Low cost activated carbon prepared from *Dipterocarpus alatus* fruit

Yuvarat Ngernyen¹, Andrew J. Hunt², Ketsara Silakate¹, Chantakorn Patawat¹, Werawit Phiewruangnont¹, Narathorn Mahantadsanapong¹, Somchai Chuan-Udom³

**ABSTRACT**

*Dipterocarpus alatus* tree grows prolifically throughout Thailand and can be tapped to yield significant quantities of oil to be used as natural diesel. However, such practices lead to waste dried fruit dropping from the tree. At present, there is no utilization of this dropped fruit, therefore cost-effective processes need to be applied to obtain higher value products from this waste. A possible to utilization is the conversion to activated carbon for adsorption applications including the removal of heavy metals, dyes, and other contaminants in water purification and other decontamination process. A major challenge of current commercial activated carbon is the high production cost and recently it has been shown that chemical activators comprise a significant proportion of these costs. This feasibility study investigates the use of *Dipterocarpus alatus* fruit as raw material to produce low cost activated carbon adsorbents. Activated carbon was prepared from *Dipterocarpus alatus* fruit: endocarp, mesocarp, and wing by chemical activation with ZnCl₂, FeCl₃, and KOH. Each part of the fruit was impregnated with 30 wt% activating agent at a ratio of 1:2 for 1 h and then carbonized at 500 °C for a further 1 h. The surface area, pore volume, and average pore size of the resulting carbons were characterized by nitrogen gas adsorption. Activation of mesocarp with ZnCl₂, KOH, and FeCl₃ gave activated carbons with the surface area of 447, 256, and 199 m²/g, respectively. In the same way, ZnCl₂ activation gave a maximum surface area of 312 and 278 m²/g for wing and endocarp, respectively. All of the aforementioned samples have an average pore size of around 2 nm. In contrast, KOH and FeCl₃ activation of wing and endocarp produced activated carbon with very low surface area (below 25 m²/g), but with an average pore size of 5-14 nm. The maximum surface area of activated carbon prepared from *Dipterocarpus alatus* fruit was higher than some literature examples for activated carbon from other biomass. Consequently, *Dipterocarpus alatus* fruit demonstrated significant potential as a feedstock for the preparation of low cost activated carbons.

**Key words:** *Dipterocarpus alatus* fruit, activated carbon, chemical activation, surface area

**INTRODUCTION**

*Dipterocarpus alatus* tree grows prolifically throughout Thailand and can be tapped to yield significant quantities of oil to be used as natural diesel. However, such practices lead to waste dried fruit dropping from the tree. At present, there is no utilization of this dropped fruit, therefore cost-effective processes need to be applied to obtain higher value products from this waste. A possible to utilization is the conversion to activated carbon for adsorption applications including the removal of heavy metals, dyes, and other contaminants in wastewater treatment.

A major challenge of current commercial activated carbon is the high production cost and recently it has been shown that chemical activators comprise a significant proportion of these costs. Significant research has focussed on reducing the production cost of activated carbon. Efforts to identify of low cost alternative precursors to traditional feedstocks such as coal have been extensively investigated. Agricultural and forest wastes such as corncob, cola nut shell, *Ficus carica* bast, plantain fruit stem, Ma-core fruit shell, date seed and *Eucalyptus camaldulensis* wood have demonstrated great interest due to their accessibility and abundant availability. To the best of the author’s knowledge no research on the preparation of activated carbon prepared from *Dipterocarpus alatus* fruit have been reported in the literature.

There are two methods for activated carbon production can be employed, physical and chemical activation. Physical activation consists of carbonization of the raw material followed by activation with steam, carbon dioxide or air at high temperature of 800-1000 °C. In the chemical activation method, the feedstock is soaked in a chemical activating agent such as

**Cite this article:** Ngernyen Y, Hunt A J, Silakate K, Patawat C, Phiewruangnont W, Mahantadsanapong N, Chuan-Udom S. Low cost activated carbon prepared from *Dipterocarpus alatus* fruit. *Sci. Tech. Dev. J. – Engineering and Technology*; 3(3):S175-S180.
H₃PO₄, ZnCl₂, KOH, NaOH and H₂SO₄ prior to carboxylation at temperature of 400–800 °C.

This preliminary study aims to demonstrate feasibility of using *Dipterocarpus alatus* fruit as raw material for the preparation of low-cost activated carbon. A one-step process, with lower activation temperature will be employed that leads to higher yields and development of extensive porosity. The chemical activators ZnCl₂, FeCl₃ and KOH were selected for production of activated carbon in this work. In order to ensure that cost are kept low a maximum activator to biomass ratio of 2:1, was utilised in this study. The resultant activated carbons were determined their pore structure and proximate analysis.

