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Activated Carbons From Grape Seeds By Chemical Activation With Potassium Carbonate And Potassium Hydroxide

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ABSTRACT

Activated carbons were produced from grape seed using either potassium carbonate (K_2CO_3) or potassium hydroxide (KOH). The carbonization experiments were accomplished at 600 and 800 °C. The effects of the experimental conditions (i.e., type of activation reagents, reagent concentrations, and carbonization temperatures) on the yields and the properties of these activated carbons were analyzed under identical conditions. An increase in the temperature at the same concentrations for both K_2CO_3 and KOH led to a decrease in the yields of the activated carbons. The lowest activated carbon yields were obtained at 800 °C at the highest reagent concentration (100 wt%) for both K_2CO_3 and KOH. The activated carbon with the highest surface area of 1238 m^2g^{-1} was obtained at 800 °C in K_2CO_3 concentration of 50 wt% while KOH produced the activated carbon with the highest surface area of 1222 m^2g^{-1} in a concentration of 25wt% at 800 °C. The obtained activated carbons were mainly microporous.

1. Introduction

Activated carbons having high surface areas have been used in many applications such as wastewater treatment, the removal of harmful gases in the air, solvent recovery, color removal, and ground water improvements. Their high surface areas are caused by heterogeneous porous structures which make them perfect adsorbents. The preparation of activated carbons is accomplished using two basic processes. In the first process, which is called physical activation, the raw material is converted into carbonized material (char) and then the carbonized samples are subjected to the activation step with an oxidizing gaseous agent such as carbon dioxide, water vapor, or their mixture. In the chemical activation process, the raw material is impregnated with a chemical reagent and then the impregnated material is carbonized at different temperatures. Chemical activation is accomplished using a wide range of chemical agents. Two of the most frequently used chemical reagents for the preparation of activated carbons are basic salts and bases. [1–5]

The preparation of activated carbon from agricultural by-products has received much attention from the scientific community as they are renewable, low-cost and environmentally friendly materials. Various agricultural by-products have been used as raw materials to produce activated carbon such as soybean oil cakes [5], pumpkin seeds [6], esparto grass [7], corncob [8], coconut shells [9], apricot stones [10], and pomegranate seeds [11]. The evaluation of agricultural residues or agricultural by-products as the precursors of activated carbon seems to be promising from a sustainable viewpoint. Grape seeds and their residues account for approximately 15% of the total solid waste products from the wine processing industry [12,13]. Although grape seeds are a valuable source of phenolic antioxidants, they are generally burnt as fuel or used for animal feed [12–14]. Grape seeds are good candidates as precursors to obtain activated carbons in terms of availability, low cost, and waste utilization.

Several types of activated carbons were prepared from grape seeds and chestnut shells and used for the removal of copper [15]. The surface areas of the activated carbons were 1319 and 916 m^2g^{-1} for chestnut shells and grape seeds, respectively. The activated carbon derived from chestnut shells had greater adsorption capacity than the activated carbon from grape seeds.

Activated carbons from different agricultural by-products (almond shells, nut shells, apricot stones, cherry stones and grape seeds) via steam pyrolysis were prepared at 800 °C with a heating rate of 15 °C/min [16]. Steam pyrolysis of grape seeds gave activated carbon with a yield of 26.2 wt% and a 497 m^2/g of surface area.

In a recent study, the preparation of the activated carbon from grape seeds with phosphoric acid activation has been reported by Al Bahri et al. [13] Grape seeds were pretreated with sulfuric acid and then impregnated with phosphoric acid at different impregnation

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ratios (from 25 to 50 wt% of the raw material). The impregnated samples were carbonized at temperatures between 350 and 550 °C. The highest BET surface area (1139 m^2/g) was obtained at 500 °C with a grape seed to phosphoric acid ratio of 1:3.

In our previous study, activated carbons were produced from pomegranate seeds by $ZnCl_2$ activation at the temperatures of 600 and 800 °C. The highest BET surface area was found to be ~979 m^2/g and it was obtained at an impregnation ratio of 2.0 [11].

In this study, we prepared the activated carbons from grape seeds using either potassium carbonate or potassium hydroxide at 600 and 800 °C. The effects of these types and concentrations of chemical reagents and temperatures on the properties of the activated carbons were analyzed.

2. Experimental

2.1. Materials

The biomass used for the preparation of activated carbons was grape seeds. The grape seeds were ground and used as received from the consumer source. No drying process was undertaken. The proximate and ultimate analyses of the grape seeds are shown in Table 1. The chemicals used in these experiments were of reagent grade.

