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Effect of activation method on the physicochemical properties and NO_2 removal abilities of sorbents obtained from plum stones (*Prunus domestica*)

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ABSTRACT

Carbonaceous adsorbents from plum stones were obtained by physical and chemical activation and used as nitrogen dioxide adsorbents. The effect of activation procedure on the physicochemical and sorption properties of active carbons was tested. The materials obtained were microporous active carbons of well-developed surface area varying from 373 to 2570 m^2/g and pore volume from 0.18 to 1.35 cm^3/g, showing different acid–base character of the surface. The results obtained in our study have proved that a suitable choice of the activation procedure for plum stones can produce activated carbons with high sorption capacity of nitrogen dioxide, reaching to 65.0 and 37.5 mg NO_2/g in dry and wet conditions, respectively. The sorption capacity towards NO_2 of the adsorbents obtained was proved to be determined mainly by the surface chemistry and the reactions taking place on the surface rather than by the specific surface area development.

1. Introduction

Increased emission of toxic gases being a consequence of rapid development of industry and related to it fast urbanization of many regions has recently become a serious threat to the natural environment. Particularly harmful gases emitted to the atmosphere are nitrogen and sulphur oxides, contributing to the appearance of acid rains and to destruction of the ozone layer. Rising standards of solutions concerning protection of the natural environment and the need for development of new environmentally friendly and advanced technologies have prompted the interest in all kinds of adsorbents.

Of particular importance is active carbons used not only as adsorbents [1–4] but also as catalysts [5–7], catalyst supports [8,9], electrode materials for electrochemical capacitors [10,11] or for hydrogen storage [12]. This wide use of the active carbon follows from its unique adsorption and catalytic properties related to the well-developed surface area, microporous structure and the presence of functional groups of different types on the surface.Active carbon can be produced from various precursors such as peat, lignin, wood, fruit stones and certain waste materials [13–17], however, their most important precursors are all types of fossil coals of different degree of coalification, from brown coals to anthracites [18–21]. The reasons for the use of these precursors are relatively low cost of production, easy accessibility and desirable physicochemical properties such as high mechanical strength, high chemical resistance, easy degradation of the used material and good ion-exchange properties.

From the ecological point of view, adsorbents obtained from waste materials such as sawdust, plastics or agricultural wastes make an excellent alternative to those produced from fossil fuels. It is a very interesting method of utilisation of wastes and their conversion into valuable products.

In view of the above, the aim of this paper was to obtain a series of adsorbents by physical (with CO_2) and chemical activation (with KOH) of plum stones and to examine the effect of different activation procedures on the ability of active carbons to remove a nitrogen dioxide in dry and wet conditions.

2. Experimental

2.1. Materials and preparation of adsorbents

The starting plum stones (*Prunus domestica*) (moisture = 1.3 wt.%, Ash^d = 0.4 wt.%, VM^{daf} = 80.6 wt.%, C^{daf} = 46.4 wt.%, H^{daf} = 5.5 wt.%, N^{daf} = 0.1 wt.%, S^{daf} = 0.0 wt.%, O^{daf} = 48.0 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 plum stones were subjected to carbonisation.

The carbonisation process (C) was carried out in a horizontal furnace under a stream of argon with a flow rate of 0.170 L/min. The sample was heated (5 °C/min) from room temperature to the final carbonisation temperature of 400 °C. In the

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Table 1
Active carbon sample identification and activation process conditions.

Sample code	Activating agent	Temperature (°C)	Heating mode, holding time
PCAc7 PCAc8	KOH	700 800	Constant temperature, time = 30 min
PCAc4-7 PCAc4-8	KOH	700 800	Temperature increasing 10 °C/min from 400 to 700 or 800 °C, time = 30 min
PCAp7 PCAp8	CO_2	700 800	Constant temperature, time = 60 min

final temperature, sample was kept 1 h and then cooled in inert atmosphere.

