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Organic bio-wastes as potential precursors used for preparation of activated carbons- review

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Currently significant amounts of wastes, which pose a real threat to the natural environment and human health, are produced worldwide. One way to get rid of waste materials is to dispose them in landfills but some of them no longer perform their function due to overfilling. For this reason, scientists pay more and more attention to the search for their possible disposal and/or recycling as it is impossible to prevent its generation completely.

Recently many researchers have taken up the topic of the use of agri-food wastes due to their low cost and widespread availability as a starting material for the production of activated carbons. As a result, it was found out that organic wastes are very successful precursors of organic matter and the obtained activated carbons are characterized by a very well developed porous structure. The paper presents the literature review regarding the possibility of using various waste materials under different impregnation and preparation conditions to obtain activated carbons with a developed surface area and good adsorption properties.

Keywords: bio-wastes utilization, pyrolysis, activated carbons

1. INTRODUCTION

The development of civilization, associated primarily with the consumers' lifestyle, results in the production of a significant amount of goods and thus contributes also to generation of a huge amount of wastes [1]. Dozen million of tons of municipal and industrial wastes are disposed of each year [2]. According to the Central Statistical Office (GUS) data in 2017, 11,968.7 tons of wastes were collected in Poland due to human and economic activities. The main source of such wastes is the household [3]. Municipal wastes collected in 2017 produced by the households (9,971.2 tons) make the vast majority that is about 83.3%. The amount of these wastes increased by 4.3% compared to that in 2016 [3]. On the average, 312 kg of wastes were collected per one inhabitant in Poland. Compared to 2016, this amount increased by 9 kg.

Municipal wastes are a diverse mixture, among others, of packaging, green wastes (often biodegradable), mineral components and hazardous wastes [4]. About 40% of municipal wastes are organic wastes whose main advantage is that they contain over 50% of carbon [5].

Due to the fact that the wastes generation process can not be fully eliminated, the main focus is on finding possibilities of reducing their amount and developing methods for their effective disposal or reuse. Currently one of the ways to utilize wastes is to store them in landfills. This method is the cheapest from the economic point of view, however, it can cause hazardous environmental problems. Methane, a strong greenhouse gas which intensifies climate changes, is released from the landfilled wastes. It is estimated that methane emissions from the landfills constitute about 30% of its global emissions due to human activities [2]. In addition, depending on the structure of the landfill, destruction can be a result of soil and groundwater contamination [2, 6].

With the increasing human awareness of environmental pollution, there is a tendency to prepare biodegradable materials. Such wastes are usually stored, incinerated or discharged into the soil. Biodegradation processes involving microorganisms are beneficial but very slow and often lead to the production of gas (methane) as well as toxic leaks [2].

Large diversity of wastes, primarily municipal ones, deposited in landfills leads to a loss of raw material resources and an environmental burden. Recycling, disposal and utilization of secondary raw materials contribute to reduction of the total amount of wastes. Therefore, an important element of waste management is its processing and sorting, enabling the recovery of raw materials of the required degree of purity [6]. Such materials can be converted into energy sources through pyrolysis or fermentation, e.g. methane, which produces methane-rich biogas, used for energy production [7]. Another way to reuse organic wastes or biomass is to transform them into activated carbon [7, 8]. One of the most important challenges for commercial activated carbon producers is the reduction of carbon material production costs. Therefore the use of cheap raw materials, such as waste materials with a large carbon content and a low content of inorganic compounds allows to minimize production costs and thus partially solve problems with residual wastes [8, 9].

2. ACTIVATED CARBON

Activated carbons belong to the group of carbon materials that are characterized by an amorphous structure, a large internal surface and a high degree of porosity. These materials are characterized by high efficiency of electrical conductivity, good thermal stability as well as surface reactivity. Activated carbons owe their adsorption capacity to a well-developed porous structure which is created by micropores (<2 nm), mesopores (2-50 nm) and macropores (> 50 nm) [10].

Depending on the method of production and potential applications [11], there are distinguished:

- powdered activated carbon (PAC);
- granulated activated carbon (GAC);
- extruded activated carbon (EAC) [12];
- cylindrical, columnar (in the form of pellets) activated carbon [13];
- carbon nanofibers, nanorods [12];
- fibrous activated carbon [14].