2.2. Preparation of the activated carbons

The preparation of activated carbons from grape seeds was accomplished using either potassium carbonate (K_2CO_3) or potassium hydroxide (KOH). 40 g of biomass (on a dry basis) was impregnated with the activating agent for 24 hours. The concentrations of the chemicals used were 25, 50, and 100 wt% which refer to the impregnation ratios of 0.25:1, 0.5:1, 1:1 of the weight of chemicals and the weight of biomass, respectively. The slurry was then dried at 105 °C.

The impregnate samples were set at the bottom of the vertical reactor (a fixed bed design of stainless steel with 6 cm diameter and 21 cm height) and the reactor was heated by an electrical furnace. The impregnated samples were carbonized at 600 and 800 °C for 1 hour under a nitrogen (N_2) flow (30 mL min^{-1}) at a heating rate of 7 °C min^{-1}. After cooling in nitrogen overnight, the solid products (carbonized products) were taken from the reactor. The carbonized samples were boiled with a concentrated hydrochloric acid solution under reflux. Then, the activated carbons were washed with hot distilled water, and then with cold distilled water until chloride ions were not detected. After these steps, the activated carbons were dried at 105 °C for 24 h. The yields of activated carbons were calculated according to the following equation:

$$\text{Yield of activated carbon (wt\%)} = \frac{\text{weight of activated carbon}}{\text{weight of grape seeds}} \times 100$$

Table 1
Proximate and ultimate analyses of grape seeds.

Proximate Analysis (as received, wt %)	
moisture	8.5
volatile matter	72.8
fixed carbon[a]	14.0
ash	4.7
Ultimate Analysis (dry basis, wt%)	
C	48.7
H	6.5
N	1.1
S	-
O[a]	43.7

[a] by difference.

2.3. Characterization of the activated carbons

A surface analyzer (Quantachrome Inst., Nova 2200e) was used to determine the porosity of the activated carbons by N_2 adsorption at 77 K. A t-plot method was used to determine the micropore volume (Vmicro). Novawin 2 software was used to obtain the results. The mesopore volume (Vmeso) was calculated by the subtraction of Vmicro from Vtotal (Vmeso = Vtotal −Vmicro). The activated carbons were pulverized and analyzed in terms of their surface topology using a scanning electron microscopy instrument (JEOL JSM-6060). The elemental compositiosn of the prepared activated carbons were determined using a LECO CHNS 932 Elemental Analyzer.

3. Results and Discussion

3.1. Product yields, proximate and ultimate analyses of activated carbons

The product yields of activated carbons from grape seeds by chemical activation with either K_2CO_3 or KOH are tabulated in Table 2. Results indicate that both the concentrations and carbonization temperatures influenced the yields of the activated carbons. An increase in the reagent concentration at the same temperatures for both K_2CO_3 and KOH resulted in a decrease in the yields of the activated carbons. An increase in the temperature at the same concentrations for both K_2CO_3 and KOH led to a decrease in the yields of the activated carbons. These findings show that both K_2CO_3 and KOH worked efficaciously as activating reagents at 800 °C [17]. Many reactions such as dehydration and elimination occur during carbonization due the release of low molecular compounds via cracking of chemical bonds in the lignocellulosic network with the help K_2CO_3 and KOH. Thus, carbon yields abated when the carbonization temperature was raised at the same concentrations. In a previous study, Hayashi and co-workers prepared activated carbons from lignin by chemical activation using $ZnCl_2$, H_3PO_4 and some alkali metal compounds [4]. The results from that study showed that the yields of activated carbons abated at an impregnation ratio of 1.0 for K_2CO_3 when temperatures were raised from 700 and 900 °C.

The production of activated carbons from palm shells was accomplished using K_2CO_3 activation [18]. The findings of this study demonstrated that when carbonization temperature and impregnation ratios were raised, the yields of the activated carbons were abated. Our findings are in consistent with these previous reports [5,17,18].

The highest activated carbon yields for both K_2CO_3 and KOH were obtained at 600 °C at a concentration of 25 wt%. Lower carbon yields occurred at 800 °C when the activating concentration was raised from 50 to 100 wt% for both K_2CO_3 and KOH.

The preparation of activated carbons from *Euphorbia rigida* using $ZnCl_2$, K_2CO_3, NaOH and H_3PO_4 in different impregnation ratios (from 25 to 100 wt%) was carried out at 700 °C [19]. In general, higher impregnation ratios yielded lower carbon yields at 700 °C.

In general, activated carbons from KOH activation yielded lower product yields than those from K_2CO_3 activation. The same trend was observed in our previous report, which was concerned with the production of activated carbons from K_2CO_3 and KOH activation (at an impregnation ratio of 1.0) from soybean oil cake at 600 and 800 °C [5].

As the carbonization temperature was raised from 600 to 800 °C for each concentration of chemicals used, the volatile content for both K_2CO_3 and KOH abated. The lowest volatile content for both K_2CO_3 and KOH was obtained at 800 °C with a chemical concentration of 25 wt%. In general, the ash contents of the activated carbons

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