EKSAKTA
Journal of Sciences and Data Analysis

E-ISSN: 2720-9326
P-ISSN: 2716-0459
DOI: 10.20885/EKSAKTA.vol1.iss1.art7

Research Article

Synthesis and Characterization of Nano Activated Carbon from Annatto Peels (*Bixa orellana* L.) Viewed from Temperature Activation and Impregnation Ratio of H_3PO_4

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Received: 15 December 2019; Accepted: 2 February 2020; Published: 7 February 2020

Abstract: Nano activated carbon is activated carbon with nano-sized carbon particles and can be synthesized from cellulose-containing materials such as the Annatto peels. In this study, the synthesis of nano activated carbon of the Annatto peels was carried out in terms of activation temperature variations and the carbon impregnation ratio of 50% H_3PO_4 acid and determining the characteristics of nano activated carbon from Annatto peels (NAPAC). The activation method used is the impregnation of carbon in 50% H_3PO_4 with a ratio of 1: 3; 1: 4; 1: 5; 1: 6; and 1: 7 (w/w) for 24 hours and heating at 400; 500; 600; 700; and 800 °C for one hour. Nano activated carbon from Annatto peels (NAPAC) was characterized by Infrared Spectrophotometer (FTIR), X-ray Diffractometer (XRD), and Transmission Electron Microscope (TEM). The results of the study, showed that the NAPAC can be synthesized from Annatto peels with activation by 50% H_3PO_4 at the temperature of 500 °C and the impregnation ratio of 1:5 (w/w). The results of characterization using FT-IR, XRD, and TEM showed that the NAPAC contains a group of functions O–H, C–H, C≡C, C=C, dan C–O/P=O with an amorphous carbon structure and the range of particles diameter at 22-36 nm.

Keywords: annatto peels, chemical and physical activation, nano activated carbon

Introduction

Technological developments in various fields provide many advantages. In the period 2010 to 2020, there will be an extraordinary acceleration in the application of nanotechnology in the industrial field [1]. Nanotechnology is a technology with ingredients whose components are less than 100 nm in one dimension and can be applied in various fields [2]. In the material field, a nanotechnology that can be developed is nano activated carbon.

In its development, nano activated carbon is carbon with the size of nano surrounded by active electrons with high purity and activated carbon atoms [3]. The difference between activated carbon and nano active carbon lies in the size of the constituent carbon particles, where the nanoparticle size of activated carbon is below 10^{-9} m, whereas activated carbon can be larger [4]. According to [5] and [3], nano activated carbon has an advantage in making biosensors because this material is relatively inexpensive, has a very large surface area and is a semiconductor. In addition, nano activated carbon can also be used as carbon nano paper for wrapping carrots because it can maintain freshness and nutrition [6].

According to [7], the material containing cellulose has the potential as a raw material for activated carbon nano because it is composed of carbon, hydrogen, and oxygen. Some cellulose materials that have been synthesized and produced nano-sized activated carbon are rice straw [8], nata-de-coco [7], Chinese herbal medicine waste [9], fiber coconut [10], and sugarcane stems [11]. Other materials that have the potential to produce nanocarbon and are rarely used, one of which is the Annatto peels. Annatto peels is an ingredient that contains pigment, cellulose, sugar, and a little oil [12].

Bixa orellana or Annatto is one of the plants that has long been known and used by most Indonesian people for medicine and health [13]. All parts of this plant can be utilized, starting from the roots, stems, leaves, even the seed skin can be utilized [14]. However, most of its use so far has been limited to the leaves and seeds, whereas the peel is rarely used, so research is needed related to Annatto peels.

In making nanocarbon, important things to consider besides the raw material used are the chemical and physical activation stages [11]. Chemical activation of activated carbon is carried out by immersing carbon in acidic chemical solutions (H_3PO_4 and H_2SO_4), bases (KOH and NaOH), and salt ($ZnCl_2$ and NaCl) [15]. The use of H_3PO_4 as a chemical activator is often used because it can produce nano carbon or activated carbon which has a large surface and large pores [11].

