

The Effect of Ammoxidation Process on NO₂ Sorption Abilities of Active Carbons

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The paper presents results of a study on obtaining N-enriched active carbons from Polish brown coal and on their use as adsorbents for removal of pollution from gas phase. The crushed precursor was subjected to carbonisation at 500, 600 and 700 °C in argon atmosphere. The chars obtained were activated by KOH at 800 °C. The active carbons were further subjected to the ammoxidation at 350 °C for 3 h, by a mixture of ammonia and air at the ratio of 1:3. The final products were microporous active carbons of well-developed surface area reaching to 2849 m²/g and pore volume to 1.49 cm³/g, showing mixed acid-base character of the surface. The results have shown that a suitable choice of the carbonisation, activation and ammoxidation procedures for brown coal can lead to obtaining activated carbons with high nitrogen dioxide adsorption ability, reaching from 16.9 to 36.4 mg NO₂/g.

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1. Introduction

Intense development of chemical industry, increasing number of motor vehicles and increased emission of products of fossil fuels combustion pose serious threat to the natural environment [1]. Particularly harmful is the pollution with nitrogen and sulphur oxides emitted to the atmosphere as their presence is related to smog, acid rains and destruction of the ozone layer. The problem of limitation of the gas pollutants emission is tackled in two ways. The first is to implement new highly-effective and environmentally friendly technologies, e.g. preliminary purification of raw products and air-tight control of industrial processes, while the second is to purify the outlet gases by adsorption, absorption or by catalytic reduction.

Of great importance in purification of post-production gases in dry conditions is active carbon that can be used as adsorbent, catalyst and catalyst support [2–4]. This wide use of 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. From among the carbon adsorbents used for removal of gas pollutants of acidic character the most promising are the nitrogen enriched active carbons. The presence of nitrogen functional groups of basic character in the structure or on the surface of active carbons significantly improves their sorption properties towards SO₂, NO_x or CO₂ [5–9].

The nitrogen-enriched active carbon can be obtained in a number of ways. The most often used is thermal treatment of carbon in the presence of nitrogen supplying agent such as ammonia, urea, melamine or nitrogen oxides [10–13]. Equally effective is carbonisation and activation of plastics including nitrogen groups in their structure, e.g. polyacrylonitrile, polyamides [14, 15]. Another effective method is deposition of amines and imines of different order (e.g. polyethyleneimine [16] or ethylene diamine [17]) on the carbon surface.

The study presented was undertaken to obtain nitrogen-enriched active carbon by the ammoxidation (simultaneous oxidation and nitrogenation) of brown coal, to establish the optimum preparation conditions of this material and to test the performance of the ability of such sorbents to remove nitrogen(IV) oxide in dry and wet conditions.

2. Experimental

2.1. Sample preparation

The starting raw sample (B) was prepared from a Polish brown coal from the Konin colliery. It was milled and sieved to the grain size of 2–4 mm. Then the crushed coal was subjected to carbonisation at 500, 600 and 700 °C in argon atmosphere for 1 h. The chars obtained (BC5, BC6 and BC7) were activated by KOH at 800 °C, at the weight ratio of char/KOH of 1:4, in argon atmosphere for 45 min. The active carbons (BC5A, BC6A and BC7A) were further subjected to the ammoxidation (N). This process was conducted at 350 °C for 3 h, by a mixture of ammonia and air at the ratio 1:3.

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2.2. Analytical procedures

The elemental analyses (C, H, N, S) of the products obtained at each stage of the processing 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 basis of low-temperature nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micrometrics Instrument Corp. (USA). The surface oxide functional groups were determined by the Boehm method. The pH of samples was measured using the following procedure: a portion of 0.4 g of the sample of dry char 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.

The evaluation of NO₂ sorption capacity was carried out according to the procedures described in [18]. The samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume between 1 cm³). Dry ("Ed") or moist (70% humidity) air ("Em") with 0.1% of NO₂ (accelerated test) was passed through the column with the adsorbent at 0.450 l/min for NO₂. The breakthrough of NO₂ and the concentration of NO were moni-

tored using Q-RAE PLUS PGM-2000/2020 with electrochemical sensors. The tests were stopped at the breakthrough concentration of 20 ppm. To check the NO₂ reduction, the concentration of NO was also monitored till 200 ppm (electrochemical sensor limit).

