Preparation and characterization of activated carbon from grape stalk by zinc chloride activation

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ABSTRACT

In this study, low cost activated carbon was prepared from the grape stalk by chemical activation with $ZnCl_2$ in CO_2 atmosphere and its characteristics were determined. Experiments were carried out at different carbonization temperature and time, impregnation time and impregnation ratio, which had significant effect on the pore structure and surface area of carbon. The prepared activated carbon was characterized by proximate-ultimate analysis, BET surface area, iodine number, surface functional group analysis by Boehm's titration and FT-IR analysis, pHzpc, SEM-EDX and particle size distribution. Results showed that the carbonization temperature and impregnation ratio have significant effect on the surface area and pore structure of the prepared activated carbon. The optimum conditions for preparing the activated carbon having the highest surface area were found to be a carbonization temperature of 700 °C, carbonization time of 120 min, impregnation time of 36 h and $ZnCl_2$/grape stalk ratio of 2. The results showed that the BET surface area, total pore volume, iodine number, pHzpc and the yield of activated carbon prepared under the optimum conditions were 1411 m^2/g, 0.723 cm^3/g, 1760 mg/g, 2.84 and 26.48%, respectively, and the activated carbon has acidic surface functional groups and highly porous surface with cracks, channels and large holes.

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1. Introduction

Activated carbon is the most widely used on the industrial scale as an adsorbent for the purification and separation processes, as a catalyst or a catalyst support in the catalytic processes and as electrode materials in electrochemical devices and processes due to its high specific surface area, adequate pore size distribution, variable characteristics of surface chemistry and relatively high mechanical strength [1]. Therefore, the demand for activated carbon is increasing day by day. However, the cost limits widespread use of the activated carbon. This fact has prompted a growing interest into the production of low cost activated carbon. Activated carbons are generally produced from the carbonaceous materials with high carbon but low inorganic content and relatively expensive. In order to drop the cost of the activated carbon, cheaper and readily available precursors such as agricultural and agro-based by-products or waste have been tried recently. Agricultural by-products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price. They can be used for the production of activated carbon with a high adsorption capacity, considerable mechanical strength and low ash content [2]. Many researches have been reported for preparing activated carbon

from these type of materials such as bamboo [3], bagasse [4], olive stones [5], cherry stones [6], oil-palm stones [7], apricot stones [8], walnut shells [5], nutshells [9], pine cone [10], acorn shells [11], groundnut shells [12], peanut shells [13,14], coconut shells [15], palm shell [16], cotton stalk [17], tobacco residues [18], coffee husks [19], tea industry waste [20].

Activated carbon can be produced through physical and chemical activation. In the physical activation, there are two steps: carbonization step and activation step. The raw material is first carbonized under inert atmosphere and then resulting char is activated at high temperature by steam or carbon dioxide. In the chemical activation, raw material is impregnated with an activation reagent and heated in an inert atmosphere. The chemicals used in the chemical activation are alkali (KOH, K_2CO_3, NaOH and Na_2CO_3), alkali earth metal salts ($AlCl_3$ and $ZnCl_2$) and some acids (H_3PO_4 and H_2SO_4). These chemicals are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar. In the case of chemical activation, the effect of KOH and $ZnCl_2$ on the carbonization of precursors has been particular interest and $ZnCl_2$ in particular is a widely used chemical agent in the preparation of activated carbon [21,22].

Although many papers have been published in recent years on the preparation of activated carbon from various cheaper and alternative agricultural wastes and by products with chemical activation, only one study concerning the production of activated carbon from grape stalk activated chemically with H_3PO_4 has been made by Deiana et al., 2009

[23]. No studies have been reported regarding the preparation of activated carbon from grape stalk chemically activated with $ZnCl_2$.

Therefore, the purpose of this work is to determine the optimal conditions for preparing activated carbon from grape stalk with $ZnCl_2$ activation. The effects of activation temperature and time, impregnation time and ratio on the yield and BET surface area of the activated carbon were investigated. Moreover, the obtained activated carbon was characterized by proximate-ultimate analysis, BET surface area, iodine number, surface functional group analysis by Boehm's titration and FT-IR analysis, pHzpc, SEM-EDX and particle size distribution.

2. Materials and methods

2.1. Materials

Grape stalk used in this study were provided from a wine production plant located near Malatya, Turkey. The precursor was washed with deionized water, dried at room temperature for 10 days and then at 80 °C for 6 hours prior to use in the experiments. The dried sample was ground and sieved to obtain a uniform particle size. Since the grape stalks have tin, long and flat structure, the uniform particles could be obtained in the fraction smaller than 50 mesh. In the preliminary studies, it was observed that the particles smaller than 80 mesh was carried by CO_2 gas being passed from the activation reactor and clogged the pipes. Therefore, the particle size of $-50 + 80$ mesh (0.3–0.177 mm) was used in the study.

Analytical reagents grade chemicals purchased from Merck were used in the study.

