Carbonaceous adsorbents prepared by physical activation of pine sawdust and their application for removal of NO_2 in dry and wet conditions

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ABSTRACT

Carbonaceous adsorbents from sawdust pellets from coniferous trees (pines) were obtained by CO_2 activation and used as nitrogen dioxide adsorbents. Activation was performed at 800 °C for four different periods of time (30, 60, 90 and 120 min). The effect of NO_2 adsorption in dry and wet conditions on the sorption ability of the activated samples obtained was tested. The results have shown that NO_2 sorption properties of the activates increase with increasing time of activation and reach maximum for the samples activated for 90 min. On the basis of measurements in dry and wet conditions, the presence of water was found to increase the NO_2 breakthrough capacity. The sorption capacity of the adsorbents obtained towards NO_2 was proved to be determined by the surface chemistry and the reactions taking place on the surface rather than by the specific surface area development.

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1. Introduction

In view of increasing awareness of the need of the environment protection, also adsorption of pollutants from the gas phase has become of increasing interest. Among the most threatening and widespread air pollutants are nitrogen oxides (NO_x). They are emitted in the process of combustion of nitrogen-containing fossil fuels so in many industrial technologies but also in motor vehicle engines. NO_x emission is known to contribute to global warming (greenhouse effect), acidification (acid rain), photochemical smog and ozone layer depletion (Inglezaks and Poulopoulos, 2006). Their emission can be limited directly at the source of their generation or by purification of exhaust gases by processes of reduction or oxidation in the gas or liquid phase accompanied by sorption in or on solid sorbents.

New technologies bound to meet the regulations related to the environment protection often use the process of adsorption and the problem they face is the access to cheap and effective adsorbents. The most effective have been those obtained from a variety of materials of organic origin, in particular activated carbons produced from fossil coals of different coalification degree, from brown coal to anthracites (Pietrzak, 2009a; Nowicki et al., 2009). However, relatively high cost of production of activated carbon from fossil coal has stimulated the search for new materials and technologies, among which much promising is the use of waste products (Mozammel et al., 2002; Tsai et al., 2001; Kazemipour et al., 2008; Girgis et al., 2002; Ahmedna et al., 2000). Activated carbon can be produced from almost any material containing carbon in organic connections and low amounts of inorganic components (Ioannidou and Zabaniotou, 2007). Agricultural waste products are low-cost adsorbents and their use is much promising way of utilization.

Carbon sorbents, including activated carbons obtained from waste products, are often for adsorption from the liquid phase, e.g. for water purification and waste water treatment (Ioannidou and Zabaniotou, 2007; Moreno-Castilla, 2004). They are also used for removal of phenols, phenolic compounds, heavy metal ions and dyes from aqueous solutions (Dabrowski et al., 2005; Dursun et al., 2005; Chuah et al., 2005; Kadirvelu et al., 2003; Nasiruddin Khan and Farooq Wahab, 2007). Attempts were made to use these sorbents for adsorption from the gas phase, for removal of volatile organic compounds (VOCs) from air pollution sources (Yates et al., 2000), for the purification of effluent gas streams (Yates et al., 2003) or removal of acidic compounds such as SO_x or NO_x (Mochida et al., 2000).

From among the low-cost adsorbents, the sawdust is one of the most promising adsorbents. It has been frequently used for removal of dyes of different types and some other unwanted materials from aqueous solutions (Özacar and Şengil, 2005; Gupta and Babu, 2009; Šćiban et al., 2007; Kaczala et al., 2009; Crini, 2006). The adsorbents obtained from the precursors of this type have attracted much interest for removal of pollutants from the liquid phase, whereas not many authors have studied their use for removal of pollutants from the gas phase.

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The previous study (Pietrzak, 2010) has shown that the carbonaceous adsorbents obtained by carbonization of sawdust pellets from coniferous tree species can be efficient for NO_2 removal. The adsorption properties of these materials towards NO_2 depend on the conditions of pyrolysis and adsorption. The sorption ability of the chars obtained has been found to increase with increasing temperature of the initial material pyrolysis and with increasing acidity of the initial adsorbent. Moreover, the presence of water significantly improves the sorption ability of the chars. In view of the above, we wanted to check if the process of activation of sawdust pellets from coniferous tree species with CO_2 improves the sorptive capacity of the adsorbents obtained towards NO_2 relative to the sorptive capacity of the chars obtained from the same precursor.

