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Physicochemical and adsorption properties of carbonaceous sorbents prepared by activation of tropical fruit skins with potassium carbonate

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ABSTRACT

A series of new carbonaceous adsorbents has been obtained by means of chemical activation of common tropical fruit peels with potassium carbonate. The influence of the precursor on the porous structure development, acidic and basic surface group generation, as well as the sorptive properties of the adsorbents prepared towards liquid pollutants, was tested.

The products of thermo-chemical treatment of grapefruit, mandarin, pomelo and banana peels were microporous carbonaceous sorbents with relatively high contribution of mesopores (of diameters within the range of 2–10 nm), characterised by well-developed surface area ranging between 836 and 1198 m^2/g, containing mainly acidic surface functional groups. Moreover, the results obtained during the study proved that a proper selection of biomass treatment process allows getting adsorbents with a very high sorption capacity towards methylene blue and methyl red as well as inorganic pollutants of molecules of size similar to that of iodine molecules.

1. Introduction

Growing interest in the carbonaceous sorbents is connected with development of modern industrial technologies as well as rising standards concerning protection of the natural environment. From a wide panoply of materials applied for that purpose, the most popular are activated carbons, which can be used for the removal of organic and inorganic contaminants from liquid and gas phases, as well as in catalysis, electrochemistry and for gas storage [1].

The worldwide production of activated carbons is based mainly on the natural precursors with a high content of elemental carbon, in particular brown and hard coals [2], wood and sawdust [3–5] or local waste materials such as coconut shells [6]. Very attractive, but at the same time expensive precursors of carbonaceous adsorbents are synthetic polymers and used tyres [7]. In view of high cost of fossil coals as well as taking into regard economic and ecological aspects, recently much attention has been paid to the production of activated carbons from waste materials of plant origin [8–11].

As has been shown by many authors, activated carbons characterised by well-developed porous structure and good sorptive properties towards pollutants of different types can be obtained from the fruit peels [12–19] and other biowastes [20–26]. Most of the hitherto reported studies have described carbon activation by CO_2 (physical activation) [12], and chemical activation by H_3PO_4 [13], NaOH [14,15] or KOH [16,23,26] as activators. Much less interest has been paid to production of activated carbons by the activation with K_2CO_3 [17–19]. For this reason the main goal of this study was to prepare a series of low-cost carbonaceous sorbents by chemical activation of four types of tropical fruit peels with potassium carbonate and to characterise their physicochemical properties as well as sorption capacity towards liquid pollutants represented by methylene blue, methyl red and iodine.

2. Experimental

2.1. Preparation of activated carbons

At the beginning, each of the precursors — banana (B), grapefruit (G), mandarin (M) and pomelo (P) peels were air-dried at 110 °C and crushed to the grain size of 4–6 mm. After that the precursors were impregnated with K_2CO_3 solution (weight ratio 2:1), dried to constant mass at 110 °C and then subjected to thermal treatment in nitrogen atmosphere (AC). The impregnated samples were heated (10 °C/min) from room temperature to 800 °C and kept at the final activation temperature for 30 min and then cooled down in nitrogen flow. After the activation process, the final products were subjected to two-steps washing procedure, with a hot 5% solution of hydrochloric acid and later with demineralised water. The weight ratio of activator/precursors used has been chosen on the basis of our earlier studies in which we have shown that the weight ratio of 1:1 is too low to ensure effective development of the surface area and porous structure. As the parameters have a substantial effect on the sorption capacity of activated carbon towards liquid pollutants, we have decided to use higher ratios of 2:1 and 3:1. However, the 3:1 ratio ensures insignificantly better textural

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Table 1
Elemental analysis of the activated carbons and the yield of activation process (wt.%).

Sample	Ash	C^{daf*}	H^{daf}	N^{daf}	S^{daf}	O^{daf**}	Yield
BAC	2.1	83.1	0.4	2.4	0.0	14.1	28.1
GAC	1.4	90.2	0.3	1.1	0.1	8.3	22.0
MAC	1.3	89.5	0.4	1.1	0.1	8.9	23.4
PAC	1.0	86.2	0.9	1.3	0.1	11.5	26.5

BAC, GAC, MAC, PAC — activated carbons obtained from banana, grapefruit, mandarin and pomelo peels, respectively.
* Dry-ash-free basis.
** Determined by difference.

parameters than 2:1 and also similarly as the application of higher activation temperature, e.g. 900 °C, leads to a significant decrease in the yield of activation process.