3. Results

3.1. Elemental composition of samples obtained

As follows from the data presented in Table I, carbonisation of brown coal brings essential changes in its elementary composition and the scale of the changes depends significantly on the temperature of the process. With increasing temperature of pyrolysis the contents of oxygen and hydrogen decrease, while that of carbon increases. Moreover, carbonisation of brown coal brings almost total removal of sulphur present in the precursor. Relatively small changes in the content of N^{daf} suggest that brown coal contains nitrogen in the form of thermally stable functional groups. Further analysis of the data presented in Table I also indicates that carbonisation leads to a significant decrease in the content of volatile matter and to an increase in the ash content.

TABLE I
Characteristics of the precursor and chars obtained at 500, 600 and 700 °C (wt%).

Sample	Yield	VM ^{daf}	Ash ^d	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf*}
B	–	53.6	28.0	63.4	4.9	0.7	2.0	29.0
BC5	76	24.2	35.4	73.9	4.0	0.7	0.1	21.3
BC6	70	18.3	37.2	79.5	3.0	0.6	0.1	16.9
BC7	59	10.7	41.6	86.3	2.3	0.6	0.0	10.8

*by difference

TABLE II
Yield and elemental composition of the active carbons obtained (wt%).

Sample	Yield	Ash ^d	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf*}
BC5A	19	14.6	90.9	0.6	0.2	0.0	8.3
BC6A	23	16.0	91.6	0.7	0.4	0.0	7.3
BC7A	31	15.5	95.6	0.7	0.6	0.0	3.1

*by difference

According to Table II, the process of activation leads to a further increase in the content of carbon and a decrease in the contents of the other elements, in particular nitrogen and hydrogen, relative to their presence in the initial chars (Table I). Much lower content of H^{daf}

in the active carbon is a consequence of gasification of the hydrogen-rich fragments of coal structure and aromatic structures formed upon carbonisation. The activation by KOH brings total removal of sulphur from the coal structure. The active carbon samples obtained

TABLE III

Yield and elemental composition of the nitrogen-enriched active carbons (wt%).

Sample	Yield	Ash ^d	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf*}
BC5AN	95	16.1	85.5	0.8	2.0	0.0	11.7
BC6AN	96	16.0	90.3	0.5	1.9	0.0	7.3
BC7AN	96	14.4	93.0	0.6	1.7	0.0	4.7

*by difference

have much lower contents of ashes than the initial chars (Table I). The lower content of ashes follows from the fact that some mineral substances present in the coal structure are removed upon activation (with KOH) and upon washing active carbon with a 5% solution of hydrochloric acid applied to eliminate excess of KOH and the side products of the reaction.

As follows from Table II, the efficiency of activation is determined by the temperature of carbonisation of the initial coal. The efficiency of activation of BC7 char obtained at 700 °C was much higher than those of BC6 and BC5 samples, carbonised at 600 and 500 °C, respectively. The reason can be much greater degree of ordering of BC7 char.

To determine the effect of nitrogen on the physico-chemical properties and sorption abilities of active carbon samples, they were subjected to ammoxidation, i.e. is to simultaneous oxidation and nitrogenation. The modified active carbons were subjected to elementary analysis whose results are collected in Table III.

These results imply that the ammoxidation of active carbon causes an increase in the contents of nitrogen and oxygen and a decrease in the content of carbon and hydrogen. As to the influence of the carbonisation temperature of the initial coal on the amount of nitrogen introduced, it slightly decreases with increasing pyrolysis temperature, however, the differences are small, which means

that the activation temperature (800 °C) has greater influence on the effectiveness of ammoxidation. After the thermal treatment at so high temperature, the reactivity of active carbon towards a mixture of air and ammonia is probably much lower as the amount of nitrogen built into the active carbon structure reached from 1.1 wt% of nitrogen for BC7AN to 1.8 wt% of nitrogen for BC5AN.

3.2. Textural studies of active carbons

As follows from Table IV, the chemical activation of BC5, BC6 and BC7 chars at 800 °C gives active carbon samples of well-developed surface area of over 2100 m²/g and the total pore volume of over 1.0 cm³/g. The data presented in Table IV also imply that the textural parameters of the active carbon samples obtained, such as specific surface area, total pore volume and total micropore volume, significantly depend on the temperature of carbonisation. The best textural parameters: specific surface area of 2849 m²/g, pore volume of 1.49 cm³/g and micropore volume of 1.38 cm³/g belong to sample BC6A, carbonised at 600 °C. All active carbon samples not modified with nitrogen (BCA) have porous structure with a dominant contribution of micropores. The ratio of the micropore volume (V_m) to the total pore volume (V_t) is in the range 87–96%.