According to [11] in addition to the type of activator, an important thing to consider to produce nano-sized activated carbon is the impregnation ratio. The impregnation ratio can also affect functional groups in the activated carbon produced [16]. On the other hand, the advantage of the chemical activation stage is that it can produce good quality activated carbon with low physical activation temperatures [17]. Optimal activation temperatures have been reported between 400 °C to 600 °C by most previous researchers, regardless of the time of activation and the impregnation ratio for different raw materials [18][19].

Based on the background above, this research will synthesize activated carbon nano from Annatto peels in terms of the H_3PO_4 impregnation ratio and activation temperature and determine the characteristics of nano activated carbon from Annatto peels (NAPAC).

Materials and Methods

Materials

Annatto peels (*B. orellana*) sample were obtained from the UKSW Notohamidjojo Library area. The chemicals used include aquadest, 50% H_3PO_4, and NaOH. All chemicals used in the PA (Pro-Analysis) degree were obtained from E-Merck Germany, except aquadest.

The tools used in this study include a balance of 0.01 g (Ohaus TAJ601), analytical balance with an accuracy of 0.1 mg (Ohaus PA214), moisture analyzer (Ohaus MB 25), pH meter (Hanna HI 9812), furnace (Vulcan A-550), and reflux apparatus, also Buchner vacuum. Tools used to characterize the results are Infrared Spectrophotometer (FT-IR, Shimadzu Prestige 21), X-ray Diffractometer (XRD, Rigaku Multiflex 2kW), and Transmission Electron Microscope (TEM, JEM 1400 JEOL/EO).

Sample Preparation

Samples were prepared according to the modified [20] method

100 g of Annatto peels are washed with hot distilled water and then dried for 4 hours (T = 105 °C). After drying, the sample is mashed and sieved with a 60 mesh sieve.

Carbonization and Activation of Samples [21] modified

The carbonization of the sample is done by inserting the sample into the furnace (T = 400 °C) for an hour. Carbon is impregnated in 50% H_3PO_4 at a ratio of 1: 3; 1: 4; 1: 5; 1: 6; and 1: 7 (w/w) for 24 hours. After that, the sample is filtered under the Buchner vacuum and roasted (T = 105 °C) overnight. Then activated for 1 hour at a temperature of 400; 500; 600; 700; and 800 °C. The results of activation are then washed with 1M NaOH and rinsed with distilled water to pH 7. Activated carbon is heated in an oven (T = 110 °C) for 24 hours.

Characterization of results

Analysis of activated carbon functional groups can be observed with Infrared Spectrophotometer (IR) at wavenumbers 4000-400 cm^{-1}. Analysis of the crystal properties of the results was tested with X-Ray Diffractometer (XRD) and to determine the particle size of the results was carried out using the Transmission Electron Microscope (TEM) on the best results of the impregnation ratio and activation temperature.

Results and Discussion

Analysis of Annatto Peels Activated Carbon Functional Groups

In Figure 1. we can see the comparison of FTIR spectra of commercial activated carbon (standard) as literature with activated carbon from Annatto peels (APAC) activated by 50% H_3PO_4 at different temperatures. In the spectra (Figure 1. (a)) the standard activated carbon is detected peak at wavenumber 3510.45 cm^{-1}; 2931.80 cm^{-1}; 2291.43 cm^{-1}; 1635.64 cm^{-1}; 1388.75 cm^{-1}; 1126.43 cm^{-1}; and 617.22 cm^{-1} which is the vibration of the O–H group [22]; C–H [23]; C≡C [23]; C=C stretching [24]; C–H bending [8]; C–O stretching, and C–H aromatic [25] respectively.

