

## REMOVAL OF NO<sub>2</sub> ON MODIFIED CARBONACEOUS ADSORBENTS

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### **Introduction**

In recent years emission of toxic gases to the atmosphere creates a very important worldwide environmental problem. Nitrogen oxides, NO<sub>x</sub> are the group of the most environmentally detrimental species. They are emitted to the atmosphere mainly from power plants where fossil fuel is burned and from exhaust gases of automobiles. Their chemical reactivity is of the great importance in atmospheric chemistry because NO<sub>x</sub> (including NO and NO<sub>2</sub>) contribute to the acid rain, photochemical smog, depletion of the stratospheric ozone layer, and global warming. Moreover the presence of these gases in the air affects human health (Lee et al., 2003). It is well known that although a main component of NO<sub>x</sub> is NO NO<sub>2</sub> is much more harmful. It is formed in the atmosphere as a result of photochemical oxidation of NO (Shirahama et al., 2002) and directly in automobiles engines where even up to 30% of NO<sub>x</sub> can be emitted as NO<sub>2</sub> (Tabor et al, 1994). Therefore, continuous control and minimization of NO<sub>x</sub> emission is an important issue.

Adsorption and reduction of NO<sub>2</sub> has been a subject of interested of various research groups. Studies of these processes have been performed with many different carbonaceous materials including soot (Azambre et al., 2006; Muckenhuber and Grothe, 2007), carbon black (Jeguirim, 2004; Muckenhuber and Grothe, 2007), char (Kong and Cha, 1996), activated carbon fibers (Shirahama et al., 2002), carbon nanotubes (Ellison et al., 2004) and activated carbon (Lee et al., 2003; Rubel and Stencel, 1996; Illán-Gómez et al., 1996; Klose and Rincón, 2007). The most promising materials used for adsorption and reduction of NO<sub>2</sub> are activated carbons. Their application is governed by developed porous structure. Unique surface properties of active carbons are not only determined by the well-developed surface area but they are also related to the type, number and bonding mode of heteroatoms on their surface. Modification of the active carbon changes the physical and chemical properties of the product. The chemical structure of their surface essentially affects their adsorption, electrochemical, catalytic, acid-base, redox, hydrophilic or hydrophobic character and other properties [Pietrzak et al., 2007]

This paper reports the effect of modification with impregnation or calcinations on the adsorption and reduction of NO<sub>2</sub> by activated carbon.

### **Experimental**

*Materials* Wood-based activated carbon BAX-1500 manufactured by Mead Westvaco was used in this study. The initial sample is designated as B. Impregnation (designation "I") was performed with 10 wt% of suspension containing inorganic species extracted with 18% HCl from pyrolyzed sewage sludge at 950°C added to the carbon in volume equal to the volume of its pores. After impregnation the sample was dried at 120°C overnight. Heat treatment (designation "HT") was performed in a horizontal furnace under nitrogen flow (flow rate 100 ml/min). The samples were heated (10°C/min) from room temperature to final temperature 950°C. At the final temperatures samples were maintained for 60 min and then cooled in inert gas atmosphere.

*Evaluation of NO<sub>2</sub> sorption capacity* The home designed dynamic test was used to evaluate NO<sub>2</sub> adsorption from gas streams (Bagreev et al., 2001). Samples were packed into a glass column (length 370 mm, internal diameter 9 mm, bed volume between 2 cm<sup>3</sup>) and used as received. Dry (designation "DA") or moisture air (designation "WA") with 0.1% of NO<sub>2</sub> was passed through the column of adsorbent at 0.450 L/min for NO<sub>2</sub>. The flow rate was controlled using Cole Parmer flow meters. The breakthrough of NO<sub>2</sub> was monitored using electrochemical sensor or photoionization sensors. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of mg of toxic gases per g of adsorbent were calculated by integration of the area above the breakthrough curves, and from the NO<sub>2</sub> concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent.

*pH* a sample of 0.4 g of dry carbon powder was added to 20 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then the pH of suspension was measured.

**Thermal analysis** Thermal analysis was carried out using a TA Instruments Thermal Analyzer. The instrument settings were: heating rate, 10°C/min and a nitrogen atmosphere at 100 ml/min flow rate. For each measurement about 30 mg of a ground adsorbent were used.

