

Influence of Temperature and Impregnation Ratio of H_3PO_4 on the Production of Activated Carbon from Hazelnut Shell

Y. ÖRKÜN^a, N. KARATEPE^{a,*} AND R. YAVUZ^b

^aEnergy Institute, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

^bEngineering Department, Istanbul Technical University, Chemical 34469 Maslak, Istanbul, Turkey

Hazelnut shell was used as a precursor in the production of activated carbon by chemical activation with H_3PO_4 since there is a huge volume of such a solid waste resulting from the hazelnut production in eastern Black Sea region of Turkey. Effects of final activation temperature, time and H_3PO_4 concentration used in the impregnation stage on the porous development were investigated. Activation at low temperature represented that micropores were developed first and then mesoporosity developed, enhanced up to 400 °C and then started to decrease due to possible shrinking of pores. The optimum temperature for hazelnut shell was found to be around 400 °C on the basis of total pore volume and the Brunauer–Emmett–Teller surface area. It was clearly demonstrated that H_3PO_4 concentration used in the impregnation stage was not only effective for development of surface area and pore volumes but also an effective tool for tailoring the pore structure and size distribution.

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1. Introduction

Activated carbon is a generic term for a family of highly porous carbonaceous materials, none of which can be characterized by chemical analysis. The volume of the pores in activated carbons is generally defined as being greater than 0.2 ml/g, and in the internal surface area is generally larger than 400 m²/g as measured by the nitrogen Brunauer–Emmett–Teller (BET) method. The width of the pores varies from 3 Å to several thousands angstroms. Activated carbons having enormous internal surface areas, make them effective adsorbents.

The characteristics of activated carbon depend on the physical and chemical properties of the precursor as well as on the activation method [1]. The choice of precursor is largely dependent on its availability, cost and purity, but the manufacturing process and intended application of the product are also important considerations. Agricultural wastes are considered to be a very important feedstock because they are renewable sources and low cost materials. Several researches on the preparation of activated carbons from agricultural wastes, such as fruit stones, sugar canes, almond shells, nut shells etc., have been reported [2–6]. Hazelnut is one of the most important agricultural products of Turkey. North coasts of Turkey are so suitable to grow hazelnut that approximately 80% of the total hazelnut production in the world is supplied from this region [7]. Therefore, there is a great potential of hazelnut shell to use in activated carbon production in that region.

There are two methods of preparing activated carbons: physical or chemical activation. Chemical activation has some advantages over physical activation method when a lignocellulosic material is especially used as a raw material. Besides some disadvantages of chemical activation, yield is relatively high in this process, and activation temperature is low making the process more economical compared to physical activation. In a chemical activation, a raw material is impregnated with an activating reagent and the impregnated material is heated in an inert atmosphere. There will be a reaction leading to developments in porosity between the precursor and the activating agent used in activation. Several activating agents, such as $ZnCl_2$, KOH , $NaOH$, $AlCl_3$, H_3PO_4 , $CaCl_2$, etc., are used in chemical activation processes so far. Activating agents generally act as dehydrating materials and they may promote the formation of crosslinks. Among the numerous dehydrating agents for chemical activation, the use of phosphoric acid is preferred recently due to some environmental and economical concerns [8].

If chemical activation is essentially considered as a reaction between the solid precursor and the chemical, the concentration of the activating agent, temperature, and activation time will be the main factors affecting the extents of reaction. These parameters were investigated in this study to represent the effects of operation conditions on developments of pore volume and pore size distributions of activated carbons prepared from hazelnut shell activated by H_3PO_4 .

2. Experimental

Hazelnut shell was obtained from the Akçakoca area in the eastern Black Sea region of Turkey. They were

* corresponding author; e-mail: kmnilgun@itu.edu.tr

sized and the fraction of particle sizes between 0.85 mm and 1.0 mm used in the impregnation stage. 50 g of this sample were impregnated with 100 ml of H₃PO₄ solutions having different concentrations (35 wt%, 50 wt%, and 65 wt%). This mixture was stirred at 85 °C for 4 h and then it was dried within an air circulated oven at 110 °C. All impregnated materials were carbonized in a quartz reactor, under the same experimental conditions: a flow of N₂ of 300 cm³/min, heating rate of 5 °C/min up to a final temperature and a given activation time. After carbonization, the carbon was cooled down to room temperature in a flow of nitrogen. To remove the excess of H₃PO₄, the activated carbon after carbonization was extensively washed with hot water until neutral pH. Then the sample was dried in an oven at 110 °C. Samples are designated as “AC” followed by their respective carbonization temperatures (°C), times (h), and H₃PO₄ concentrations (%), e.g. AC500-120-50.