2.2. Sample characterisation

2.2.1. Analytical procedures

Elemental analysis of all the samples under investigation was carried out using the Elementar Analysensysteme instrument, model Vario EL III. The ash content was determined according to the ISO 1171:2002 standard: the dried sample was burned in a microwave oven at 850 °C for 60 min. The ash content was expressed as: %Ash = [(mass of crucible and ash − mass of crucible) / (mass of crucible and sample − mass of crucible)] ∗ 100%.

2.2.2. Porous structure

Nitrogen adsorption/desorption isotherms were measured at −196 °C using the Quantachrome Autosorb iQ surface area analyser. Prior to the isotherm measurements, the samples were outgassed at 150 °C for 10 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 ~ 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.

2.2.3. Surface oxygen groups and surface pH

To evaluate the content of oxygen functional groups of acidic and basic character the Boehm method was applied [27], whereas the pH of the materials was evaluated using the procedure described in detail in our previous study [28].

2.2.4. Scanning electron microscopy (SEM)

SEM images were obtained using a scanning electron microscope (SEM) made by PHILIPS (Netherlands) in the following conditions: working distance of 14 mm, accelerating voltage of 15 kV and digital image recording by DISS.

2.3. Adsorption from liquid phase

Determination of the iodine adsorption was performed according to the ASTM D4607-94(2006) standard. Portions of 0.1 g of the samples sieved to a particle size of 0.09 mm were placed in 250 mL flasks and 5 mL of 5% HCl was added. Then 10 mL of stock iodine solution of 0.1 M 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 at 25 mL of water. The resulting solution was titrated with a 0.1 M sodium thiosulphate (1% starch solution as an indicator) until the solution becomes colourless. A blank was prepared without adding a sample. The amount of adsorbed iodine was calculated by applying the following formula: [(mL of sodium thiosulphate used for blank − mL thiosulphate used for sample) ∗ initial concentration of iodine solution ∗ molar mass of iodine molecule] / mass carbon.

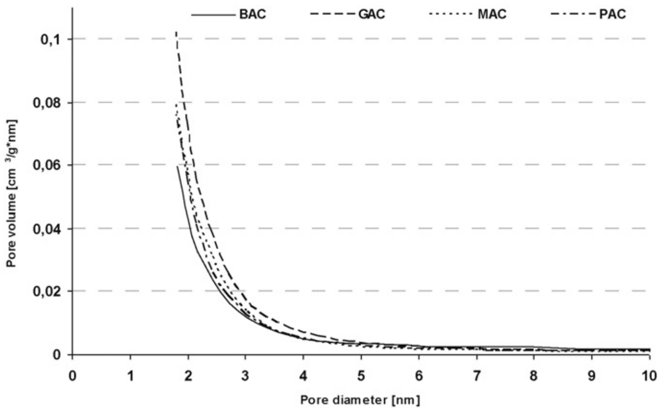

Fig. 1. Pore size distribution of the activated carbons.

Methylene blue and methyl red adsorption was determined according to the following procedure. Samples of the prepared activated carbons in the same portions of 0.020 g with the particle size 0.09 mm were added to 0.05 l of methylene blue or methyl red solution with initial concentrations in the range from 40 to 220 mg/L and the suspension was stirred to reach equilibrium for 24 h. The equilibrium time of 24 h was chosen on the basis of preliminary kinetic studies. After the adsorption equilibrium had been achieved, the solution was separated from the sorbent by filtration. The adsorbent was separated by syringe filters ABLUO™–CAMEO™ (pore size: 1,2 μm). In order to avoid the change in dye concentrations, a preliminary filtration was performed prior to sampling, and the solution used for dye proportioning was collected from the second filtration on the same filter.

The dye concentrations in the solution before and after adsorption were determined using a double beam UV–Vis spectrophotometer (CaryBio100, Varian) at a wavelength of 665 and 429 nm, respectively. All experiments were made in triplicate. The equilibrium adsorption amounts (mg/g) were calculated according to the following formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}, \tag{1}$$

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

Table 2
Textural parameters of the activated carbons obtained.

Sample	Total surface area [m^2/g]	Micropore area [m^2/g]	Total pore volume [cm^3/g]	Micropore volume [cm^3/g]	V_{mic}/V_t	Average pore diameter [nm]
BAC	1188	993	0.65	0.48	0.74	2.19
GAC	1198	883	0.64	0.43	0.67	2.16
MAC	1077	833	0.57	0.41	0.72	2.15
PAC	836	603	0.46	0.29	0.63	2.19

BAC, GAC, MAC, PAC — activated carbons obtained from banana, grapefruit, mandarin and pomelo peels, respectively.