TABLE IV

Porous structure of the active carbons obtained.

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_m/V_t	Average pore diameter [nm]
BC5A	2195	2168	1.14	1.10	0.96	2.07
BC6A	2849	2816	1.49	1.38	0.92	2.09
BC7A	2235	2147	1.24	1.08	0.87	2.22
BC5AN	1260	1210	0.68	0.59	0.87	2.17
BC6AN	1345	1294	0.72	0.62	0.86	2.14
BC7AN	2002	1954	1.01	0.91	0.90	2.20

Table IV also presents the textural parameters of the active carbon samples enriched in nitrogen (BCAN). Ammoxidation of the active carbon samples BC5A and BC6A considerably deteriorates their textural parameters. Samples BC5AN and BC6AN have much lower specific surface area (about 1000 m²/g) and lower total pore volume and micropore volume than the unmodified samples. The situation is somewhat different for sample BC7AN whose specific surface area and pore volumes are a bit smaller than those of the corresponding unmodified sample. The data from Table IV also reveal that the structure of nitrogen-enriched samples is substantially dominated by micropores. In the ammoxidised samples the contribution of micropores is lower than in non-ammoxidised samples and varies from 86 to 90%. The nitrogen-enriched samples have slightly greater average pore diameter than the unmodified ones.

3.3. Acid-base properties of active carbons

In order to characterise the chemical properties of the surfaces of the active carbon samples obtained (unmodified and modified), the contents of the surface oxygen functional groups of acidic and basic type as well as pH were measured.

The results presented in Table V indicate that the activation of brown coal chars gives active carbon samples with relatively high content of surface oxides, exceeding 2 mmol/g. The total content of the oxygen functional groups on the active carbon samples obtained significantly depends on the temperature of pyrolysis. It was the greatest for BC5A of 2.38 mmol/g, while the lowest for BC7A of 2.03 mmol/g.

TABLE V

Acid-base properties of active carbons obtained.

Sample	Acidic groups [mmol/g]	Basic groups [mmol/g]	Total [mmol/g]	pH
BC5A	1.78	0.60	2.38	6.21
BC6A	1.45	0.67	2.12	6.53
BC7A	1.10	0.93	2.03	7.06
BC5AN	1.57	1.04	2.61	8.88
BC6AN	1.40	1.25	2.65	9.08
BC7AN	1.08	1.46	2.54	9.11

According to the data from Table V, the temperature of carbonisation determines not only the total content of oxygen functional groups but also their acid-base character. All BCA samples show the dominant content of acidic oxygen groups, but with increasing temperature of pyrolysis the dominance decreases. From among the unmodified samples, the greatest prevalence of acidic functional surface groups was noted for BC5A, proved to have almost three times greater acidic (1.78 mmol/g) than basic (0.60 mmol/g) groups. The smallest prevalence of acidic groups was found for BC7A, containing 1.1 mmol/g of acidic groups and 0.93 mmol/g of basic groups.

As follows from pH results the active carbon samples were characterised by neutral (BC7A) or slightly acidic (BC5A and BC6A) surface character.

After exposing BCA samples to the reaction with a mixture of air and ammonia, both the content and type of the oxygen functional groups and pH of the samples' surfaces were changed. The nitrogen-enriched active carbon samples have only a little greater content of oxygen functional groups than the unmodified ones. Much greater differences are revealed in the acid-base character of the oxygen groups.

BCAN samples contain less acidic groups and much more basic groups than BCA samples. A significant increase in the content of acidic groups is probably a result of the presence of numerous oxygen–nitrogen complexes generated on the surface of the samples in the process of ammoxidation. Table V data also reveal that the ammoxidised carbon samples have much higher pH than the corresponding BCA ones, which is a consequence of the presence of much greater amount of the basic oxygen groups on the surface of the former and the presence of the nitrogen functional groups introduced upon ammoxidation.