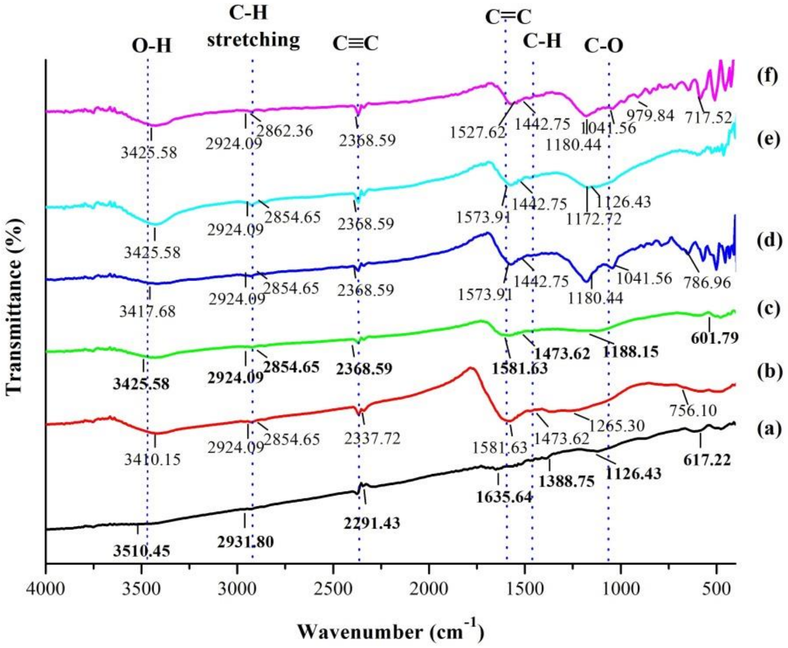

Figure 1. FTIR spectra: (a) standard activated carbon; APAC with variations in the activation temperature: (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 700 °C, and (f) 800 °C.

In Figure 1., it can be seen that the APAC spectra at an activation temperature of 400; 500; 600 and 700 °C have functional groups that are similar to standard activated carbon spectra namely O–H stretching [22]; C–H stretching and –CH– deformed groups [24]; C=C stretching [26]; C≡C stretching [23] and C–O stretching or P=O stretching [16]. At an activation temperature of 800 °C the emergence of new absorption bands at wave number 979.84 cm^{-1} due to vibration stretching P–O–P polyphosphate groups [27]. According to [28] at an activation temperature of 800 °C, the presence of oxygen is temperature-dependent, just like phosphorus. This causes the proportion of oxygen and phosphorus bound to carbon to increase so that at a temperature of 800 °C vibrations of oxygen and phosphorus are more visible.

In Figure 1., it can be seen that the treatment temperature of 500 °C has a significant decrease in absorption at the C–O or P=O peak with a width of wavenumber of about 1000-1300 cm^{-1} compared to other temperature activation treatments so that the resulting spectra is closer to the spectra standard activated carbon. According to [29] at an activation temperature above 450 °C, there is a release of bonds between carbon from cellulose material with $[H_2PO_4]^-$ or $[H_2P_2O_7]^{2-}$ which is lost in the washing stage so that there is a decrease in the number of C–O (P–O–C) and P=O. However, when using an H_3PO_4 activator and the activation temperature rises above 500 °C, a change in H_3PO_4 to P_2O_5 can react with carbon [30].

After knowing the effect of the activation temperature of the FTIR results, the next step is to study the effect of the impregnation ratio on the functional groups of the APAC.

In Figure 2., it can be seen that activated carbon at all impregnation ratios (1:3 to 1:7, w/w) has functional groups that are similar to standard activated carbon functional groups namely O–H stretching vibrations [22]; C–H stretching; –CH– deformed [24]; C≡C [23]; C=C stretching group [26]; and the C–O stretching group or P=O stretching [16]. In Figure 2., it can be seen that in the impregnation ratio of 1: 3 and 1: 4 (w/w) (Figure 2. (b) and Figure 2. (c)) there are wide absorption bands at wavenumbers 1000-1300 cm^{-1} (C–O or P=O).

