

Preparation and Characterization of Activated Carbons from Furfural Production Wastes

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ABSTRACT: This study has been focused on research activated carbons which were prepared from furfural production wastes. The effects of the lower impregnation ratios to chemical structure and surface texture were determined. The Fourier transform infrared spectroscopy (FTIR) and SEM analysis were studied for characterization. The FTIR results showed that there was no important change among the activated carbon samples with different acid impregnation ratios. Micro and mezopore formations were observed at lower impregnation ratios compared with the pyrolyzed char and increasing the impregnation ratio caused to macropore formation on the surface texture at SEM photographs.

Keywords: Activated carbon, furfural, chemical activation, characterization

ORIGINAL ARTICLE

INTRODUCTION

Activated carbon (AC) is a highly porous carbon based material and due to its well-developed porosity and surface functional groups it is one of the most widely used adsorbents for the various gas separation and purification processes, the recovery of solvents, the removal of organic pollutants from drinking water and as a catalyst support.¹⁻⁵

Many kinds of materials can be used as the precursors for producing ACs. Among them, wood, charcoal, agricultural by-products like nut shells, fruit pits, rice husk, corncob wastes and synthetic polymers are commonly used as the starting material [2,4,6,7,8,9].

There are basically two methods for preparing activated carbon: physical and chemical activation. Physical activation consists of two steps: the carbonization of starting material at 400-500 °C to eliminate the bulk of the volatile matter and the activation of char by using carbon dioxide and water steam at 800-1000 °C or with air at low temperature. In chemical activation both the carbonization and the activation steps proceed simultaneously [3,4,6].

As for chemical activation, pyrolysis char would be impregnated with some chemical reagents such as H₃PO₄, ZnCl₂, KOH, CaCl₂ and H₂SO₄ [1,2,3,5,6,10,11,12]. Chemical agents act as dehydration agents and they may restrict the formation of tar and volume contraction during carbonization [5,12,13]. Major advantages of chemical activation compared to physical activation are lower treatment temperatures and shorter treatment times. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation [8,12,13]. However, there are some disadvantages of the chemical

activation process, such as corrosiveness of the process and the washing steps after carbonization [13].

The high porosity and the large surface area, achieved after the activation process, ensures very high adsorption capacity to activated carbons, which is difficult to obtain with other sorbents [1].

Furfural and its derivatives are strategic chemicals due to several possible applications. Furfural is a selective solvent for separating saturated from unsaturated compounds in petroleum refining and it is useful for production of gas, oil and diesel fuel. Furfural derivatives, especially furfuryl alcohol, is an important component for furan resins [14-16].

All pentosans containing materials could be used for furfural production but industrial production of furfural requires a minimum content of 18-20% pentosans, because only about one third of the pentosans in the raw materials can be converted into furfural [14,17].

Furfural production from raw material consists of two steps: The first step involves acid-catalysed hydrolysis, where the pentose chains are hydrolysed at nearly 100 °C temperature and lower acid concentrations to monomeric pentoses. In second step pentoses are converted into furfural by the dehydration. H₂SO₄ and Ti, Zn or Al salts are commonly used catalysts for first step [14,16,17].

In this study, effects of lower acid concentrations to chemical structure and surface texture of ACs were investigated. For this purpose, waste materials which were used in first step of furfural production in which acid concentrations relatively lower than AC production were converted into ACs and compared with the ACs which were prepared at higher acid concentrations. Fourier transform infrared spectroscopy (FTIR) and scanning

electron microscopy (SEM) analysis were studied for characterization of ACs.

Experimental

Hazelnut shells obtained from Giresun, Turkey were dried, crushed and sieved to a particle size fraction of 1.0-2.0 mm which is commonly used precursor size for producing commercial adsorbents for gas-phase applications. A portion of 2.5 g of this processed starting material was impregnated with 10 ml of H₂SO₄ solution of 5-50% concentrations at 85 °C for 7 h. This part of the study simulates the hydrolysis step of furfural production. Acid impregnated sample was then evaporated at 110 °C for 12 h. The mixture was carbonized at 450 °C in the absence of the air for 2 h. After carbonization has been completed, the residual impregnating agent was removed by washing with hot distilled water until the pH of water reached 6-7. Final char was dried at 105 °C for 12 h and kept in a desiccator for characterization [5,10,17,18,19,20].