**Potentiometric titration** Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator (Metrohm). The instrument was set at the mode when the equilibrium pH was collected. Subsamples of the materials studied of about 0.100 g in 50 mL 0.01 M NaNO<sub>3</sub> were placed in a container thermostatted at 298 K and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO<sub>2</sub>, the suspension was continuously saturated with N<sub>2</sub>. The carbon suspension was stirred throughout the measurements. Volumetric standard NaOH (0.1 M) was used as the titrant. The experiments were done in the pH range of 3-10. Each sample was titrated with base after acidifying the sample suspension.

The surface properties were evaluated first using potentiometric titration experiments (Jagiello et al., 1994; Jagiello, 1994). Here, it is assumed that the population of sites can be described by a continuous pK<sub>a</sub> distribution, f(pK<sub>a</sub>). The experimental data can be transformed into a proton binding isotherm, Q, representing the total amount of protonated sites, which is related to the pK<sub>a</sub> distribution by the following integral equation

$$Q(pH) = \int_{-\infty}^{\infty} q(pH, pK_a) f(pK_a) dpK_a \quad (1)$$

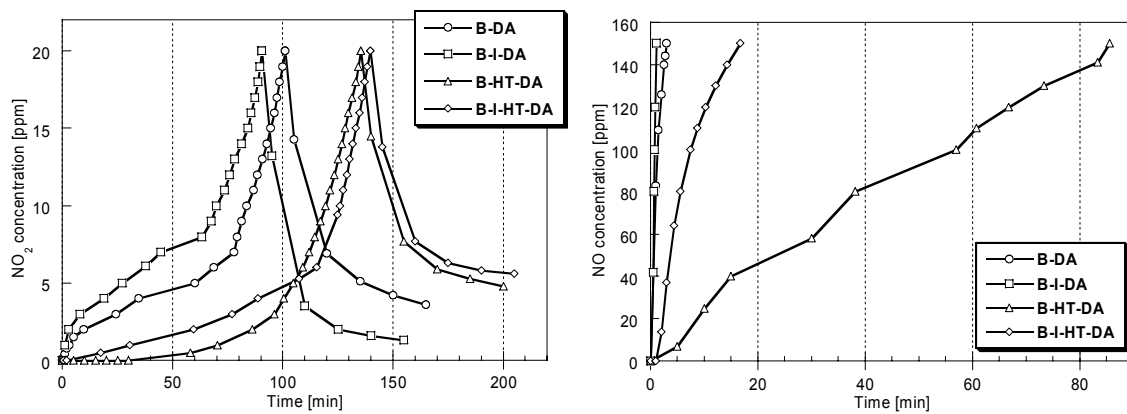
The solution of this equation is obtained using the numerical procedure (Jagiello et al., 1994; Jagiello, 1994), which applies regularization combined with non-negativity constraints. Based on the spectrum of acidity constants and the history of the samples, the detailed surface chemistry was evaluated.

### Results and discussion

The results of NO<sub>2</sub> breakthrough capacity experiments for materials studied in dry conditions are presented in Table 1 and Figure 1.

**Table 1.** NO<sub>2</sub> breakthrough capacities and surface pH values for the initial and exhausted samples.

Sample	NO <sub>2</sub> breakthrough capacity		pH	
	mg/g of ads	mg/cm <sup>3</sup> of ads	initial	exhausted
B-DA	42.7	10.6	6.01	2.42
B-I-DA	29.4	8.5	2.98	2.26
B-HT-DA	50.5	17.0	8.03	1.86
B-I-HT-DA	45.8	16.8	8.34	2.82



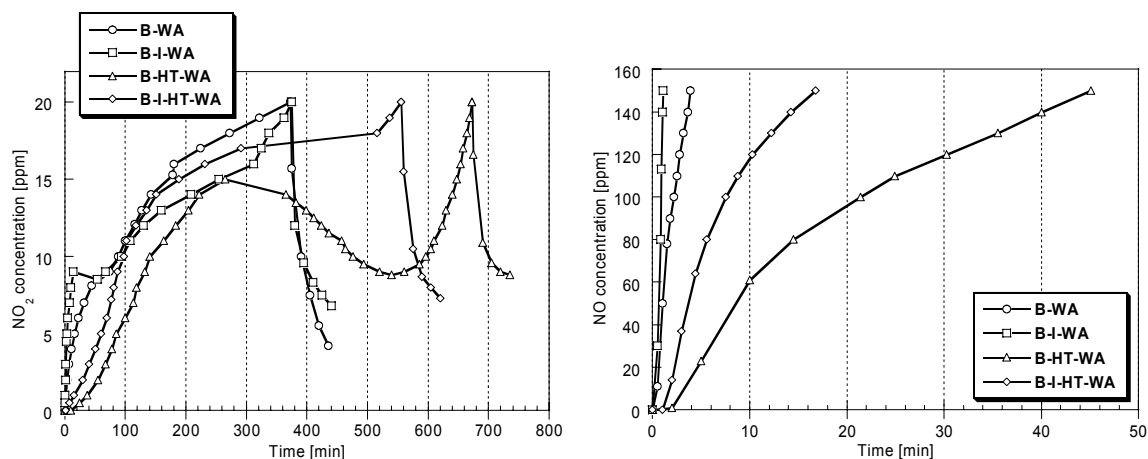
**Figure 1.** NO<sub>2</sub> breakthrough curves and NO concentration curves for materials studied in dry condition.

