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Characterization of nanoporous carbon fibrous materials obtained by chemical activation of plane tree seed under ultrasonic irradiation

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ABSTRACT

An ultrasonic irradiation was applied for the impregnation by chemical agents in the chemical activation process of new type of active carbon precursor. Plane tree seed, due to the unique fibrous structure and low cost is a promising eco-friendly raw material for the preparation of activated carbon materials. Ultrasonic irradiation was used for the impregnation step allowing the chemical activation by different agents: potassium or sodium hydroxide, hydrogen peroxide and pyrogallol. The porous structures were examined by nitrogen adsorption/desorption isotherms at 77 K and electrochemically by cyclic voltammetry. The textures of these materials were observed by scanning electron microscopy. The application of ultrasonic irradiation in the impregnation step increased surface area of the final material more than two times in comparison to the material which impregnation in the activation process was by conventional stirring. Ultrasonic irradiation enhances the chemical activation process and the activated carbon fibrous materials with nanoporous structure were obtained by impregnation of seeds with alkaline hydroxides. Total surface areas of these samples were 976 $m^2 g^{-1}$ and 1130 $m^2 g^{-1}$. These fibers have total specific capacitance as high as 125 F g^{-1} and 53 F g^{-1} which major fraction in both cases originate from internal micropores structure.

1. Introduction

Carbon materials can be made from any carbon containing substances (almost all naturally occurring organic medium) with a wide range of structures, compositions and properties [1]. Activated carbon is widely used in environment protection for adsorption of pollutants from gaseous and liquid streams, for recovery of solvents, in catalysis as a catalyst support, in electrochemistry etc. [2–5]. A challenge in the field of carbon adsorbents is to produce activated carbon from cheap and readily available and renewable raw material by low cost process. Commonly used materials are: various stones and nutshells, forest and agricultural residues, corn hulls and corn stover, seed coat, waste tea, natural fibers [2–4,6–10], etc.

In order to get a high surface area, chemical or/and physical activation processes of material usually have been employed. The physical method consists of the pyrolysis of the precursor material and gasification of the resulting char in steam or carbon dioxide [7]. Chemical activation offers some advantages over physical activation such as: it uses lower temperatures and heat treatment times, it usually consists of one step and the obtained carbon yields are usually higher. Disadvantages are the need for a washing step of activated material to remove the chemical agent and the inorganic reaction products. Chemical reagents which are commonly used in the chemical activation process are: NaOH, KOH, H_3PO_4, $ZnCl_2$, K_2CO_3 [2–4,6–10], etc.

Ultrasonic irradiation could enhance the reaction rates in a broad range of reacting systems: biological, chemical and electrochemical. Ultrasonication could increase the conversion factor, change the reaction pathway by forming free radicals that accelerate the reaction, improve the yield and/or initiate the reaction. Also, ultrasonic irradiation may have mechanical effects on the chemical reaction, such as accelerating dissolution, or increasing the surface area between the raw materials and activating agents and/or renewing the surface of a solid reactant [11]. The physics and chemistry of nonlinearly oscillating acoustic cavitation bubbles induced by ultrasonication are strongly influenced by the dissolved gas in the surrounding liquid [12]. Informations available in the literature about application of ultrasound in the field of active carbons are mostly related to improvement of sorption processes [13,14] while those regarding regeneration [15] or preparation [16,17] of activated carbon are only sporadic.

Plane tree (Platanaceae) contains several species of trees distributed around the Northern Hemisphere. The hairy, dry, seed like fruits are densely packed into a hard drap ball. The ball contains

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several hundred achenes each of which has a single seed and is conical with a tuft consisting of many thin stiff bristle fibers attached to the base of each achene. The seeds could be collected from the tree in autumn as it matures, even over the winter to early spring. They are cheap and renewable raw material which, can be collected for several months each year.

In this study we examined new type of a precursor for preparation of active carbon fibrous material-plane tree seeds. Also, the influence of different chemical activating agents on the adsorption and electrochemical properties of obtained carbon material were investigated. Ultrasonic irradiation has been chosen for dispersion and better mixing of the raw material with the solution, due to its specific form. KOH and more recently NaOH are the two most used hydroxides for the preparation of active carbons [3]. Apart from the known alkali hydroxide agents in our experiment other forms of oxygen such as hydroxyl groups and peroxide, were examined. 1,2,3-Trihydroxybenzene Pyrogallic acid (pyrogallol) chemically is a phenol with three phenolic hydroxyl groups that exhibits weak acidic properties. H_2O_2 is the simplest peroxide that is well known as a strong oxidizer, while pyrogallol is a strong reducing agent. But there was no literature data for influence of ultrasound irradiation on pyrogallol characteristics neither for interaction between pyrogallol and botanical precursor.