The char PC was then subjected to chemical activation (Ac) or physical activation (Ap) at temperatures in the range of 700–800 °C. Chemical activation by KOH was preformed with an alkali/char weight ratio of 4/1 for 30 min, in argon atmosphere (flow rate 0.330 L/min). Two modes of heating during activation were applied: (a) activation at constant temperature (samples were put into reaction zone heated to 700 or 800 °C and held in this condition for 30 min) and (b) activation accompanied by a temperature increase (10 °C/min) from 400 °C to the final activation point of 700 or 800 °C (samples were placed into reaction zone heated to 400 °C next heated to final activation temperatures and held in this condition for 30 min). Physical activation was carried out in a horizontal furnace under a stream of carbon dioxide with a flow rate of 0.170 L/min, for 60 min.

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 then 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. NO_2 adsorption experiments

The home designed dynamic test was used to evaluate NO_2 adsorption from gas streams [22]. Samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 3 cm^3) and used as received. Dry or wet air (75% humidity) with 0.1% of NO_2 was passed through the column of adsorbent at 0.450 L/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 milligram of NO_2 per gram 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. To check the NO_2 reduction, the concentration of NO was also monitored till 200 ppm (electrochemical sensor limit). All experiments were made in triplicate

2.3. Instruments and characterisation of the adsorbents

2.3.1. Analytical procedures

The elemental analysis of the initial plum stones, char and active carbons was performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany). All experiments of elemental analysis were performed in triplicate.

2.3.2. Porous structure

Characterisation of the pore structure of activated carbons was performed on the grounds of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micromeritics Instrument Corp. (USA). Before the isotherm measurements, the samples were out-gassed 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 the *t*-plot method.

2.3.3. Surface oxygen groups

The contents of surface oxygen functional groups were determined by the Boehm method [23,24]. All experiments were performed twice.

2.3.4. Measurement of surface pH

The pH of active carbons was measured using the following procedure: a portion of 0.4 g of dry active carbon powder was added to 20 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then pH of the suspension was measured.

3. Results and discussion

According to the results of proximate and elemental analysis, the raw plum stones used for the study were characterised by a high content of volatile matter (over 80 wt.%) and a low content of C^{daf} (below 50 wt.%) (Table 2). It is well known that a good precursor of active carbons should be characterised by high content of carbon, low content of mineral substance and low content of volatile matter. Therefore, the plum stones were at first subjected to carbonisation at 400 °C.

Changes in the elementary composition of the precursor are mainly as a result of high temperature. On heating, the least stable fragments of the coal structure (e.g. methylene and oxygen bridges) undergo decomposition leading to formation of the side products of carbonisation rich in hydrogen and oxygen, such as water and simple hydrocarbons.

Analysis of the elementary composition of the active carbon samples obtained (Table 2) shows that the process of activation (irrespective of the heating variant, temperature of activation and type of activating agent) leads to a further significant increase in the content of carbon and a decrease in the contents of hydrogen and oxygen, but has no significant effect on the content of nitrogen.

Table 2
Elemental analysis of the precursor, char and active carbons obtained and yield of carbonisation and activation processes (wt.%).

Sample	VM^{daf}	Ash	C^{daf}	H^{daf}	N^{daf}	$O^{daf\,a}$	Yield
P	80.6	0.4	46.4	5.5	0.1	48.0	–
PC	25.7	0.9	79.4	3.6	0.1	16.9	35
PCAc7	–	0.6	91.2	0.5	0.1	8.2	55
PCAc8	–	0.4	92.3	0.6	0.0	7.1	49
PCAc4-7	–	0.7	93.3	0.8	0.0	5.9	40
PCAc4-8	–	0.5	94.0	0.7	0.0	3.3	38
PCAp7	–	1.1	93.8	1.8	0.3	4.1	62
PCAp8	–	1.5	94.0	0.9	0.3	3.8	52

VM, volatile matter; daf, dry-ash-free basis.
[a] Determined by difference.

Table 3
Textural parameters of the active carbons obtained.