In the 1:5 impregnation ratio (w/w) (Figure 2. (d)) there was a decrease in absorption at the wave number 1000-1300 cm^{-1} but in the impregnation ratio 1:6 and 1:7 (w/w) (Figure 2. (e) and Figure 2. (f)) the absorption band returned to rise marked by the widening of the absorption band at wavenumbers 1000-1300 cm^{-1} (C–O or P=O). This is because the small volume of phosphoric acid is insufficient to decompose or cleanse impurities in carbon. However, if the volume of phosphoric acid is excessive it will increase the occurrence of P–O–C bonds in activated carbon more and more [31][16].

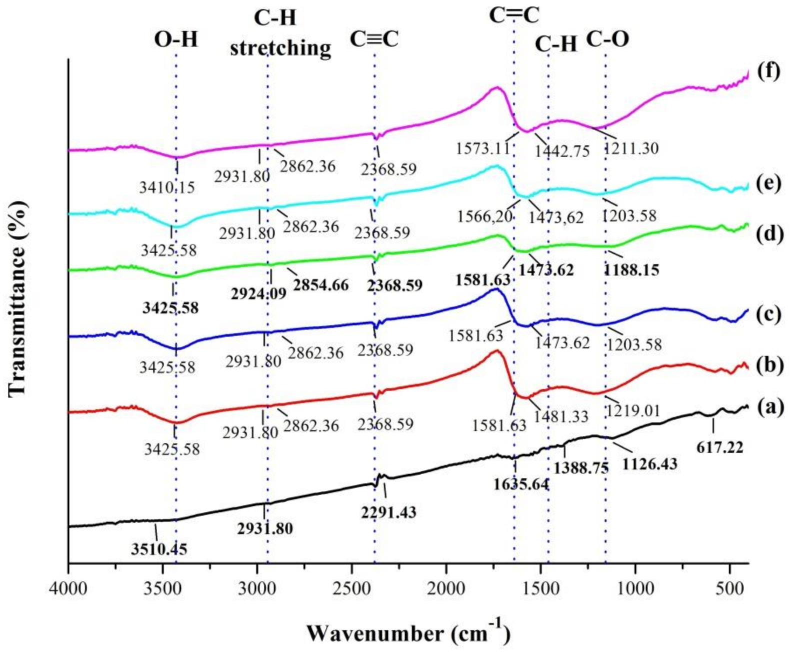

Figure 2. FTIR spectra: (a) standard activated carbon; APAC with various impregnation ratios (carbon: H_3PO_4, w/w): (b) 1:3, (c) 1:4, (d) 1:5, (e) 1:6, and (f) 1:7 at an activation temperature of 500 °C.

Based on Figure 2., the results show that the APAC spectra with an impregnation ratio of 1:5 (w/w) are closer to the standard activated carbon.

The CrystallinityAnalysis of Activated Carbon

Figure 3. shows the results of X-ray diffraction from standard activated carbon (Figure 3. (a)) and APAC with a treatment temperature of 500 °C activation and carbon impregnation ratio of H_3PO_4 1:5 (w/w) (Figure 3. (b)).

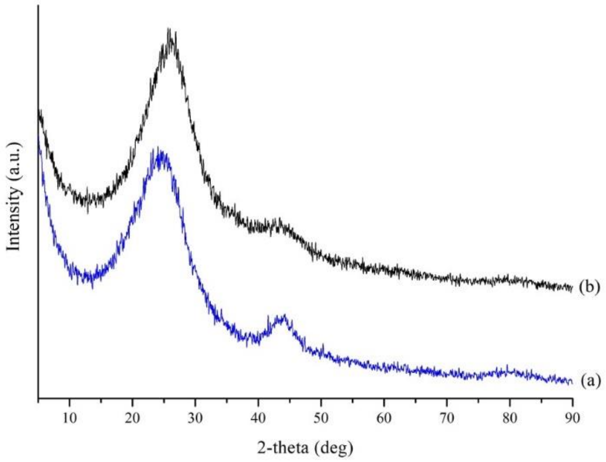

Figure 3. XRD diffractogram: (a) standard activated carbon and (b) APAC with an activation temperature of 500 °C the ratio of carbon impregnation to H_3PO_4 1: 5 (w/w).

