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Sorption properties of active carbons obtained from walnut shells by chemical and physical activation

Piotr Nowicki, Robert Pietrzak [*], Helena Wachowska

Laboratory of Coal Chemistry and Technology, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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ABSTRACT

A technology of obtaining active carbon from common walnut shells is described. The effect of activation methods, temperature and heating mode on the surface properties has been tested. The resulting carbons were characterised by elemental analysis, low-temperature nitrogen sorption and determination of the number of surface oxygen groups. The sorption properties of the active carbons obtained were characterised by determination of nitrogen dioxide adsorption in dry conditions and the number of iodine adsorption.

The final products were microporous active carbons of well-developed surface area reaching to 2305 m^2/g and pore volume to 1.15 cm^3/g, showing diverse acid–base character of the surface. The results have shown that the important effect on the content and type of surface oxides generated on the active carbons surface have both the temperature and the method of activation. The results obtained in our study have proved that a suitable choice of the activation procedure for walnut shells can produce activated carbons with high capacity of nitrogen dioxide, reaching to 66 mg NO_2/g. The results of our study have also shown that the adsorption ability of carbonaceous sorbents depends on the method and procedure of activation as well as on their textural parameters and acid–base properties of their surface.

1. Introduction

The development of many branches of industry and the use of modern technologies that are accompanied by tougher and tougher requirements for environmental protection justify the ceaseless search for possibly cheap and most effective adsorption materials. Among many materials considered the most promising are active carbons, because of low cost of production and abundant resources as well as specific beneficial properties, such as: high mechanical and chemical resistance, ease of degradation of the used material and good ion-exchange properties.

Active carbons have been widely applied not only for selective adsorption of different pollutants from gas and liquid phase but also in catalysis (as direct catalysts or catalyst supports system for variety of reactions), in electrochemistry (for the manufacture of electrodes for electrochemical capacitors) or for gas storage [1–6].

The wide spectrum of their use is first of all a result of their unique physicochemical properties determined both by the very well-developed surface area and the type, number and bonding mode of different heteroatoms on their surface. Such heteroatoms can be oxygen, nitrogen or sulphur, which can essentially affect the acidic/basic or hydrophilic/hydrophobic character and change the adsorption, catalytic or electrochemical properties of active carbons [7–9].

Precursors for the manufacture of active carbons can be different carbonaceous materials, for instance wood, lignin, cellulose, peat and coals, beginning from brown coals and ending with anthracites [10–13]. The main reason for application of coals as precursor material is the high content of carbon and their primary porous structure, which permit getting materials of well-developed porous structure. Unfortunately, the pores present in natural coals are very small and they cannot be accessible to many adsorbates. Therefore coals must be subjected to carbonisation and/or activation. The activation of coals can be realized in two ways: physical method—using gas agents such as steam or carbon dioxide [14,15] or by chemical method—in which the precursor impregnated or mixed with an activating agent e.g. KOH, K_2CO_3, $ZnCl_2$, H_3PO_4, is subjected to the process of pyrolysis [12,16–18].

Economy and the measures aimed at the environment protection instigate the search for new precursors and new technologies for production of active carbon. For these reasons recently certain waste products have been used as precursors of active carbons, for example waste tyres, polymers and resins, as well as agricultural byproducts such as: nut shells, fruit stones,

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[*] Corresponding author. Tel.: +48 618291476; fax: +48 618291505.
E-mail address: pietrob@amu.edu.pl (R. Pietrzak).

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sawdust, sugar cane bagasse, corncobs, rice husks and straw [19–26]. The use of these raw products permits obtaining active carbons of new physicochemical properties and convert these waste materials to valuable products.

The objective of this paper was to obtain the series of active carbons from common walnut shells and physicochemical characterisation of the active carbons obtained. Different preparation parameters, particularly activation procedures, were examined in order to evaluate the influence of the activation conditions on the textural parameters and acid–base properties of the final product. Finally, we will correlate the surface properties with ability of active carbons to remove a nitrogen dioxide.

2. Experimental

2.1. Preparation of active carbons

The starting walnut shells WS (Ash = 0.9 wt.%, Moisture = 0.1 wt.%, volatile matter = 81.5 wt.%, C^{daf} = 48.2 wt.%, H^{daf} = 5.6 wt.%, N^{daf} = 0.2 wt.%, O^{daf} = 46.0 wt.%) were manually chosen, cleaned with distilled water and dried at 110 °C for 24 h. Then they were ground with a roller mill and sieved to a uniform size range of 1.5–2.5 mm. Next the crushed walnuts were subjected to carbonisation. The carbonisation (C) was carried out in a horizontal furnace under a stream of argon with a flow rate of 170 mL/min. The sample was heated (5 °C/min) from room temperature to the final carbonisation temperature of 400 °C. In the final temperature, sample was kept 60 min and then cooled in inert atmosphere. The carbonisate WSC (Ash = 2.6 wt.%, Moisture = 0.0 wt.%, Volatile matter = 23.2 wt.%, C^{daf} = 83.0 wt.%, H^{daf} = 3.9 wt.%, N^{daf} = 0.2 wt.%, O^{daf} = 12.9 wt.%) was then subjected to chemical activation (with potassium hydroxide) or physical activation (with carbon dioxide) at temperatures in the range 500–800 °C. Additionally, one part of the walnut shells WS was subjected to direct activation with CO_2. The preparation conditions and sample identification codes of the carbons are listed in Table 1.

The chemically activated samples were washed first with 5% solution of HCl and later with distilled water until the pH of the washed solution was about 6–7. The physically activated samples were rinsed only in distilled water. The washed active carbons were dried at 110 °C for 24 h.