2. Materials and methods

2.1. Materials

The material used in our study was harvested from single trees of plane tree (*Platanus orientalis*) growing in the Belgrade's parks (Serbia) in September. *P. orientalis* is widespread in the eastern Mediterranean region of Europe (Southern Italy, Balkan Peninsula where Serbia is, and Turkey) and Western Asia. The fruits diameter was about 2–3 cm. Achenes with their thin bristle fibers were used for the experimental work. Their length was up to 1 cm and about 1 mm thick while bristles were shorter and a few times thinner. Achenes and bristles because of its fibrous shape were marked as natural fibers (NF). The activation agents were: NaOH, KOH and H_2O_2 manufactured by Centrohem, Serbia. The reducing agent was pyrogallol, manufactured by AnalaR NORMAPUR®, UK. Argon with a purity of 99.998%, supplied from a compressed gas cylinder, provided the inert atmosphere during carbonization and activation process. Liquid nitrogen and ultra-pure compressed nitrogen (nitrogen content of 99.9995%) served as coolant and adsorbate for the gas adsorption/desorption experiments, respectively.

2.2. Sample preparation

The plane fruit was first peeled off and washed with water to remove dirt and then dried in an oven. Achenes with the bristles (denoted as nature fibers – NF) were soaked in the 10% (w/w) aqueous solutions of NaOH (NF-1), Pyrogallol (NF2), KOH (NF-3) or H_2O_2 (NF-4). The ratio of the dry sample to each solution was 1:13 (mass basis). The sample bottles were placed on the bottom of the ultrasonic cleaner (Velleman VTUSC3, 42 kHz, 170 W) for 1 h at 333 K. Filtrated samples were partially dried in oven at the 373 K for 2 h. After that wet samples of NF were carbonized and activated in one step by pyrolysis under Ar flow up to 1173 K and kept at this temperature for 1 h. The heating rate during pyrolysis was 300 K/h. After cooling under Ar flow the samples were washed with distilled water for several times and last one was in ultrasound bath at the 333 K for h. The wet samples were dried at the 373 K and stored in desiccator. The samples were grounded in electronic grinder to ensure easy handling during electrochemical experiments. Another set of the samples was prepared without use of ultrasound, thus just soaked in the previously mentioned solutions for h, than carbonized as described above and washed in distilled water for several times [18]. These samples were denoted with *.

The mass yield of NF after impregnation process Y is calculated with following equation:

$$Y = ((mi - m)/m) \times 100\% \quad (1)$$

where m is the mass of the starting material before impregnation process and mi is mass of the material after impregnation and drying.

The mass loss of NF during carbonization and activation are calculated in a similar manner as shown in Eq. (2):

$$W = ((mc - mi)/mi) \times 100\% \quad (2)$$

where mc is the mass of the material after one step process of carbonization and activation.

2.3. Adsorption characteristics

The adsorption characteristics were determined from nitrogen adsorption/desorption isotherms at 77 K using the homemade gravimetric balance based on the McBain method. Before obtaining isotherms, the samples were degassed at a temperature of 523 K to remove any contaminants that may be present on the sample surface. The specific surface area, S_{BET} was calculated using Brunauer-Emmet–Teller (BET) method, from the adsorption branch of the isotherm [19]. The calculations of S_{BET} were performed in the relative pressure range from 0.0011 to 0.07. But for the carbonized NF, NF2 and NF4, which adsorption characteristics were significantly lower than for previously mentioned samples (NF-1 and NF-3) there were problems during the experimental work. It was not possible to ensure sufficient time for each point in adsorption process to come in a state of complete equilibrium. So, it was necessary to adopt a simplified experimental procedure, which involves the determination of the specific surface area in a single point on the adsorption isotherm within the BET range of relative pressure.

The high resolution α_s-plot proposed by Kaneko et al. [20], was used to calculate the external surface area, S_{ext}, as well as the total surface area, S_{tot} and the micropore volume, $V_{mic\alpha}$. External surface area, presents surface area of mesopores and macropores.

In order to analyze pore size distribution of samples slit pore geometry was select to represent the individual pores. The characteristic size of the slit shaped pores is their average pore width, L_{sr}. The pore size distribution in the micropore range (pore size is less than 2 nm) was estimated by applying the Horvath and Kawazoe (HK) method [21]. The HK method has been originally proposed for slit-like carbonaceous micropores and often employed for evaluation of the micropore size distribution of active carbons [21,22]. The pore size of mesopores (pore size is between 2 and 50 nm) were calculated by applying the Pierce modified by Orr and Dalla Valle method to the desorption branch of the isotherm. [19].

There are numerous other theoretical models that consider molecular modeling of adsorption isotherms for different pore widths using the Grand Canonical Monte Carlo method [23,24], Non Local Density Functional Theory [17] that were connected with their own specific assumptions of the description of the porous structure and/or mechanism of adsorption.

2.4. Structural characterization

The texture of the obtained active carbon nature fibers were investigated by scanning electron microscopy (SEM, JEOL JSM-35 model).