Production of new activated bio-carbons by chemical activation of residue left after supercritical extraction of hops

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ABSTRACT

A technology of activated bio-carbons production from the residue left after supercritical extraction of hops is described. The effect of the variant of chemical activation and impregnation ratio on the physicochemical properties as well as sorption capacity towards toxic gas of acidic character (nitrogen dioxide), basic organic dye (aqueous solution of methylene blue - MB) and iodine was investigated. The materials obtained were activated bio-carbons of well-developed surface area ranging between 897 and 1095 m^2/g, showing clearly acidic character of the surface. The sorption tests results proved that chemical activation of the residue left after supercritical extraction of hops allows obtaining activated bio-carbons with very high sorption capacity towards nitrogen dioxide, reaching to 77.2 and 155.3 mg/g in dry and wet conditions, respectively. The maximum sorption capacity of the adsorbents towards methylene blue was 328.75 mg/g, while towards iodine 1815 mg/g. The equilibrium data for aqueous solution of MB were analyzed by the Langmuir and Freundlich models, whereas the kinetics of the adsorption process was studied using pseudo-first and second-order models. According to the obtained data, the adsorption of MB from aqueous solution is better described by Langmuir model and pseudo-second order kinetic model.

1. Introduction

The production of hop has been continuously developing along with beer industry. The greatest producers of hop are Germany and USA (Turner et al., 2011). Although it is mostly used for beer production, the properties of hop have made it an attractive raw product for medicine, pharmacy or in cosmetic and food industry (Bland et al., 2015; Formato et al., 2013; Sakamoto and Kanings, 2003). Thanks to its regenerating, relaxing, calming and soothing properties, hop has been used in hair care preparations, bath fluids, creams and face masks (Kumhala and Blahovec, 2014; Mizobuchi and Sato, 1985). In the kitchen hop is used as a component of soups and salads (Maikhunthod and Marriott, 2013; Yamaguchi et al., 2009). On industrial scale extract from hop is obtained by supercritical CO_2 extraction (Bazan et al., 2016a; Capuzzo et al., 2013). This type of plants extraction leaves much waste that has to be utilized (Millao and Uquiche, 2016; Van Opstaele et al., 2012) and one of the methods proposed for their utilization is production of carbon adsorbents (Bagreev and Bandosz, 2001; Bazan et al., 2016b; Bazan-Wozniak et al., 2017; Hofman and Pietrzak, 2012; Nowicki et al., 2012). Carbon adsorbents are commonly used for purification of ex-

haust gases (Pietrzak and Bandosz, 2007; Seredych and Bandosz, 2009) or for water treatment (Isiuku et al., 2014; Wiśniewska et al., 2017). The activated bio-carbons obtained from the waste left after plant extraction should show high sorption capacity, short time of adsorption processes and the lack of side products that could form during adsorption (Bazan et al., 2016c; Nowicki et al., 2016; Senthilkumaar et al., 2006). Moreover, taking into account the technological and economic demands, it would be most desirable to obtain universal adsorbents showing high sorption capacities towards gas and liquid pollutants. The method allowing production of such adsorbents is chemical activation by a series of activating agents such as: NaOH, KOH, K_2CO_3, H_3PO_4, $ZnCl_2$ (Elmouwahidi et al., 2017; Kılıç et al., 2012), as it gives bio-carbons of highly developed surface area and pore size distribution needed (Benaddi et al., 2000; Foo and Hameed, 2011; Nowicki et al., 2014).

The aim of the study presented was to obtain activated bio-carbons by chemical activation of the residue left after supercritical CO_2 extraction of hops. The bio-carbon sorbents obtained were then tested for removal of gas pollutant of acidic character (nitrogen dioxide) and liquid organic (methylene blue) and inorganic (iodine) pollutants.

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2. Materials and methods

2.1. Precursor and activated bio-carbons preparation

The residue left after supercritical extraction of hops was used as the precursor in this study. The starting material was powder with grain size range of 0.10–0.80 mm and moisture content in air-dry state of 5.6 wt%. The raw material was divided into two parts. One of them was impregnated with Na_2CO_3 solution (weight ratio Na_2CO_3:precursor, 2:1 or 3:1), dried to constant mass at 110 °C and then subjected to thermal treatment in nitrogen (flow rate of 0.330 L/min). The impregnated samples were heated (10 °C/min) from room temperature to 700 °C and kept at the final activation (A) temperature for 45 min and then cooled down in nitrogen flow. The activated bio-carbons obtained were labelled as A2 and A3, which refers to the precursor impregnated with Na_2CO_3 at the weight ratio alkali: precursor 2:1 or 3:1, respectively, and activated at 700 °C.

The second part of the starting material was firstly subjected to pyrolysis at 500 °C (P), carried out in a quartz tubular reactor heated by horizontal laboratory furnace under a stream of nitrogen at the flow rate of 0.170 L/min. The sample was heated at 10 °C/min from room temperature to the final pyrolysis temperature, kept at 500 °C for 1 h and then it was cooled down in an inert atmosphere. Pyrolysis product was next subjected to chemical activation with Na_2CO_3. Chemical activation by Na_2CO_3 was performed at 750 °C with an alkali/bio-char weight ratio of 2:1 or 3:1 in nitrogen atmosphere (flow rate 0.330 L/min), for 45 min. The activated bio-carbons obtained were labelled as PA2 and PA3, which refers to the bio-char impregnated with Na_2CO_3 at the weight ratio alkali: bio-char 2:1 or 3:1, respectively, and activated at 750 °C.

