Comparison of activated carbon produced from natural biomass and equivalent chemical compositions

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ABSTRACT

Activated carbon was prepared from natural biomass (almond shell, waste tea, tomato stems and leaves) and also from commercial lignin, cellulose and hemicellulose by the chemical activation method using concentrated phosphoric acid as the activation agent. Further activated carbon was generated by the same method using biomass equivalent mixtures of commercial lignin, cellulose and hemicellulose as the precursor. Thermogravimetric analysis of the biomass was performed and the tomato leaves showed a significantly different decomposition profile compared with the other biomass, reflecting the higher proportion of extraneous material present. The activated carbon produced from each natural biomass was characterised in terms of its surface area and pore volume. The surface area values of the activated carbon produced from the waste tea and its equivalent composition were similar. The waste tea had the lowest ash content (3.45%). Comparison of the surface area measured on the other biomass materials and their equivalent compositions, showed noticeable differences. It was concluded that extraneous components particularly mineral matter in the biomass might have a significant impact on the surface area created during the heat treatment process. In general, mesopore rich material was produced with the starting materials except when commercial lignin was the precursor. Variation of the surface area of the activated carbon between the equivalent chemical composition and calculated values using commercial composition was in the range 5.34–11.43%.

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1. Introduction

Various types of precursors are used to produce activated carbon. These precursors are generally fossil based hydrocarbons (such as bituminous coal, lignite), natural biomass (lignocellulosic materials), biomass waste, polymers and carbonaceous wastes. The use of natural biomass is important as it is the most abundant renewable raw materials [1–6]. The surface characteristics of the activated carbon products are strongly influenced by the chemical nature of the raw material, the activation method (chemical or physical), the activation agent and the heat treatment process. A great number of studies are available in the literature reporting the effects of these factors on the final product. In addition to these factors, several investigations have researched the production of activated carbon directly from lignin, cellulose and hemicellulose, which are the main constituent components of natural biomass. However,

there is only limited discussion regarding interaction between the extraneous components (extractives and ash) and the main biomass components (lignin, cellulose and hemicellulose) during production of activated carbon in the presence of phosphoric acid. Furthermore, there is no literature comparing the properties of activated carbon produced by chemical activation with phosphoric acid of natural biomass with that produced from equivalent mixtures of their constituent components.

Phosphoric acid is widely employed to prepare activated carbon using various types of natural biomass such as waste tea [2,4], corncobs [3,6], rice husks [7,8], fruit seeds and stones [9,10], coconut shells [11], bamboo [12] in addition to KOH [13,14], $ZnCl_2$ [15,16] and K_2CO_3 [5,17]. The main objectives of these studies were to determine the surface characteristics of the activated carbon and the adsorption behaviour for various toxic and non-toxic materials and heavy metals from an aqueous phase. The determinations of surface characteristics were generally based on the BET surface area, porosity and functionality of the surface. The effects of various process parameters on the activated production were also extensively investigated and interpreted in these studies.

The main components of natural plant based biomass; lignin, cellulose and hemicellulose were used individually in many studies for several purposes, such as thermal decomposition [18–21]

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and the production of porous materials. The majority of these studies focused on thermal investigations applying thermoanalytical techniques (including thermogravimetric analysis, TGA, derivative thermogravimetry, DTG, differential thermal analysis, DTA, differential scanning calorimetry, DSC). Physical [11,21,22] and/or chemical [11,14,15,23–25] techniques using H_3PO_4, KOH, $ZnCl_2$ and K_2CO_3 were used to produce activated carbon from pure compositions. Cagnon et al. [21] used coconut shell and its artificial mixture (which corresponds to the coconut shell composition) to determine the contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors. There is no available study using phosphoric acid or chemical activation agent.

The objective of this research was to investigate the nature of activated carbon synthesised from a range of raw biomass relative to that produced from equivalent mixtures of lignin, cellulose and hemicellulose. Analysis of composition and experimental measurement of surface area and pore size distribution were performed to consider the influence of extraneous components (extractives and ash) and the original biomass form on the nature of the activated carbon produced.

2. Experimental

2.1. Materials

Activated carbon was prepared from four different raw biomass materials: almond shell (AS), factory waste tea (WT), tomato stems (TS) and tomato leaves (TL). The raw material particle size (diameter) was less than 500 μm. Additionally, activated carbon was produced directly from lignin, cellulose and hemicellulose individually and also in equivalent mixtures to the raw biomass. Commercial lignin and cellulose were sourced from Sigma–Aldrich and hemicellulose from Merck.