As seen from Table 1, heat treatment at 950°C causes an increase in the NO<sub>2</sub> removal capacity. It is important to mention that that increase is much smaller for the unmodified sample (20%) in comparison with the impregnated one (55%). If the capacity is considered per unit volume of the adsorbent, which is important form, the point of view of practical applications, a 60% increase is noticed for the unmodified sample and almost 100% for the modified one. Generally speaking, in comparison with the initial sample, impregnation is not beneficial for the performance of adsorbents. For the B-I-DA sample the capacity per mass decreases about 45% and per volume about 25% in comparison with the initial sample, B-DA. These differences are much smaller for heat-treated samples, B-HT-DA and B-I-HT-DA, and are about 10 and 1%, respectively.

Based on the changes in the pH, impregnation increases the acidity of the materials. This is the result of the high acidity of suspension used for the impregnation, which is equal to 1.59. Heat treatment of the impregnated sample results in the greater increase in the pH than in the case of the unmodified sample. As a result of NO<sub>2</sub> adsorption the pH of all samples significantly decreases. This can be linked to the adsorption of NO<sub>2</sub> and formation of nitric acid. In spite of the fact that the process was run in dry conditions water molecules needed for formation of HNO<sub>3</sub> have their source in surface OH groups (Lee et al., 1998).

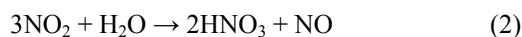
**Table 2.** NO<sub>2</sub> breakthrough capacity results and surface pH for adsorption in wet condition (at 20 ppm).

Sample	NO <sub>2</sub> breakthrough capacity		pH	
	mg/g of ads	mg/cm <sup>3</sup> of ads	Initial	Exhausted
B-WA	63.8	16.0	6.01	1.96
B-I-WA	67.1	19.3	2.98	black 1.69 gray 2.42
B-HT-WA	139.6	47.6	8.03	1.45
B-I-HT-WA	66.0	23.6	8.34	1.75



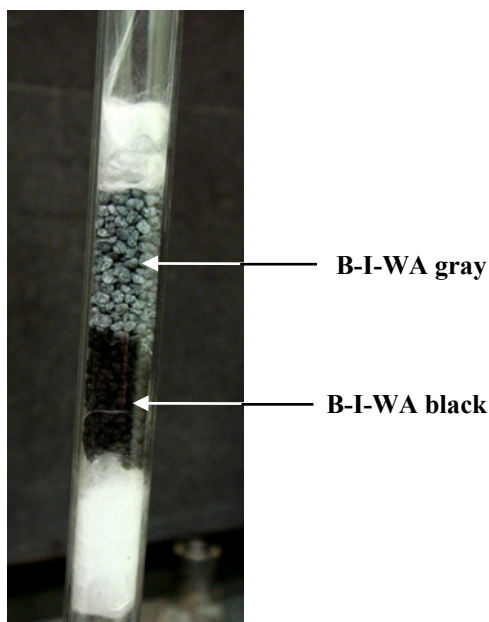
**Figure 2.** NO<sub>2</sub> breakthrough curves and NO concentration curves for materials studied in dry condition.

The results obtained in wet conditions are presented in Table 2 and Figure 2. It is clearly seen that the presence of water significantly increases the NO<sub>2</sub> breakthrough capacity. It is likely that responsible for this is reaction of NO<sub>2</sub> with water with formation of nitric acid according to the following reaction [Lee et al., 1998]:



Support for this is in higher surface acidity of the exhausted carbons in comparison with those used in dry conditions (Table 1). In spite of the fact that in dry conditions nitric acid was also formed as the surface reaction product its amount is limited by the amount of surface hydroxyl groups.