2.2. Analytical procedures

The elemental analysis (C,H,N,S) of the starting walnut shells, carbonisate and active carbons were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

Characterisation of the pore structure of activated carbons was performed on the ground of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micrometrics Instrument Corp. (USA). Before the isotherm measurements samples were outgassed at 150 °C for 10 h. Surface area and pore size distribution were calculated by BET and BJH methods, respectively. Total pore volume and average pore diameter were determined as well. Micropore volume and micropore surface area were calculated using *t*-plot method.

The surface oxide functional groups were determined by the Boehm method [27].

Evaluation of NO_2 sorption capacity: the home designed dynamic test was used to evaluate NO_2 adsorption from gas streams [28]. Samples were packed into a glass column (length 350 mm, internal diameter 9 mm, bed volume 2 cm^3) and used as received. The bed density was calculated from quotient of the initial mass of the sorbent and the bed volume. Dry air with 0.1% of NO_2 was passed through the column of adsorbent at 450 mL/min. The breakthrough of NO_2 was monitored using electrochemical sensor. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of mg of NO_2 per g of adsorbent were calculated by integration of the area above the breakthrough curves, and from the NO_2 concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent.

The iodine sorption ability of the active carbon samples was determined according to the ASTM Standard [29]. To measure the adsorption capacity of the activated carbons in a powdered form, the granular samples were pulverized manually in a mortar.

3. Results and discussion

3.1. Preparation and characterisation of activated carbons from walnut shells

Elemental analysis of the active carbons obtained has shown that their elemental composition depends to a significant degree on the method and temperature of activation. The content of carbon varied from 75.3 to 94.8 wt.%, the content of hydrogen – from 0.4 to 3.4 wt.%, that of nitrogen – from 0.1 to 0.6 wt.% and that of oxygen – from 3.4 to 22.3 wt.%. As according to our earlier study [30], there is no clear correlation between the elementary composition of the unmodified active carbons and their sorption capacities towards NO_2, in this work no detail information on the

Table 1
Active carbon sample identification, description of activation methods and yield.

Sample	Activation conditions	Temperature [°C]	Heating rate [°C/min]	Time [min]	Yield [%]
WSCAKOH5	KOH:carbonisate wt. ratio = 4:1	500	–	30	45
WSCAKOH6	Ar flow: 330 mL/min	600	–	30	35
WSCAKOH7	Temp. = constant	700	–	30	32
WSCAKOH8		800	–	30	23
WSCAKOH4–5	KOH:carbonisate wt. ratio = 4:1	500	10	30	65
WSCAKOH4–6	Ar flow 330 mL/min	600	10	30	56
WSCAKOH4–7	Temp. = increasing from 400 °C to final activation temp.	700	10	30	45
WSCAKOH4–8		800	10	30	44
$WSCACO_25$	CO_2 flow:170 mL/min	500	–	60	75
$WSCACO_26$	Temp. = constant	600	–	60	72
$WSCACO_27$		700	–	60	71
$WSCACO_28$		800	–	60	70
$WSACO_25$	CO_2 flow 170 mL/min	500	10	60	21
$WSACO_26$	Temp. = increasing from 25 °C to final activation temp.	600	10	60	19
$WSACO_27$		700	10	60	17
$WSACO_28$		800	10	60	16

Table 2
Porous structure of the samples obtained by chemical activation.

Sample	Total surface area (BET) [m^2/g]	Micropore area [m^2/g]	Total pore volume [cm^3/g]	Micropore volume [cm^3/g]	V_{mic}/V_t	Average pore diameter [nm]
WSCAKOH5	490	479	0.25	0.23	0.92	2.00
WSCAKOH6	821	813	0.38	0.37	0.97	1.94
WSCAKOH7	1184	1176	0.57	0.55	0.96	1.92
WSCAKOH8	2305	2288	1.15	1.12	0.97	1.99
WSCAKOH4–5	1049	1039	0.51	0.50	0.98	1.95
WSCAKOH4–6	1398	1389	0.68	0.66	0.97	1.94
WSCAKOH4–7	2139	2124	1.04	1.02	0.98	1.95
WSCAKOH4–8	2263	2249	1.10	1.07	0.97	1.94

Table 3
Porous structure of the samples obtained by physical activation.

Sample	Total surface area (BET) [m^2/g]	Micropore area [m^2/g]	Total pore volume [cm^3/g]	Micropore volume [cm^3/g]	V_{mic}/V_t	Average pore diameter [nm]
WSCA$CO_2$5	165	162	0.08	0.07	0.88	2.01
WSCA$CO_2$6	379	355	0.18	0.17	0.94	1.93
WSCA$CO_2$7	437	433	0.22	0.21	0.95	2.00
WSCA$CO_2$8	469	456	0.25	0.23	0.92	2.14
WSA$CO_2$5	191	188	0.09	0.08	0.89	1.91
WSA$CO_2$6	356	352	0.17	0.16	0.94	1.92
WSA$CO_2$7	481	469	0.25	0.24	0.96	2.11
WSA$CO_2$8	697	677	0.37	0.34	0.92	2.14

elementary composition is given. Our main concern was to check the relation between the textural parameters and acid–base character of the active carbon surfaces and their sorption properties.

The surface area measured for the active carbon samples, presented in Tables 2 and 3, clearly illustrate a considerable influence of the activating agent, heating mode and temperature on the structure of the final product. The greatest effect on the surface area definitely has the method of coal activation. The chemically activated samples have much more developed surface area and porous structure than the samples activated by the physical method. The greatest surface area of 2305 m^2/g and the greatest total pore volume of 1.15 cm^3/g has WSCAKOH8 sample, while the least beneficial textural parameters has WSCA$CO_2$5 sample whose surface area is 165 m^2/g and the total pore volume is 0.08 cm^3/g.