Surface functional groups on the raw material and ACs were studied on thin films between KBr plates by a Fourier transform infrared spectrometer for chemical characterization. By comparison to the standard frequency patterns, various characteristic chemical bonds (or stretchings) were determined, from which certain surface functional groups could be derived. The surface microstructure of ACs were analyzed using SEM. For this analyses a few particles of prepared ACs were fixed on a sample holder, then the sample holder was located within the SEM chamber and vacuumed down at high vacuum mode and the microstructure of the samples were observed at 250-1500 X [3,21,22].

RESULTS AND DISCUSSION

The FTIR results of precursor and pyrolyzed char (without any acid impregnation) are shown in Figure 1. According to FTIR spectra, precursor displayed the following bands: the broad band in the region 3200-3600 cm⁻¹ was attributed to O-H stretching in hydroxyl functional groups, 2894 and 2937 cm⁻¹ bands were ascribed to symmetrical and asymmetrical C-H stretching vibrations of aliphatic CH₃ and CH₂ groups, the bands at

1742 and 1632 cm⁻¹ were ascribed to C=O stretching from ketones, aldehydes or carboxyls groups, the bands in the region 1430-1560 cm⁻¹ were ascribed to C=C stretching vibrations in the aromatic rings and the bands in the region 1000-1300 cm⁻¹ were ascribed to C-O or C-O-C stretchings in lactonic, ether, phenol etc. Figure 2 also depicted the FTIR spectra of AC samples prepared at different concentrations (5 to 50%). It was found that pyrolyzed char and acid impregnated activated carbons had similar bands. According to FTIR spectra of ACs and pyrolyzed char the following bands were displayed: For all carbonized products, the broad band in the region 3200-3600 cm⁻¹ and the sharp bands at 2894 and 2937 cm⁻¹ which were viewed at precursor spectra were disappeared. Many weak bands were appeared in these regions, this change was attributed to effect of carbonization. C=O stretching from ketones, aldehydes or carboxyls groups in the region 1625-1750 cm⁻¹, C=C symmetric stretching of aromatic rings at 1580 cm⁻¹ and broad band in the region 1000-1300 cm⁻¹ from C-O stretching from ethers were viewed for all AC samples and pyrolyzed char. Weak peaks in the region 100-500 cm⁻¹ were attributed to C-H deformations. The bands in the region 1380-1460 cm⁻¹ were ascribed to alkane groups for the samples of AC but these bands are not exist for pyrolyzed char. Thus the chemical structure of ACs surface was relatively combined with different C-O, C=O, C-O-C, C=C and C-H bands [5,7,9,13,21].

SEM technique was employed to observe the surface physical morphology of samples. A significant difference of the surface topography between pyrolyzed char and AC samples was observed. It could be seen from the micrographs that there were no pores on the external surface of pyrolyzed char but a homogenous surface morphology was observed. Well developed and uniformly sized micro and mezopores were generally distributed throughout the AC samples which were impregnated 5 and 10% chemical agent. More rough surface texture were observed at this samples compared with the pyrolyzed char. A heterogeneous macropore structure with the micro and mezopores were observed from the micrographs of AC samples which were impregnated 30-40 and 50% chemical agent (Figure 3) [3,9,12].

