

# NO<sub>2</sub> removal on adsorbents prepared from coffee industry waste materials

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**Abstract** A technology for obtaining carbonaceous adsorbents by physical and chemical activation of waste materials from coffee industry is described. The effect of pyrolysis temperature and type of activation procedure on the textural parameters, acid–base character of the surface and sorption properties of activated carbons has been tested. The resulting carbons were characterized by low-temperature nitrogen sorption, determination of pH and the number of surface oxygen groups. The sorption properties of the activated carbons obtained were characterized by evaluation of nitrogen dioxide adsorption in dry and wet conditions. The final products were adsorbents of specific surface area ranging from 5 to 2,076 m<sup>2</sup>/g and pore volume from 0.03 to 1.25 cm<sup>3</sup>/g, showing very diverse acidic–basic character of the surface. The results obtained in our study have proved that a suitable choice of the pyrolysis and activation procedure for coffee industry wastes permits production of adsorbents with high sorption capacity of nitrogen dioxide, reaching to 44.5 and 84.1 mg NO<sub>2</sub>/g in dry and wet conditions, respectively.

**Keywords** Activated carbon · Industrial waste materials · Chemical/physical activation · Nitrogen dioxide adsorption/reduction

## 1 Introduction

Everyday large amounts of harmful and toxic pollutants are released to the natural environment as a result of human activity. To curb their amount, numerous legal solutions have been proposed and new technologies aimed at minimisation of pollutants emission have been searched. One of such technologies is based on adsorption, a mass-exchange involving process, as a result of which gases, vapours or dissolved substances accumulate on the surface or in the porous structure of an adsorbent (Bansal and Goyal 2005).

The best known and commonly used adsorbents are activated carbons belonging to the group of carbonaceous materials showing strong sorption properties both from gas and liquid phase (Karagöz et al. 2008; Lach et al. 2008; Nakagawa et al. 2003; Przepiórski 2006). The activated carbons are microcrystalline porous materials characterised by large specific surface area per a mass unit, reaching even a few thousand m<sup>2</sup>/g (Lozano-Castello et al. 2001; Nowicki and Pietrzak 2011). Their internal structure is an intricate network of pores of diverse shapes and size.

The main precursors of activated carbons used on industrial scale are fossil coals of different degrees of metamorphism, timber, peat and coconut shells (Duggan and Allen 1997; Guo et al. 2009; Hsu and Teng 2000; Veksha et al. 2008; Wang et al. 2009; Yang et al. 2010). Literature provides many reports on obtaining activated carbon by physical and chemical activation of all kinds of waste materials of plant or industrial origin (Cabal et al. 2009; Chand et al. 2009; Nakagawa et al. 2003, 2004; San Miguel et al. 2002; Toles et al. 1999). Such solutions are appreciated not only from the ecological viewpoint but also for economical reasons (reduced cost of production). Moreover, it has been shown that some of the activated carbons obtained from waste materials show comparable or

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even better sorption properties than those obtained from traditional precursors.

The main aim of this study was to obtain a series of carbonaceous adsorbents from coffee industry waste materials and perform their physicochemical characterization. Different preparation parameters were examined in order to evaluate the influence of pyrolysis and activation conditions on the properties of the final product. Finally, we tried to correlate the surface properties with the ability of the activated carbons to remove nitrogen dioxide, which is a toxic and fast acting compound whose harmful effect is a few times greater than that of CO and SO<sub>2</sub>. In order to check the influence of the presence of water on the sorption abilities of the materials obtained toward NO<sub>2</sub>, adsorption measurements were conducted in dry and wet conditions.

## 2 Experimental section

### 2.1 Samples preparation

#### 2.1.1 Raw material

The starting material was coffee industry waste (C) in the form of cylinders of length 25 and 6 mm in diameter. After drying for 24 h at 110 °C it was subjected to pyrolysis (P) or direct activation processes (CAd).

#### 2.1.2 Pyrolysis

Pyrolysis process was carried out in a horizontal furnace under a stream of argon supplied at a flow rate of 0.170 L/min. The samples were heated at the rate of 10 °C/min from room temperature to the final pyrolysis temperature of 500 (P5) or 800 °C (P8). At the final temperature, the samples were kept for 60 min and then they were cooled down in an inert gas atmosphere. Pyrolysis products (CP5 and CP8, were split into cylinders of about 10 mm in length and 4 mm in diameter) and then subjected to chemical activation by KOH or physical activation with carbon dioxide.

