



## Production of activated carbon and fungicidal oil from peach stone by two-stage process



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### ABSTRACT

In this study, the production of activated carbons from peach stone with zinc chloride activation was investigated by means of a two-stage process: precarbonization and chemical activation. Precarbonization was performed at two different temperatures 300 °C and 400 °C in order to obtain the bio-oil. Then the activation of precarbonized chars after impregnation with zinc chloride was carried out. The activation temperatures varied from 500 °C to 700 °C to determine the optimal processing conditions. For comparison, traditional chemical activation was also performed. In two-stage process, the precarbonization temperature had important effect on the surface area of activated carbon as well as activation temperature. The surface area of activated carbons obtained from the two-stage process was lower than that those from the one-stage process. The bio-oil obtained from precarbonization step showed fungicidal activity against fungi *Coriulus versicolor*. The adsorption capacities of activated carbons for phenol and methylene blue were found to be in the range of 51.6–64.9 mg g<sup>-1</sup> and 104.2–121.9 mg g<sup>-1</sup>, respectively.

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### 1. Introduction

Activated carbon has been widely used for the separation of gases, the recovery of solvents, and the removal of pollutants from water/wastewater and as a catalyst support. Adsorption capacity is based on the physical properties of the pores, namely the specific surface area, the pore size and distribution as well as its surface chemistry [1]. These properties vary depending on the precursor and activation conditions used to produce activated carbons.

Although commercial activated carbon is mainly produced from coal, wood, and coconut shell, a number of researchers have used many carbonaceous materials which are cheap and readily available.

Because of its low ash content and reasonable good hardness, production of activated carbon from fruit stones such as peach stone [2], olive stone [3,4], apricot stone [5], date stone [6,7], cherry stone [8,9], plum stone [10], besides other lignocellulosic wastes, such as almond shell [3,5], palm shell [11], tea wastes [12], pine cone [13], tobacco wastes [14] etc. was studied by a number of researchers. Activated carbons can be basically produced by two methods: Physical or chemical activation or a combination of both

of them. The physical activation method involves carbonization of the raw material and the subsequent activation at high temperature in a carbon dioxide or steam atmosphere. The chemical activation method involves the carbonization of the raw material previously impregnated with a chemical agent such as zinc chloride, phosphoric acid, potassium hydroxide etc. Since a large number of studies have been carried out on activated carbon production, the general mechanism for both the chemical and physical activation is well known.

The advantage of chemical activation over physical activation is that chemical activation produces much higher yield and better-developed, more uniformly sized pores compared to physical activation, and leads to a decrease in the mineral matter content. It also uses lower temperatures for carbonization. Nevertheless, there are also some disadvantages of the chemical activation process, one of which is the prevention of the utilization of valuable volatiles. For example, the pyrolysis liquids obtained from lignocellulosic materials can be used as sterilizing agent, smoke flavors, environmentally friendly wood preservative, antimicrobial and growth promoting agent, etc. [15]. Because of this, the physical activation method compares favorably with the chemical activation process if the bio-oil derived from carbonization step is used as a chemical feedstock. Our previous study showed that pistachio shell could be used for production of both fungicidal oil and activated carbon. In that study, the microporous activated carbon having a BET surface

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708 m<sup>2</sup> g<sup>-1</sup> with a loss of char mass 57.5 wt% was obtained from pistachio shell by CO<sub>2</sub> activation at 900 °C [16].

One of the biomass sources in Turkey is food processing wastes. Currently, food-processing industries, such as the fruit juice industry, are growing fast and, as a result, several by-products are being produced in large quantities. One of the main food processing wastes is peach stone which is disposed by burning. However, peach stone contains hydrocyanic acid or cyanide, in the form of cyanogenic glycosides, which may lead to environmental problems when burned. Peach stone is a valuable agro industrial by-product that is available not only in Turkey but also in many countries (especially in the Mediterranean region). The low ash content and the absence of transportation costs make peach stones an ideal precursor for activated carbon production.

The preparation of activated carbon by chemical activation using H<sub>3</sub>PO<sub>4</sub> [17–23] and K<sub>2</sub>CO<sub>3</sub> [24,25] and physical activation [2,26–29] of peach stones have been previously studied. The chemical activation of peach stone using K<sub>2</sub>CO<sub>3</sub> was studied to obtain activated carbons for the removal of dyes [24] and acetaminophen [25]. Molina-Sabio and Rodriguez-Reinoso compared the activating agents on the porosity development in production of activated carbon from peach stone [23]. They observed that KOH only produced a widening of micropore width, ZnCl<sub>2</sub> additionally developed small mesoporosity and H<sub>3</sub>PO<sub>4</sub> led to a more heterogeneous pore size distribution. On the other hand, it was observed that steam activation of peach stone chars led to the development of microporosity accompanied by an increase in the number of oxygen surface groups [26]. Duranoglu et al. [2] prepared microporous activated carbon from peach stone by steam activation. They determined that activated carbon had acidic oxygen functionalities, mainly in the form of phenolic groups. Similarly, Galiatsatou et al. [28] produced the activated carbon with microporous structure steam activation. It was found that chemical functionality of the activated carbon surface depend on the type of the activating agent (steam and carbon dioxide) in physical activation of peach stone [29].