These considerable differences in the specific surface area and the total pore volume between the samples obtained by chemical and physical activation of WSC carbonisate provide the evidence proving the differences in the intensity of the process of gasification by KOH and CO_2 and illustrating the influence of the method of activation on the reactivity of WSC carbonisate.

From among the chemically activated samples, the best textural parameters are achieved on activation of WSC carbonisate accompanied by a temperature increase from 400 °C to the final activation point. The surface area of thus obtained WSCAKOH4-X varies from 1049 to 2263 m^2/g, while the parameters of WSCAKOH samples obtained by the activation of the same carbonisate at a constant temperature are bit worse: S_{BET} varies from 490 to 2305 m^2/g.

This difference can follow from the fact that on heating of the mixture of WSC carbonisate with KOH from 400 °C to the final temperature of activation (500, 600, 700 or 800 °C) the particular stages of gasification take longer time and therefore not only the surface of the carbonisate grains undergoes gasification but also its deeper layers, so the porous structure of the active carbons obtained is better developed.

For the samples activated by the physical method (WSCACO_2 and WSACO_2), the mode of activation has some effect on the textural parameters, but the differences are not so much pronounced as in the chemically activated ones. Somewhat better are the textural parameters of WSACO_2 obtained by direct activation (S_{BET} 191–697 m^2/g) heated in the stream of carbon dioxide from room temperature to the final temperature of activation.

The difference between the textural parameters of WSCACO_2 and WSACO_2 could be explained by the fact that upon carbonisation of walnut shells their carbon structure undergoes ordering to some or even substantial degree and therefore, the carbonisate obtained becomes less susceptible to CO_2 and the porous structure is poorly developed. Upon activation of non-carbonised walnut shells ("direct activation") the time of contact between the carbon substance and the activating agent is much longer (similarly as for WSCAKOH4-X) so the final WSACO_2 have more beneficial textural parameters.

Another factor having important effect on the textural parameters of the activated carbons is the temperature of activation. With increasing temperature of activation (irrespective of the method of activation) the textural parameters of the carbon improve. The samples obtained at 800 °C have much better developed surface area and greater total pore volume than the samples activated at 500 °C. The differences are the most pronounced for WSCAKOH samples; the surface area of the sample activated in the highest temperature is almost five times greater than that activated in the lowest temperature. A possible explanation is that upon activation at 700 °C and even more at 800 °C, the intensity of gasification of WSC carbonisate is much higher than at 500 or 600 °C, so the process is more rapid and the porous structure becomes more developed. The lowest influence of the activation temperature on the textural parameters is observed for WSCAKOH4-X samples. The surface area S_{BET} of the sample activated at 800 °C (WSCAKOH4–8) is only twice greater than that of WSCAKOH4–5 activated at 500 °C.

The effect of the activation temperature on the textural parameters of the active carbons is also significant for the samples activated with CO_2; the samples activated at 800 °C show the surface area and total pore volume about three times greater than the samples activated at 500 °C. However, the differences are much smaller than for the samples activated with KOH.

According to the data presented in Tables 2 and 3, the active carbon samples obtained are characterised by microporous structure as the contribution of micropores in the total pore volume is over 88%. The highest contribution of micropores of 97–98% was found in WSCAKOH4-X samples obtained by chemical activation of WSC carbonisate accompanied by temperature increase from 400 °C to the final activation temperature. A bit lower contribution of micropores was noted in WSCAKOH samples obtained by chemical activation at a constant temperature. The least contribution of micropores of 88–95% was determined for $WSCACO_2$ samples obtained by physical activation of WSC carbonisate by carbon dioxide.

The microporous character of the chemically activated carbon samples was confirmed by the adsorption–desorption isotherms presented in Fig. 1A and B. Their shape is similar to that of the reversible isotherm type I, according to IUPAC classification assigned to microporous substances of small external area and much developed internal area. The majority of the isotherms have narrow and open hysteresis loops in the range of low pressures, whose shape is close to that of H4 loop according to IUPAC classification. The isotherms obtained for $WSCACO_2$ samples obtained by physical activation of the carbonisate (Fig. 2A and B) show certain deformations and wide hysteresis loops indicating the presence of a greater contribution of mesopores.