#### 2.1.3 Activation

Chemical activation (Ac) was performed at 700 °C with an alkali:char weight ratio of 2:1, for 30 min, in argon atmosphere (flow rate 0.330 L/min). The obtained activated carbons were washed first with a 5 % solution of HCl and later with hot distilled water until free of chloride ions.

Physical activation (Ap) was carried out at 800 °C in a horizontal furnace under a stream of carbon dioxide with a flow rate of 0.250 L/min, for 30 min.

Direct activation of the precursor (Ad) was performed in the same conditions as physical activation. All samples activated by CO<sub>2</sub> were rinsed in distilled water and dried at 110 °C for 24 h.

### 2.2 Analytical procedures

Elemental analyses of all materials under investigation were performed on an elemental analyser CHNS Vario EL III. The content of ash and volatile matter was performed according to the Data National Standards ISO 1171:2002 and ISO 562:2000, respectively.

Characterization of the pore structure of chars and activated carbons was performed on the grounds of low-temperature nitrogen adsorption–desorption isotherms measured on Autosorb iQ surface area analyser manufactured by Quantachrome Instruments. Surface area and pore size distribution (from the adsorption branch of the isotherm) were calculated by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. To evaluate the total pore volume and average pore diameter, the criteria for cylindrical pores were used. Micropore volume and micropore surface area were calculated using *t*-plots method.

The acid–base surface properties were evaluated using potentiometric titration experiments using 809 Titrand equipment manufactured by Metrohm. Materials studied of about 0.1 g in 50 mL 0.01 M NaNO<sub>3</sub> were placed in a glass container thermostated at 25 °C and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric carbon dioxide, the suspension was continuously saturated with nitrogen. Volumetric standard HCl (0.1 M) and NaOH (0.1 M) were used as the titrants.

The pH of chars and activated carbons was measured using the following procedure: a portion of 0.2 g the sample of dry powder was added to 10 mL of demineralised water and the suspension was stirred overnight to reach equilibrium. Then pH of the suspension was measured.

Evaluation of NO<sub>2</sub> sorption capacity: The samples (in the form of granules of 0.75–1.5 mm in diameter) were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 3 cm<sup>3</sup>). Dry (D) or wet (M, 70 % humidity) air with 0.1 % of NO<sub>2</sub> was passed through the dry bed of the adsorbent at 0.450 L/min. The breakthrough of NO<sub>2</sub> were monitored using Multi-Gas Monitor Q-RAE PLUS PGM-2000/2020. The tests were stopped at the breakthrough concentration of 20 ppm, because of the electrochemical sensor limit. The capacities of each material in terms of milligram of nitrogen dioxide per gram of adsorbent were calculated by integration of the area above the breakthrough curves, and from the breakthrough time, NO<sub>2</sub> concentration in the inlet gas, flow rate as well as mass of adsorbent (Nowicki et al. 2010).

In order to check the NO<sub>2</sub> reduction as a result of its reaction with surface oxygen groups, the concentration of nitrogen oxide in the system (which is also very harmful compound) was monitored till 200 ppm (electrochemical sensor limit). All experiments were made in triplicate, using a new portion of the carbon sample each time.

### 3 Results and discussion

#### 3.1 Elemental composition of the chars and activated carbons

As follows from the data presented in Table 1, the coffee industry waste materials used are characterised with a low content of carbon (a little more than 40 wt %), very high content of volatiles (over 80 wt %) and a considerable content of mineral substances (ash). Because of these properties the waste material studied was a not attractive precursor of activated carbon. In order to increase the degree of coalification and to decrease the content of volatiles, the initial waste material was subjected to pyrolysis at two temperature variants at 500 or 800 °C.

Analysis of the data collected in Table 1 has shown that pyrolysis brings significant changes in the structure of initial material. Chars CP5 and CP8 have a much lower content of volatiles and a much greater content of carbon than the initial sample (C). Unfortunately, the content of ash also considerably increases. The intensity of these changes is greater in the sample subjected to pyrolysis at 800 °C. The increase in the pyrolysis temperature from 500 to 800 °C proved beneficial not only by increasing the coalification degree of the material obtained but also by leading to more pronounced changes in the content of the other heteroatoms present in the precursor structure.