The surface of activated carbons may contain heteroatoms, among which phosphorus, oxygen, sulfur, hydrogen, nitrogen and halogens stand out [15, 16]. These elements can come from carbon material precursors (wastes) and are incorporated into the carbon structure in the pyrolysis process. In addition, they can be introduced additionally to modify the properties of the resulting carbon materials or as a result of contact of the carbon material with the surrounding atmosphere [16]. Heteroatoms give specific adsorption or catalytic properties to carbons. The dominant element is *oxygen* which is part of the surface functional groups of acid or basic nature [17]. The chemical nature and amount of surface oxygen functional groups depend largely on the starting material as well as the method and activation conditions [18]. *Phosphorus* is attached to the carbon skeleton mainly through oxygen. The most common form is pentavalent phosphorus in the form of phosphate groups, however, in the process of modification some phosphorus-oxygen bonds can be replaced by phosphorus carbon ones. Carbons containing phosphorus are characterized by a hydrophilic acid surface and chemical stability as well as high adsorption capacity in relation to metal ions and organic molecules and significant catalytic activity used, for example, in biomass processing [16]. In activated carbons *sulfur* can occur at various degrees of oxidation. This element can be introduced into the carbon structure as a result of impregnation, surface functionnalization, intercalation or doping [19]. The presence of sulfur increases the sorption capacity of carbon relative to heavy metal ions. Sulfur-doped carbons are used for hydrogen storage and carbon dioxide capture or for photocatalytic degradation of pollutants [19-22]. Sulfonated carbons (containing -SO_3H groups) serve, among others, as catalysts in biomass processing and biodiesel production [19].

Activated carbon may have also protonated ($C–OH_2^+$), neutral (COH) or ionized (CO^-) groups on its surface. Carbons containing protonated surface groups are called the H-type carbons while those with the ionized groups are called L-type carbons [23].

2.1. Features of the starting materials used for AC production

The activated carbon can be obtained from any material that contains significant amounts of elemental carbon. The properties of the obtained carbon materials depend on the type and characteristics of the starting material. On a large scale there are applied organic materials with insignificant contamination, such as fossil coal, peat, lignin, wood [24]. However, organic municipal wastes have been increasingly used in recent years. They come mainly from households. Due to their low cost, universal access and significant amounts, they are an excellent starting material for the production of activated carbons [25]. Chestnut oak shells [26], potato skins [27], spent tea [28], tomato paste [29], fruits of *Artocarpus integer* [30], plum stones [31], cotton [32], nut shells [33] as well as cassava stalks [34], coconut shells [35], rice husks [36], corncob [37], acorn husks [38], olive seeds [39], corn stalks [40], reedy grass leaves [41], pomegranate seeds [42], spent coffee grounds, pomelo skin [43] are used.

Activated carbon produced from the agricultural/household wastes can come from various parts of the plant, such as root, stem, bark, flower, fruit peel, husk or stone which can be divided into wood and non-wood raw materials. Wood raw materials consist mainly of cellulose, hemicellulose and lignin while the composition of non-wood raw materials is much richer. They contain cellulose, hemicellulose, lignins, lipids, proteins, sugars, water, hydrocarbons and starch. The basic criteria taken into account when choosing a raw material include, among others, high carbon content and density, low content of inorganic volatile substances, prevalence as well as the possibility of producing activated carbon with high efficiency [10].

2.2. Methods for obtaining activated carbons

Active carbons are obtained as a result of the pyrolysis (carbonization) process and the activation of carbon materials. The product obtained as a result of the pyrolysis of the initial raw material (so-called pyrolysate or carbonizate) is adsorption-inactive and has a very poorly developed surface. In order to develop the adsorbent surface, the obtained carbonizate is activated [44]. The basic properties of the activated carbon depend mainly on the selection of appropriate starting material as well as the type of activating agent and the conditions of the pyrolysis process [45].

