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Preparation of high-surface area activated carbons from Paulownia wood by $ZnCl_2$ activation

Sait Yorgun *, Naile Vural, Hakan Demiral

Department of Chemical Engineering, Engineering and Architecture Faculty, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey

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ABSTRACT

In this study, an activated carbon with high-surface area was prepared from Paulownia (*P. tomentose*) wood by chemical activation with $ZnCl_2$. The influences of carbonization temperature and impregnation ratio on the pore structure of the activated carbon were investigated. Activation temperatures and impregnation ratios were selected in the range of 400–700 °C and 0.5–4.0, respectively. Under the experimental conditions investigated, a carbonization temperature of 400 °C and impregnation ratio of 4.0 were found to be suitable for producing high-surface area activated carbon. It was shown that $ZnCl_2$ works effectively as dehydration reagent below 500 °C. The obtained carbons were characterized by nitrogen adsorption–desorption isotherms at 77 K. The results showed that the surface area and micropore volume of activated carbons, which were determined by application of the Brunauer–Emmett–Teller (BET) and *t*-plot methods, were achieved as high as 2736 m^2/g and 0.69 cm^3/g, respectively. The chemically activated carbons were found to be mainly type I carbons. The microstructures of the char and activated carbons were also examined with scanning electron microscopy (SEM).

1. Introduction

Biomass is a renewable resource that can be better managed and utilized to provide a wide range of useful chemicals, materials and energy. A possible utilization of biomass resources is converting it into activated carbon.

The environmental constraints and a growing demand in adsorbing materials need to intensify research works on activated carbon produced from non-fossil sources. In this perspective, lignocellulosic wastes from agriculture and forestry are of great interest [1]. In recent years, evaluation of agricultural and forestry wastes as raw materials for the production of activated carbons has increased remarkably due to their low cost and large supply.

Activated carbon is predominantly an amorphous solid with a large internal surface area and pore volume. It consists of a basic structural unit building up of condensed aromatic rings. The pores in the carbon contribute to the increase in its surface area and to textural properties before and after activation [2]. Activated carbon is one of the most important adsorbents used in industry. This adsorbent is mainly used for separation and purification of gaseous and liquid mixtures [3–6]. The nature of the precursor, activation method, and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, pore shape and surface chemistry [2,6,7].

Activated carbons can be produced basically by two methods: physical activation or chemical activation. The former involves primary carbonization of the raw material (below 700 °C) followed by controlled gasification at higher temperatures (>850 °C) in a stream of an oxidizing gas (steam, CO_2, air or a mixture) [8–10]. Chemical activation is known as a single step method of preparation of activated carbon in the presence of chemical agents which are normally alkali and alkaline earth metal containing substances and some acid such as KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $ZnCl_2$, $MgCl_2$, H_3PO_4 and H_2SO_4 [2,9]. Chemical activation is the process that normally takes place at a lower temperature and shorter time than those used in physical activation. Moreover, the development of a porous structure is better for the chemical activation. The carbon yield in chemical activation is usually higher than in physical activation since the chemical agents are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile substances [5,10–12]. Among the chemical activating agents, in particular, zinc chloride is the most widely used chemical in the preparation of activated carbon [13]. Zinc chloride activation has been applied to different materials [6,11,13–23].

Woods are one of the most important materials for preparing activated carbons, which have particular porous characteristics and are appropriate for the adsorption of solute in liquid-phase [5]. There are many studies in the literature relating to preparation and characterization of activated carbon from forest wastes [24].

Paulownia is scrophulariacease, with nine species of the very adaptable and fast-growing timber trees. Paulownia, which is

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* Corresponding author. Tel.: +90 222 239 37 50x32 76; fax: +90 222 239 36 13.
E-mail address: syorgun@ogu.edu.tr (S. Yorgun).

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indigenous to China, has been naturalized in Japan, Australia, Brazil, Europe and USA [25]. In recent years, Paulownia is receiving increasing attention as a genus suitable for use as a short-rotation woody crop in Turkey. The climate of Turkey is suitable for Paulownia plantation. If appropriate conditions are provided, the tree can reach about 15–25 m high in a 5-year period [26,27]. Paulownia trees have been used for different purposes such as to produce leaves useful as fodder or fertilizer, flower for honey production, and wood for solid products over the years [25,28,29].

In this study, the use of Paulownia wood to produce activated carbon has been considered. For this purpose, activated carbons were prepared from Paulownia wood (*P. tomentose*) by chemical activation with zinc chloride, and the influences of carbonization temperature, and impregnation ratio on the pore structure (specific surface area, pore volume, and pore size distribution) were investigated. In addition, scanning electron microscopy (SEM) has been used to visually observe the differences in the development of the microstructure of the activated carbons.