**Table 1** Elemental analysis of the precursor, chars and activated carbons obtained and the yield of pyrolysis and activation processes (wt%)

Sample	Ash	VM	C <sup>daf,a</sup>	H <sup>daf</sup>	N <sup>daf</sup>	S <sup>daf</sup>	O <sup>daf,b</sup>	Yield
C	16.0	82.4	41.5	5.8	3.2	0.1	49.4	–
CP5	38.3	43.1	68.7	2.7	4.0	0.9	23.8	37.7
CP8	49.7	39.8	79.7	1.5	6.0	1.3	11.5	29.6
CAd	69.9	–	63.4	1.6	13.3	1.6	20.3	22.0
CP5Ac	1.7	–	84.4	1.0	2.2	0.1	12.2	25.5
CP5Ap	54.1	–	63.5	1.6	6.5	1.8	26.7	29.2
CP8Ac	1.2	–	87.9	0.6	1.3	0.0	10.2	69.2
CP8Ap	58.4	–	68.1	1.2	7.6	2.0	21.2	83.5

VM volatile matter

<sup>a</sup> Dry-ash-free basis

<sup>b</sup> Determined by difference

Sample CP8 shows a much lower content of hydrogen and oxygen than CP5 char and a greater content of nitrogen and sulphur. An increase in the content of N<sup>daf</sup> and S<sup>daf</sup> suggested that these elements occur in the precursor in the form of heterocyclic compounds resistant to elevated temperature and as the carbon substance has lost oxygen, the contribution of these heterocyclic compounds has increased.

The process of activation leads to further changes in the elemental composition dependent on the type of activation. The greatest changes were obtained as a result of direct activation of the precursor—sample CAd. The activated carbon obtained shows a much higher (by 21.9 wt %) content of carbon than the precursor, but the increase in the content of C<sup>daf</sup> is not as much as that observed as a result of pyrolysis, especially that at 800 °C. In samples CP5Ap and CP8Ap obtained by activation with CO<sub>2</sub> a decrease in the content of C<sup>daf</sup> (in comparison with the appropriate chars) by a few percent is observed, while in samples CP5Ac and CP8Ac obtained by activation with potassium hydroxide the content of C<sup>daf</sup> increases. The differences follow from different mechanisms of activation with these two agents (Marsh and Rodriguez-Reinoso 2006).

A certain influence on the content of C<sup>daf</sup> also has the temperature of pyrolysis as follows from the fact that the activated carbons obtained by (physical or chemical) activation of CP8 char show a greater content of C<sup>daf</sup> than those obtained by activation of CP5. Much less complicated are the changes in the content of hydrogen upon activation as all activated carbon samples show a lower content of hydrogen than the precursor and the chars. The most pronounced decrease in H<sup>daf</sup> is observed in sample CAd obtained by direct activation of the precursor because the processes of pyrolysis and activation take place simultaneously. For the samples obtained by activation of chars CP5 and CP8 a somewhat greater decrease in the content of hydrogen is observed as a result of activation with KOH. The changes of the hydrogen content also depend on the pyrolysis temperature.

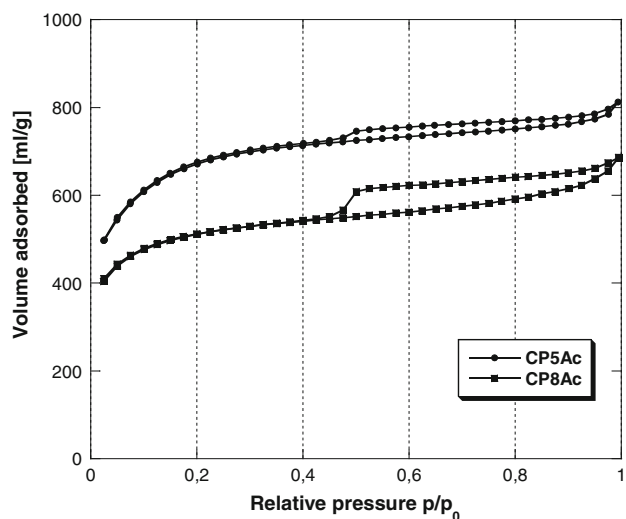
Activation also results in significant changes in the content of nitrogen, sulphur and oxygen. In sample CAd obtained by direct activation of the precursor, a significant increase in the contents of N<sup>daf</sup> and S<sup>daf</sup> relative to those in the precursor (C), follow from a considerable loss of volatiles and oxygen. The contents of N<sup>daf</sup> and S<sup>daf</sup> in the samples (CP5Ap and CP8Ap) obtained by physical activation of the chars also increase but not as much as in sample CAd. Physical activation also brings a significant increase in the content of oxygen relative to the relevant chars, which is a consequence of oxidation of their grains as a result of reaction with CO<sub>2</sub>. A different tendency in changes in the content of nitrogen, sulphur and oxygen is observed in the carbon samples obtained by chemical