Carbonization is the initial stage of the process of obtaining activated carbons. During this time, volatile components are desorbed and the organic material is carbonized. The original porous structure is also shaped and undergoes significant development in the next stage (activation). In the initial stage, the starting material is dried at a temperature of about 200°C to reduce the amount of moisture and fractions with lower boiling points. Such a process increases the material mechanical strength. The carbonization process is carried out in the absence of air, in an atmosphere of inert gas, most often nitrogen at a temperature of 500-800°C. In this temperature range, as a result of the release of volatile substances, the organic mass of the starting material is reduced and the content of elemental carbon increases [24, 44].

The parameters of the obtained carbon are significantly affected by those of the pyrolysis process:

- the *atmosphere* of the process affects the thermal decomposition as well as the course of reactions that occur between the pyrolysis products and the carbonaceous material. Inert gas removes gases and vapours formed during pyrolysis thereby increasing the carbonizate reactivity [44].
- *rate of temperature rise*: rapid temperature rise makes it difficult to control the formation of the porous structure because the individual phases of thermal decomposition and the secondary reactions of the pyrolysis products overlap. Significant amounts of volatiles are released in a short time, which leads to larger pores. The obtained carbonizates are characterized by a greater reactivity than those obtained at a slow temperature rise.
- the *final temperature of the carbonization process* affects the arrangement of the carbon material in the carbonate. As the temperature increases, more energy is needed to break the chemical bonds, and the volatile products are distilled off. At higher temperatures, condensation processes occur more intensively and the resulting material is characterized by a greater mechanical strength.
- the ordering of the carbon material is influenced by *the time it is kept at the final temperature*. When the final temperature is lower than that at which the main thermal decomposition reactions end, a further slow decomposition of the carbonaceous material takes place. However, some of these processes are inhibited. At a temperature higher than that at which the basic processes of thermal decomposition of carbon matter end, further internal ordering takes place [44].
- the *number of intermediate stages* of the pyrolysis process affects the creation of the porous structure of the carbon material. Based on the research (own study), it was found

> that the extension of pyrolysis time allowed to obtain active carbons with a very well developed surface by introducing intermediate stages. The surface of the activated carbons obtained, e.g., as a result of pyrolysis with two intermediate stages was twice as large as that of the materials obtained from the pyrolysis with one intermediate stage.

Figure 1 shows the examples of pyrolysis processes.

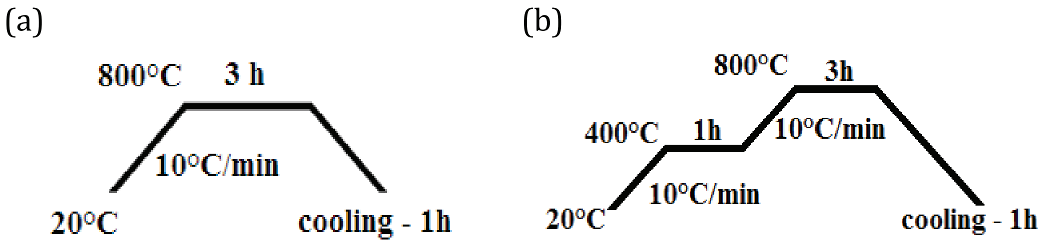

Fig. 1. Exemplary diagrams of the pyrolysis process: with one intermediate stage (a) and two intermediate stages (b).

2.3. Activation of carbon material

Activation is a key step to develop the pore structures of carbon materials obtained in the carbonization process. It can be carried out in two ways, using physical and chemical activation.

In the case of *physical activation*, the material obtained after carbonization is activated using an oxidizing gas to develop and strengthen the structure of the pores [23]. In the initial phase of activation, the oxidizing gas removes more reactive carbon, resulting in the opening of previously inaccessible pores and the creation of new ones. Further oxidation causes the existing pores to expand. The most commonly used oxidizing agents are: steam, carbon dioxide, air or mixtures of these gases [23, 24].

Below are the equations for the oxidation of the carbon surface using the selected oxidants: air (reactions 1, 2), CO_2 (reaction 3) and steam (reactions 4-8). The basic reaction of carbon with steam is represented by reaction 4, reactions 5 and 6 occur simultaneously. Reactions 6 and 7 show the possibility of obtaining methane [10, 24, 44, 46].