2.2. Preparation of activated carbon

Dried grape stalks were impregnated with different weight ratios of $ZnCl_2$/grape stalk. The impregnation was performed by shaking at 150 rev/min by using an orbital flask shaker (Gallenkamp) for contact times of 24, 36 and 48 h. The impregnated materials were filtered and dried at 105 °C for 24 h and then activated. The activation experiments were carried out in a cylindrical stainless steel reactor with 15 cm height and 6 cm in diameter. In a typical run, 40 g of the dry sample impregnated with $ZnCl_2$ was placed into the reactor and CO_2 was passed through at a flow rate of 0.1 dm^3/min; the system was heated at a rate of 20 °C min^{-1} in a muffle furnace. In the experiments devoted to the study of temperature, the sample was heated to 500, 600 and 700 °C and maintained in each case at that temperature for 120 min. The influence of carbonization time was explored using 30, 60, 90 and 120 min times at the best temperature selected in the previous series of experiments. After the activation, the sample was allowed to cool down under CO_2 flow prior to remove it from the furnace. The activated samples were washed with 3 M HCl solution to remove the zinc compounds. Then, they were washed several times with hot and finally cold distilled water until the pH of the wash water was neutral. The wet samples were dried at 105 °C for 24 h. After these procedures applied, the production yield of activated carbon was calculated by dividing the mass of the resultant activated carbon by the initial mass of grape stalk used for activation.

2.3. Sample characterization

Grape stalk was characterized by proximate and ultimate analysis, SEM (JEOL/JSM-6510 LV), FT-IR (Perkin Elmer Spectrum One), TG (Perkin Elmer Pyris TG/DTA) analysis while the activated carbons obtained was characterized by proximate and ultimate analysis, BET surface area, iodine number, surface functional group analysis by Boehm's titration [24] and FT-IR, pHzpc, SEM-EDX and particle size distribution.

Ash content of the activated carbon was determined according to ASTM D3174-73 standard. The specific surface area and pore structure parameters of the activated carbons were determined by using a surface

area analyzer (Micromeritics ASAP 2020). Iodine number of the activated carbon was determined using the sodium thiosulfate volumetric method [25]. In order to determine quantitatively and qualitatively surface functional groups of the activated carbon, Boehm's titration method [24] and FT-IR analysis were applied, respectively. pHzpc value of the carbon was measured by using Malvern Nanosize ZS-3600 zetasizer. A scanning electron microscope was used to examine the surface morphology of the grape stalk and activated carbons obtained. The samples for SEM analysis were prepared by sputter-coating the surfaces with Au. The elemental composition was analyzed by EDX. Particle size distribution and elemental analysis of the samples were performed using Malvern Master Sizer 3000 and LECO CHNS 932 Elemental Analyzer, respectively.

3. Results and discussion

3.1. Characterization of the grape stalk

The results of the proximate and ultimate analysis of the grape stalk are shown in Table 1. The grape stalk contains 8.7% ash, 63.13% volatile matter and 21.17 fixed carbon. The ultimate analysis revealed that the grape stalk used was composed mainly of carbon (41.58%), hydrogen (4.92%) and oxygen (52.16%), as expected for most lignocellulosic material.

Fig. 1 shows that the FT-IR spectra of the grape stalk. The broad band at 3340 cm^{-1} indicates hydroxyl groups. The peaks observed at 2921 cm^{-1} and 1620 cm^{-1} can be assigned to the C-H group and C $=$ C stretching, respectively. The region between 1610 and 1500 cm^{-1} is associated with C-C stretching in aromatic rings found on the lignin structure [26]. Fig. 2a shows scanning electron micrograph of the grape stalk. As seen the figure, the grape stalk has a rough surface with cracks and voids.

In order to determine general decomposition characteristics of the grape stalk during the activation, the sample was subjected to thermogravimetric analysis (Fig. 3). TG profiles display a weight loss in the temperature range of 50–180 °C due to dehydration of the sample. 6.17% weight loss was determined at this temperature range. This value is close to the moisture percentage of the grape stalk (Table 1). The highest weight loses was observed between 184–550 °C, which indicate the thermal decompositions of the cellulose, hemicellulose and lignin. In this range, the weight loss is about 81%. At temperatures above 600 °C, it was not observed significant weight losses. Therefore, it can be stated that the temperatures above 600 °C is more appropriate for activation.

3.2. Preparation of activated carbon

In order to obtain activated carbon from the grape stalk chemically activated with $ZnCl_2$, the effects of the carbonization temperature and carbonization time, impregnation time of $ZnCl_2$ and weight ratio of

Table 1
Proximate and ultimate analysis of the grape stalk.

Proximate analysis	wt.% (db)
Ash	8.7
Moisture	7.0
Volatile matter	63.13
Fixed carbon	21.17
Ultimate analysis	*wt.% (db)*
C	41.58
H	4.92
N	1.18
S	0.16
O*	52.16

db: dry basis; *: by difference.