2. Experimental

2.1. Materials

Paulownia wood used in this study as a raw material was obtained from Çorum, Black Sea region in Turkey. Prior to use, sample was air dried, grounded in high-speed rotary cutting mill and then screened to give the fraction of 0.6 < Dp < 1.8 mm particle size for use in the chemical activation experiments. Elemental analyses of the raw material and activated carbon were performed on a Carlo Erba Model EA 1108 elemental analyzer. ASTM standard test procedures were applied for ash content, ASTM D 1102-84; volatile matter content, ASTM E 897-82; higher heating value, ASTM D 3286 and moisture content, ASTM D 2016-74. Fixed carbon was calculated from the difference. The proximate and ultimate analyses of the raw material and activated carbon are given in Table 1.

2.2. Preparation of activated carbon

In this study, the impregnation ratio was calculated as the ratio of the weight of $ZnCl_2$ in solution to the weight of the used Paulownia wood. The impregnation ratio was varied between 0.5 and 4. Chemical activation of Paulownia wood was performed using zinc chloride. Ten to eighty grams of $ZnCl_2$ were dissolved in 200 mL of distilled water, and then 20 g of the raw material was mixed with the $ZnCl_2$ solution and stirred at approximately 80 °C for 7 h to ensure a complete reaction between $ZnCl_2$ and wood particles. The mixtures were then filtered and the remaining solids were dried at 110 °C for about 12 h.

Carbonization of the impregnated sample was carried out in a 316 stainless steel tubular reactor with a length of 104 mm and an internal diameter of 70 mm, with a sweep gas (N_2) connection. The fixed-bed reactor was externally heated by an electrical furnace. In the carbonization system, heating rate and final carbonization temperature were controlled. The temperature was measured with a Ni–Cr thermocouple inside the bed. More detailed descriptions of the carbonization procedure can be found elsewhere [30]. About 10 g of the impregnated sample was placed on a metal mesh in the reactor and heated up to the final carbonization temperature under the nitrogen flow (150 cm^3/min) at heating rate of 10 °C/min and held for 1 h at this final temperature. The final carbonization temperature was varied from 400 to 700 °C. The resulting solids after carbonization were boiled at about 90 °C with 100 mL of 1 N HCl solution for 30 min to leach out the activating agent, filtered and rinsed by warm distilled water several times to remove excess acid. They were then dried at 110 °C for 12 h, and weighed to calculate the yield.

Table 1
Proximate and ultimate analyses of Paulownia wood and an activated carbon (prepared at impregnation ratio of 3.0 and carbonization temperature of 400 °C).

Analysis	Raw material (wt%)	Activated carbon (wt%)
Proximate		
Moisture	6.50	3.20
Ash	1.06	2.65
Volatile matter	71.80	13.80
Fixed carbon	20.64	80.35
Ultimate		
Carbon	44.73	71.36
Hydrogen	6.12	2.25
Oxygen[a]	48.28	25.93
Nitrogen	0.87	0.46
H/C molar ratio	1.64	0.38
O/C molar ratio	0.81	0.72
Calorific value (MJ/kg)	20.6	25.3
Empirical formula	$CH_{1.64}O_{0.81}N_{0.02}$	$CH_{0.38}O_{0.27}N_{0.005}$

[a] By difference.

2.3. Characterization of the prepared activated carbon

The pore structure characteristics of the resulting activated carbons were determined by nitrogen adsorption at 77 K using an automatic adsorption instrument (Quantachrome, Autosorb-1 C). Prior to gas adsorption measurements, the samples were degassed at 300 °C in a vacuum condition for 3 h. Adsorption data were obtained over a relative pressure, P/P_o, ranging from approximately 10^{-6} to 1. The surface area, pore volume and pore size distribution of the activated carbons were determined by the application of the Brunauer–Emmett–Teller (BET) and *t*-plot analysis software available with instrument, respectively. The BET surface areas were assessed by applying relative pressures ranging from 0.01 to 0.15 [8]. The total pore volumes (V_t, cm^3/g) were estimated to be the liquid volumes of N_2 at a high relative pressure near unity (~0.99). The *t*-plot method was applied to the micropore volume and mesopore surface area, and the mesopore volume was obtained by deducting the micropore volume from the total pore volume. Pore size distribution of the activated carbons was obtained by applying the micromeritics density functional theory (DFT) method to the nitrogen adsorption isotherms using the software supplied by Autosorb-1 C [31]. The microstructures of char and activated carbons produced from Paulownia wood were examined using scanning electron microscopy (JEOL JSM-5600 LV Model SEM).

3. Results and discussion

3.1. Yield of activated carbon

The high volatile matter and low ash content of a biomass resource make it a good starting material for preparing activated carbon [31]. As can be seen from Table 1, the raw material Paulownia wood used in this study has low ash and high volatile matter contents. The yield of activated carbon was calculated from the weight of resultant activated carbons divided by the weight of dried Paulownia wood [7,21]. The final carbonization temperature and impregnation ratio play an important role on the yield of activated carbon. As seen in Fig. 1, it is observed that the activated carbon yields are higher than those of chars with no impregnation in the carbonization temperature range of 400–700 °C. The activation of Paulownia sawdust without $ZnCl_2$ impregnation resulted in a relatively low active carbon yield in the range of 28.3–21.9% since a large amount of carbons were removed as CO, CO_2, CH_4 and tar coupling with O and H atoms [32]. The activating agent in the inte-