



The use of microwave radiation for obtaining activated carbons enriched in nitrogen



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ARTICLE INFO

Article history:

Received 24 August 2014

Received in revised form 12 December 2014

Accepted 20 December 2014

Available online 27 December 2014

Keywords:

Activated carbon

Microwave radiation

Physical activation

Urea

Physicochemical properties

ABSTRACT

The activated carbons were synthesized from hay with CO₂ as an activating agent. Furthermore hay and the chars obtained by pyrolysis were treated with urea, in order to introduce nitrogen to their structure, and then subjected to physical activation. The porous structure of activated carbons before and after impregnation was characterised by nitrogen adsorption using BET and BJH methods. The thermal properties of the samples were investigated by thermogravimetric (TG) analysis and differential thermogravimetry (DTG).

The final products were activated carbons of low surface area varying from 84 to 196 m²/g and showing basic character of the surface. The impregnation of hay and chars with urea leads to a decrease in activated carbon surface area and pore volume. However, the materials modified by urea show a very high content of nitrogen (from 8.1 to 12.8 wt.%), which could be achieved thanks to the use of microwave heating as this method of heating permits a considerable reduction of the temperatures of pyrolysis and activation and a shortening of the time of activation. Following the character of TG and DTG curves, the nitrogen functional groups introduced into the activated carbon structure have relatively low thermal stability, as evidenced by the distinct loss of mass above the temperature of approximately 400 °C, observed both for unmodified carbon and the carbon enriched in nitrogen.

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1. Introduction

Porous carbon materials have been for many years successfully used for the removal of pollutants from water [1–3] and air [4–6], for the separation of gas mixtures [7,8] and for the recovery of valuable substances such as gold or silver [9]. So far a few methods for the synthesis of activated carbon have been proposed, however, all of them have been based on one of the two mechanisms of physical or chemical activation. Physical activation is realised in two stages, carbonization of the initial material at an elevated temperature in neutral gas atmosphere followed by activation of the carbonizate obtained [10,11]. Chemical activation is usually realised in one stage, of impregnation or physical mixing of the activating agent with precursor which is then subjected to thermal treatment in neutral gas atmosphere [12–14]. Increasing demands in the traditional areas of activated carbon applications and new fields of their potential use have stimulated the search for new carbon materials of improved and strictly defined properties. Literature provides many reports on the synthesis of activated carbons from all kinds of materials with the help of conventional heating [15–18]. However, this method has many drawbacks, such as non-uniform heating of the sample volume or the necessity to perform pyrolysis and activation in high temperatures (>800 °C), so the search for new and more effective methods

for the synthesis of carbon adsorbents is continued. An interesting alternative can be the use of microwave radiation. The heating by microwave radiation has many advantages over the conventional one. The most important are: selectivity, no need of contact and uniform heating of the whole volume of the material. Microwave heating is based on the conversion of electromagnetic energy into heat, in contrast to classical heating, based on the convection mechanism involving conduction and radiation. The difference permits a shortening of the time of heating which saves energy [19–21].

Activated carbons are used in the industry for the adsorption from gas and liquid phases, which means that they must be characterised by high sorption capacity and selectivity. Because of these demands the carbon materials are subjected to processes of modification to change their certain physicochemical parameters. For example attempts have been made to obtain carbonaceous adsorbents showing increased adsorption towards selected adsorbates. Nowicki et al. [22] have found that the removal of acidic gases is more intense on the activated carbons of increased basicity. Another type of modification is enrichment of the carbons in nitrogen, which improves the capacity for nitrogen(IV) oxide adsorption [23]. One of the methods to achieve the nitrogen enrichment is thermal treatment of carbon in the presence of a nitrogenating agent. Most often used N-reagents are ammonia [24–26] and urea [27–29]. Another method leading to nitrogen enrichment is pyrolysis, followed by activation of nitrogen containing polymers [30,31]. By these methods it is possible to obtain a wide range of

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carbonaceous materials of different contents of nitrogen present in the form of different chemical species.

The main purpose of our study was to prepare a series of nitrogen-enriched activated carbons from low quality hay using microwave radiation and to determine their physicochemical properties. Moreover, thermogravimetric analysis was used to study thermal stability of activated carbons before and after nitrogen introduction.

2. Materials and methods

2.1. Samples preparation

The precursor of activated carbon was the post-agricultural waste – low quality hay (H) in the form of cylinders of 0.8 cm in diameter and 1 cm in length. The initial material was first subjected to pyrolysis in a microwave oven (Phoenix, CEM) at two temperatures 400 °C (H40), and 500 °C (H50). This process was carried out under a stream of nitrogen (Linde Gas, Poland) with a flow rate of 0.330 L/min. In the final temperature, samples were kept for 60 min and then cooled down in an inert gas atmosphere. The chars obtained were next subjected to physical activation (A) and the products were labelled H40A and H50A. This process was carried out at 500 °C, under a stream of carbon dioxide (Linde Gas, Poland) with a flow rate of 0.250 L/min, for 15 min. Some part of the chars obtained were subjected to impregnation with a solution of urea obtained from Avantor Performance Materials Poland S.A. (Gliwice, Poland) (impregnation ratio 1:1) and dried at 105 °C to constant mass. Then the samples were subjected to physical activation in a microwave oven. The samples were heated (10 °C/min) from room temperature to 500 °C and kept at the final activation temperature for 15 min. The activating agent was carbon(IV) oxide (Linde Gas, Poland), supplied at the rate of 250 mL/min. The treated carbon samples were washed with water to remove urea decomposition products and dried. The nitrogen-enriched carbons were labelled as H40UA and H50UA, respectively. Activation process (called direct activation) was also performed for the precursor and impregnated precursor in the same conditions as for the chars and the products were labelled as HDA and HUDA, respectively.

