawdust (CS).

Table 4: Textural properties of carbonized sawdust and prepared activated carbons

	CS	KOH-1	KOH-2	NaOH-1	NaOH-2
S_{BET} (m^2/g)	245	784	899	177	513
V_{total} (mm$_{liq}^3$/g)	190	456	504	108	331
S_{meso} (m^2/g)	67	106	92	94	142
V_{micro} (mm$_{liq}^3$/g)	88	346	412	72	187
$w_{micropore,\ max}$ (nm)	0.37	0.34	0.37	0.47	0.34, 0.43
ρ_{He} (g/cm^3)		1.818	2.223	1.813	1.962

	HCl-1	HCl-2	ZnCl$_2$-RS	ZnCl$_2$-CS	MgCO$_3$-RS	MgCO$_3$-CS
S_{BET} (m^2/g)	468	538	504	347	349	264
V_{total} (mm$_{liq}^3$/g)	283	337	207	289	183	351
S_{meso} (m^2/g)	64	73	48	52	104	53
V_{micro} (mm$_{liq}^3$/g)	207	238	233	151	125	108
$w_{micropore,\ max}$ (nm)	0.35	0.35	0.44	0.36	0.35, 0.49	0.35
ρ_{He} (g/cm^3)	1.963	1.862	2.065	1.867	1.958	2.250

S_{BET} specific surface area
V_{total} total pore volume at relative pressure $p/p_0=0.99$
S_{meso} mesopore (external) surface area
V_{micro} micropore volume
$w_{micropore,\ max}$ maximum of micropore-size distribution
ρ_{He} true (skeletal) density

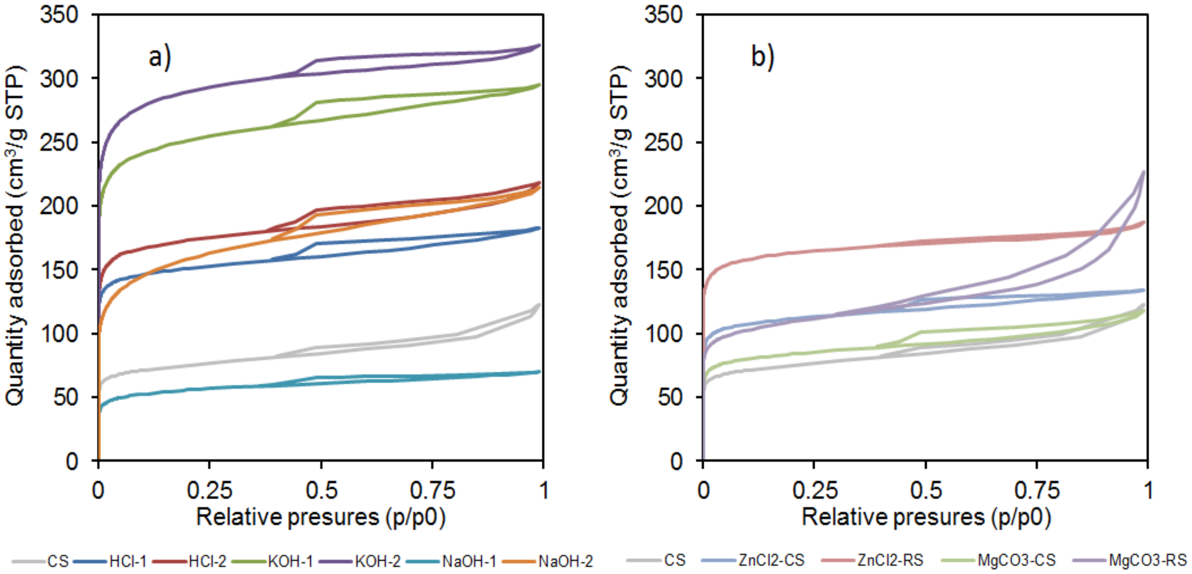

Figure 1: Adsorption-desorption isotherms of carbonized sawdust and activated carbons a) acid and base as activation reagent, b) salts as activation reagent

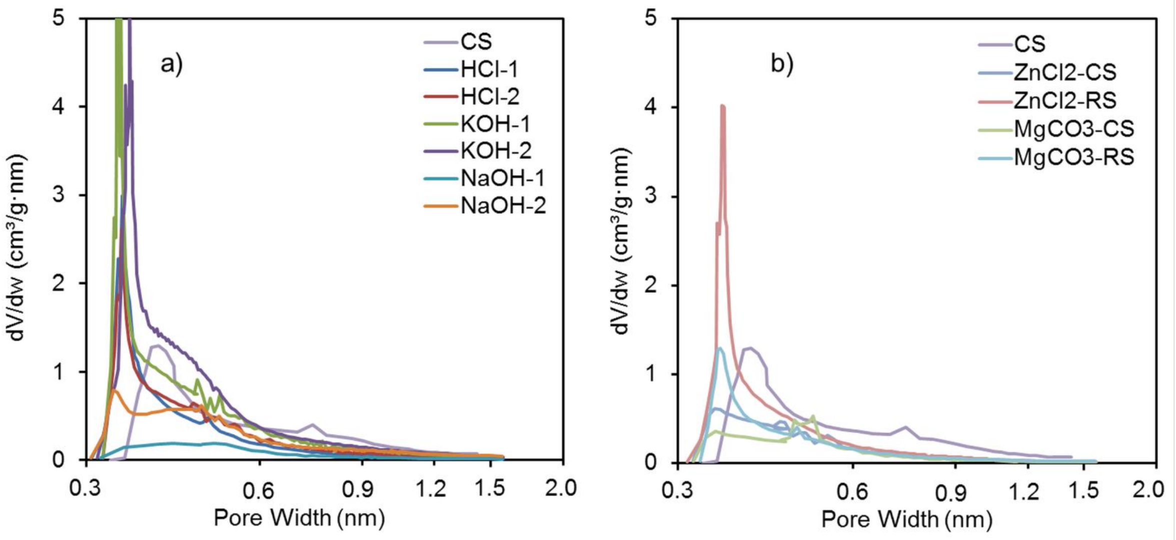

Figure 2: Micropore-size distributions of carbonized sawdust and activated carbons a) acid and base as activation reagent, b) salts as activation reagent

4. Conclusions

The parent carbonized sawdust shows well-developed microporous structure. Increasing activation ratio with HCl does not cause any significant changes within micropores width contrary to increasing activation ratio with NaOH and KOH (Figure 2a, Table 4) when the formation of micropores of different width can be observed. Concerning the production of activated carbons, the activation of raw sawdust by $ZnCl_2$ and $MgCO_3$ is more effective than activation of carbonized sawdust by $ZnCl_2$ and $MgCO_3$;

From the statistics based on the literature review it could be suggested that research in activated carbon will continue developing along the years. Sawdust carbonate itself has a surface area of only 245 m^2/g with a strong microporous structure. The micropores were well developed. In contrast, the maximum surface areas of activated carbon prepared with alkali metal compounds, were generally larger than surface areas of the original carbonaceous material. In general, as the concentration of alkali metal increases the porous structure developed gives higher surface and higher total pore volume carbons. On the other side, the acid environment produces higher marcopore surface structure. Of course, the properties of activated carbon are suitable for the types of applications, since it is clear that the adsorption of large organic macromolecules will not take place in the micropores. In addition to the usual activating agents, it is possible to use CO_2 activation, but it does not produce high-quality porous structures, although it is on the other hand very cheap (Seixas et al., 2017).

The influence of the activating agent itself in terms of adsorption of harmful substances from waste water will be the subject of further research for these prepared activated carbons.

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