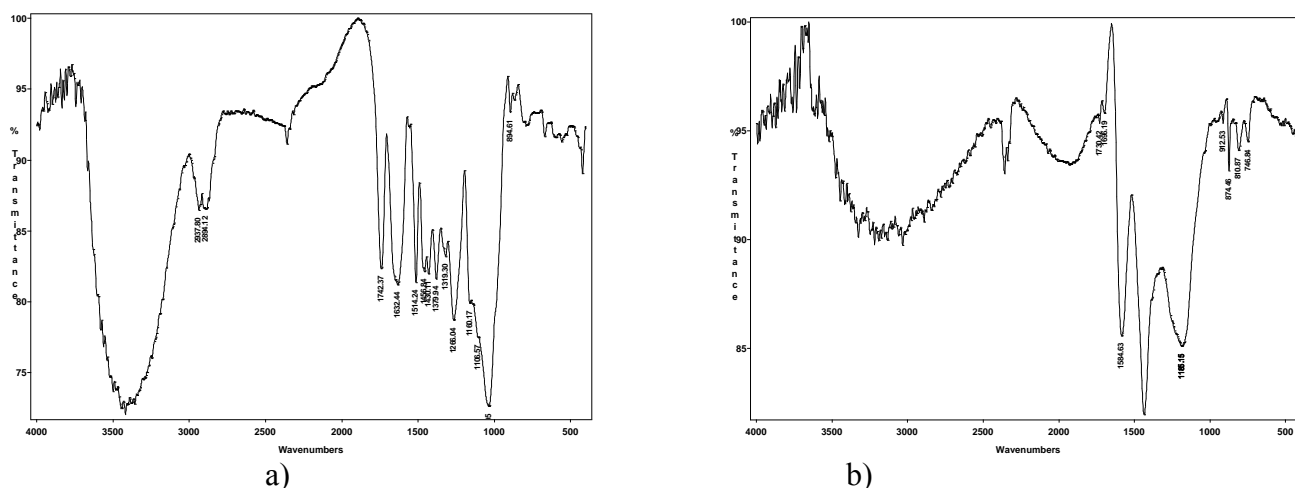
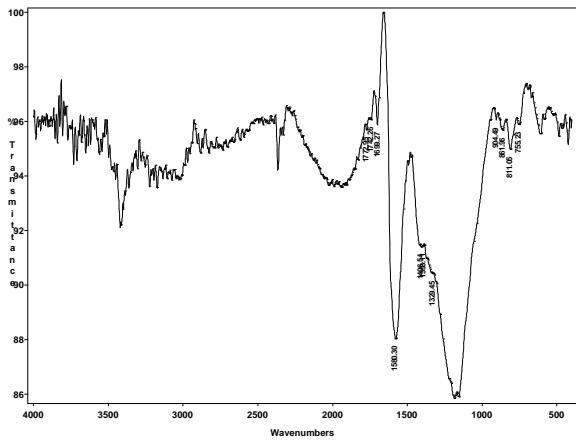
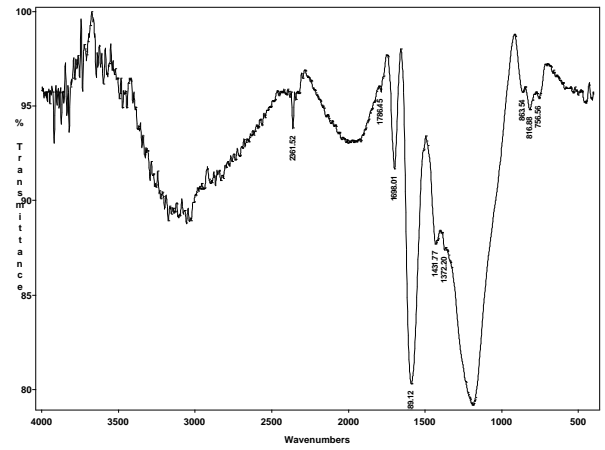


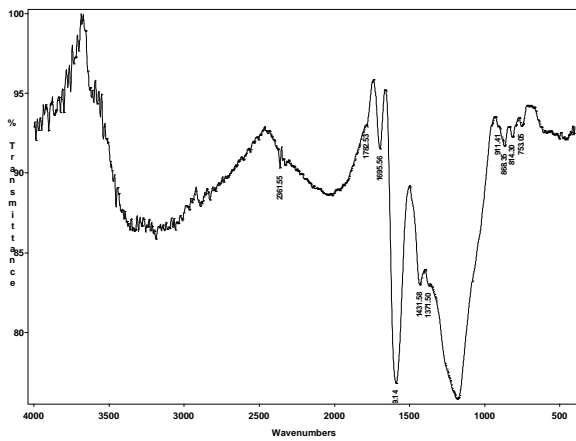
Figure 1. Functional groups of precursor (a) and pyrolyzed char (b)