Information on the carbon pore structure was derived from N₂ adsorption isotherms obtained at -196 °C on an ASAP 1020 apparatus (Micromeritics). Samples were de-

gassed under vacuum at 200 °C for 2 h prior to all adsorption measurements. The BET surface areas (SBET) of the activated carbon samples were calculated from the N₂ adsorption isotherms using the BET equation. The micropore volumes (V_{mi}) of the AC samples have been calculated by applying *t*-plot method, Dubinin–Radushkevich (DR) and Horvath–Kawazoe (HK) methods to the experimental N₂ isotherms measured at -196 °C. Total pore volume (VT) was assessed from the amount of N₂ adsorbed at *p/p*₀ = 0.95. The volume of mesopores (V_{meso}) was calculated by subtracting the volume of micropores (V_{mi}) from the VT. The density functional theory (DFT) was used to calculate the pore size distribution from the N₂ desorption isotherms with the software supplied by Quantachrome, USA. N₂ at -196 °C on carbon, slit pore, NLDFT equilibrium model was used in the interpretation of the N₂ desorption data. The average pore diameter (*D*) of the sample was calculated by assuming a cylindrical shape of pores from the BET surface area and pore volume, $D = 4VT/SBET$. The results are given in Table.

Porous textural properties of the activated carbon samples.

TABLE

Sample	S_{BET} [m ² /g]	V_{mi}^a [cm ³ /g]	V_T [cm ³ /g]	V_{mi}^b [cm ³ /g]	V_{mi}^c [cm ³ /g]	V_{meso} [cm ³ /g]	<i>D</i> [Å]
AC400_2_50	2245.9	1.012	1.1736	1.075	0.90	0.1616	20.90
AC450_2_50	2192.4	0.975	1.1575	1.052	0.89	0.1825	21.12
AC500_2_50	1958.8	0.869	1.0025	0.928	0.79	0.1335	20.47
AC400_2_35	2120.7	0.939	0.9932	0.922	0.86	0.0542	18.73
AC400_2_65	2322.5	1.012	1.3629	1.202	0.93	0.3509	23.47
AC400_1_50	2328.2	1.043	1.2438	1.124	0.93	0.2008	21.37
AC400_3_50	2963.9	1.332	1.5638	1.441	1.19	0.2318	21.10

^a Calculated by applying DR equation to N₂ adsorption data.

^b Calculated by applying *t*-plot equation to N₂ adsorption data.

^c Calculated by applying HK equation to N₂ adsorption data.

3. Results and discussions

Figure 1 shows the N₂ adsorption isotherms of various activated carbons classified with respect to the parameters affecting the production of activated carbon from hazelnut shell with H₃PO₄. They represent type I isotherm according to the Brunauer, Deming, and Teller (BDT) classification, depending on the activation conditions. Type I isotherm represents unimolecular adsorption and applies to microporous adsorbents with small pore sizes.

Activation temperature is one of the most important factors affecting the textural properties of the activated carbons. The N₂ adsorption isotherms of activated carbons prepared with 50 wt% H₃PO₄ at temperatures be-

tween 400, 450 and 500 °C for 2 h activation time are shown in Fig. 1a. N₂ adsorption isotherm gives some approximate assessment of the pore size distributions. At these temperature ranges there seems to be a pore size and pore volume enhancements up to 450 °C and then a shrinking of the pores due to an increase in the temperature. Pore sizes, volumes and pore size distribution of an activated carbon are the crucial properties for a specific application.

The pore size distributions of the activated carbons obtained by applying the DFT method are shown in Fig. 2a. Pore size distributions of the activated carbons are mostly similar to each other indicating that the porous structure is already formed at the temperatures

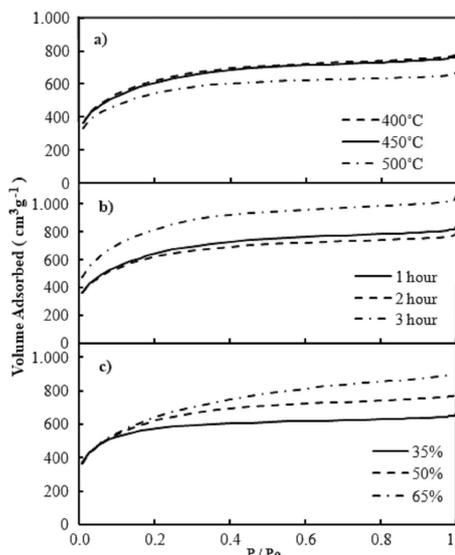


Fig. 1. N_2 adsorption isotherms of the activated carbons prepared at different conditions ((a) activation temperature, (b) activation time, (c) H_3PO_4 concentration).