**MATERIALS AND METHODS**

**Materials**

*Dipterocarpus alatus* fruits were collected from Khon Kaen University. The fruits divided into 3 parts: endocarp, mesocarp and wing as shown in Figure 1. Each part was cut into small piece and sieved with the size lower than 4 mm (mesh no. 5).

**Preparation of activated carbon**

10 g of the of *Dipterocarpus alatus* fruit sample was mixed with 30 wt% ZnCl₂, FeCl₃ or KOH at a impregnation ratio of sample: activating agent 1:2 for 1 h. It was noted that, at this ratio the chemicals were able to promote activation within the raw material, while leading to no excess unutilised activator. No drying step as employed and the resulting sample was carbonized inside fixed-bed stainless steel reactor (5 cm in the diameter and 30 cm in the height) at 500 °C for 1 h under high purity flow of nitrogen (200 cm³/min). The chosen carbonization temperature was found from thermal analysis as explained in section 3.1. The sample was washed with distilled water until the solution was pH neutral. The carbon was then oven dried at 110 °C for 3 h and kept in air tight pack for further analysis. The yield of the activated carbon is defined as the ratio of mass of final activated carbon to that of the dried original sample (10 g).

**Characterization**

Thermal stability of endocarp, mesocarp and wing of *Dipterocarpus alatus* fruit samples were investigated by thermogravimetric analyser or TGA (TGA-50 Shimadzu). A typical analysis was conducted by heating a 10 mg sample up to 700 °C at a heating rate of 10 °C min⁻¹ under N₂ at a purge rate of 10 ml min⁻¹.

In order to characterise the BET surface area, pore volume and average pore size of activated carbon, N₂ adsorption isotherm at ~196 °C was determined by gas adsorption analyser (ASAP2460, Micromeritics). Adsorption data were obtained over the relative pressure or P/P° ranging from 0.01 to 0.99. The sample was degassed in a vacuum at 250 °C for 5 h before adsorption test. Specific surface area (S_BET) was calculated using the Brunauer-Emmett-Teller equation. The total pore volume (V_T) was estimated at a P/P° of 0.99. Micropore volume (V_mic) was determined using t-plot method. Mesopore volume (V_meso) was calculated by the different between total pore volume and micropore volume. Average pore size (D_P) was obtained by applying Barrett-Joyner-Halenda or BJH method. Proximate analysis that include moisture, ash, volatile matters and fixed carbon of the raw material and activated carbon was carried out using standard method. The contents of volatile matters and moisture were determined based on ASTM D5832-98 by heated sample at 950 °C for 30 min and ASTM D2867 by heated sample at 150 °C for 3 h, respectively. For ash content, sample was heated at temperature of 800 °C for 2 h. Finally, fixed carbon content calculated by the difference as 100 – moisture(%) – ash(%) – volatile matters(%).

**RESULTS AND DISCUSSION**

**Properties of raw materials**

The proximate analysis of each part of the *Dipterocarpus alatus* fruit based on the average of three samples was demonstrated in Table 1. For all parts, the content showed similar values; with a moisture content of 8 wt%, volatile matter content of 72–73 wt%, ash 2 wt% and fixed carbon of 16–17
wt%. *Dipterocarpus alatus* fruit exhibit low ash and high volatile contents, similar to other biomass wastes that have already been reported in literature. The fixed carbon content is also higher or comparable with those materials such as oil palm wood (9.63 wt%)\(^1\), kenaf core fibre (11 wt%)\(^1\), waste tea (11.34 wt%)\(^1\), *Eucalyptus camaldulensis* wood (14.65 wt%)\(^2\), bagasse (16.4 wt%)\(^3\), barley straw (17.3 wt%)\(^4\) and rice-straw (17.8 wt%)\(^5\). Therefore, *Dipterocarpus alatus* fruit is a suitable feedstock for preparation of activated carbon.

The thermal behaviour as analysed by TGA for the endocarp, mesocarp and wing of *Dipterocarpus alatus* fruit are presented in Figure 2. The TG curve of *Dipterocarpus alatus* fruit is like that of any other biomass comprised mainly of cellulose, hemicellulose and lignin. It indicates three mass loss steps: the evaporation of adsorbed moisture up to 110 °C, the decomposition of hemicellulose in the biomass at 200–340 °C and the cellulose decomposition at about 380–500 °C\(^6\). It can also be seen that the moisture the evaporated from the structure 10 wt%, which is consistent with the results of proximate analysis. Moreover, the main decomposition occurring between 200–480 °C is the devolatilisation process resulting in the remaining of carbon content in the structure. Therefore, the suitable temperature for preparation of activated carbon from this fruit should be higher than these temperatures, therefore 500 °C was used to prepare activate carbon in this work.