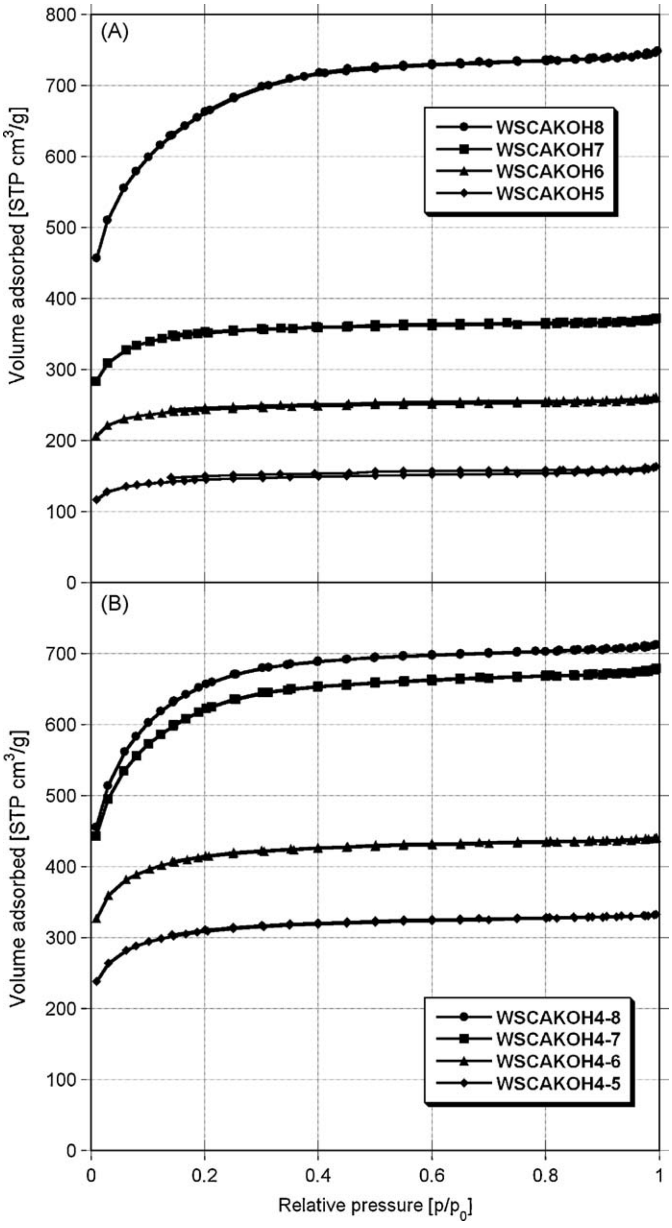

Fig. 1. Nitrogen adsorption isotherms of the samples obtained by chemical activation.

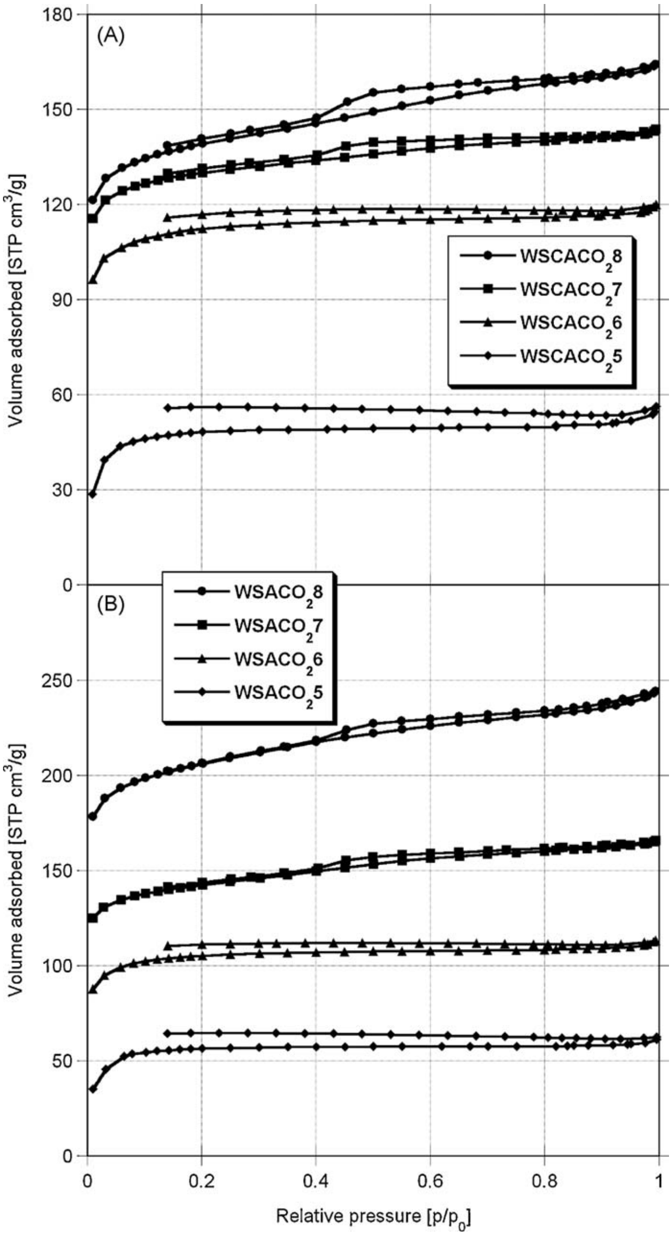

Fig. 2. Nitrogen adsorption isotherms of the samples obtained by physical activation.

To establish the acid–base properties of the activated carbon samples obtained, the contents of functional groups of acidic and those of basic character were determined. Analysis of the data collected in Tables 4 and 5 has shown that the activated carbon samples obtained are characterised by different content of surface oxygen functional groups; from 0.60 to 3.37 mmol/g. The content of the surface oxides is determined mainly by the method of activation. The carbon samples activated by the chemical method have much greater content of the surface oxygen groups than those activated by the physical method. The greatest content of the surface oxides of over 3 mmol/1 g of carbon was found in WSCAKOH5 and WSCAKOH4–5 samples, obtained by the chemical activation of WSC carbonisate, while the lowest content of the

Table 4
Acid–base properties of samples obtained by chemical activation.

Sample	Total content of surface oxides [mmol/g]	Acidic groups [mmol/g]	Basic groups [mmol/g]
WSCAKOH5	3.02	2.69	0.33
WSCAKOH6	1.68	1.31	0.37
WSCAKOH7	1.67	1.19	0.48
WSCAKOH8	1.64	1.00	0.64
WSCAKOH4–5	3.37	3.17	0.20
WSCAKOH4–6	2.54	2.19	0.35
WSCAKOH4–7	1.79	1.24	0.55
WSCAKOH4–8	1.64	1.00	0.64

Table 5
Acid–base properties of samples obtained by physical activation.

