



## Original Research Paper

## Preparation, structural evaluation and adsorptive properties of activated carbon from agricultural waste biomass



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## ABSTRACT

The purpose of this study is to produce the low-cost activated carbon from the orange peel, known as a waste of fruit juice industry, by chemical activation using zinc chloride ( $\text{ZnCl}_2$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ). The effects of the activation temperature and type of activation reagents on the surface and chemical properties of activated carbon were investigated. The activation temperatures and impregnation ratios were selected at the range of 500–1000 °C and 1:1, respectively. The carbon content of activated carbons resulted 70% while BET surface area of activated carbons prepared with  $\text{K}_2\text{CO}_3$  and  $\text{ZnCl}_2$  activation is 1352  $\text{m}^2 \text{g}^{-1}$  and 1215  $\text{m}^2 \text{g}^{-1}$  respectively. An increase in the temperature for both  $\text{K}_2\text{CO}_3$  and  $\text{ZnCl}_2$  led to a decrease in the yields of the activated carbons. The yield of  $\text{ZnCl}_2$  series is higher than that of  $\text{K}_2\text{CO}_3$ . The obtained activated carbons were heteroporous with the micropore.

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## 1. Introduction

Activated carbon (AC) obtained from agricultural by-products has the some advantage like efficiency and low cost If they are compared with non-renewable coal-based granular activated carbons [1]. The abundance and availability of agricultural by-products makes them good sources of raw materials for activated carbon production [2]. In recent years, this has promoted a growing research interest in the use of alternative waste materials from industry and agriculture for activated carbon production [3–5]. One of the main challenges in the commercial manufacture of activated carbons is to identify new precursors that are cheap, therefore, a lot of research has been reported on activated carbons from agricultural wastes, including corn cob [6], coconut shell [7], palm shell [8], apple pulp [9], chickpea husks [10], grain sorghum [11], pistachio nut shell [12], jute fiber [13], olive stones and walnut shell [14], cherry stones [15], coir pith [16], wild rose seeds [17], rice bran [18], gopher plant [19], jackfruit shell waste [4], oil palm shell [20], rubber tree seed coat [21], cotton stalk [22], flamboyant [23], beach casuarina, lantana weed, tea waste, sugarcane bagasse and empty oil palm fruit bunches [24]. Palmyra tree leaves, inflorescence and fruit nutshell waste [25] have been found to be suitable precursors owing to their high carbon and low ash contents [26–31]. Chemical activation of AC has been reported as more advantageous over physical activation due

to higher yields, more surface area and better development of porous structures in carbon [32–35]. According to the Food and Agriculture Organization (FAO), the annual production of orange fruit in 2010 is projected at 66.4 million tonnes, translating to approximately 32 million tonnes of peels as the byproducts [36].

Traditionally, orange peel (OP) were processed to obtain the volatile and nonvolatile fractions of essential oils and flavoring in the carbonated drinks, ice creams, cakes, air-fresheners, perfumes and cosmetic products [37]. Besides, OP have been reported to have germicidal, antioxidant and anti-carcinogenic properties as a remedy against breast and colon cancer, stomach upset, skin inflammation, muscle pain, and ringworm infections [38]. However, the application of these extracted constituents is limited due the overall demands for these value-added products are relatively insignificant. Therefore, it is necessary to find a rapid and easy route toward upgrading of the citrus processing biomass.

Thus the object of the present research work has been to explore an economically viable carbon precursor for the production of activated carbon materials. To our knowledge, this is the first time that the production of activated carbon are provided by chemical activation with  $\text{ZnCl}_2$  and  $\text{K}_2\text{CO}_3$

## 2. Materials and methods

## 2.1. Preparation activated carbon

Orange peel (OP), outer skin with white inner skin, a by-product collected from the local restaurant and fruit juice industries, was

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the precursor used in the present study. The raw precursor was washed exhaustively with deionized water to remove adhering dirt particles from the surface. Dried (at 110 °C) OP was cut, sized to a particle size of 4 mm. The results of proximate and ultimate analysis of orange peel are given in Table 1.

In the first step of activation, the starting material was mixed with ZnCl<sub>2</sub> at the ZnCl<sub>2</sub>/starting material weight ratio of 1:1 and the mixture was knead with adding distilled water. The mixture was then dried at 110 °C to prepare the impregnated sample. In the second step, the impregnated sample was placed on a quartz dish, which was then inserted in a quartz tube (inlet diameter 60 mm). The same method and ratio also is applied for K<sub>2</sub>CO<sub>3</sub>.

Carbonization of the impregnated samples was carried out in a 316 stainless steel tubular reactor (Protherm PTF 12, Fig. 1) with a length of 90 mm and an internal diameter of 105 mm under nitrogen flow. The impregnated sample was heated up to activation temperature under N<sub>2</sub> flow (100 ml min<sup>-1</sup>) at heating rate of 10 °C min<sup>-1</sup> and held for 1 h at this activation temperature. The activation temperature varied from 400 to 1000 °C (samples are coded OPZn4, OPZn5, OPZn6, OPZn7, OPZn8, and OPZn9). Adsorbents (OPKC5, OPKC7, OPKC8, OPKC9, OPKC95, and OPKC10) were prepared from orange peels by chemical activation with K<sub>2</sub>CO<sub>3</sub>. After activation, the sample was cooled down under N<sub>2</sub> flow and 0.5 N HCl was added on to OPZn activated samples. HCl were not added on to OPKC activated carbons. The activated carbons were further washed with distilled water until no chloride could be detected in the wash-water, filtered and rinsed by warm distilled water several times until the pH value was 6–7. The washed sample was dried at 110 °C. The yields of activated carbons were calculated according to the following equation:

$$\text{Yield of AC (wt\%)} = \frac{\text{Weight of activated carbon}}{\text{Weight of orange peel}} \times 100 \quad (1)$$