Sample	Total surface area, S_{BET} (m^2/g)	Total pore volume, V_t (cm^3/g)	V_{mic}/V_t	Average pore diameter, D (nm)
PCAc7	1796	0.89	0.96	1.98
PCAc8	2175	1.09	0.97	2.05
PCAc4-7	1888	0.91	0.98	1.92
PCAc4-8	2570	1.35	0.96	2.10
PCAp7	373	0.18	0.94	1.94
PCAp8	470	0.23	0.96	1.97

The surface areas measured for the active carbon samples, presented in Table 3, clearly illustrate a considerable influence of the activating agent, heating mode and temperature of activation on the porous structure of the final product. The greatest effect on the surface area definitely has the method of plum stones 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 2570 m^2/g and the greatest total pore volume of 1.35 cm^3/g has sample PCAc4-8 obtained by chemical activation accompanied by a temperature increase from 400 to 800 °C, while the least beneficial textural parameters has sample PCAp7 obtained by physical activation at 700 °C, whose surface area is 373 m^2/g and the total pore volume is 0.18 cm^3/g. The considerable differences in the textural parameters of samples obtained by chemical and physical activation clearly illustrate differences in the intensity of the process of gasification by KOH and CO_2 and show the influence of the method of activation on the reactivity of char obtained from plum stones.

The second 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 procedure of activation) the textural parameters of the active carbons improve. For the samples activated at a constant temperature (PCAc7 and PCAc8) the effect of temperature on the surface area development is smaller. This difference follows probably from the fact that on heating of the mixture of the carbonisation product PC with KOH from 400 °C to the final temperature of activation, the particular stages of gasification process take longer time and therefore not only the surface of the char grains undergoes gasification but also their deeper layers, so the porous structure of the active carbons obtained is better developed. 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 25% greater than the samples activated at 700 °C.

In order to characterise the chemical properties of the surfaces of the active carbon samples obtained, the contents of the surface oxygen functional groups of acidic and basic types as well as pH were measured. According to the data collected in Table 4, the amount of oxygen groups depends first of all on the method of activation. The greatest content of oxygen-containing functional groups of over 2.0 mmol/g of carbon was found in the samples obtained by activation of PC char accompanied by a temperature increase from 400 °C to the final activation point, while the lowest – about 1.0 mmol/g of carbon – in the samples obtained by physical activation. The content of the surface oxygen groups in chemically activated samples depends also on the mode of heating during activation. Somewhat lower amount of oxygen groups was determined in samples PCAc7 and PCAc8 obtained by activation of PC char at a constant temperature.

The results presented in Table 4 indicate that the method of activation also affects the acid–base character of the oxygen-containing functional groups, not only their amount. The samples activated with KOH show clearly prevalence of acidic groups, particularly sample PCAc4-7 which contains almost 3 times more acidic groups than basic ones, while the samples obtained upon activation with CO_2 contain similar amounts of basic and acidic groups. The most acidic character of the surface of pH 5.3 was found to show sample PCAc4-7, while the least acidic properties had sample PCAp8 whose pH was 8.5.

According to the data presented in Table 4, an important effect on the content and type of the surface oxygen groups generated on the active carbon surfaces also has the temperature of activation. An increase in the temperature of activation from 700 to 800 °C leads to a decrease in the amount of groups of acidic character and an increase both in the number of basic groups (especially for the PCAc4-X samples) and pH of the surface. However, for the samples activated with carbon dioxide, the effect of temperature of activation on the content of the oxygen-containing functional groups is much weaker, particularly on the groups of acidic character.

As follows from further analysis of Table 4, the basic groups present on the surface of the majority of the active carbons studied are probably strong bases. It is evidenced by the fact that inspite of comparable contents of groups of acidic and basic character, samples PCAp7 and PCAp8 have the surface pH of above 8. This supposition is also confirmed by the behaviour of sample PCAc4-8 containing more acidic groups than basic ones, whose pH is 7.1.

All the activated samples produced were tested for the NO_2 adsorption in dry and wet conditions. The results are collected in Table 5 and reveal that the active carbon samples obtained show different sorption abilities towards nitrogen dioxide, but they are generally greater in dry conditions. The greatest influence on the NO_2 adsorption by the active carbon samples studied in dry conditions has the method of activation. Chemically activated samples

Table 4
pH and content of the surface oxygen functional groups for active carbons obtained.