3.4. Nitrogen dioxide adsorption

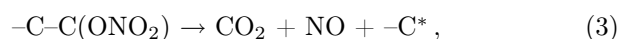
According to Table VI, from among the unmodified active carbon samples the greatest sorption capacity towards NO₂ of 30.4 mg/g was found for BC6A sample. The lowest capacity, almost twice lower than that of BC6A was determined for sample BC7A. Taking into regard the fact that BC6A is characterised by the best developed porous structure from among BCA samples and the fact that it shows the highest capacity for NO₂ adsorption suggests that the adsorption capacity of these samples depends much more on the textural parameters than on the chemical nature of the surface.

TABLE VI

NO₂ breakthrough capacities of active carbons in dry (Ed) and wet (Em) conditions.

Sample	NO ₂ adsorption [mg/g]	
	Ed	Em
BC5A	28.7	30.2
BC6A	30.4	35.7
BC7A	16.9	31.0
BC5AN	30.0	35.1
BC6AN	26.2	30.4
BC7AN	28.9	36.4

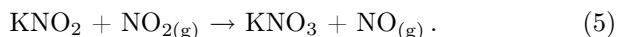
According to Jeguirim [19], the mechanism of NO₂ adsorption in dry conditions could be described as





where $-C^*$ are the active sites and $-C(O)$ are the carbon-oxygen complexes.

The adsorption capacity can be also influenced by potassium hydroxide used in the activation, which reacts with carbon leading to formation of hydrogen, metallic potassium and carbonates. Upon NO₂ adsorption, the metallic potassium left after the activation in the presence of oxygen can react with NO₂ giving KNO₂, which can further react according to the equation [20]:



Figures 1a and b present the NO₂ adsorption curves and NO concentration changes for the active carbon samples. The shape and course of the NO₂ adsorption curves obtained for the active carbon samples are very similar (Fig. 1a), which means that the mechanism of nitrogen dioxide sorption on all of them must be similar. The concentration of NO₂ in the outlet gas after the beginning of desorption rather quickly decreases but it does not reach zero. This observation can indicate that a great amount of NO₂ has been weakly adsorbed, in particular in sample BC6A.

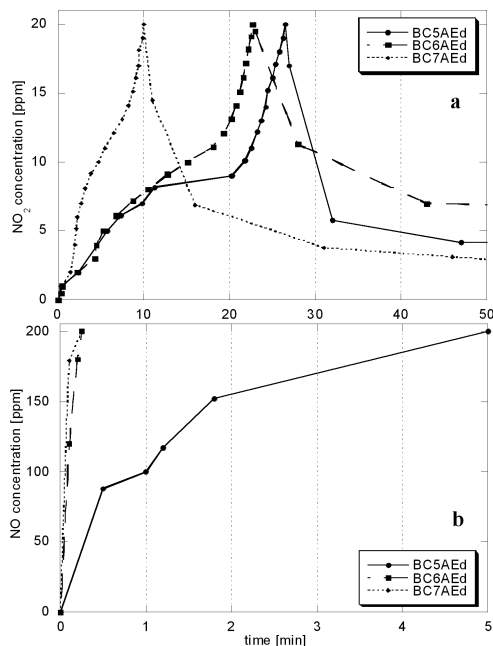
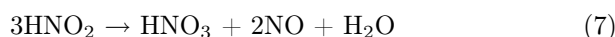
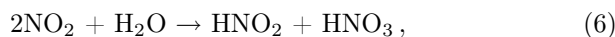


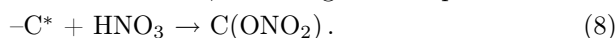
Fig. 1. NO₂ breakthrough curves (a) and NO concentration curves (b) for BCA samples in dry conditions.

The curves illustrating changes in NO concentration presented in Fig. 1b, inform about the process of NO₂ reduction to NO taking place on the active carbon surface. As follows from the course of the curves, the active carbon samples show rather great reducing potential towards NO₂. The greatest reducing potential has BC6A for which the maximum NO concentration of 200 ppm was reached in one minute, while the least effective NO₂ reduction occurred on BC5A.