After the activation process, the final products were subjected to two-step washing procedure, firstly with a hot 5% solution of HCl and later with demineralized water until free of chloride ions. Finally, the samples were dried to constant mass at 110 °C.
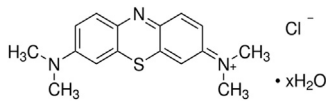
2.2. NO_2 adsorption tests

The evaluation of sorption capacity: samples in the form of powder (0.10–0.50 mm in diameter) were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume 3 mL). The samples were tested in dry (D) and wet (W) conditions. Dry or wet air (70% humidity) with 0.1% of NO_2 was passed through the bed of the adsorbent with a total flow rate of 0.450 L/min. The concentration of NO_2 was monitored using Multi-Gas Monitor Q-RAE PLUS PGM-2000/2020. The tests were stopped at the breakthrough concentration of 20 ppm because of the electrochemical sensor limit. After that, the desorption of NO_2 from the adsorbent bed was monitored. The interaction capacities of each sorbent in terms of milligram of NO_2 per gram of adsorbent were calculated according to the formula proposed by Nowicki et al. (2012).

2.3. Adsorption of methylene blue

Methylene blue was obtained from POCH S.A., Gliwice and was used without further purification. A stock solution of methylene blue (MB) was prepared 1000 mg/L by dissolving the required amount of dye powder in distilled water. All working solutions of desired concentrations were prepared by diluting the stock solution with distilled water.

Adsorption of methylene blue (MB, Table 1) from aqueous solution was performed using the following procedure. Samples of the prepared bio-carbons of 0.025 g with the particle size of 0.09 mm were added to 50 mL of dye solution with initial concentration in the range from 50 to 180 mg/L and the suspension was stirred to reach equilibrium for 24 h. After the adsorption equilibrium had been achieved, the solution was separated from the sorbent by centrifugation at 6000 rpm, for 5 min. The concentration of dyes solution was determined using double beam UV–Vis spectrophotometer (Carry 100 Bio) at 665 nm. The equilibrium

Table 1
Properties of methylene blue.

Name	3,7-bis(dimethylamino)phenothiazin-5-ium chloride
Chemical formula Molecular structure	$[C_{16}H_{18}N_3S]^+Cl^-$
Colour	Blue
Molecular weight	319.85 g/mol
Class	Thiazin
Maximum wavelength	665 nm

adsorption capacities q_e (mg/g) were calculated according to the following formula:

$$q_e = \frac{(C_o - C_e)}{m} \times V$$

where in C_O is the initial concentration (mg/L), C_e is the residual concentration (mg/L), V is the volume of the solution (L), m is the mass of the adsorbent (g).

The effect of pH on dye removal efficiency was studied in a pH range of 2–12. The initial pH of the dye solution was adjusted by the addition of 0.1 mol/L solution of HCl or NaOH. The effect of the contact time was investigated by varying the contact time from 0 to 720 min at the room temperature.

2.4. Adsorption of iodine

The iodine sorption ability of the adsorbents was determined according to the following procedure: Portions of 0.2 g of the samples sieved to a particle size below 1 mm were placed in 250 mL flasks and 4 mL of 5% HCl was added. Then 20 mL of stock 0.1 mol/L iodine solution was added to it and the mixture was shaken for 4 min in a shaker. All the samples were filtered through filter paper and next washed with 50 mL of water. The resulting solution was titrated with 0.1 mol/L sodiumthiosulphate (1% starch solution was used as an indicator) until the solution become colorless.

2.5. Sample characterization

2.5.1. Low-temperature nitrogen adsorption
Nitrogen adsorption/desorption isotherms were measured at −196 °C using the QuantachromeAutosorbiQ surface area analyser. Prior to the isotherm measurements, the samples were outgassed at 150 °C for 8 h. BET specific surface areas were evaluated in the range of relative pressures p/p_0 of 0.05–0.30. Total pore volumes were calculated by converting the amount adsorbed at $p/p_0 \sim 0.99$ to the volume of liquid adsorbate. Average pore sizes and pore distributions were calculated from the adsorption branches of isotherms using the BJH method. Additionally, external surface areas, micropore volumes and areas were determined by the t-plot method.

2.5.2. Measurement of surface pH
The pH of activated bio-carbons was measured using the following procedure: a portion of 0.2 g the sample of dry powder was added to 10 mL of distilled water and the suspension was stirred overnight to reach equilibrium. Then the pH of the suspension was measured on a pH-meter manufactured by Metrohm Ion Analysis (Switzerland) equipped in Unitrode Pt1000 (combined glass pH electrode with temperature sensor).

2.5.3. Surface oxygen functional groups
The content of surface oxygen functional groups was determined according to the Boehm method (Boehm, 1994). A portion of 0.25 g of