Sample	pH	Total content of surface oxides (mmol/g)	Acidic groups (mmol/g)	Basic groups (mmol/g)
PCAc7	5.8	1.98	1.36	0.62
PCAc8	6.4	1.85	1.20	0.65
PCAc4-7	5.3	2.14	1.55	0.59
PCAc4-8	7.1	2.06	1.17	0.89
PCAp7	8.2	0.94	0.49	0.45
PCAp8	8.5	1.04	0.43	0.61

Table 5
NO_2 breakthrough capacities of the active carbons obtained.

Sample	In dry conditions (mg/g_{ads})	In wet conditions (mg/g_{ads})
PCAc7	41.5	26.0
PCAc8	35.5	29.0
PCAc4-7	46.5	34.0
PCAc4-8	65.0	37.5
PCAp7	2.0	4.0
PCAp8	11.0	16.5

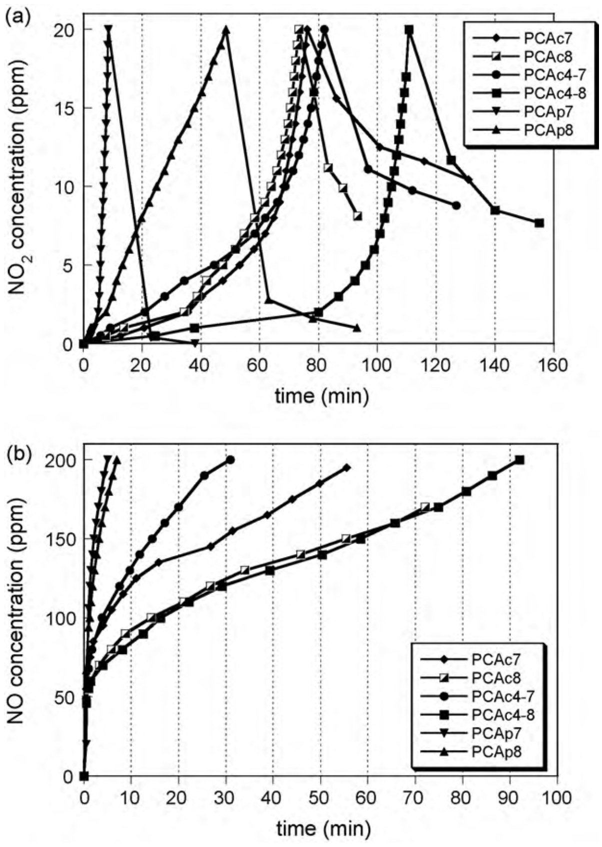

Fig. 1. NO_2 breakthrough curves (a) and NO concentration curves (b) for active carbons obtained studied in dry condition.

are able to adsorb several times greater amount of NO_2 than the active carbons obtained by physical activation. The greatest adsorption capacity in dry conditions (65 mg/g) was found for PCAc4-8 sample obtained by chemical activation of PC char accompanied by a temperature increase from 400 °C to the final activation point of 800 °C, while the least effective adsorbents, of sorption capacity much smaller than those of the other samples, proved PCAp7 and PCAp8, whose sorption ability towards NO_2 were only 2 and 11 mg/g, respectively. These considerable differences in the sorption abilities between the active carbons obtained by chemical and physical activation follow mainly from the fact that samples activated with potassium hydroxide have much more developed surface area and porous structure, than the active carbons obtained by activation with carbon dioxide (Table 3). The second reason for these differences could be the higher (about 2 times) content of the surface oxygen functional groups in the chemically activated samples (Table 4). Moreover, it should be noted that the active carbon samples obtained by chemical activation with increasing temperature (PCAc4-7 and PCAc4-8) are characterised by greater sorption abilities towards NO_2 in dry conditions than the commercial wood-based activated carbon BAX-1500 manufactured by Mead Westvaco [25].

The sorption ability of the samples activated by KOH depends also to a significant degree on the mode of heating during activation as the sorption capacities of the samples obtained by activation of PC char accompanied by temperature increase from 400 °C to the final activation point (especially PCAc4-8) are greater than those of analogous samples activated at a constant temperature. This dependence is probably a consequence of differences in porous structure development and surface oxygen groups content between PCAcX and PCAc4-X samples.