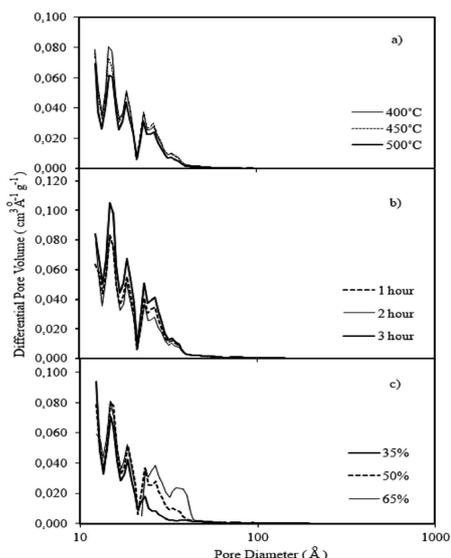


Fig. 2. DFT differential pore size distributions for the samples prepared at different conditions ((a) activation temperature, (b) activation time, (c) H_3PO_4 concentration).

of 400–500°C. The calculated results presented that any significant pore size was not observed above 50 Å. From the pore size distributions, it is clearly seen that the activated carbon samples represent three distinct pore sizes at ≈ 15 , ≈ 18.5 , and ≈ 25 Å. The peaks at 15 and 18.5 Å are the main and small peaks within the micropore region, respectively. The peak at around 25 Å is a broad peak, compared to the other peaks, representing a wide pore size within the mesopore region up to 50 Å.

The N_2 adsorption isotherms of activated carbons prepared with 50 wt% H_3PO_4 at 400°C for different activation times are shown in Fig. 1b. The pore size and distribution of the activated carbon was gradually increased and widened as the activation time was increased to 3 h. The increases in the surface area and pore volumes with activation time indicate that prolonged heat treatment is required for the full development of porosity at 400°C. Pore size distributions and volumes calculated from the N_2 desorption isotherms by DFT method are given in Fig. 2b. These curves represent the effect of activation time on pore size development under the experimental conditions mentioned above. Results clearly demonstrate that there is no considerable pore size above 100 Å expected for the activated carbon prepared at 3 h.

The N_2 adsorption isotherms of activated carbons prepared at 400°C for 2 h using the raw materials impregnated with 35 wt%, 50 wt%, and 65 wt% H_3PO_4 are shown in Fig. 1c. As it can be clearly seen from this figure, effect of H_3PO_4 concentration used in impregnation stage on the final activated carbon product is incontestable. H_3PO_4 concentration does not only affect the surface area and the pore volumes but also tailor the pore nature and size distribution of the activated carbon. As the concentration is increased, highly microporous nature of activated carbon switches to another form, where the mesopores are also dominant in the overall pore size distribution, after a certain H_3PO_4 concentration for a given activation condition. After a given concentration, H_3PO_4 concentration influences to change the nature of the pore size developments from micropores to higher pores due to the possible changes in phosphorous materials and/or higher phosphorus contents that will react with lignocellulosic materials during both impregnation and activation stages. Some authors [9] consider that several polyphosphoric acids such as $H_4P_2O_7$, $H_5P_3O_{10}$ and $H_{n+2}P_nO_{3n+1}$, each one having different molecular sizes, should have played a role in porosity development.

Pore size distributions and volumes calculated from the N_2 desorption isotherms by DFT method are given in Fig. 2c. It is clearly seen that increasing the H_3PO_4 concentration in the impregnation stage leads to increase in volumes and/or widening of the pores depending on the concentration. In summary at high H_3PO_4 concentration pore sizes of the activated carbons are created or developed by different ways resulting in activated carbons having wider micro and mesopores. After a given high H_3PO_4 concentration, mesopores become more dominant.

4. Conclusions

It is clearly demonstrated that activated carbons having high surface area and pore volumes can be prepared from hazelnut shell by chemical activation with H_3PO_4 . Hazelnut shell among the lignocellulosic renewable materials can be considered as competitive precursor in the preparation of microporous activated carbons. From the

overall results, it is clearly represented that the activated carbons from hazelnut shell by H_3PO_4 can be produced for some unique applications by tailoring of the porosity with appropriate adjustments of temperature, H_3PO_4 concentration and time, mainly.

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