activation (CP5Ac and CP8Ac). In these samples the content of nitrogen is much lower than in the chars and activated carbon samples obtained by physical activation and they do not contain sulphur. These facts suggest that the nitrogen and in particular sulphur groups present in the precursor have low chemical resistance to potassium hydroxide. As a result of chemical activation the content of oxygen decreases, in contrast to its increase in the samples activated with CO<sub>2</sub>, which confirms the earlier assumption about different mechanisms of reactions of these two agents with carbonaceous substance.

It should be noted that the activated carbon samples obtained significantly differ in the content of mineral matter. The content of ash (A<sup>d</sup>) substantially depends on the type of activation. It was the highest (A<sup>d</sup> of 69.9 wt %) in sample CAd obtained by direct activation of the precursor. In the samples obtained by physical activation of the chars, the content of mineral substance is 54–58 wt %, which is most probably a consequence of a rather high content of metal ions such as Al, Ca, Fe, K, Mn, Na, Rb, Sr, Zn detected in the precursor by ICP-OES method. In the samples obtained by chemical activation the content of ash is much lower than in the precursor. This observation can be explained by the fact that a considerable part of mineral substance undergoes decomposition in the reaction with potassium hydroxide and much is removed by the washing of the activation products with a 5 % HCl solution.

### 3.2 Textural parameters of the chars and activated carbons

Analysis of the data presented in Table 2 permits concluding that irrespective of the pyrolysis temperature, the chars obtained have a poorly developed specific surface area, ranging from 9 to 12 m<sup>2</sup>/g. The porous structure of both chars includes mainly mesopores as follows from high average pore diameter and the lack of micropores. Interestingly, the activation with CO<sub>2</sub> is also not favourable for development of porous structure. Only the sample obtained by direct activation of the precursor (CAd) shows a bit



**Fig. 1** Nitrogen adsorption isotherms of the chemically activated carbons

larger specific surface area and pore volume, but the values of these parameters are still much smaller than for the commercial activated carbon obtained by physical activation. One of the reasons for so poor textural parameters of the materials obtained probably is a very high content of inorganic substance, which can be deposited in the pores and block the access of the adsorbate to smaller pores. This situation can also follow from the fact that the parameters of the activation process (mainly the temperature of 800 °C) could be too drastic for the precursor applied, leading to combustion of a considerable part of organic substance and thus to destruction of the porous structure. This interpretation is based on a considerable increase in average pore diameter with respect to that of chars CP5 and CP8.

The situation is different for samples CP5Ac and CP8Ac activated with potassium hydroxide, whose specific surface area is 2,076 and 1,553 m<sup>2</sup>/g, respectively. In contrast to samples CP5Ap, CP8Ap and CAd, samples CP5Ac and CP8Ac not only have much developed porous structure with predominance of micropores (Fig. 1), but also a very

**Table 2** Textural parameters of the chars and activated carbons obtained

Sample	Surface area (m <sup>2</sup> /g)	Micropore area (m <sup>2</sup> /g)	External area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
CP5	9	0.1	8.7	0.022	~0	9.69
CP8	12	3.8	8.1	0.038	0.002	12.51
CAd	29	1.6	27.2	0.003	~0	5.76
CP5Ac	2,076	1,983	93.1	1.252	1.06	2.42
CP5Ap	5	0.4	5.0	0.030	~0	23.70
CP8Ac	1,553	1,404	149.1	1.061	0.76	2.74
CP8Ap	10	0.1	9.7	0.035	~0	14.53

low content of mineral substance (Table 1). Lower surface area and total pore volume of CP8Ac sample follow from the fact that this carbon has much more mesopores in its structure (formed as a result of broadening of small pores), as indicated by a greater average pore diameter and a hysteresis loop observed in nitrogen adsorption isotherm much greater than that recorded for the analogous sample CP5Ac (Fig. 1).

