

SORPTION PERFORMANCE TOWARDS NO₂ OF NITROGEN-ENRICHED ADSORBENTS OBTAINED FROM SAWDUST PINE

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Introduction

Modification of the precursors or ready activated carbons permits getting materials of improved adsorption and catalytic properties or of specific acid-base or hydrophobic-hydrophilic character. Particularly promising are the activated carbons enriched in nitrogen because of wide possibilities of use of such materials. In particular, they can find applications related to protection of the natural environment, e.g. for low temperature selective catalytic reduction of NO, for removal of harmful exhaust gases, for adsorption of metal ions from the liquid phase and in electrochemistry for production of electrodes for electrochemical capacitors [1-6].

Nitrogen-enriched activated carbon can be produced from various precursors such as wood, plastics containing nitrogen in their structure and fossil coals of different degree of coalification, from brown coals to anthracites [7-8]. From the ecological point of view, N-enriched activated carbons obtained from waste materials such as sawdust 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.

For this reason the objective of this paper was to obtain adsorbents from sawdust pine, enrichment of the products in nitrogen in the reaction with urea and characterisation of the products adsorption capacities towards NO₂, in dry and wet conditions.

Experimental

Adsorbents were prepared from sawdust from coniferous trees via carbonization and physical activation of sawdust pellets (SP) (length 15 mm and diameter 5 mm). The carbonization (C) was carried out in a horizontal furnace under argon with a flow rate of 170 mL/min. The sample was heated (5°C/min) from room temperature to the final carbonization temperature of 600°C. In the final temperature, samples were kept 60 min and then cooled in inert atmosphere. Activation (A) was performed in a horizontal furnace at 800°C in CO₂ flow at the rate of 0.330 L/min for 60 (A60) or 120 min (A120).

Incorporation of nitrogen (U). Urea was applied as a reagent introducing nitrogen functions into the carbon structure. The sample was mixed with urea at the weight ratio of 1:1 and then oxidized with oxygen from air at 350°C. The reaction proceeded in a glass reactor under atmospheric pressure for 3 h. The obtained nitrogen-enriched carbons were

washed with hot distilled water to remove the unreacted part urea and dried.

The elemental analysis of the products obtained at each stage of the processing were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

Characterization 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). 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 t-plot method.

Evaluation of NO₂ was carried out according to the procedures described in [9] with some modifications. Samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 2 cm³). Dry air with 0.1% of NO₂ was passed through the column of adsorbent at 0.450 L/min. The breakthrough of NO₂ was monitored using electrochemical sensor.

Results and Discussion

As a result of carbonization of the sawdust pellets at 600°C (SPC), the content of the elemental carbon increases, the content of hydrogen decreases and that of oxygen significantly decreases. The content of nitrogen does not change significantly, which testifies to the thermal resistance of the nitrogen species originally contained in the sawdust.

Table 1. Characteristics of Sawdust Pellets, Chars and Activated Carbons Obtained (wt.%).

Sample	Ash ^d	C ^{daf}	H ^{daf}	N ^{daf}	O ^{daf}
SP	0.5	46.7	6.4	0.1	46.8
SPC	0.9	91.9	2.7	0.2	5.2
SPCA60	1.6	95.1	0.8	0.2	3.9
SPCA120	2.4	94.0	0.8	0.2	5.0
SPCU	0.8	79.1	4.6	4.6	13.4
SPCUA60	1.2	90.6	0.8	2.9	5.7
SPCUA120	1.0	90.9	0.8	2.9	5.4

*by difference

The reaction of SPC char with urea (SPCU) permits introduce about 5% wt of nitrogen into the coal structure. This reaction leads also to an increase in the content of oxygen and a decrease in the content of elemental carbon and hydrogen, as a consequence of the oxidizing conditions of the process. The activation of SPC and SPCU samples with CO₂ (irrespective of the time of activation) brings a further increase in the content of elemental carbon and decrease in the content of hydrogen and nitrogen (for SPCU sample) as well as an

insignificant changes in the oxygen content. Significant decrease in the content of nitrogen suggests that some part of the functional groups introduced during reaction with urea are thermally unstable and undergo decomposition.

The surface area measured for active carbon samples, presented in Table 2, clearly illustrate a considerable influence of the time of activation and method of preparation on the porous structure of final products.

Table 2. Textural Parameters of Samples Obtained.

Sample	S_{BET} [m ² /g]	V_t [cm ³ /g]	A [nm]
SPC	390	0.18	1.95
SPCA60	482	0.28	2.32
SPCA120	536	0.29	2.23
SPCUA60	497	0.23	1.92
SPCUA120	583	0.28	1.93

Better textural parameters (about 15%) are achieved by activation of SPC and SPCU chars for 2 hours. Moreover, samples SPCUA60 and SPCUA120, obtained from sawdust enriched in nitrogen at stage of the char have insignificant better developed porous structure than analogous samples produced from non-modified sawdust.

All the samples produced were tested for the NO₂ adsorption in dry and wet conditions. The calculated breakthrough capacities for the chars obtained presents Table 3.

Table 3. NO₂ Breakthrough Capacities of the Active Carbons Obtained.

Sample	NO ₂ breakthrough capacity [mg/g _{ads}]	
	Dry conditions	Wet conditions
SPCA60	22.7	31.2
SPCA120	46.1	43.4
SPCUA60	35.9	28.1
SPCUA120	60.7	29.9

According to these data, the activated carbons obtained from sawdust are characterised by diverse sorption capacities of NO₂. The results indicate that the sorption ability of the samples obtained, both in dry and wet conditions, increases significantly with increasing time of activation. Introduction of nitrogen improves the NO₂ breakthrough capacity in dry conditions, however in wet conditions it contributes to worsening of the sorption abilities. The highest NO₂ sorption capacity in dry conditions (60.7 mg/g) was obtained for sample SPCUA120 enriched in nitrogen and activated for 2 hours, while the lowest of (22.7 mg/g) for SPCA60. The best

sorption ability in wet condition 43.4 mg of NO₂ per gram of adsorbent is observed for SPCA120 sample, whereas the worst (28.1 mg) reveals sample SPCUA60.

The improvement of the sorption capacity in dry conditions after introduction of nitrogen follows most probably from the fact that as a result of reaction with urea 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, may favour the reduction of nitrogen dioxide to nitrogen monoxide, which also contributes to the improvement of the sorption capacities of activated carbon towards NO₂.

Conclusions

The above presented and discussed results have shown, that a suitable choice of the nitrogenation and activation procedure for sawdust pellets, can produce active carbons with high adsorption ability of nitrogen dioxide, both in dry and wet conditions.

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