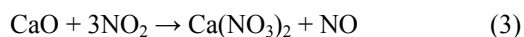
It is interesting that contrary to the runs in dry conditions impregnation increased the capacity when experiments are run in the presence of water. It is likely caused by reactions of NO<sub>2</sub> and nitric acid with inorganic compounds introduced to the carbon surface. The TA analysis indicates that the ash content increased after impregnation from 4 to 9%.



**Figure 3.** Image for B-I-WA

Figure 3 shows the column with impregnated carbon after the NO<sub>2</sub> adsorption process in wet conditions. The initial carbon was gray in color as the upper level of the bed. Apparent change in color from gray to black of the bottom part of the bed (first in contact with NO<sub>2</sub>) shows the changes in the chemical nature of an inorganic phase deposited on the carbon surface. Another important aspect is the relatively large size of the reaction zone, which can be judged based on the fact that high concentration of NO<sub>2</sub> is detected in the effluent gas, even though the color is still unchanged. For better understanding of the removal process, the two layers of bed were separated and analyzed. They are referred to as „black” and „gray”.

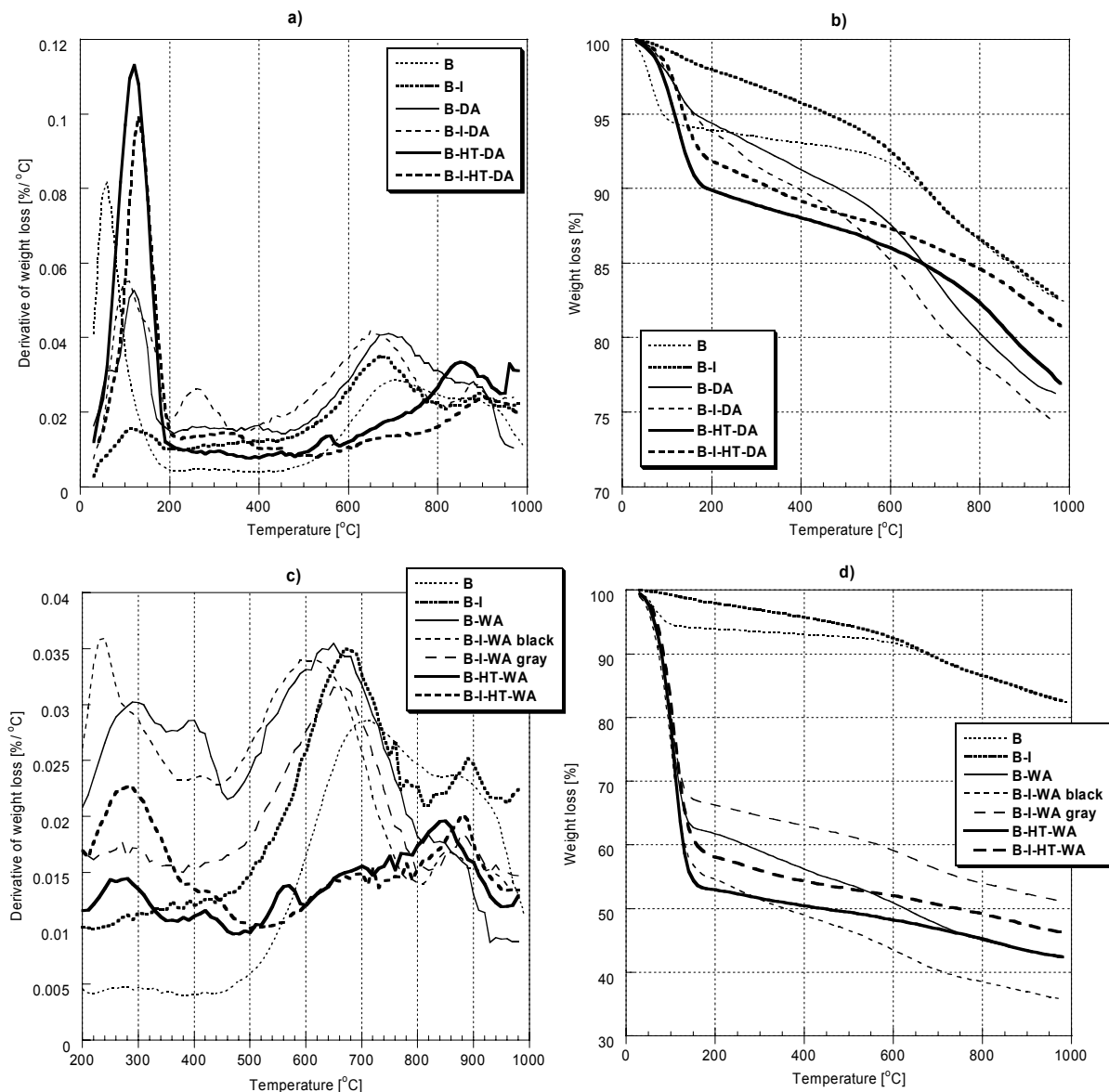
XRF results showed that the inorganic phase used for impregnation consists of mainly Cl, Fe, Ca, Al and Zn. Although the chlorides are water-soluble the yellowish color of suspension and its high pH suggests also existence of insoluble oxides, likely formed by decomposition of nitrates when the evaporation of the water from the original extract was carried out. According to the results discussed in the literature (Underwood et al., 1999; Lee et al., 1998) metal oxides react with NO<sub>2</sub> forming nitrates:



Moreover, nitrates are also formed via reaction of these oxides with nitric acid:



Since water is a product of this reaction it may contribute to the formation of more nitric acid, which results in further oxidation of the carbon surface. On the other hand, it is well known that nitrates are very water-soluble and it is likely that they move to the pore system of carbon resulting in returning of its original black color. All of these results in an increase in surface acidity as a result of formation of new salts and, oxidation of the carbon surface and inorganic compounds present there.



**Figure 4.** DTG and TG curve in nitrogen.

All initial and exhausted carbons were investigated using thermal analysis. The DTG and TG curves in nitrogen are presented in Figure 4. The DTG curve for the initial carbon B shows peaks at 60°C and at 710°C (Fig. 4a). The former is related to the removal of physically adsorbed water and the latter to the extended carbonization and removal of volatile compounds since this carbon was obtained at about 650°C.

The analysis of the behavior of other samples (Fig 4a) indicates that both impregnation and reaction with  $\text{NO}_2$  in dry conditions results in the shift of the first peak to higher temperatures. In the case of B-I the maximum is found at 100°C whereas for the exhausted samples that maximum is at about 125°C. While for B-I water is expected to have high affinity to an inorganic phase, in the case of the exhausted sample this can be the effect of oxidation of the carbon surface and inorganic phase. In the case the B-I-DA sample a peak at about 260°C is revealed. It likely represents nitrates of such metals as calcium and iron formed following reaction (3). The lack of this peak for the heat-treated samples can be related to the transformation of metal oxides in spinel like structures via solid-state reactions at high temperatures [Bandosz and Block, 2006]. This limits reaction (3) to occur. Moreover, the small amount of acid formed in this case was not enough for oxidation of those stable inorganic compounds. In the case of nonimpregnated samples, carbon surface oxidation is a result of the exposure to  $\text{NO}_2$ . Support for this is a shift in the

position of that last huge peak toward lower temperature, which is the result of decomposition of more oxygen groups formed on the surface.

Figure 4c shows DTG curves for the samples exposed to  $\text{NO}_2$  in wet conditions. For clarity, the intense water peak is removed and only the data in the range 200-1000°C is presented. The analysis of the data indicates that only B-I-WA black reveals a peak at about 240°C assigned to nitrates. It is more pronounced than in the case of B-I-DA. This is related to the fact that in wet conditions metal oxides react not only with  $\text{NO}_2$  according to reaction (3) but also with  $\text{HNO}_3$  (according to reaction (4)), which is formed when the sample is exposed to nitric oxide (according to reaction (2)). Comparison of DTG curves for B-I and B-I-WA black and gray shows differences related to the reactions in wet conditions. It supports the hypothesis the bottom part of the bed was more reactive towards retention of  $\text{NO}_2$ .

Comparison of all DTG curves obtained suggests that the process run in wet conditions affects surface chemistry to a much greater extent than that in dry conditions. All curves but the one for B-I-WA gray have peaks at about 280°C and between 400 and 420°C. They likely represent nitrates being the products of surface interactions of either  $\text{NO}_2$  or  $\text{HNO}_3$  with inorganic phase and/or carbonaceous phase. As mentioned above support for the extensive carbon surface oxidation is shift of the peak over 650°C towards lower temperatures in comparison with the results obtained in dry conditions. These changes are also seen on TG curves (Figs. 4b and 4d) where the extent of weight loss can be linked to severity of surface changes/oxidation.