The third factor which influences the NO_2 adsorption by the active carbon samples studied is the temperature of activation. An increase in temperature of this process from 700 to 800 °C brings a considerable increase in the NO_2 breakthrough capacity, with the exception of samples PCAcX. This effect is particularly visible for the samples obtained by physical activation, as sample PCAp8 (activated at higher temperature) adsorbs 5 times more NO_2 than an analogous sample PCAp7, activated at 700 °C.

As already mentioned, the majority of the active carbon samples studied shows much poorer sorption capacities towards NO_2 in wet than in dry conditions. Only the samples activated with CO_2 adsorb greater amount of nitrogen dioxide in the presence of water. The greatest decrease in the adsorption capacity (by 42%), caused by the conditions of adsorption was found for PCAc4-8, while the smallest (by 18%) for PCAc8. Despite the fact that for the former sample we observed the greatest deterioration of sorption abilities, it shows the greatest adsorption of NO_2 in wet conditions (37.5 mg/g). The least effective adsorbent in the presence of water, similarly as in dry conditions, proved sample PCAp7, which adsorbed only 4 mg NO_2 per gram.

According to the data presented in Table 5, the sorption abilities of the active carbons studied in wet conditions (similarly as in dry conditions) are influenced first of all by the method of activation. The samples activated with potassium hydroxide show greater sorption capacity toward NO_2 (reaching from 26 to 37.5 mg/g) than those obtained by the activation with carbon dioxide. However, the differences between samples PCAc and PCAp are not so pronounced as it was observed in dry conditions. This observation suggests that in wet conditions the sorption capacities of the adsorbents obtained are determined not only by the porous structure development but also by the surface chemistry and the reactions taking place on the surface (e.g. reduction of NO_2 to NO, nitric acid formation).

Further analysis of the data collected in Table 5 indicates that the sorption abilities of active carbons studied depend also to some degree on the thermal conditions of the activation process. The increase in the temperature of activation from 700 to 800 °C caused an increase of NO_2 adsorption for all active carbons studied (especially for sample PCApX), but in contrast to the results for dry conditions, the differences between particular samples are not so large – only several milligram per gram. For the chemically activated samples, the heating mode during activation has greater effect on the sorption abilities than the temperature of activation.

Different sorption capacities of the same samples in different conditions indicate, that adsorption of NO_2 in dry and wet conditions takes place according to different mechanisms. This presumption is to some degree confirmed by the shape of the NO_2 breakthrough curves presented in Figs. 1 and 2, showing also the NO concentration curves, as nitrogen monoxide is known to be the product of surface reduction of NO_2, on carbonaceous adsorbents [26].

The shapes of the majority of NO_2 breakthrough curves of the samples exhausted in dry conditions (Fig. 1a) (with the exception of PCAp7 and PCAp8 samples) are considerably different from those recorded in wet conditions (Fig. 2a). The shape of the curves obtained in dry conditions (particularly for PCAc4-8 sample) is sim-