A. Air:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -387\ \text{kJ/mol} \qquad (1)$$
$$2C + O_2 \rightarrow 2CO \qquad \Delta H = -226\ \text{kJ/mol} \qquad (2)$$

B. Carbon dioxide:

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +159\ \text{kJ/mol} \qquad (3)$$

C. Steam:

$$C + H_2O \rightarrow H_2 + CO \qquad \Delta H = +130\ \text{kJ/mol} \qquad (4)$$
$$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad \Delta H = +77\ \text{kJ/mol} \qquad (5)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42\ \text{kJ/mol} \qquad (6)$$
$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -86\ \text{kJ/mol} \qquad (7)$$
$$2C + 2H_2O \rightarrow CH4 + CO2 \qquad \Delta H = -9\ \text{kJ/mol} \qquad (8)$$

Carbon oxidation is a complex process, consisting of many intermediate stages which include, among others, transport of reagents to the surface of carbon particles, penetration into the pores, surface chemisorption, chemical reactions and release of reaction products [24]. The reaction with air is exothermic (reactions 1, 2), so it is difficult to maintain a suitable, constant temperature. In addition, oxygen is an aggressive reagent and using it as an oxidizing agent causes many difficulties. In many processes, oxygen activation is carried out at low temperatures and is combined with the additional steam treatment. This method is used for materials with low reactivity.

The main reactions using carbon dioxide (reaction 3) and steam (reaction 4) are endothermic. The rate of interactions of carbon dioxide with carbon at a given temperature is 30% slower than in the case of reaction with steam [24, 44]. However, often slower reactions allow better process control.

One of the most effective methods of surface modification of adsorbents with a porous structure is hydrothermal treatment (HTT). The course of the process depends on many factors, including the primary (initial) adsorbent structure, time and temperature at which the process is carried out, phase type (gas, liquid) or environmental pH [47]. This process can be carried out in a gaseous environment using oxygen, ozone and nitrogen oxides or in the liquid phase using hydrogen peroxide, nitric acid, perchloric acid, potassium permanganate [48, 49]. The hydrothermal steam treatment at a high pressure is one of the most effective methods of modifying the porous structure and adsorbent surface. Under these conditions, particularly at temperatures above 200°C, water changes its properties due to the disappearance of the original tetrahedral structure [50], gaining unusual properties as a solvent or oxidizing medium.

The amount and type of created oxygen groups depend largely on the type of oxidizing agent and temperature conditions of the pyrolysis process. Liquid phase oxidation usually leads to the formation of significant amounts of acidic oxygen groups. In turn, basic groups are formed mainly as a result of chemisorption of oxygen on the surface of carbon materials or during the heating of acid-type carbons in an inert gas or hydrogen atmosphere [51].

Chemical activation is also called wet oxidation. The starting material is impregnated or mixed with the activating agent and then heat treated at a temperature of 500-900°C in an inert atmosphere. The activating factors include $ZnCl_2$, H_3PO_4, H_2SO_4, K_2S, KCNS, HNO_3, H_2O_2, $KMnO_4$, $(NH_4)_2S_2O_8$, NaOH, KOH or K_2CO_3 [10, 23]. Of these activating agents, $ZnCl_2$, H_3PO_4, NaOH and KOH are the most commonly used ones. Many experiments were performed to study the effect of individual activating agents on the structure of the obtained activated carbons. On their basis, it was found, for example, that the activated carbon impregnated with H_3PO_4 had mesopores in its structure whereas the use of $ZnCl_2$ led to the formation of both micro- and mesopores [10].

Activators basically act as drainage and oxidizing agents. They can also prevent the formation of tar or ash, thereby increasing the surface of the resulting carbon. Due to the greater reactivity of the activating factors, it is often possible to skip the carbonization stage, reduce the process temperature as well as the time needed to develop the pore structure [23, 51, 52].

One of the most important factors taken into account during chemical activation is the degree of impregnation (I) with the activating factor. It is defined as the ratio of the mass of the activating agent to that of the impregnated starting material [25]. The impregnation ratio has a very large impact on the pores development.

The higher impregnation ratio leads to the formation of mesopores while the lower one results in the formation of micropores. This is due to the fact that a higher impregnation factor causes greater swelling and greater release of volatiles which leads to pores widening. A lower impregnation coefficient promotes the removal of volatile substances but at the same time it prevents from the tarry substances accumulation [53].