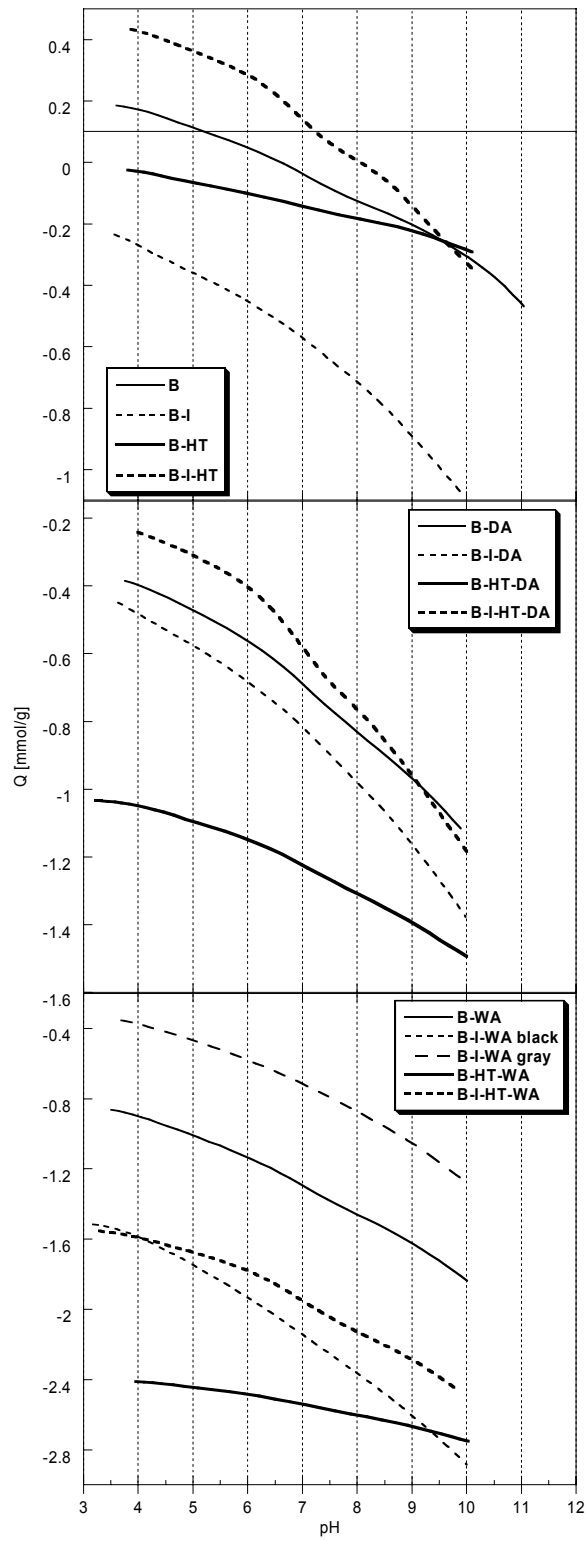
The alteration in surface chemistry as a result of  $\text{NO}_2$  exposure is also seen on proton uptake curves presented in Figure 5. They show that both experimental conditions result in an increase in surface acidity (proton release). This is the result of oxidation effects of  $\text{NO}_2$  and  $\text{HNO}_3$ . Here, as from other experiments, it is seen that wet conditions result in a more acidic surface.

### ***Conclusions***

The results of this research showed an important role of water for the removal of  $\text{NO}_2$  carbonaceous materials. The adsorption of nitric dioxide is enhanced in wet conditions. This is caused by interaction of  $\text{NO}_2$  and formed  $\text{HNO}_3$  with the carbon and inorganic oxide surface. In dry conditions the reaction of carbonaceous material with  $\text{NO}_2$  is predominant. Inorganic species introduced to the carbon surface generally cause a decrease in capacity, likely due to the blocking of the porosity. When the sample is heat treated, the capacity increases. When the experiment is run in wet conditions impregnation slightly increases the capacity owing to the activity of inorganic phase via retention of  $\text{NO}_2$  via nitrates and nitrites formation. Due to their solubility they can migrate further to carbon pores increasing the available surface area.

### ***Acknowledgement***

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**Figure 5.** Proton uptake curves for the initial samples and after exposure to  $\text{NO}_2$ .

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