Sample	Total content of surface oxides [mmol/g]	Acidic groups [mmol/g]	Basic groups [mmol/g]
WSCACO$_2$5	0.60	0.10	0.50
WSCACO$_2$6	0.75	0.15	0.60
WSCACO$_2$7	0.82	0.12	0.70
WSCACO$_2$8	1.00	0.20	0.80
WSACO$_2$5	0.60	0.28	0.32
WSACO$_2$6	0.73	0.26	0.47
WSACO$_2$7	1.09	0.35	0.74
WSACO$_2$8	1.09	0.34	0.75

surface oxides of 0.6 mmol/g was determined in WSCACO$_2$5 and WSACO$_2$5 samples obtained by the physical activation of the WSC carbonisate and WS precursor. These results are in agreement with the data on the elemental composition if the carbon samples studied, in particular with a much greater content of oxygen in the samples activated with KOH than those activated with CO$_2$. This difference follows from the fact that gasification of the carbonisate grains upon chemical activation is much more intense and the surface of the grains undergoes oxidation to a significant degree. According to literature data [31] the increase of oxygen content is a result of KOH decomposition and the reaction of K$_2$O with the carbon, which is consistent with the mechanism of coal gasification upon the activation with alkalies.

The method of activation also affects the acid–base character of the surface oxides, not only their amount. The carbon samples activated by KOH (Table 4) contain more groups of acidic character than those activated by carbon dioxide (Table 5). The majority of chemically activated samples show distinctly acidic character of the surface. The most acidic of all samples are WSCAKOH4–5 and WSCAKOH5, containing 15 and 8 times more acidic groups than basic ones. The majority of the physically activated samples (obtained by both WS and WSC activation) show the prevalence of basic functional groups. The differences in the content of the acidic and basic groups are not so profound as for the samples activated with KOH. The most basic character was the surface of WSCACO$_2$7, containing over 5 times more basic than acidic groups. WSACO$_2$5 sample showed intermediate acid–base properties.

As follows from Tables 4 and 5, the temperature of activation also had a significant effect on the amount and type of the surface oxides (especially for the samples activated with KOH). The samples activated with KOH at 500 °C contain the greatest amount of acidic groups and the lowest amount of basic groups. An increase in the temperature of activation to 600, 700 or 800 °C leads to a significant decrease in the amount of groups of acidic character and an increase in the number of basic groups. The samples activated at 800 °C contain 2–3 times less acidic groups and 2–3 times more basic groups than the samples activated at 500 °C.

In the samples activated with carbon dioxide, the effect of temperature of activation on the content of the surface oxygen functional groups is much weaker, especially on the groups of acidic character. The number of groups of this type changes in a small range and it is difficult to note any general correlation between their number and the temperature of activation. Similarly as for the samples activated with KOH, the higher activation temperature favors generation of a greater number of basic groups. However, the differences in their number among particular samples are much smaller than for the samples activated by KOH.

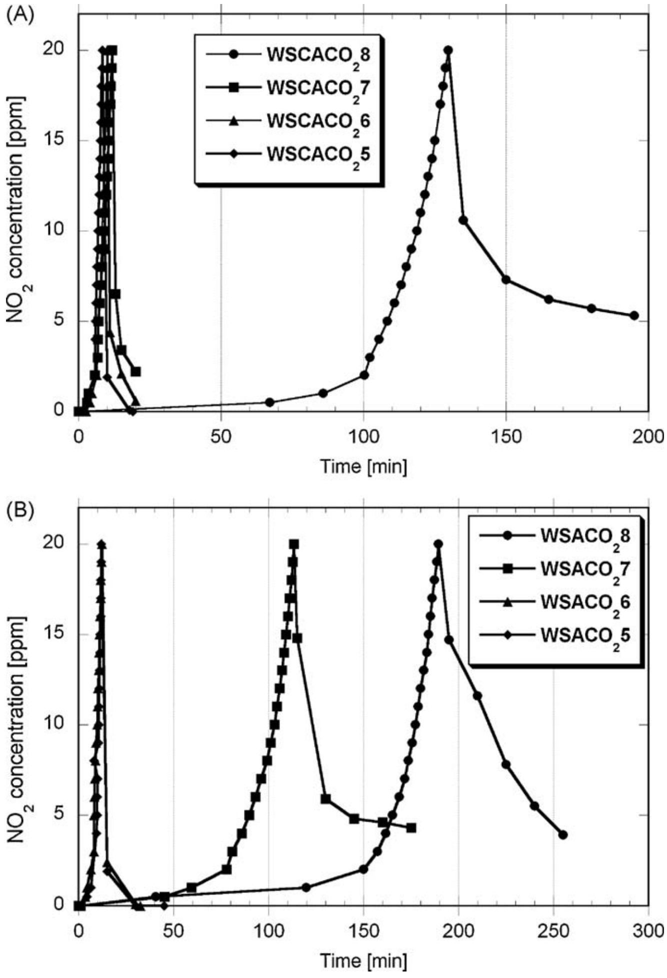

Fig. 3. NO$_2$ breakthrough curves for samples obtained by physical activation.

3.2. Nitrogen dioxide adsorption properties

The NO$_2$ breakthrough curves obtained for our materials are presented in Figs. 3 and 4. The shapes of the NO$_2$ breakthrough curves obtained for the samples activated by CO$_2$ (Fig. 3A and B) indicate the samples activated at the stage of carbonisate at 800 °C and at the stage of precursor at 700 and 800 °C show the best performance as NO$_2$ adsorbents. The shapes of the breakthrough curves obtained for the samples activated by KOH (Fig. 4A and B) are completely different. According to the shapes of the breakthrough curve, in the first step of the reaction the concentration of NO$_2$ in the outlet gas rapidly increases (especially for WSCAKOH4–7 and WSCAKOH4–8 Fig. 4B), followed by a slow down of the increase or even a decrease in the NO$_2$ concentration for WSCAKOH4–5 (Fig. 4B) followed by a steep rise in the NO$_2$. This shape is most probably related to the surface chemical character determined by the activating agent and the conditions of the activation process.

