Powder Technology 319 (2017) 302–312

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Characterization and application of bio-activated carbons prepared by direct activation of hay with the use of microwave radiation

Justyna Kazmierczak-Razna, Piotr Nowicki, Robert Pietrzak *

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Laboratory of Applied Chemistry, Umultowska 89b, 61-614 Poznań, Poland

ARTICLE INFO

Article history:
Received 29 January 2017
Received in revised form 20 June 2017
Accepted 28 June 2017
Available online 05 July 2017

Keywords:
Biomaterials
Microwave radiation
Direct activation
Carbonaceous bio-adsorbents
NO_2 removal
Wastewater treatment

ABSTRACT

Preparation of bio-activated carbons from hay by direct activation with the use of microwave radiation was studied. The influence of process variables such as the temperature and activation time on textural, chemical-surface properties and sorption properties of the products obtained was studied. The resulting bio-carbons were characterized by low-temperature nitrogen sorption and determination of pH as well as the content of surface oxygen groups. The sorption properties of the bio-activated carbons obtained were characterized by determination of nitrogen dioxide adsorption in dry and wet (70% humidity) conditions and tested by iodine, methylene blue and Congo red removal from aqueous solution. The products were microporous bio-carbons of rather low surface area ranging from 88 to 265 m^2/g and pore volume from 0.09 to 0.18 cm^3/g, showing basic character of the surface. The results show that the adsorption of organic and inorganic compounds depends on the activation procedure (temperature and time of activation). It is therefore concluded that the activated bio-carbons from hay are promising adsorbents for NO_2 removal from gas streams as well as different pollutants from liquid phase.

1. Introduction

Because of their unique porous structure, high accessibility and non-toxic properties, activated carbons have been very attractive for many research groups and for many applications. Production of activated carbons increases each year. Their consumption is the highest in Japan and USA, while the lowest in African countries [1]. A rapid increase in the significance of activated carbons in developed countries is a consequence of increasing demand from all branches of industry and successful development of new technologies based on the use of porous materials [2–5].

The most popular methods of activated carbons production employ conventional heating, however it means that the heating is inhomogeneous and implies the need for performance of pyrolysis and activation at rather high temperatures. An interesting alternative to avoid these drawbacks is the use of microwave energy. The benefits of microwave heating include selectivity, no need of contact and the fact that it is homogeneous in the whole volume of the sample. The heating by microwaves is based on the conversion of electromagnetic radiation into heat, in contrast to the classical convection mechanisms. The difference permits a shortening of heating time and thus saving energy, so the microwave heating has been increasingly often used in physical processes and chemical reactions [6–9].

For this reason the main aim of this study was to obtain a series of carbonaceous adsorbents from hay and to give their physicochemical characterization. Different preparation parameters (temperature and time of activation) were applied in order to evaluate the influence of the activation conditions on the properties of the final product. Our goal was also to study the correlation between activated carbons physicochemical properties and the pollutant in order to develop optimized adsorbent materials for air purification and decolourization of wastewaters.

2. Materials and methods

2.1. Samples preparation

The precursor was the post-agricultural waste – low quality hay (H) of moisture content in air-dry state of 7.8 wt%, in the form of cylinders of 0.8 cm in diameter and 1 cm in length. The initial material was subjected to direct activation (DA) in a microwave oven (the power of the microwave was 1400 W at a frequency of 2.45 GHz) under a stream of carbon dioxide with a flow rate of 0.250 L/min in two temperatures 500 (HDA5), 600 (HDA6). In the final temperature, samples were kept 15 min (HDA5-15 and HDA6-15), 30 min (HDA5-30 and HDA6-30), 60 min (HDA5-60 and HDA6-60) and then cooled down in an inert atmosphere.

2.2. Characterization of the activated carbons

Elemental analysis of samples was performed by using an elemental analyzer CHNS Vario EL III (Elementar Analysensysteme GmbH,

---

* Corresponding author.
E-mail address: pietrob@amu.edu.pl (R. Pietrzak).

http://dx.doi.org/10.1016/j.powtec.2017.06.062
0032-5910/© 2017 Elsevier B.V. All rights reserved.

Germany). The content of ash was determined according to the Data National Standards ISO 1171:2002.

Characterization of the pore structure of activated carbons was determined by nitrogen adsorption - desorption at −196 °C by Autosorb iQ surface area analyzer (Quantachrome Instruments USA). On the grounds of results of the measurements BET surface area, total pore volume and pore diameter were determined. The total pore volume (V_t) was calculated at a relative pressure of approximately $p/p_0 = 0.99$ and at this relative pressure all pores were completely filled with nitrogen. The average pore diameter (D) was determined on the basis of the surface area (S) and the total pore volume (V_t) according to formula $D = 4V_t / S$. Moreover micropore volume (V_{mic}) and micropore area (S_{mic}) were calculated using t-plot method.

The analysis of surface oxygen functional groups was based on the Boehm method [10].