In comparison with those studies, this study covered pyrolysis at low temperatures (precarbonization) and then chemical activation using ZnCl<sub>2</sub>. To our knowledge, this is the first time that the production of both activated carbon with high yields and fungicidal oil are provided by two-stage process at low temperatures. The effects of temperatures of precarbonization and activation steps on the yield and textural properties of activated carbons from peach stone were investigated. In addition, phenol and methylene blue adsorption capacities of the produced activated carbons were studied. In order to compare two methods, one-stage chemical activation was also performed.

## 2. Materials and methods

### 2.1. Materials

Peach stone (kernel + shell) was supplied by a juice company (Dimes Food Company, Turkey) and used as received. The stones consisted of approximately 6% kernel and 94% shell. The proximate, ultimate and component analyses of stones are shown in Table 1.

### 2.2. Experimental setup

#### 2.2.1. TG analysis

Thermo gravimetric analysis of raw stone, precarbonized stone, and ZnCl<sub>2</sub>-impregnated raw- or precarbonized stone at ratio of ZnCl<sub>2</sub> to biomass 1:1 by weight was performed in a thermogravimetric (TG) analyzer (Perkin-Elmer Diamond TG/DTA) under N<sub>2</sub> atmosphere. The impregnated samples were prepared as follows. The raw stones or precarbonized stones were impregnated with

**Table 1**  
Proximate, ultimate and component analyses of Peach Stone.

|                                        |       |
|----------------------------------------|-------|
| Proximate analysis (as received, wt %) |       |
| Moisture                               | 9.3   |
| Volatile matter                        | 71.7  |
| Fixed carbon                           | 17.9  |
| Ash                                    | 1.1   |
| Ultimate analysis (dry, %wt)           |       |
| C                                      | 45.92 |
| H                                      | 6.09  |
| N                                      | 0.58  |
| S                                      | 0.03  |
| O <sup>a</sup>                         | 47.38 |
| HHV, <sup>b</sup> MJ kg <sup>-1</sup>  | 19.33 |
| Component analysis (dry, %wt)          |       |
| Cellulose                              | 46    |
| Hemicellulose                          | 14    |
| Lignin                                 | 33    |
| Extractives <sup>c</sup>               | 7     |

<sup>a</sup> Calculated from difference.

<sup>b</sup> High heating value.

<sup>c</sup> Toluene/alcohol (2/1) (v/v).

ZnCl<sub>2</sub> solution by the wet method. After impregnation, the samples were dried overnight at 105 °C. The sample (particle size <100 μm) was about 10 mg for each TG run. The flow rate of purge gas (N<sub>2</sub>, 99.99%) was kept at 200 mL min<sup>-1</sup>. The sample was heated from the ambient temperature up to 700 °C at a heating rate of 10 °C min<sup>-1</sup>. The repeatability of the experimental data was within ±2.5%.

#### 2.2.2. One-stage process

40 g of grounded raw stones (<2 mm) was mixed in a beaker with 150 mL of ZnCl<sub>2</sub> solution (1.96 M) which corresponded to an impregnation ratio of 1:1 (weight of impregnation reagent/weight of stone). The slurry was then dried overnight in a moisture oven at 105 °C. The impregnated samples were pyrolyzed in a fixed bed design and stainless steel reactor (L, 210 mm; Ø, 60 mm). The reactor was heated under nitrogen gas stream at a heating rate of 5 °C min<sup>-1</sup> to the desired activation temperature (500, 600 and 700 °C) and held at this temperature for 1 h. After pyrolysis, the furnace was cooled to room temperature in a nitrogen gas stream overnight. The char was boiled with 200 mL of 10% HCl solution for 60 min, filtered in a vacuum flask, washed with hot water and finally washed with cold water to remove the chloride ions and other inorganics. After washing, the activated carbon samples were dried at 110 °C for 24 h and weighed.

The yield of activated carbon was calculated by

$$\text{Yield (\%)} = \frac{m}{M} \times 100 \quad (1)$$

where *M* is the initial mass of raw stone, *g*; *m* is the mass of resultant activated carbon, *g*. The experiments were performed in duplicate. The repeatability of the experimental data was within ±2.8%.

#### 2.2.3. Two-stage process

In a typical run, 100 g of stones (whole stone as received) was filled in a reactor and then the reactor temperature was increased by a heating rate of 5 °C min<sup>-1</sup> up to pyrolysis temperature (300, 400 and 500 °C) and held for 1 h at this temperature. The reactor was continuously purged with nitrogen at a flow rate of 25 mL min<sup>-1</sup>. The nitrogen gas swept the volatile products from the reactor into the ice-cooled traps. All the liquid products were condensed in the traps. The non-condensable volatiles (gases) were vented to the atmosphere. After pyrolysis, the furnace was cooled to the room temperature in a nitrogen gas stream. All traps were weighted before and after each run. The total liquid amount was calculated by difference. The yields of liquid product and char were determined by weighting. The amount of gas was determined by difference. The liquid product consisted of two phases: aqueous phase and oil

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