The calculated breakthrough capacities are presented in Tables 6 and 7. For the samples activated by CO$_2$ (Table 7) the

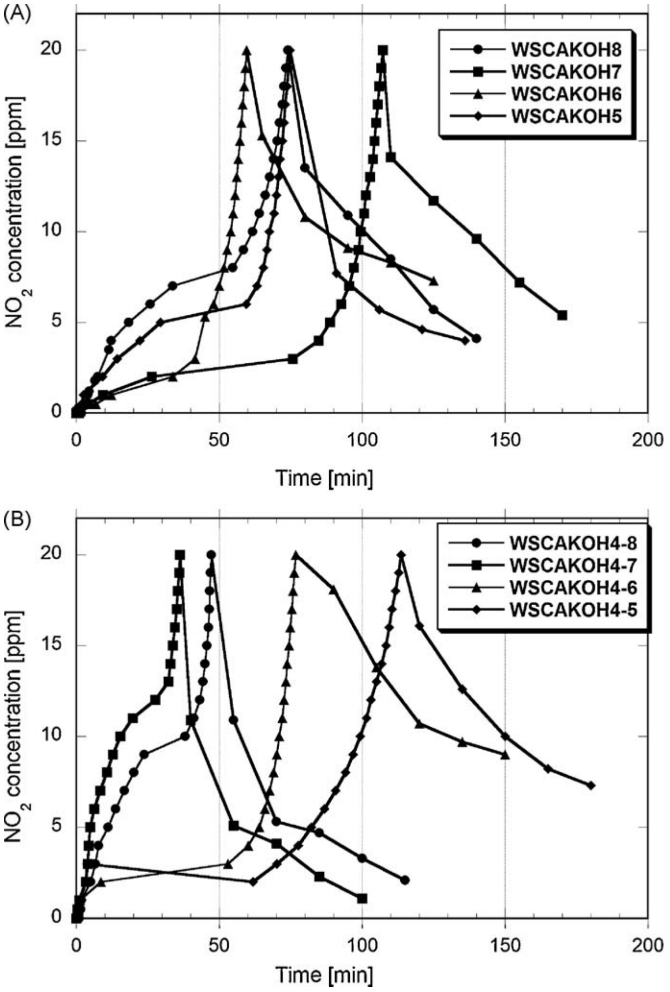

Fig. 4. NO_2 breakthrough curves for samples obtained by chemical activation.

Table 6
NO_2 breakthrough capacities and iodine adsorption of samples obtained by chemical activation.

Sample	NO_2 breakthrough capacity	
	mg/g of ads	mg/cm^3 of ads
WSCAKOH5	37.6	12.2
WSCAKOH6	36.5	10.8
WSCAKOH7	62.6	19.8
WSCAKOH8	66.3	10.7
WSCAKOH4–5	50.9	19.4
WSCAKOH4–6	47.2	13.9
WSCAKOH4–7	40.0	4.2
WSCAKOH4–8	54.8	6.5

largest breakthrough capacity is found for those activated at 800 °C ($WSCACO_28$ and $WSACO_28$). However, for the samples activated at the stage of the carbonisate (WSCA) only the one activated at 800 °C ($WSCACO_28$) shows significant NO_2 sorption capacity expressed in mg/g as well as in mg/cm^3. The other samples obtained in lower temperatures show very small and similar breakthrough capacity. Analysis of the NO_2 breakthrough capacity of the samples obtained by the precursor activation (WSA) shows that not only $WSACO_28$ sample activated at 800 °C having the greatest breakthrough capacity of all samples activated by CO_2, but also $WSACO_27$ sample activated at 700 °C shows very good sorption capacity.

Table 7
NO_2 breakthrough capacities and iodine adsorption of samples obtained by physical activation [mg/g].

Sample	NO_2 breakthrough capacity	
	mg/g of ads	mg/cm^3 of ads
$WSCACO_25$	2.0	1.5
$WSCACO_26$	3.5	1.8
$WSCACO_27$	3.7	1.9
$WSCACO_28$	33.8	24.5
$WSACO_25$	3.1	2.3
$WSACO_26$	2.7	2.1
$WSACO_27$	29.9	21.7
$WSACO_28$	58.1	37.8

Table 6 presents the calculated breakthrough capacities for the samples subjected to chemical activation by KOH. For the samples activated at constant temperatures, (WSCAKOH) the highest breakthrough capacity is found for the samples obtained at 700 and 800 °C (WSCAKOH7 and WSAKOH8). Interestingly, although the samples activated at 500 and 600 °C have almost 2x smaller NO_2 breakthrough capacity than those activated at 700 or 800 °C, still they show a very good capacity of over 35 mg/g and 10 mg/cm^3. All the samples activated with accompanying temperature increase (WSCAKOH4-X) show very good and similar breakthrough capacities expressed in mg/g, although there are considerable differences in the breakthrough capacity expressed in mg/cm^3 between WSCAKOH4–5, WSCAKOH4–6 and WSCAKOH4–7, WSCAKOH4–8. The differences are most probably a result of the physical properties, and first of all the bulk density of the samples. The bulk density of WSCAKOH4–5 is 0.38 g/cm^3, WSCAKOH4–6 is 0.30 g/cm^3, but WSCAKOH4–7 has the bulk density of 0.10 g/cm^3 and the bulk density of WSCAKOH4–8 is 0.11 g/cm^3.