## 2.2. Characterization of adsorbent

The physical, structural and chemical properties of the activated carbon were determined by several analysis methods. The surface properties and surface area of the samples were characterized by N<sub>2</sub> adsorption measurements at 77 K using a surface area analyzer (TriStar 3000). The surface area ( $S_{\text{BET}}$ ) was calculated from isotherms using the Brunauer–Emmett–Teller (BET) equation. The volume of liquid nitrogen corresponding to the amount adsorbed at a relative pressure of  $P/P_0 = 0.99$  was defined as total pore

**Table 1**  
Characteristics of the orange peel.

Characteristics	Methods	Orange peels
Moisture content (wt.%)	ASTM D 2016	9.20
Proximate analysis (wt.%)		
Volatile matter	ASTM E 872	76.52
Ash	ASTM D1102	3.09
Fixed carbon	By difference	20.39
Ultimate analysis (wt.%)	LECO 932 Instrument	
Carbon		46.63
Hydrogen		6.04
Nitrogen		0.23
Sulfur		0.05
Oxygen	By difference	47.05
Surface properties	TriStar 3000 Instrument	
BET surface area (m <sup>2</sup> g <sup>-1</sup> )		1
Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )		0.001
Mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )		5.67
Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )		n.d

n.d.: not detection.

volume (VT) [39]. The micropore volume ( $V_{\mu}$ ) was determined from Dubinin–Radushkevich equation [40] and mesopore volume was calculated from the difference between  $V_T$  and  $V_{\mu}$ . The pore diameter was calculated using the ratio  $4 VT/S_{\text{BET}}$ , and pore size distribution using the DFT method.

Fourier transforms infrared (FT-IR) spectroscopy analyses were performed using a spectrometer Perkin Elmer 283. The samples for FT-IR analyses were prepared by mixing them with KBr powder and pressing the mixture into pellets. The FT-IR spectra were recorded between 4000 and 400 cm<sup>-1</sup> (resolution of 4 cm<sup>-1</sup> and acquisition rate of 20 scan min<sup>-1</sup>).

Ultimate analysis of the carbons was carried out in a C H N S Analyzer (LECO 932). Prior to analysis, the samples were dried overnight at 105 °C and cooled in desiccators. Oxygen content was obtained by the difference between the total percentage (100 wt.%) and the sum of percentages (wt.% dry ash free) of nitrogen, carbon, hydrogen and sulfur.

Ash content determination was done according to the ASTM D2866-94 method. Dry AC sample (1.0 g) was placed into a porcelain crucible and transferred into a preheated muffle furnace set at a temperature of 1000 °C. The furnace was left on for one hour after which the crucible and its content was transferred to desiccators and allowed to cool. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample. Then the % ash content (dry basis) was calculated from Eq. (1).

$$\text{Ash \%} = \frac{W_{\text{ash}}}{W_0} \times 100 \quad (2)$$

where  $w_0$  is the dry weight of activated carbon sample before ashing.

In order to plot TGA (10 mg activated carbon, 10 °C/min, 10 ml/min N<sub>2</sub> flow rate) and DTA (10 mg activated carbon, 10 °C/min, 10 ml/min O<sub>2</sub> flow rate), curves for adsorbents, (Shimadzu DTA-50 TG/DTA thermal gravimetric analyzer) and losses in its mass were recorded. Heating procedures were started at room temperature and reached up to 800 °C by gradually increasing the temperature. The heating process is allowed to continue at this temperature for awhile; when no change in mass observed, the process is terminated. TGA and DTA graphs were plotted as a function of changes versus time and then construed.

SEM (Zeiss EVO 50 Model) was carried out to show the pore structure of obtained activated carbons. The SEM images were taken in secondary electrons; the acceleration voltage was equal to 20 kV, and the emission current was 20 pA.

The structures of these samples were checked by the powder XRD technology with Cu K $\alpha$  radiation at room temperature, using a Rigaku diffractometer (MXP-AHP18) for  $2\theta = 2-60^\circ$ .

To specify MB numbers (Methylene blue number), 0.02 g of adsorbent was agitated with 10 mL 1000 mg L<sup>-1</sup> MB solutions for 12 h. Then, the mixture was filtrated through 0.45  $\mu\text{m}$  nitrocellulose membrane. MB concentration left in the filtrate was determined by carrying out measurements in UV vis spectrophotometer (Shimadzu 2100S) at 668 nm [31]. Iodine numbers of adsorbent was defined according to ASTM D4607-94(1999) [32].

## 3. Results and discussion

### 3.1. Characterization results

#### 3.1.1. Ultimate analysis

Ultimate analysis results are given in Table 2. Results indicate that the carbonization temperatures influenced the yields of the activated carbons. An increase in the temperature at the same concentrations for both K<sub>2</sub>CO<sub>3</sub> and ZnCl<sub>2</sub> led to a decrease in the yields of the activated carbons. These findings show that both K<sub>2</sub>CO<sub>3</sub> and

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