The data from Table VI also imply that in wet conditions the sorption capacity of all BCA samples increases by 5–45% relative to that in dry conditions. The greatest adsorption capacity of NO₂ in wet conditions of 35.7 mg/g was noted for BC6A, whereas the greatest increase in adsorption relative to that in dry conditions was found for BC7A, whose adsorption capacity in wet conditions was almost twice greater than in dry ones. Greater sorption capacities in wet conditions most probably follow from a different mechanism of NO₂ adsorption. According to Jeguirim [19], the presence of water in the reaction environment can be responsible for the changed mechanism of adsorption. In the wet conditions the reactions



can lead to formation of a mixture of HNO₂ and HNO₃ acids and the nitric(V) acid formed can react with the active carbon surface, according to the equation



The shape and character of the NO₂ adsorption-desorption curves shown in Fig. 2a are considerably different from those recorded in dry conditions (Fig. 1a), which indicates differences in the mechanism of the adsorption process. The character of NO₂ adsorption curves recorded for BCA samples is similar, only for BC6A some differences are noted in the NO₂ concentration range 10–15 ppm, which can explain slightly greater sorption capacity of this sample. The shapes of desorption curves recorded for all BCA samples are also similar and prove that most of NO₂ has been strongly adsorbed.

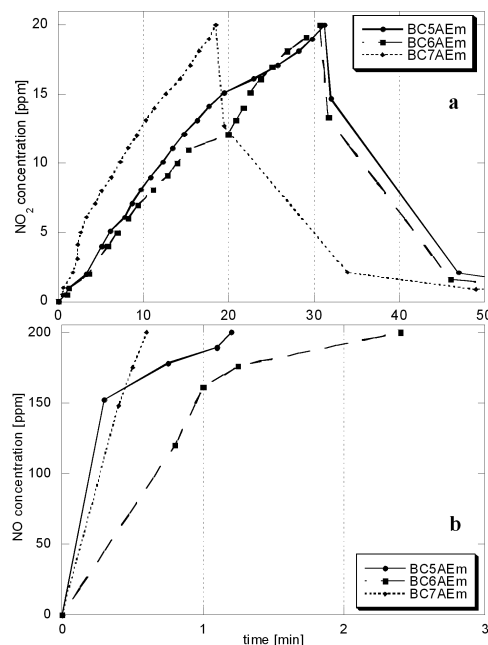


Fig. 2. NO₂ breakthrough curves (a) and NO concentration curves (b) for BCA samples in wet conditions.

The curves illustrating changes in the NO concentration, shown in Fig. 2b, imply that the active carbon samples studied have very high reducing potential also in wet conditions. The maximum concentration of NO for BC5A and BC6A samples is reached in about 1 min, while for BC7A in about 2–3 min.

The active carbon samples subjected to amoxidation (BCAN series) were subjected to analogous NO₂ sorption studies in the same conditions as the unmodified samples. The NO₂ adsorption–desorption curves and those illustrating changes in NO concentration obtained for the amoxidised samples are shown in Figs. 3 and 4, respectively, while the sorption capacity values are given in Table VI.

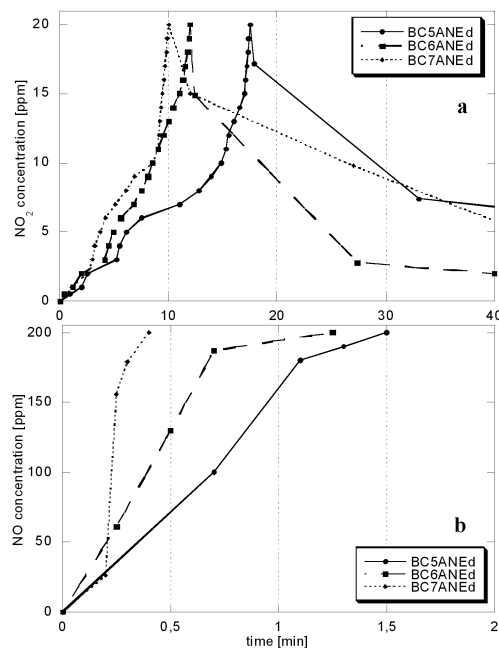


Fig. 3. NO₂ breakthrough curves (a) and NO concentration curves (b) for BCAN samples in dry conditions.