According to the results the differences in the NO_2 breakthrough capacity of these samples follow mainly from differences in the total surface. However, analysis of our results does not bring a definite answer to the question which factor determines the sorption properties of carbons towards NO_2 to the greatest degree. As mentioned in Section 3.1, the active carbon samples activated with KOH show much better developed porous structure than those activated with CO_2 so the sorption properties of the former are much better. However, there is no direct correlation between the surface area and total pore volume and the NO_2 sorption, especially for WSCAKOH4-X.

Analysis of the data collected in Table 4 indicates that it is the chemical character of the surface of active carbons obtained by activation with KOH that determines their sorption capacity as these carbon samples have high content of oxygen functional groups, especially those of acidic character. Comparison of the data from Tables 4 and 6 reveals that the samples WSCAKOH8 and WSCAKOH4–8 with the greatest content of basic groups and the lowest content of acidic groups show the best sorption abilities. However, it is difficult to conclude the presence of which type of oxygen groups is more beneficial for the sorption abilities. It is the more difficult because the other carbon samples containing more groups of acidic character and less groups of basic character (in particular WSCAKOH4–5) also show very good sorption properties towards NO_2.

The sorption abilities of chemically activated samples can also be influenced by the type of the activating agent. According to literature data [32], KOH reacts with carbon leading to formation of hydrogen, metallic potassium and carbonates:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3.$$

When the active carbon surface is exposed to gas NO_2, the metallic potassium left after the activation can – in the presence of oxygen – react with NO_2 to give KNO_2, which could undergo further reactions according to the following equation [33]:

$$KNO_2 + NO_{2(g)} \rightarrow KNO_3 + NO_{(g)}$$

Analysis of the data presented in Tables 3 and 5 suggests that for the samples activated by CO_2, the NO_2 breakthrough capacity is determined not only by the total surface area but first of all by the type of the porous structure, the average pore diameter and the content of surface oxides. The samples $WSCACO_28$ and $WSCACO_28$ having similar values of the specific surface areas of 437 and 469 m^2/g, respectively, show much different sorption properties towards NO_2; the sorption capacity of $WSCACO_28$ towards NO_2 is nine times greater than that of $WSCACO_27$.

According to Table 3, only the samples with the average pore diameter above 2.1 nm ($WSACO_28$–2.14 nm; $WSACO_27$–2.11 nm; $WSACO_28$–2.14 nm) have high breakthrough capacity. It is known that the rate of gas diffusion is an important parameter characterising the process of gas adsorption, therefore, much greater sorption ability of $WSACO_28$ can follow from the fact that this carbon has a greater contribution of mesopores, greater mean diameter of pores and greater width (so also availability) of micropores (as indicated by the iodine numbers of these carbon samples, discussed in more detail in Section 3.3). Adsorption of nitrogen dioxide also depends on the chemical composition of the active carbon surfaces, in particular on the presence of the basic functional groups, whose presence favors sorption of gases of acidic character. However, it is difficult to estimate the effect of this factor for the carbon samples activated with CO_2 as the sample $WSCACO_28$ with only a little more basic and acidic groups on the surface than $WSCACO_27$, shows the sorption capacity nine times greater. Interpretation of the effect of the surface oxygen groups on the NO_2 adsorption is even more difficult in view of the fact that the samples $WSACO_27$ and $WSACO_28$, containing similar amounts of basic and acidic surface groups, show significantly different sorption capacities towards NO_2. It should be noted however, that these samples were obtained in a different way than $WSCACO_27$ and $WSCACO_28$ (without carbonisation), so the type of the oxygen groups generated upon activation can be completely different.

It should also be emphasized that the results on the sorption abilities of the carbon samples activated with carbon dioxide can hardly be compared with those of other works on NO_2 adsorption.