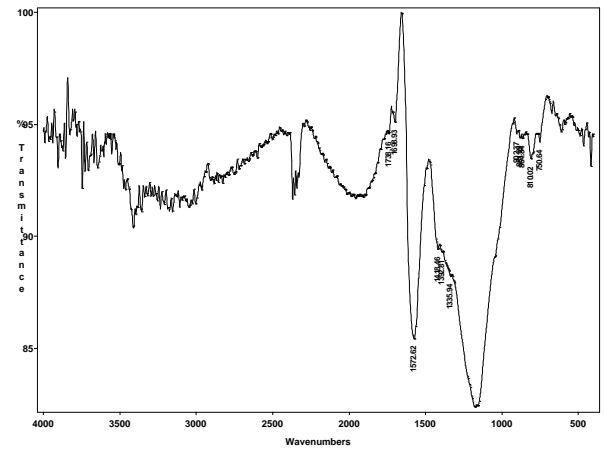
a)



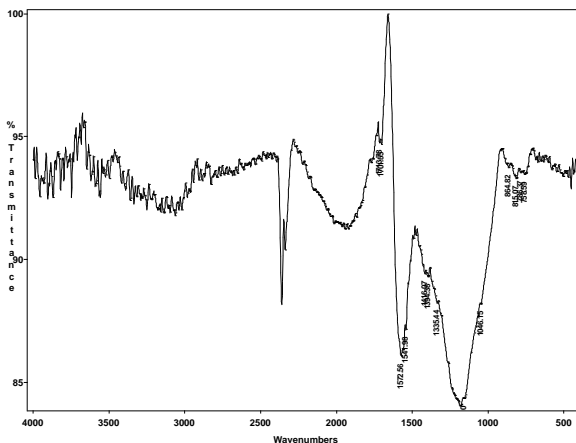
b)



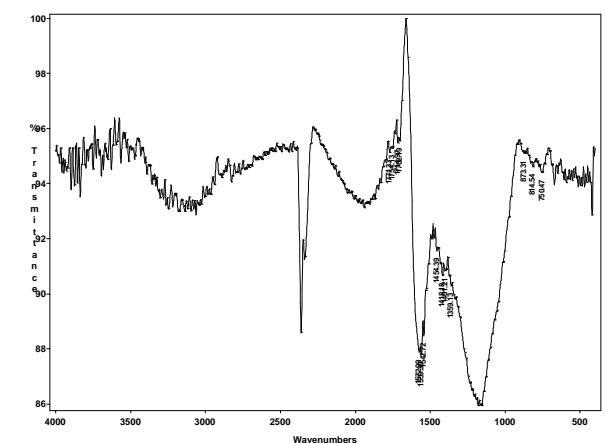
c)



d)



e)



f)

Figure 2. Functional groups of AC with 5% impregnation ratio (a), AC with 5.5% impregnation ratio (b), AC with 7% impregnation ratio (c), AC with 10% impregnation ratio (d), AC with 40% impregnation ratio (e), AC with 50% impregnation ratio (f)