2.2. Sample characterisation

2.2.1. Analytical procedures

The elemental analyses of the starting hay, chars and activated carbons were performed on an elemental analyser CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany). The content of ash was established according to the Data National Standards ISO 1171:2002.

2.2.2. Porous structure

Characterisation 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 (Quantachrome Instruments USA). On the grounds the BET surface area measured, the total pore volume and pore diameter were determined. Moreover micropore volume and micropore surface area were calculated using the t-plot method.

2.2.3. Surface oxygen groups

The content of surface oxygen functional groups was determined by the Boehm method. 0.25 g of carbon sample was placed in 25 mL of 0.1 M solutions of either sodium hydroxide or hydrochloric acid (Avantor Performance Materials Poland S.A.). The vials were sealed and shaken for 24 h and then 10 mL of each filtrate was pipetted and the excess of the base or acid was titrated with 0.1 M HCl or NaOH, as required. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes all acidic groups and HCl reacts with all basic groups.

2.2.4. Measurement of surface pH

The pH of the adsorbent surface was obtained by mixing a sample of carbon (0.2 g) with deionized water (10 mL), stirring the suspension overnight to equilibrate, and then measuring the pH of this suspension.

2.2.5. Thermal analysis

Thermogravimetric analysis of the non-modified as well as nitrogen-enriched activated carbon was performed on a SETSYS 12 made by Setaram. The samples (10 mg, particle size below 0.06 mm) were heated at the rate 10 °C/min, in helium atmosphere. Analysis lasted for 100 min and the temperature during the decomposition varied from 20 to 1000 °C.

3. Results and discussion

Because of the low content of carbon in the initial material (H, Table 1) it was at first subjected to pyrolysis and then to physical activation by CO₂. The processes are known to lead to significant changes in the elemental composition of the material. The higher the temperature of pyrolysis, the greater the increase in the content of carbon and ash in the products. Thermochemical treatment of hay leads also to a significant decrease in the content of hydrogen and oxygen and to an increase in the content of nitrogen. The contents of H^{daf} and N^{daf} in all products of physical activation are similar, while the content of O^{daf} significantly decreases with increasing temperature of pyrolysis. The greatest changes in the elemental composition with respect to that of the initial material, that is the greatest increase in C^{daf} and the greatest decrease in O^{daf}, were observed for the sample subjected to direct activation (HDA) that is to simultaneous pyrolysis and activation. The efficiency of activation depends first of all on the variant of activation, which is evidenced by the fact that the efficiency of direct activation is by over 50% lower than that of physical activation. For the samples obtained by two-stage activation, the efficiency of activation depends also on the temperature of pyrolysis, as illustrated by a few percent difference in efficiency of activation between samples HA40 and HA50.

Different relations were observed for the activated carbon enriched in nitrogen by impregnation with urea. The yield of activation was higher (about 10 wt.%) for sample HUDA obtained by direct activation of the impregnated precursor. Lower yield obtained for the samples modified with nitrogen at the stage of the char (H40UA and H50UA) is most probably related to the fact that the structure of the pyrolysis products is less susceptible to modification and the nitrogen functional groups are incorporated only on the surface graphene layers, so a large part of them undergo destruction upon activation. Sample HUA has the highest content of nitrogen (12.8 wt.%) and the lowest content of carbon and ash, from among all samples studied. In samples H40UA and H50UA, the content of nitrogen is lower (9.5 and 8.1 wt.%) and decreases significantly with increasing temperature of pyrolysis, while the content of C^{daf} is similar to that in the unmodified samples. It should be emphasised that the content of nitrogen in the structure of all activated carbon samples obtained was much higher than that in similar carbon adsorbents obtained from sawdust with the use of conventional heating

Table 1

Elemental analysis of the precursor and activated carbons obtained as well as the yield of activation process (wt.%).

Sample	Ash	C ^{dafa}	H ^{daf}	N ^{daf}	O ^{dafb}	Yield
H	5.7	48.1	6.1	1.6	44.2	–
HDA	17.8	80.8	3.0	2.9	13.3	31.9
H40A	20.0	75.5	3.4	2.9	18.2	82.4
H50A	22.3	80.1	3.2	2.9	13.8	87.8
HUDA	10.9	70.4	3.3	12.8	13.5	90.8
H40UA	15.9	76.5	2.7	9.5	11.3	81.2
H50UA	16.8	78.5	2.8	8.1	10.6	84.1

^a Dry-ash-free basis.

^b Determined by difference.

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