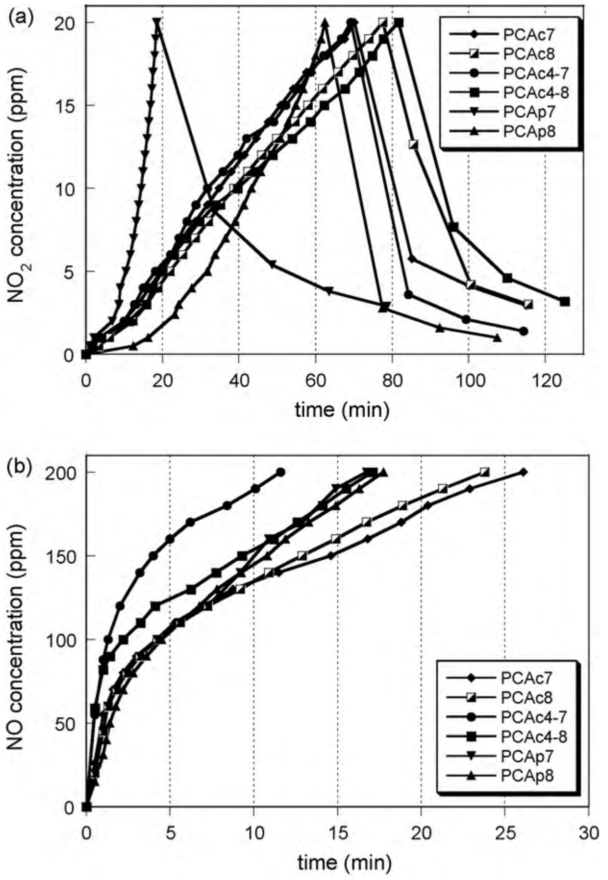

Fig. 2. NO_2 breakthrough curves (a) and NO concentration curves (b) for active carbons obtained studied in wet condition.

ilar to that of the breakthrough curve typical of the ideal adsorbent (with zero emissions for a relatively long period of time followed by a steep rise in the concentration of the emitted gas) and indicates that the activated samples obtained can be used as efficient adsorbents for NO_2 removal in such conditions. In wet conditions the shape of the breakthrough curves is close to a straight line which suggests not only a different mechanism of NO_2 adsorption but also lower usefulness for NO_2 adsorption purposes. The exception is sample PCAp8 (Fig. 2a), whose adsorption–desorption curve is close to that recorded for chemically activated carbons in dry conditions, which is probably responsible for their better sorption abilities towards NO_2.

On the basis of the shapes of the NO_2 desorption curves (Figs. 1a and 2a) it can be concluded that some part of NO_2 is weakly adsorbed and it is detected in the outlet gas when the source of NO_2 is disconnected. It is probably the reversibly physisorbed NO_2, which at this stage of the process is released from the carbon surface. This supposition is supported by results of Chughtai et al. [27], who studied the NO_2 adsorption at ambient temperature and proved that in such conditions about 10% of NO_2 is reversibly physisorbed, whereas the rest is chemisorbed. It should be emphasized that in the samples exhausted in wet conditions the concentration of NO_2 detected in outlet gas is lower.

The data presented in Figs. 1b and 2b also evidence that the active carbon samples studied show not only good sorption abilities towards nitrogen dioxide but are also capable of its reduction and/or adsorption as significant amounts of nitrogen(II) oxide are formed in the process of adsorption. This phenomenon is unfavourable for the natural environment as nitrogen(II) oxide formed is a serious threat to the atmosphere. On the basis of the shape of the curves from Fig. 1b and the data from Table 5 it can be concluded that the chemically activated samples, showing high sorption capacity towards NO_2 in dry conditions (i.e. PCAc4-8 and PCAc8), are also characterised by the low potential of NO_2 reduction to NO or by high adsorption capacity for NO, which is very important from the ecological point of view. On the contrary, the samples activated by CO_2 showing very high potential of $NO_2 \rightarrow NO$ reduction (or low adsorption ability for NO) are characterised by very poor sorption capacity towards NO_2. A possible explanation of this relation is that nitrogen(II) oxide forming in great amounts is subjected to competitive adsorption in pores or on the surface of carbons blocking the access to NO_2 molecules.

On the basis of comparison of the NO concentration changes presented in Figs. 1b and 2b, it can be concluded that in wet conditions the process of $NO_2 \rightarrow NO$ reduction is more effective than in dry conditions. This difference is particularly well pronounced for PCAc4-8 sample, which reached the maximum concentration of NO (200 ppm) about 5 times faster, than in dry conditions. The exceptions are PCAp7 and PCAp8 samples, on which the NO_2 reduction to NO is about 2–3 times more effective in dry conditions. The decrease in the potential of $NO_2 \rightarrow NO$ reduction of these samples, in comparison to that in dry conditions, may be responsible for their better sorption abilities towards NO_2.

In order to characterise the effect of NO_2 adsorption on the textural parameters and the chemical properties of the surfaces of the active carbon samples studied, all samples exhausted in dry and wet conditions were subjected to surface area measurements (Table 6) as well as determination of pH and surface oxygen groups content (Fig. 3).