After applying chemical activation a washing step is necessary because the pores of the obtained activated carbon can be occupied or blocked by an excessive activating agent or by-products. Depending on the activating agent, carbon is washed with acid, alkali or water [23]. Unfortunately, washing the final product is often a time consuming and expensive stage which confines possibility of the obtained materials application.

3. LITERATURE REVIEW

Activated carbon is one of the materials widely used in both everyday life and industry, due to its very well developed surface and porous structure, high reactivity or exceptional physicochemical properties, especially those regarding adsorption. Porous carbon materials are very often exploited by scientists and representatives of the industrial circle owing to the possibility of their use in, among others, adsorption, catalysis or separation processes. Due to the high adsorption capacity of inorganic and organic substances, they are commonly used as adsorbents in the processes of pollution removal from air, water and industrial gases [54].

The properties of activated carbons depend primarily on the type of starting material, activation method and pyrolysis process conditions. Optimization of carbonization and activation conditions allows obtaining carbons with a well-developed surface and porosity [55].

Table 1 presents the examples of selected waste materials, types of activation, pyrolysis process conditions as well as selected structural parameters and sorption capacities of specific adsorbents.

Table 1. Activation conditions and pyrolysis process as well as sorption capacities of selected precursors.

Precursor	A	I	Conditions	S_{BET} [m^2/g]	q$_e$	Ref.
Coffee residues	H_3PO_4	0	450°C –1h	253	–	56
		25		610	–	
		50		728	*Cd(II): 46.95; *Pb(II): 89.28	
		75		817	–	
		100		1003	–	
	$ZnCl_2$	0	450°C –1h	253	–	
		25		526	–	
		50		682	–	
		75		858	*Cd(II): 37.04; *Pb(II): 63.29	
		100		889	–	
Coffee residues	CO_2	–	600°C –4h	11 ± 2	–	57
	steam	–		469 ± 14	–	
	$ZnCl_2$	–		470 ± 12	*Formaldehyde: 245	
	$ZnCl_2$ + CO_2	–		914 ± 21	*Formaldehyde:130	
	$ZnCl_2$ + steam	–		305 ± 25	–	
Coffee grounds	KOH	9	800°C –1h	1348	**MB: 280, **Ph: 1288	58
		18		1455	**MB: 514, **Ph: 1566	
		36		1778	**MB: 906, **Ph: 1615	

cont. Table 1.

Coffee husks	$ZnCl_2$	1:1	550°C –4h	1522	*MB: 263 *Ph: 117	59
	$ZnCl_2 + FeCl_3$	1:1		1374	*Ph: 167	
	$FeCl_3$	1:1		965	*Ph: 65	
Coffee pulp	Na_2HPO_4	4:1	825°C –1h	140	–	60
		2:1		155	–	
		5:4		451	*MB: 150; *DR: 120	
		1:1		444	*MB: 110; *DR: 98	
Spent coffee grounds	H_3PO_4	2	800°C –3h	219.3	–	(*)
			400°C – 1h → 800°C – 3h	464.2	*MB: 236	
Chestnut oak shells	H_3PO_4	–	450°C –2.5h	989.4	*Cr(VI): 17.50	26
Waste potato peels	H_3PO_4	–	400°C – 2h	904.6	*Co(II): 373	27
			600°C – 2h	1041.4	*Co(II): 405	
			800°C – 2h	0.9	–	
Plum stone	H_3PO_4	3:1	500°C –1h	–	*Cu(II): 48.31; *Pb(II): 80.65	31
Pecan nutshell	$CaCl_2$	–	700°C –2h	490	–	33
	NaCl	–		786		
	KCl	–		808		

cont. Table 1.