The diffractogram of standard activated carbon and APAC has a similar pattern. The appearance of the display in the form of a wide-angle range and the absence of sharp peaks on the activated carbon diffractogram shows the dominant structure is amorphous [32][11]. The XRD pattern of standard activated carbon shows two peaks at ~ 24 ° and ~ 44 ° (weak) diffraction angles (Figure 3. (a)). In the XRD pattern, the APAC showed two broad peaks at ~ 25 ° and ~ 43 ° (weak) diffraction angles (Figure 3. (b)). Figure 3. (a) and Figure 3. (b) show that the standard activated carbon and APAC is amorphous.

Size Analysis of Active Carbon Particles

Figure 4. shows the results of the TEM analysis of APAC with a treatment temperature of 500 °C activation and an impregnation ratio of 1:5 (w/w) (carbon: H_3PO_4).

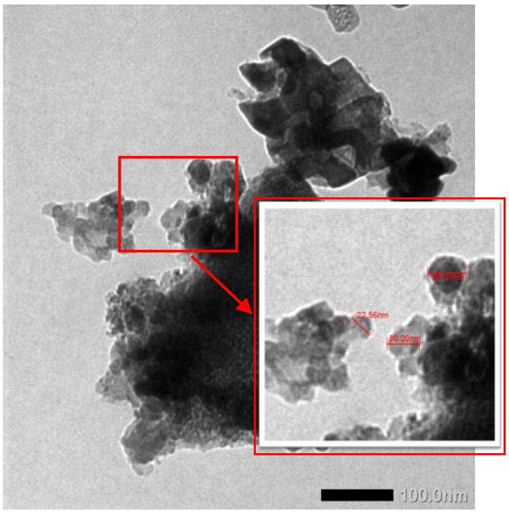

Figure 4. TEM micrograph results of APAC at an activation temperature of 500 °C the ratio of carbon impregnation to H_3PO_4 1:5 (w/w), magnification of 40,000x.

APAC particles are round with particle diameters ranging from 22-36 nm at a magnification of 40,000x. A similar result was obtained by [33] in the manufacture of nanocarbon from coconut shells, where cellulose-based carbon nano produces a single round carbon that is characterized by light shading (slightly black) from TEM results with particle sizes ranging from 20-40 nm. These results indicate that APAC is nano-sized, where the diameter of APAC particles is still in the range of nanoparticles which is 1-100 nm. This result is also confirmed by the research of [7] and [11] in the manufacture of activated carbon from nata-de-coco and sugarcane stems which states that cellulose-based materials can potentially produce activated carbon with irregular (amorphous) and non-uniform carbon particles, also, carbon particles produced nano-sized.

Conclusion

Based on the analysis results, nano activated carbon from Annatto peels (NAPAC) was obtained through the activation process with H_3PO_4 50% with the best activation temperature and impregnation ratio at 500 °C with a ratio of 1:5 (w/w) with %yield is 18.2%. The results of the characterization using FT-IR, XRD, and TEM show that the NAPAC contains O-H, C–H, C≡C, C=C, and C–O/P=O functional groups with amorphous carbon structures and the diameter of particles ranges from 22-36 nm.

Acknowledgement

The researcher would like to thank Universitas Kristen Satya Wacana for funding support for the XRD and TEM analysis through the Internal Research Grant Scheme namely *Skema Hibah Penelitian Internal Skim Penelitian Perseorangan/Kelompok Wajib* for the 2018-2019 Fiscal Year.

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