On the basis of comparison of the data presented in Tables 3 and 6, it can be concluded that after adsorption the textural parameters of all samples deteriorate significantly, but the changes depend to significant degree on the conditions of adsorption. After adsorption in dry conditions, the surface area decreases by 51–73% and 20–61% for chemically and physically activated carbons, respectively, whereas the pore volume decreases by 22–74%. For the samples activated with KOH exhausted in wet condition the decrease in the textural parameters is less pronounced; surface area decreases by 52–62% and the pore volume by 53–64%. The opposite tendency, greater deterioration of textural parameters in wet than in dry conditions (S_{BET} by 59–70%, V_t by 57–61%) is

Table 6
Textural parameters of the active carbons after adsorption in dry and wet conditions.

Sample	In dry conditions			In wet conditions		
	S_{BET} (m^2/g)	V_t (cm^3/g)	D (nm)	S_{BET} (m^2/g)	V_t (cm^3/g)	D (nm)
PCAc7	491	0.23	1.92	676	0.32	1.92
PCAc8	795	0.38	1.95	918	0.44	1.96
PCAc4-7	924	0.44	1.91	908	0.43	1.91
PCAc4-8	989	0.48	1.98	1151	0.55	1.95
PCAp7	297	0.14	1.95	152	0.07	1.98
PCAp8	185	0.08	2.18	140	0.10	2.07