Tomato paste	$ZnCl_2$	6:1	500°C –1h	787	*MB: 400 *MY: 385	29
Palm shell	K_2CO_3	1.0	800°C –2h	1170	–	35
Rice husk	NaOH	–	800°C –1h	2681	–	36
Corncob	H_3PO_4	1:2	400°C – 2h	700	*IN: 632	37
			500°C – 2h	633	*IN: 945	
			600°C – 2h	600	*IN: 485	
Acorn shell	$ZnCl_2$	–	400°C –15min	997	*IN: 951	38
			500°C –30min	1289	*IN: 1209	
			600°C –45min	966	*IN: 910	
Olive stones	H_3PO_4	60	500°C –2h	257	–	39
		70		779		
		80		1218		
Reedy grass leaves	H_3PO_4	–	400°C – 2h	690	*IN: 455	41
			500°C – 2h	1474	*IN: 1128	
			600°C – 2h	1223	*IN: 1082	
			500°C – 1h	1320	*IN: 1109	
			500°C – 3h	1376	*IN: 1117	
			500°C – 4h	1298	*IN: 1100	
			500°C – 5h	1107	*IN: 1070	

cont. Table 1.

Pome-granate seeds	$ZnCl_2$	2.0	600°C – 1h 800°C – 1h	978.8 823.7	–	42

A – activating agent ,
I – impregnation ratio,
S_{BET} – specific surface area [m^2/g],
q_e – adsorption capacity,
* – adsorption capacity [mg/g],
** – adsorption capacity [μmol/g] ,
MB –methylene blue,
Ph – phenol,
|R- Direct Red,
MY – metanil yellow,
IN – iodine number,
(*) – own results (unpublished).

3.1. Effects of temperature and pyrolysis time

Kyzas et al. [27] obtained activated carbons from the potato peel impregnated with phosphoric acid (V) (Table 1). They conducted carbonization in the three temperature variants: 400ºC, 600ºC, 800ºC. At the final temperature, the sample was soaked for 2 hours. As a result of pyrolysis, carbons were obtained with a yield of 55, 51 and 49%, respectively. It was found that the increase in carbonization temperature caused a gradual decrease in efficiency. This can be attributed to the thermal degradation of phosphor-carbon compounds present in the carbon material and reduction of phosphates to elemental phosphorus, resulting in the formation of volatile phosphorus compounds (phosphorus oxide (V) and elemental phosphorus). An increase in the temperature from 400 to 600ºC caused a 15% increase in the surface area while a further increase in the carbonization temperature to 800ºC caused a decrease in the specific surface area. It was found that the reduction in the surface area could have been caused by the breakdown of the structure associated with excessive oxidation of the pore walls inside the material.

A similar relationship was observed by Xu et al. [41], using reedy grass leaves impregnated with phosphoric acid (V) as a starting material. They carried out the tests changing the temperature (400ºC, 500ºC and 600ºC for 2 hours) and time (500ºC for 1, 3, 4 and 5 hours). It was found that the S_{BET} surface area, total pore volume, iodine number and micropore volume with the increasing temperature activations initially increased and then decreased. The research results indicate that the development of porosity below 500°C involves primarily the creation of new micropores (or even ultra-micropores, r <0.7 nm), which expand with the increasing temperature. This may be due to the fact that phosphorus in the form of various structures present in the impregnated reedy grass leaves under such heating conditions tends to boil which causes the structure of the carbonized product to develop. At the temperature of 500ºC, the extension of the activation time caused an initial increase in the surface and then its decrease, which could be due to the destruction of some pores. The adsorption capacity was determined on the basis of the iodine number which was even up to about 1100 mg/g for the tested carbons [41].

Research on the use of spent coffee (coffee grounds) impregnated with phosphoric acid (V) allowed obtaining carbons with the surface area of approx. 460 m^2/g (unpublished results). The extension of pyrolysis time and the use of intermediate heating stages resulted in an almost 2-fold increase in the surface area of these materials (Table 1).

3.2. Effects of the impregnation ratio of the activating agent

Boudrahem et al. [56] used coffee wastes impregnated with various amounts of H_3PO_4 and $ZnCl_2$. They found that the surface development was strongly influenced by the amount and nature of the activating agent. In the case of both activating agents, they obtained the best specific surface parameters at the highest impregnation ratio (100%). They showed that with the increasing impregnation ratio, the specific surface area of the obtained material increases. This may be due to the action of a chemical agent that promotes condensation which mainly occurs between the aromatic hydrocarbons and tar-forming compounds. They are responsible for the formation of large molecules (polycyclic aromatic compounds) in the structure of activated products and cause an increase in the S_{BET} surface area. The surface areas of activated carbons made from the coffee residues impregnated with H_3PO_4 were much larger than the activated carbons impregnated with $ZnCl_2$. The results of heavy metal ions (Pb^{2+} and Cd^{2+}) adsorption tests have shown that the adsorbed amount of metal ions increases with the increasing impregnation coefficient. This is closely related to the increase in the adsorbent surface area, development of microporosity, the presence of acid functional groups and a greater number of available adsorption centers associated with the increase in the amount of activating agent.