2.2. Activated carbon preparation

The process used to prepare the activated carbon is shown schematically in Fig. 1. Each precursor was mixed with H_3PO_4 (wt, 85%) at the desired acid:precursor ratio in a Teflon beaker. Each test was performed using 5 g of precursor. The H_3PO_4 impregnated precursor was directly subjected to microwave (MW) treatment for 30 s. Microwave pretreatment improves the surface area of the final product as reported by Yagmur et al. [1,2,4]. This pretreatment for each precursor was conducted in a domestic type microwave oven (Vestel, MDG-620). The frequency and the input power of the

microwave equipment were 2.45 GHz and 900 W, respectively. The sample was removed from the MW oven directly after the 30 s radiation time and a Raytek IR thermometer was used to evaluate the temperature as the sample cooled. Extrapolation of the temperature profile suggested that the sample temperature was in the range between 355 and 375 °C when extracted from the oven. The error was in the range between 1.4% and 5.6%.

Carbonisation of the samples was carried out in a quartz tube reactor located in a temperature programmable rotary tube furnace under nitrogen flow. The heating rate for all the samples was 10 °C/min and each sample was held in the furnace at the desired carbonisation temperature for 1 h [1,2]. The carbonised sample was mixed in hot distilled water (500 ml) for 12 h then washed and filtered. This process was repeated until the filtrate became neutral pH. The washed sample was dried in an oven at 110 °C for 12 h. The dry sample was powdered in a mill (IKA, M20 Universal Mill) at 20 000 rpm for 3 min. The sample was subjected to a further washing stage with hot distilled water to remove any residual phosphoric acid, filtered and dried prior to further analysis.

The yield of each run was calculated from the following equation:

$$\text{Yield}, \quad \% = \frac{\text{Activated carbon (dry), g}}{\text{Precursor (dry), g}} \times 100$$

2.3. Analyses

The hemicellulose, cellulose and lignin weight fractions of the natural biomass; almond shell, the waste tea and tomato plant (stems and leaves) were determined in the University of Maine, USA, following a procedure described in the literature [26,27].

The ash and moisture content of the starting materials were determined according to the TAPPI standard method T211 om-85 and Turkish Standards (TS 1561). A LECO CHNS 932 Elemental Analyser was employed to determine the carbon, hydrogen, nitrogen and sulphur content of the raw materials and the activated carbons; the oxygen content was calculated by difference.

The specific surface area and pore size distributions of the samples were determined using a Quantachrome NOVA 2200 series volumetric gas adsorption instrument. The surface area of the sample (degassed at 120 °C for 12 h) was computed using multipoint nitrogen adsorption data according to the BET method [28]. The calculated deviation in the BET measurements was between 0.4% and 1.95%. The pore volume of each sample was determined in accordance with the Non Local Density Functional Theory (NLDFT) method. Recently, the method has been broadly used for the pore analyses of activated carbon [1,4,5,29,30]. The total pore volume
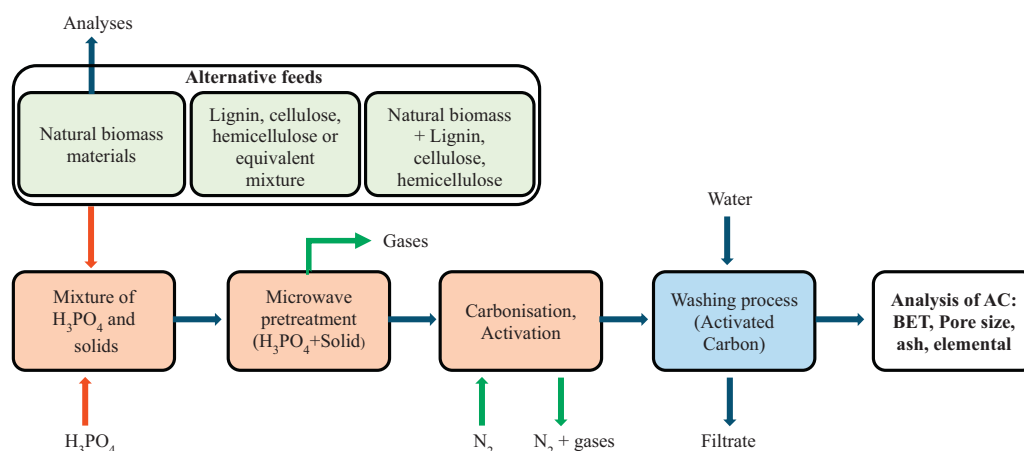

Fig. 1. Schematic of activated carbon production process.