### 3.3 Acid–base properties of the chars and activated carbons

According to the data presented in Table 3, the materials obtained show a diversity of acid–base properties as can be concluded from the content of oxygen functional groups varying in the range 2.88–13.90 mmol/g and pH values varying from 4.4 to 12.7.

The content and type of oxygen functional groups depend first of all on the variant of activation. The greatest number of such groups is on the surface of carbon samples obtained by direct activation of precursor (CAAd) and physical activated chars (CP5Ap and CP8Ap)—on whose surface the number of such groups considerably exceeds 10 mmol/g.

High content of oxygen groups is also obtained for the chars, especially CP8. Much lower numbers of oxygen functional groups (only 2.88 and 3.25 mmol/g) are found on the surface of the carbon samples obtained by chemical activation. It is probably the effect of removal of a significant part of metal compounds present in the ash, during the acid washing step.

The number of oxygen functional groups also to some degree depends on the pyrolysis temperature. Char CP5 as well as the carbon samples obtained from its physical and chemical activation have a smaller content of oxygen groups than the analogous samples obtained from char CP8.

As mentioned earlier, the method of precursor modification also affects the type of oxygen groups formed. As follows from Table 3, the treatment of coffee industry waste materials at a high temperature and in carbon dioxide atmosphere leads to obtaining carbon materials with only basic functional groups on the surface. However, the samples obtained by chemical activation of the chars, have both acidic and basic groups on their surface and the acidic ones are dominant. The unexpectedly high content of basic functional groups on the surfaces of products of direct and physical activation can be a result of a high susceptibility of the precursor and chars obtained by its pyrolysis to the oxidation with CO<sub>2</sub>. Undoubtedly, such a strongly basic character of these materials is a consequence of the content of metal compounds present in the structure of the precursor, which undergo different transformations as a result

**Table 3** Acid–base properties of the chars and activated carbons obtained

Sample	Total content of surface oxides (mmol/g)	Acidic groups (mmol/g)	Basic groups (mmol/g)	pH
C	1.86	0.67	1.19	6.4
CP5	6.38	0.00	6.38	12.2
CP8	8.90	0.00	8.90	12.7
CAAd	13.90	0.00	13.90	11.9
CP5Ac	2.88	1.95	0.93	4.4
CP5Ap	10.25	0.00	10.25	12.0
CP8Ac	3.25	2.35	0.90	4.9
CP8Ap	11.32	0.00	11.32	12.4

of high–temperature treatment on pyrolysis or activation. The content of inorganic substances is much lower in the samples obtained by chemical activation, so probably that is why the number of basic oxygen groups on their surface is smaller.

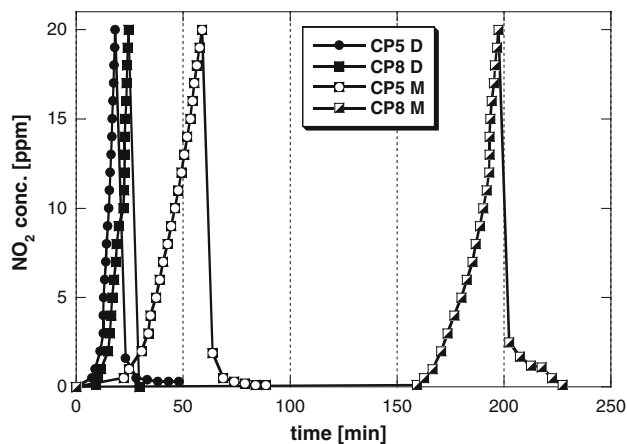
### 3.4 Sorption abilities of the chars and activated carbons toward nitrogen dioxide

High values of pH as well as the presence of a high number of oxygen functional groups on the majority of the samples obtained suggest that when applied as adsorbents they should show high affinity to pollutants of acidic character. In view of this expectation the main aim of this study was to evaluate the usefulness of the adsorbents obtained from the coffee industry waste materials in removal of nitrogen dioxide. Results of the relevant measurements are presented in Table 4 and in Figs. 2, 3 and 4 and prove that the chars and activated carbons show different sorption properties towards NO<sub>2</sub>.