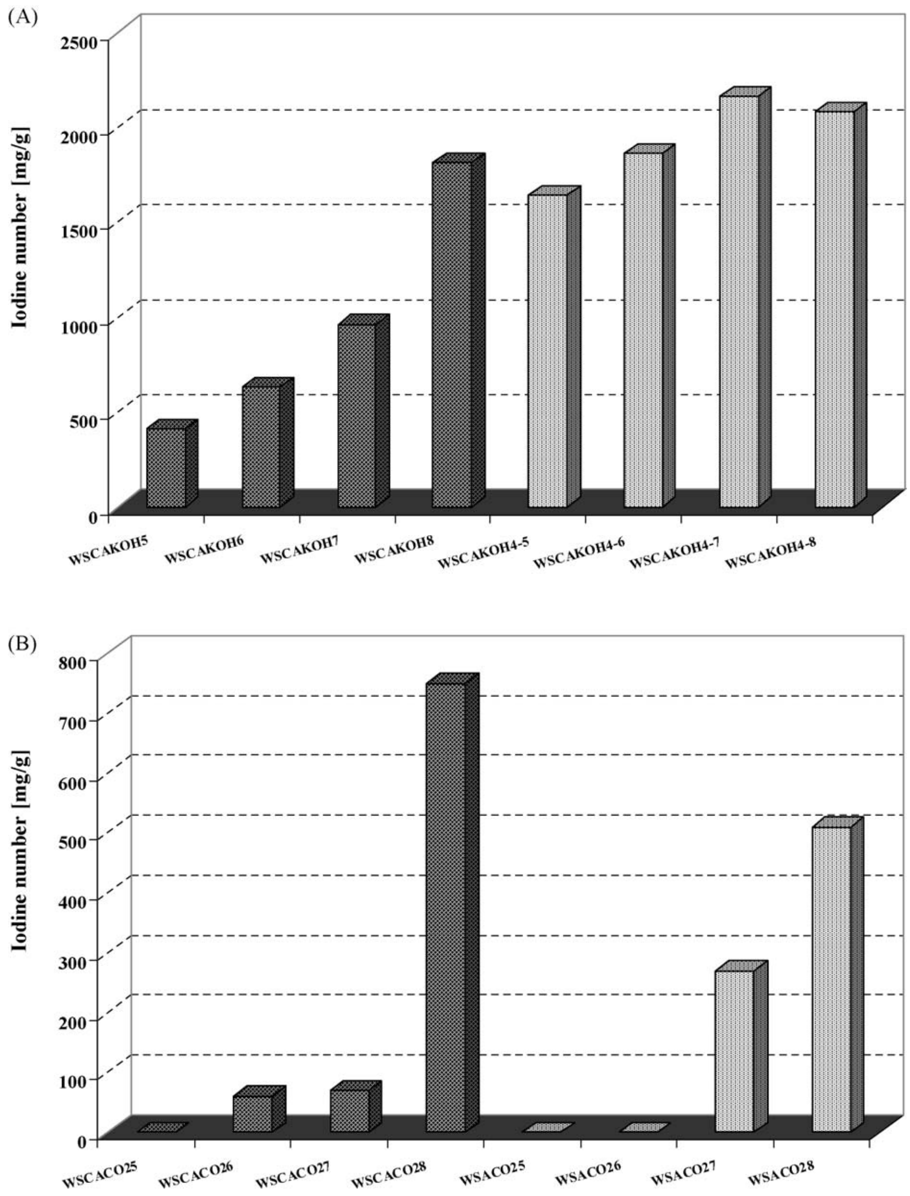

Fig. 5. Iodine number for active carbons obtained.

The problem is that the materials studied by other research groups were characterised by much better developed surface area and porous structure [28] or had much different chemical composition [33].

3.3. Adsorption value of iodine

To characterise the sorption properties from the liquid phase, the iodine adsorption number was determined for all samples. According to the data presented in Fig. 5, many samples are characterised by very good sorption capacities from the liquid phase as their iodine number exceed 2000 mg/g. The highest adsorption capacity from the liquid phase (from 1640 to 2160 mg/g) is found for WSCAKOH4-X samples obtained by chemical activation of the carbonisate WSC accompanied by temperature increase from 400 °C to the final activation temperature. The other samples activated with KOH proved much less effective adsorbents as their sorption capacity varied from 410 to 1810 mg/g. The least effective sorbents are the samples activated by carbon dioxide, in particular $WSCACO_25$, $WSACO_25$ and $WSACO_26$, showing practically no adsorption from the liquid phase.

The reasons for the very low iodine adsorption number of the samples obtained by activation with carbon dioxide most probably are the poorer textural parameters. As follows from the data collected in Tables 2 and 3, these carbon samples have much lower total pore volume and much poorer developed surface area than the analogous samples activated with KOH.

Another parameter of relative importance in the iodine adsorption is the temperature of activation. Irrespective of the method of activation, the adsorption capacity from the liquid phase increases with increasing temperature of activation, which is particularly pronounced for the samples WSCAKOH and $WSACO_2$.

4. Conclusions

The above-presented and discussed results permit drawing some important conclusions on the method of physicochemical and sorption properties of activated carbon obtained from walnut shells.

The textural parameters of the activated carbon samples obtained from walnut shell are determined by the method of activation and temperature of activation. The samples activated by KOH have much better textural parameters than those activated by CO_2. With the temperature of activation increasing from 400 to 800 °C (irrespective of the method of activation) the structural parameters of the samples improve. In all activated carbon samples obtained the dominant presence of micropores was established with a small contribution of mesopores. The lowest contribution of micropores was found in $WSCACO_2$ obtained by activation of the carbonisates by CO_2, whereas the greatest contribution of micropores was found in WSCAKOH4-X activated by KOH with temperature increased from 400 °C to the final activation temperature.

The content of the surface oxygen functional groups varied from 0.60 to 3.37 mmol/g. The content and type of the surface oxygen functional groups depended first of all on the method of activation. The samples activated with KOH show much higher content of the surface oxides and acidic surface character, whereas the samples activated with CO_2 show much lower content of the surface oxides and basic surface character.

For the samples activated with CO_2, the breakthrough NO_2 capacity depends mainly on the temperature of activation. The highest adsorption capacity was obtained for the sample activated at 800 °C ($WSCACO_28$–33.8 mg/g). From among the samples activated at the stage of precursor the best adsorbers were those activated at 700 ($WSACO_27$–29.9 mg/g) and 800 °C ($WSACO_28$–58.1 mg/g). All the samples activated with KOH show very good NO_2 sorption properties. However, it should be noted that the samples activated at constant temperatures (without temperature increase) at 700 and 800 °C (WSCAKOH7–62.6 mg/g and WSAKOH8–66.3 mg/g) show almost twice higher NO_2 breakthrough capacity than the samples activated at 500 and 600 °C (WSCAKOH5–37.6 mg/g and WSAKOH6–36.5 mg/g). The differences are much smaller for the samples activated on increasing temperature (WSCAKOH4-X) as their breakthrough capacities are similar.

Analysis of the sorption capacities from the liquid phase, described by the iodine number has shown that WSCAKOH4-X samples obtained by chemical activation of the carbonisate WSC on increasing temperature have the highest sorption capacity, while the least effective sorbents have proved the samples activated with CO_2, in particular $WSCACO_25$, $WSACO_25$ and $WSACO_26$ samples showing practically no sorption abilities from the liquid phase.

In general, the results presented and discussed in this paper indicate that the walnut shells are suitable precursor for obtaining cheap active carbon characterised by good sorption properties from gas and liquid phases. Explanation of the effect of different types of oxygen groups on NO_2 adsorption needs further studies e.g. by XPS, FTIR, TPD or TG combined with MS, which would permit detail interpretation of the roles of acidic and basic groups.

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