The aim of the study was to obtain carbonaceous adsorbents from sawdust of coniferous trees by CO_2 activation and the use of the material for adsorption of nitrogen dioxide from the gas phase. The influence of duration of activation on the sorption properties of the products obtained was analyzed. To characterize the sorption properties of the adsorbents obtained against NO_2, the process of adsorption was conducted in dry and wet conditions.

2. Methods

2.1. Materials and preparation of adsorbents

Adsorbents were prepared from sawdust from coniferous trees via activation of sawdust pellets (SP) (length 1.5 cm and diameter 0.5 cm). Activation (A) was performed in a horizontal furnace at 800 °C in CO_2 flow at the rate of 0.330 L/min to about 70% burn-off. The samples were heated (10 °C/min) from room temperature to the final activation temperature and maintained at this temperature for 30, 60, 90 and 120 min and cooled in CO_2 atmosphere, then they were ground and sieved to the grain size of 1–2 mm. The adsorbents obtained are labeled as SP-A-X where X stands for the holding time.

2.2. NO_2 adsorption experiments

The evaluation of NO_2 sorption capacity was carried out according to the procedures described in (Pietrzak, 2010) with some modifications. The samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume between 3 cm^3). Dry or moist (70% humidity) air with 0.1% of NO_2 was passed through the column with the adsorbent at 0.450 L/min for NO_2. The samples obtained after adsorption were labeled as SP-A-X-Ed and SP-A-X-Em, where "Ed" represents a sample exhausted in dry condition, and "Em" represents a sample exhausted in moist/wet condition. The breakthrough of NO_2 and the concentration of NO were monitored using Q-RAE PLUS PGM-2000/2020 with electrochemical sensors. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of milligram of toxic gases 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 (Pietrzak and Bandosz, 2007). To check the NO_2 reduction, the concentration of NO was also monitored till 240 ppm (electrochemical sensor limit).

2.3. Instruments and characterization of the adsorbents

2.3.1. Analytical procedures

Elemental analysis (C, H, N, S) of the initial sawdust pellets and chars obtained was made on an elemental analyzer CHNS PERKIN ELMER 2400 Series II. The content of ash was performed according to the Data National Standards ISO 1171:2002.

2.3.2. Porous structure

Characterization of the pore structure of obtained samples was performed on the basis of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micromeritics Instrument Corp. (USA). 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 area were calculated using the t-plot method.

2.3.3. Surface oxygen groups

The surface oxide functional groups were determined by the Boehm method (1964, 1994).

2.3.4. Measurement of surface pH

The pH of chars was measured using the following procedure: a portion of 0.4 g 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.

2.3.5. FTIR analysis

The samples were subjected to FTIR study on Bruker Vector 22 spectrophotometer, using 1 mg sample with 200 mg KBr in standard disk form. The disc was prepared by applying pressure of about 15 MPa for about 1 min. The spectrum without any sample ("background spectrum") was scanned and was evidently subtracted from all recorded spectra. The spectrum was recorded in the range 400–4000 cm^{-1}. Sixty-four scans at a resolution of 2 cm^{-1} were made to get each spectrum.

3. Results and discussion

According to the results presented in Table 1, activation of raw pallets at 800 °C leads to a 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. Moreover, with increasing holding time of activation the content of carbon decreases, while that of the other elements (H^{daf} and O^{daf}) increases. The changes are a consequence of greater gasification of the carbonaceous material upon activation for a longer time, according to the mechanism of carbon dioxide interaction with the precursor surface (Marsh and Rodriguez-Reinoso, 2006). As known, upon activation with carbon dioxide the following reactions take place:

$$C_f + O_2 \leftrightarrow CO_2$$
$$2C_f + O_2 \leftrightarrow 2CO$$
$$C_f + CO_2 \leftrightarrow CO + C(O)$$
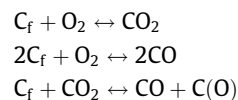
where C(O) stands for the so-called *surface oxygen complexes* acting as inhibitors of the activation process as they block the reaction

Table 1
Elemental analysis of the initial sample and the activates (wt.%).

Sample	Ash^d	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{dafA}
SP	0.5	47.0	7.7	0.1	0.0	45.2
SP-A-30	1.0	95.5	1.0	0.4	0.0	3.1
SP-A-60	1.2	95.0	1.1	0.4	0.0	3.5
SP-A-90	1.4	92.8	1.2	0.2	0.0	5.8
SP-A-120	1.4	91.4	1.3	0.3	0.0	7.0

[A] By difference.