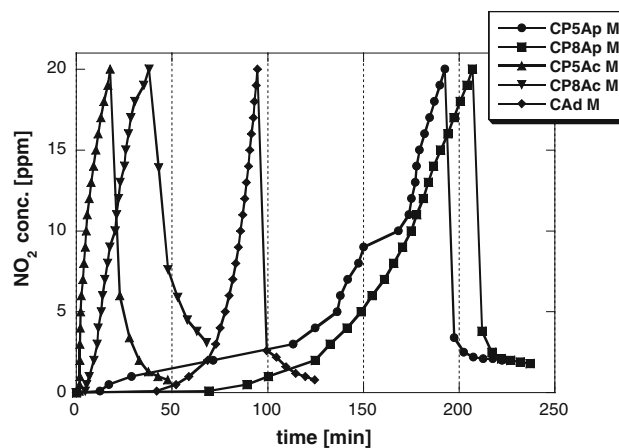
The effectiveness of nitrogen dioxide removal from a stream of gases depends significantly on the temperature of pyrolysis, variant of activation and the conditions of adsorption. All the chars and carbons obtained by

**Table 4** NO<sub>2</sub> breakthrough capacities of the chars and activated carbons obtained (mg/g<sub>ads</sub>)

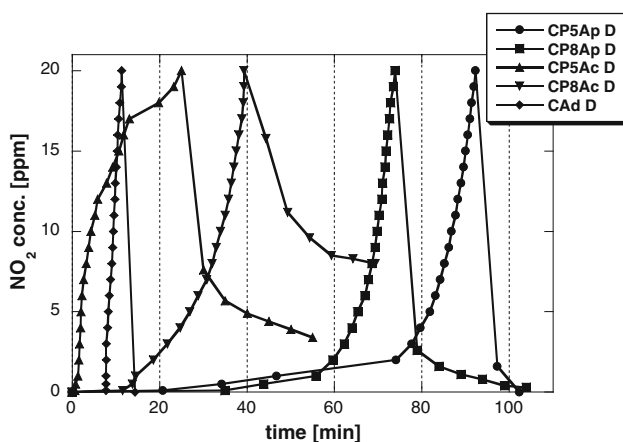
Sample	Dry conditions	Wet conditions
CP5	6.3	21.0
CP8	9.0	84.1
CAAd	3.4	31.8
CP5Ac	13.0	12.6
CP5Ap	36.4	65.8
CP8Ac	44.5	28.8
CP8Ap	31.9	76.0



**Fig. 2**  $\text{NO}_2$  breakthrough curves for the chars studied in dry (*D*) and wet (*M*) conditions



**Fig. 4**  $\text{NO}_2$  breakthrough curves for the activated carbons studied in wet (*M*) conditions



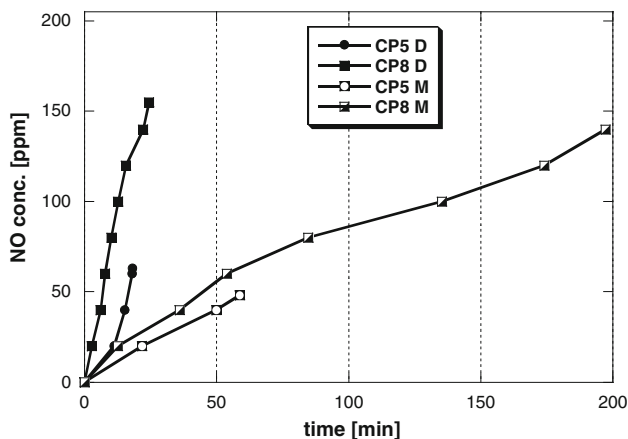
**Fig. 3**  $\text{NO}_2$  breakthrough curves for the activated carbons studied in dry (*D*) conditions

activation with  $\text{CO}_2$  show much better sorption performance in wet conditions, while those activated with potassium hydroxide—in dry conditions. The most effective adsorbent in dry conditions was CP8Ac obtained by chemical activation of CP8 char, whose sorption capacity in these conditions exceeded  $40 \text{ mg NO}_2/\text{g}_{\text{ads}}$ .