The pH surface of samples was determined with the following procedure: approximately 0.20 g of each sample was suspended on 10 mL of distilled water. Suspensions were stirred overnight to reach equilibrium and measuring the pH periodically until readings were constant.

The Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups present on the surface of HDA5-60 and HDA6-60. The measurement was conducted by means of 6700 type A FTIR spectrometer (Jasco, USA). The spectra were recorded in the range 500–4000 cm^{-1}.

Thermogravimetric analysis of the raw material 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 was varied from 20 to 1000 °C.

Morphologies of the precursor and the activated carbons (HDA5-60 and HDA6-60) were analyzed on the basis of a scanning electron microscope (Hitachi S-3400N) images recorded using acceleration voltage of electron beam adjusted to 15 keV.

2.3. Adsorption experiments

Evaluation of NO_2 sorption capacity: the home designed dynamic test was used to evaluate NO_2 adsorption from gas streams in dry and wet conditions (70% humidity), more details are contained in our earlier works [11–13]. Additionally to check the NO_2 reduction (as a result of its reaction with carbonaceous materials) the concentration of NO in the system was monitored using Q-RAE PLUS PGM-2000/2020 with electrochemical sensors till 200 ppm. After the breakthrough tests, for 30 min all samples were exposed to a flow of air (360 mL/min).

The iodine sorption ability of the adsorbents was determined according to the ASTM D4607-94(2006) standard. This method permits estimation of the ability of the adsorbents obtained to remove substances whose molecules have the size close to that of iodine molecules, so of diameters close to 1 nm, from the liquid phase.

Methylene blue (MB) and Congo red (CR) was obtained from Sigma-Aldrich and used without further purification. The MB and CR stock solution (1000 mg/L) was prepared by dissolving accurately weighed amount of the dyes in demineralized water. All working solutions of the desired concentrations were prepared by diluting the stock solution with demineralized water.

Determination of the methylene blue and Congo red adsorption was performed using the following procedure: samples of the prepared activated carbons of equal portion of 0.025 g with the particle size 0.09 mm were added to 50 mL of the MB or CR solution with initial concentrations in the range from 5 to 40 mg/L. The mixture was agitated in a shaker at room temperature with an agitation speed of 150 rpm for 24 h to reach equilibrium. Unknown concentrations of dyes were determined by finding out the absorbance at the characteristic wavelength using a double beam UV–Visible spectrophotometer (Cary Bio 100, Varian). Standard calibration chart was prepared by measuring the absorbance of different dyes concentrations at λ_{max} 665 nm for MB, 497 nm for CR and unknown concentrations of dyes before and after adsorption were computed form the calibration chart. Each experiment was carried out in triplicates under identical conditions and an average value was determined. MB and CR uptake at equilibrium, q_e (mg/g), was calculated by:

$$q_e = (C_0 - C_e)V/m$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution, and m (g) is the mass of adsorbent used.

The Langmuir equation is probably the best known and widely used adsorption isotherm and is expressed by the following relation:

$$q_e = \frac{Q_0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{1}$$

where, q_e is the amount of dye adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), Q_0 is the maximum adsorption capacity (mg/g) and K_L is the isotherm constants for Langmuir (L/mg).

The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_0} + \frac{C_e}{Q_0} \tag{2}$$

The Freundlich isotherm can be applied to no ideal adsorption on heterogeneous surfaces and multilayer sorption. The Freundlich adsorption isotherm model is represented as follows

$$q_e = K_F \cdot C_e^{1/n} \tag{3}$$

The logarithmic form of the Freundlich isotherm can be expressed as

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \cdot \log C_e \tag{4}$$

where q_e is the amount of metal ion adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), K_F is the capacity of the adsorbent and 1/n is the intensity of adsorption constant for Freundlich. The plot of log q_e versus log C_e is employed to determine the K_F and n from intercept and slope respectively.

3. Results and discussion

In order to evaluate the thermal stability of the adsorbents obtained and to verify the presence of the main components of the initial material (H) such as lignin, cellulose and hemicellulose, the samples were subjected to the thermogravimetric analysis. The thermograms are presented in Fig. 1. The data imply that the precursor was thermally stable up to about 240 °C, which is relatively high in comparison to the range of thermal stability of e.g. plum stones - 200 °C [14], wheat straw - 215 °C, soy hulls - 209 °C [15], or chitosan for which mass loss of 5% has been observed already at 80 °C [16]. A small initial mass loss, manifested on the DTG curve as a peak at about 100 °C, corresponds to desorption of water physically adsorbed in the initial material. The character of TG curves implies that the process of decomposition of low-quality hay takes place in three stages. In the first stage, up to about 200 °C the mass loss reaches about 3%. In the second stage, from about 200 °C to 390 °C, a rather rapid mass loss is observed of about 54%, then the third stage takes place from about 440 °C to 600 °C, and brings a mass loss of about 15%.

As mentioned above, such precursors as hay owe their thermal stability to the presence of cellulose, hemicellulose and lignin in their structure. The shapes of the TG and DTG curves recorded for the materials of this type depend mainly on the chemical structure and nature