Laksaci et al. [58] used coffee wastes (coffee grounds) impregnated with KOH at the three impregnation ratios: 9, 18, 36 mmol/g. They observed that with an increase in the impregnation ratio, the values of structural parameters such as specific surface area, total pore volume, volume of micro- and mesopores increase. The increase in porosity observed along with the increase in the impregnation coefficient could have been caused by the release of tar from the crosslinked structures formed as a result of chemical treatment. It was shown that the increase in the impregnation ratio led to an increase in the adsorbed amounts of phenol and methylene blue. When the impregnation coefficient increased from 9 to 36 mmol/g, the amounts adsorbed on AC increased from 280 to 906 mmol/g (MB) and from 1288 to 1615 mmol/g for phenol (Table 1).

Similar conclusions were drawn by Gonçalves et al. [60] who used coffee precursor impregnated with Na_2HPO_4. They observed that as the impregnation ratio increased, the surface area developed more efficiently and the amount of adsorbed dyes increased (phenol, MB, and Direct Red, Table 1).

3.3. Effects of activation type

Boonamnuayvitaya et al. [57] prepared activated carbon from the spent coffee using physical, chemical and physicochemical activation. They employed the following combinations of activating agents: CO_2, steam, $ZnCl_2$, $ZnCl_2$ + CO_2, $ZnCl_2$ + steam. It was observed that the surface and pore volume of activated carbon in the presence of $ZnCl_2$ were larger than in the case of the systems without $ZnCl_2$. According to the literature data [61] $ZnCl_2$ is a dehydrating agent that largely influences the pyrolysis process of carbon materials. When mixed with the $ZnCl_2$ carbon materials, it binds within the carbon structure. During the pyrolysis interactions between the zinc compounds and the carbon atoms are found. Under such conditions, the distance between the carbon monolayers increases and pores are created in the structure. $ZnCl_2$ used during pyrolysis causes that hydrogen and oxygen atoms are removed from the starting materials in the form of water, not hydrocarbons or oxidized organic compounds [61]. The best development of the surface area and porosity was observed for the $ZnCl_2$ activated sample in combination with CO_2. This was associated with the oxidation of the carbon surface area in the presence of CO_2 which resulted in the broadening and opening of closed pores, enabling the simultaneous evacuation of $ZnCl_2$. Slightly worse results were obtained for the materials activated with $ZnCl_2$ and steam. Water vapour converts $ZnCl_2$ into a liquid state which prevents its incorporation into the carbon matrix. As a consequence, $ZnCl_2$ could not react effectively and increase the pore size [57].

SUMMARY

Nowadays waste materials are one of the most serious problems for the society. The amount of waste generated increases year by year. Therefore new methods of their utilization and/or reuse are being sought. In the case of materials of organic origin, one of their management methods is their re-use as starting materials for the production of synthetic activated carbons. The paper presents the review of the latest, exemplary literature reports on the use of waste materials, e.g. solid coffee wastes, cane leaves, olive seeds, rice hulls, acorn shells to obtain effective carbon adsorbents.

The use of organic waste materials allows to obtain effective adsorbents from cheap, widely available precursors, in part it can also solve problems with the management of significant amounts of wastes. In addition, the activated carbons produced from waste materials very often have a higher sorption capacity than the commercial activated carbons. Due to the diverse compositions of the initial wastes, specific functional groups and heteroatoms can be present in the obtained active carbons, which are additional adsorption and even photocatalytic centers.

The paper presents the analysis of research results in which different starting materials, different activation methods and carbonization conditions were used. On their basis, it was found that with an increase in the impregnation ratio and longer pyrolysis time, better development of surface area and porosity is observed. The activated carbons had very good sorption properties in relation to toxic or arduous organic substances present in the environment. It has been shown that the sorption capacities of the obtained materials are closely related to the quality of the starting materials and activating factors.

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