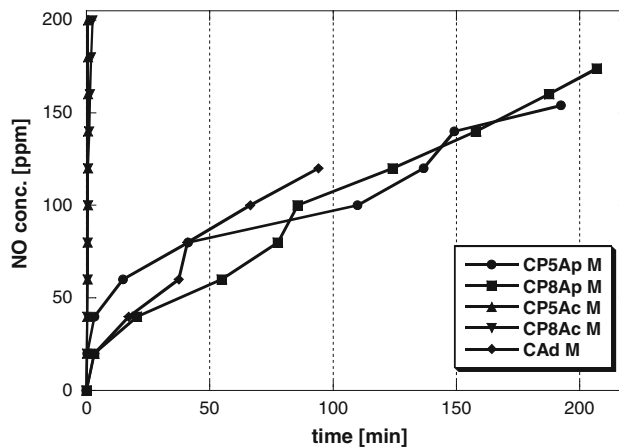
Unexpectedly, the highest sorption capacity in wet conditions was found for char CP8, whose sorption capacity towards  $\text{NO}_2$  was as high as  $84.1 \text{ mg/g}$ . High sorption capacities of  $65.8$  and  $76.0 \text{ mg NO}_2/\text{g}$  were also found for samples CP5Ap and CP8Ap, obtained by physical activation, respectively. In view of poor textural parameters of these samples (Table 2), their so high sorption capacities towards nitrogen dioxide are supposedly related to a high content of basic oxygen functional groups and mineral substance that can interact with  $\text{NO}_2$ , especially in the presence of steam.

The other materials, in particular those obtained by chemical activation, are much less effective in removal of nitrogen dioxide, and their sorption capacities vary in the range  $6.3$ – $36.4 \text{ mg/g}$ . For the chars obtained from coffee industry waste materials the effectiveness in  $\text{NO}_2$  removal from the stream of gases increases with increasing temperature of pyrolysis. It is particularly well pronounced when adsorption is realised in wet conditions, then the pyrolysis temperature increase from  $500$  to  $800 \text{ }^\circ\text{C}$  results in a fourfold increase in sorption capacity. The influence of pyrolysis temperature on the efficiency of  $\text{NO}_2$  removal is also manifested for the activated carbons obtained. Almost all samples obtained from CP8 char show much better sorption capacities than the analogous samples obtained by activation of CP5 char. Only sample CP8Ap upon adsorption in dry conditions shows somewhat poorer sorption capacity than CP5Ap.

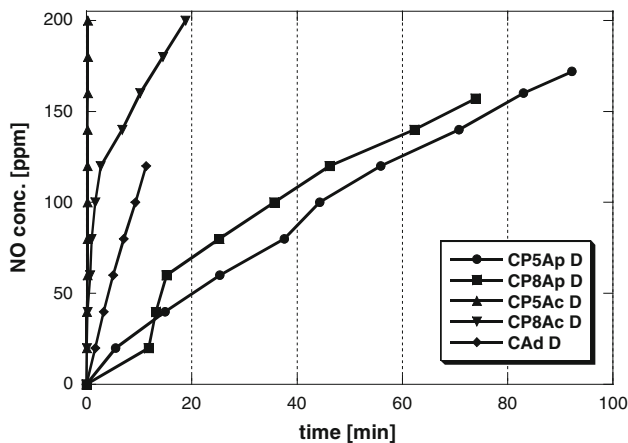
Plots 2–4 are the  $\text{NO}_2$  breakthrough curves recorded for the chars and activated carbons in dry and wet conditions. The majority of the curves have similar shapes, which suggests that  $\text{NO}_2$  adsorption on the materials obtained takes place according to similar mechanisms. For many samples studied for a long time the  $\text{NO}_2$  concentration is close to zero and the adsorption curve is almost parallel to the  $x$  axis. It is particularly well seen for the sample CP8 upon adsorption in wet conditions (Fig. 2), which as mentioned above shows the highest sorption capacity from among the samples obtained. Similar course of the adsorption curves was observed for activated carbons CP5Ap and CP8Ap, irrespective of the adsorption conditions. For the other adsorbents the adsorption curves are less smooth but for none of them a rapid increase in the nitrogen dioxide concentration to the threshold value of  $20 \text{ ppm}$  is observed in a short time. The steepest curves are obtained for the samples showing the poorest sorption capacity, i.e. CP5, CP8 (Fig. 2) and CAAd