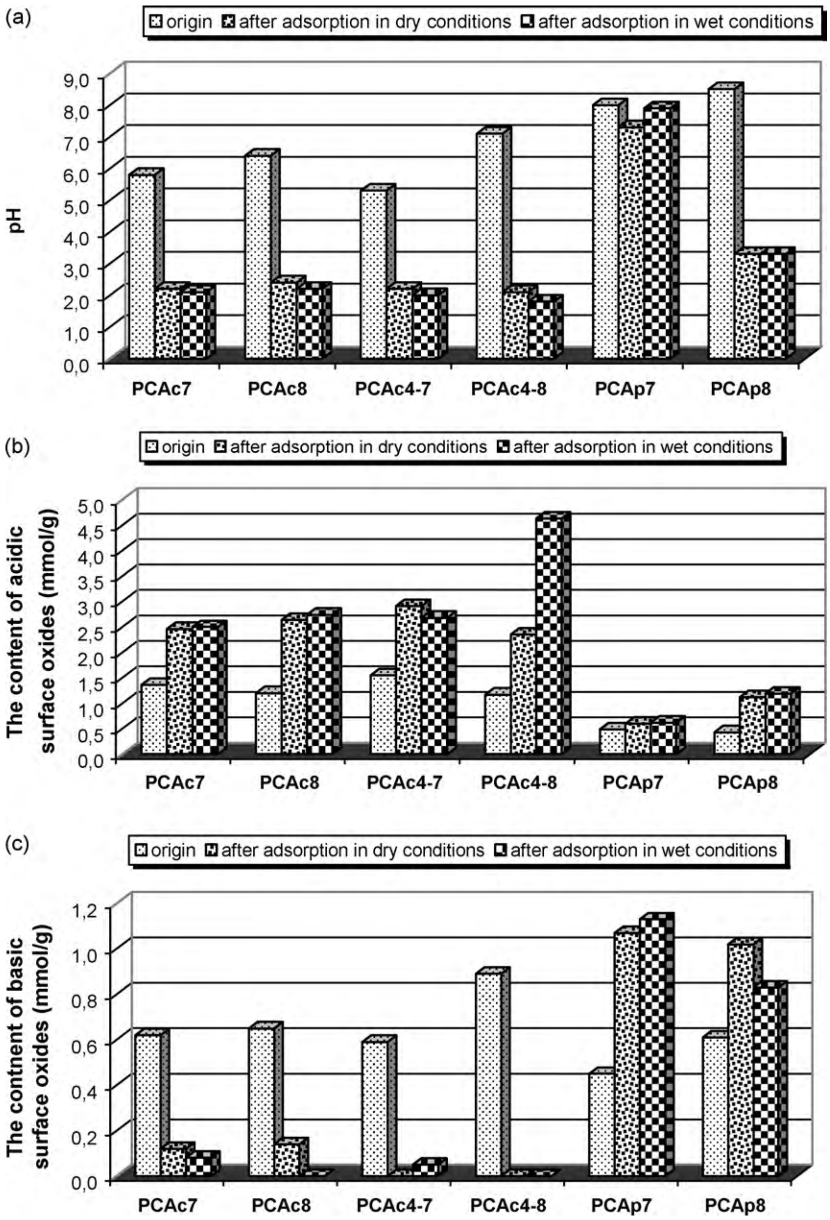

Fig. 3. The changes of pH of the surface (a), the content of acidic (b) and basic (c) surface oxygen functional groups after adsorption in dry and wet conditions.

observed for the samples activated by CO_2. The changes are caused probably by pore blocking by chemically adsorbed NO_2 and NO as well as by the changes in the content of surface oxygen functional groups taking place during the adsorption process (as a result of the surface oxidation).

For the samples exhausted in wet conditions, additional effect on the deterioration of the textural parameters of active carbons studied may have nitric acid formed in the presence of water, which can also block the pores or cause the oxidation of the surface. This fact can be responsible for the not large differences in deterioration of the surface areas and total pore volumes between the samples exhausted in dry and wet conditions, although we observed significant differences in their NO_2 adsorption capacities (Table 5).

As follows from the data presented in Fig. 3, adsorption of NO_2 causes also significant changes in the acid–base character of the active carbons surface. First of all we observed considerable decrease in pH value of the surface (Fig. 3a) (with the exception of PCAp7 sample) for the samples exhausted both in dry and wet conditions, which is a consequence of NO_2 and NO adsorption as well as nitric acid formation. The magnitude of pH changes is directly proportional to the active carbon sorption capacity towards NO_2. The comparable values of surface pH of the samples exhausted in dry and wet conditions (in spite of significant differences in their NO_2 breakthrough capacity) result probably from the fact that in wet conditions greater amounts of nitric acid are formed than in dry conditions.

According to the data presented in Fig. 3b and c, NO_2 adsorption causes also significant changes in the content and type of the surface oxygen-containing functional groups. For all samples exhausted in dry as well as in wet conditions, we observed significant increase in the content of surface oxygen groups of acidic character. This increase is particularly pronounced for chemically activated samples (PCAc), which show greater sorption capacity toward NO_2, than the physically activated carbons (PCAp).

A specific situation is observed for the surface oxygen groups of basic character (Fig. 3c). For the all samples activated by KOH we observed a drastic decrease in the amount of such groups, particularly for PCAc4-8 sample. It is probably an effect of reaction of basic oxygen groups with NO_2 or their neutralisation by nitric acid formed during adsorption process. In contrast, for the samples activated by carbon dioxide, we observed a significant increase in the content of surface oxygen-containing functional groups of basic character, especially for PCAp7 sample. It follows probably from the fact that the physically activated samples show considerably different acid–base properties (Table 4) as well as poorer adsorption capacity towards NO_2 (Table 5).

4. Conclusions

Analysis of the above presented and discussed results has shown that the textural parameters and acid–base properties of the active carbons obtained from plum stones are determined by the method, procedure and temperature of activation.

Moreover, the results have shown that the active carbons obtained from plum stones (especially by chemical activation with KOH) can be used as efficient adsorbents for NO_2 removal. The NO_2 breakthrough capacities obtained in dry and wet conditions prove that the presence of water decreases the NO_2 breakthrough capacity of the chemically activated carbons, but increases the sorption capacity of the physically activated carbon.

Analysis of the chemical properties of the surfaces and textural parameters of the samples obtained has shown that the sorption capacities of the adsorbents obtained towards NO_2 are determined to a great degree by the development of the surface area as well as the surface chemistry and the reactions taking place there.

Besides the high sorption capacities towards NO_2, the active carbon samples obtained are also capable of NO_2 reduction to NO and its adsorption.

The results have shown that a suitable choice of the activation procedure for plum stones can lead to producing active carbons with high adsorption ability of nitrogen dioxide.

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