These results prove that the introduction of nitrogen to the active carbon samples leads to improvement of their sorption abilities both in dry and wet conditions. This improvement follows most probably from the fact that as a result of amoxidation numerous nitrogen and oxygen functional groups are generated on the surface of activated carbons and they act as active sites for NO₂ adsorption. Moreover, the presence of groups of these types, especially those of basic character, favours the reduction of nitrogen dioxide to nitrogen monoxide, which also contributes to the improvement of the sorption capacities of activated carbon towards NO₂. The greatest improvement in the sorption capacity in the dry and wet conditions by 12 mg/g and 5.4 mg/g, respectively, was noted for sample BC7AN. The improvement effect upon amoxidation was weaker for BC5A, while the introduction of nitrogen to BC6A brought deterioration of its sorption capacity towards nitrogen dioxide. This deteri-

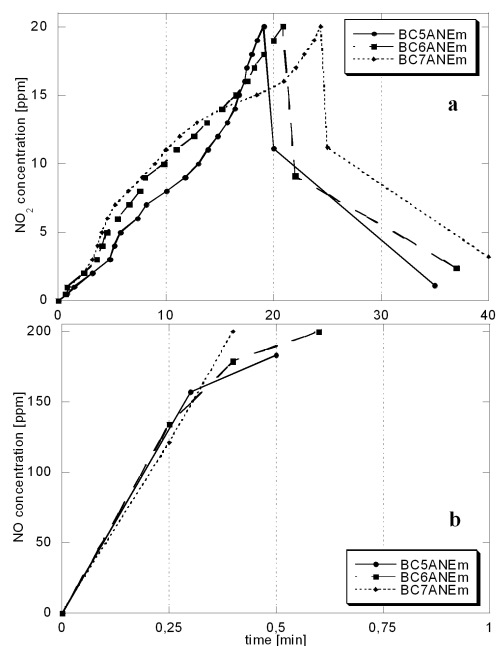


Fig. 4. NO₂ breakthrough curves (a) and NO concentration curves (b) for BCAN samples in wet conditions.

oration can follow from the fact that sample BC6AN was the only one for which no oxidation was observed to occur as a result of amoxidation (Table III), which could reduce its reactivity towards NO₂.

The adsorption–desorption curves recorded for the amoxidised samples and shown in Fig. 3a, have similar shape, which means that the mechanism of adsorption on them must be similar. The character of the NO₂ adsorption curves obtained for the amoxidised samples (BCAN) is slightly different from that of the curves recorded for the unmodified samples (BCA) (Fig. 1a). As follows from the desorption curves (Fig. 3a) after completion of adsorption in the first 20 min of desorption the concentration of NO₂ slowly decreases, in particular for sample BC7AN, which indicates that most of NO₂ has been weakly adsorbed.

A comparison of the curves illustrating changes in the NO concentration, presented in Fig. 1b and 3b, has shown that the reduction potential towards NO₂ of the amoxidised samples BCAN is similar to that of the unmodified samples BCA. Only BC7AN sample had much greater reduction potential towards NO₂ than the corresponding unmodified sample.

Figure 4a presents the NO₂ adsorption curves recorded for amoxidised active carbon samples in wet conditions. The similar shape of the curves in the adsorption and desorption sections proves that the mechanism of NO₂ adsorption on these samples is similar. A comparison of the curves from Fig. 2a (BCA) and 4a (BCAN) reveals that the introduction of nitrogen into the active carbon samples does not cause significant changes in the mechanism of adsorption in the wet conditions. As follows from

the desorption curves after the completion of adsorption the concentration of NO₂ rapidly decreases in a few minutes from the beginning of desorption, which means that most of NO₂ has been strongly adsorbed in contrast to the situation for dry conditions.

The character of the curves illustrating changes in the NO concentration, Fig. 4b, proves that the ammoxidised brown coals are capable of effective reduction of NO₂ also in wet conditions. The greatest surface reduction potential was obtained for sample BC6AN, while the lowest for sample BC5AN.

4. Conclusions

Activation of brown coal chars by KOH leads to obtaining active carbon of strongly developed surface area of over 2100 m²/g with the domination of micropores. The textural parameters of the active carbon samples obtained significantly depend on the temperature of carbonisation.

The process of ammoxidation results in the introduction of new nitrogen functional groups in the structure of the active carbon but also changes the acid-base character of their surface and deteriorates their textural parameters.

Introduction of nitrogen in the active carbon structure leads to increase in the sorption capacity of the majority of the samples both in dry and wet conditions.

Sorption capacity of NO₂ of the unmodified active carbon samples as well as the nitrogen-enriched samples is much greater in the wet conditions.

Acknowledgments

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