**Fig. 5** NO emission curves for the chars obtained during NO<sub>2</sub> adsorption in dry (D) and wet (M) conditions



**Fig. 7** NO emission curves for the activated carbons obtained during NO<sub>2</sub> adsorption in wet (M) conditions



**Fig. 6** NO emission curves for the activated carbons obtained during NO<sub>2</sub> adsorption in dry (D) conditions

(Fig. 3) in dry conditions and CP5Ac in wet conditions (Fig. 4).

For the majority of samples, both in dry and in wet conditions, the concentration of NO<sub>2</sub> rapidly decreases after its supply has been cut off. This observation suggests that the majority of nitrogen dioxide adsorbed was strongly bonded by the functional groups on their surface or by metal ions in their structure, which means that most of NO<sub>2</sub> was chemisorbed on the carbonaceous materials studied. Only for the samples obtained by chemical activation of the chars (in particular upon adsorption in dry conditions) the concentration of NO<sub>2</sub> decreases very slowly and even after 30 min remains at a high level (5–10 ppm). This fact means that a large part of nitrogen dioxide is physically adsorbed by these samples, and therefore it is released upon washing with a stream of air. Because of the microporous character of these samples the release of the adsorbate is slow.

On sorption measurements the presence of nitrogen oxide was also recorded, which can be formed upon

reduction of NO<sub>2</sub> in a reaction with oxygen functional groups on the carbon sample surfaces. As follows from the character of the curves presented in Figs. 5, 6 and 7, the samples studied have different ability to reduce NO<sub>2</sub> to NO. The rate of nitrogen dioxide reduction significantly depends on the variant of precursor modification and the conditions of adsorption.

The reduction is most intense on the carbons obtained by chemical activation, which is evidenced by the fact that for samples CP5Ac and CP8Ac, the maximum NO concentration possible to measure by the sensor studied of 200 ppm, is reached in a very short time, especially if adsorption takes place in wet conditions. The lowest reduction potential had sample CP5 on which the NO concentration at the end of adsorption in dry and wet conditions was 63 and 48 ppm, respectively.

On char CP8 and carbon samples activated by carbon dioxide, the intensity of reduction is greater than for char CP5 (especially in dry conditions), but for none of these samples the NO concentration exceeds 180 ppm, throughout the adsorption measurements.

Greater reduction potential observed in dry conditions is most probably the reason for lower sorption capacity towards NO<sub>2</sub> as nitrogen oxide formed upon the NO<sub>2</sub> reduction can undergo a competitive adsorption and hence, block the access to pores and active centres to nitrogen dioxide. This supposition is supported by the fact that the samples obtained by chemical activation despite much developed specific surface area and porous structure, adsorb very small amounts of NO<sub>2</sub>.

#### 4 Conclusions

It has been shown that as a result of pyrolysis and different variants of activation, it is possible to obtain from coffee

industry wastes some adsorbents showing interesting physicochemical properties and—what is more important—good sorption capacity towards nitrogen dioxide. Depending on the variant of chemical and thermal treatment, the adsorbents show different elemental compositions, chemical character of the surface and different porous structures. As follows from the results of our study, particularly interesting are the adsorbents obtained by physical activation. Despite very unfavourable textural parameters, they show high effectiveness in NO<sub>2</sub> removal, both in dry and wet conditions, and do not emit large amounts of nitrogen oxide (formed by reduction of NO<sub>2</sub>) which is seriously harmful to the environment. Such surprisingly good sorption properties of physically activated samples surely are a consequence of the presence of metals in their structure. The results have also revealed that more attention should be paid to optimisation of the pyrolysis process conditions of the precursors, which is indicated by excellent results of adsorption tests of the product of pyrolysis at 800 °C, although the high sorption capacity was reached only in wet conditions.

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