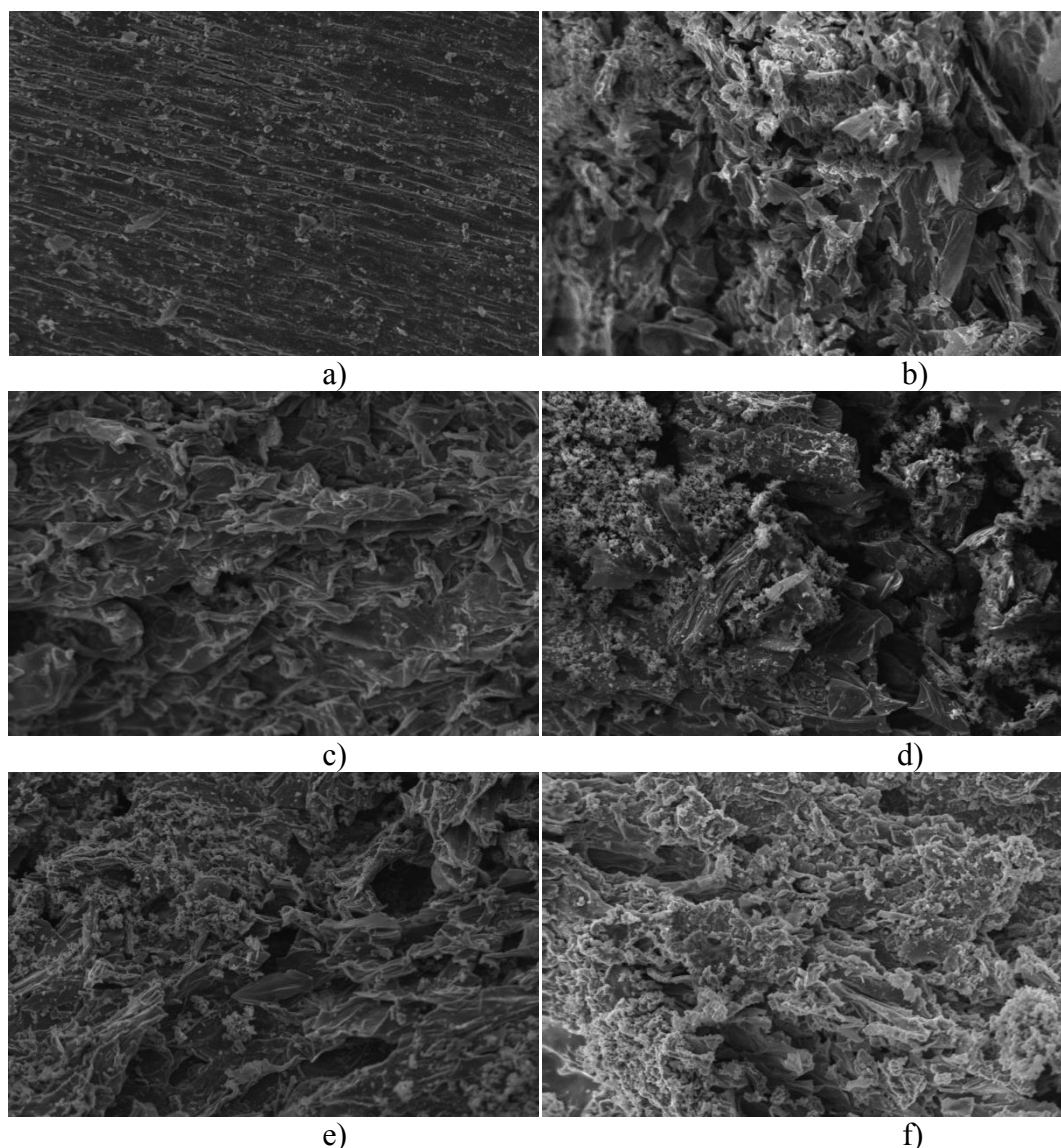


Figure 3. SEM photographs of pyrolyzed char (a), AC with 5% impregnation ratio (b), AC with 10% impregnation ratio (c), AC with 30% impregnation ratio (d), AC with 40% impregnation ratio (e), AC with 50% impregnation ratio (f)

CONCLUSIONS

Hazelnut shell was chemically activated with H_2SO_4 and pyrolyzed at $450\text{ }^\circ\text{C}$ for 2 h. The effects of chemical agent concentration especially lower concentrations which simulates the first step of furfural production were investigated. From the experimental studies on precursor, pyrolyzed char and AC samples the following conclusions can be drawn:

- When FTIR results were investigated, there were a significant difference between precursor and AC samples with the effects of activation and carbonization steps. But there was no important change among the AC samples with different acid impregnation ratios. Increasing the concentration (40-50%) caused to some extra peaks in region of alkane groups but chemical agent in the pore structure can be the reason of this peaks.
- Activation process converted pentosans to furfural but FTIR results indicated that there were still cellulosic compounds on the structure of ACs in the region of $1625\text{-}1750\text{ cm}^{-1}$. According to literature,

increasing the carbonization temperature was a solution for disappearing of this bands.²⁰

- According to SEM photographs there was no pore on the pyrolyzed char, this smooth surface texture was attributed to tar formation without any chemical agent. Micro and mezopores observed on all the AC samples but increasing the acid concentration caused to macropore formation.
- Micro and mezopores which observed on the AC samples with lower concentration were suitable for adsorption characteristics of ACs especially for gas-phase applications.
- Furfural production wastes can be used as an acid impregnated raw material and it can be an economical way for activated carbon production.

ACKNOWLEDGEMENTS

The authors express their appreciation to Assoc.Prof.Dr. Kemal SANCAK, Dr. Elvan ÜSTÜN and

Assoc.Prof.Dr. Genççağ PÜRÇEK for their generous contributions to this study.

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