![Thermogravimetric analysis plot of each part of the *Dipterocarpus alatus* fruit](image)

Figure 2: Thermogravimetric analysis plot of each part of the *Dipterocarpus alatus* fruit

**N\(^2\)** adsorption isotherms and pore structure development

Figure 3 shows the nitrogen gas adsorption-desorption isotherms at –196 °C of the prepared activated carbons. It is noted that adsorption-desorption isotherms of KOH activation for endocarp part and FeCl\(_3\) activation for wing part were not shown due to very low adsorption volumes. All the adsorption isotherms are of type I according to IUPAC or the International Union of Pure and Applied Chemistry classification, which is characteristic of microporous structures\(^6\). The adsorption rapidly increases at low relative pressures (P/P\(_o\) < 0.1). The isotherms also exhibited small hysteresis loops implying the existence of mesoporosity. Therefore, all prepared activated carbons are of a micro-mesoporous structure. Although the adsorption isotherms of all samples are similar classification, the adsorption capacities are different depend on type of activating agents. It was observed that ZnCl\(_2\) activation had higher N\(_2\) adsorption than that of FeCl\(_3\) and KOH activation. The low N\(_2\) adsorbed amount for KOH activation of wing was observed, indicating a less porous structure.

| Sample Type | Yield (wt%) | BET Surface Area (m\(^2\)/g) | Total Pore Volume (cm\(^3\)/g) |
|-------------|-------------|-----------------------------|------------------------------|
| Endocarp    | 32          | 387                         | 0.04                         |
| Mesocarp    | 35          | 412                         | 0.05                         |
| Wing        | 38          | 447                         | 0.26                         |

Table 2 is summarised the yield, \(S_{BET}\), \(V_{mic}\), \(V_{meso}\), \(V_T\) and \(D_P\) of all resulting activated carbons. A maximum yield of 43–51 wt% obtained from FeCl\(_3\) activation while ZnCl\(_2\) gave the yield of 32–38 wt%. The minimum yield of 16–25 wt% was recorded for KOH activation. As mentioned before, *Dipterocarpus alatus* fruit is a lignocellulosic material, with cellulose, hemicellulose and lignin as the main components. In activation and carbonization steps, these components decompose and liberate the non-carbon elements that is hydrogen, oxygen and nitrogen in the form of liquids and gases, remaining the carbon content\(^8\). This causes a decrease in mass of the resulting activated carbon when compare with the original material.

For all parts of the *Dipterocarpus alatus* fruit, textural analysis showed that the activated carbons synthesized with ZnCl\(_2\) had greater porosity in term of surface area and total pore volume compare to FeCl\(_3\) and KOH activated samples. It was demonstrated that activated mesocarp with ZnCl\(_2\) provide best properties of activated carbon, with BET surface area of 447 m\(^2\)/g and total pore volume of 0.265 cm\(^3\)/g. Furthermore, ZnCl\(_2\) and FeCl\(_3\) activation produced activated carbon with mostly micropore except in the case of FeCl\(_3\) activation of wing part. For KOH activation, resulting activated carbons demonstrated mainly mesoporous except for the mesocarp materials. The results from Table 2 demonstrate that chemical activation of endocarp and wing with KOH and activation of wing with FeCl\(_3\) obtaining activated carbons with low surface area and pore volume but with a pore size of 5–14 nm. It is suggested that large pore size adsorbent is suitable for adsorbed large molecule adsorbate in adsorption processes. Therefore, the use of such materials for the adsorption of large molecules
may overcome diffusion limitations resulting from the small pore size of traditional activated carbons. The adsorbent pores are classified into three groups: micropore (diameter < 2 nm), mesopore (diameter 2–50 nm) and macropore (diameter > 50 nm) according to the definition of IUPAC. Table 2 demonstrates that the average pore diameter of all activated carbons is between 2 and 14 nm, indicating they are a microporous and mesoporous materials.

For all activating agents, different parts of *Dipterocarpus alatus* fruit produced activated carbons with varying surface areas and pore volumes. This may be due to the different physical structure of each part. For example, mesocarp is hard compared to the wing part which is very thin.

The maximum surface area of activated carbon prepared from mesocarp of *Dipterocarpus alatus* fruit (447 m²/g) was higher than some chemical activated carbons from biomass such as palm flower (9.57 m²/g) 19, branches of walnut wood (32 m²/g) 20, oak wood (68 m²/g) 21, peanut shell (89 m²/g) 22, pine nut shell (296 m²/g) 23, kenaf core fiber (299 m²/g) 13, macauba seed endocarp (371 m²/g) 23 and carnauba palm leave (431 m²/g) 23.

**Proximate analysis**

According to Table 3, the volatile matters in activated carbon decreased from starting material while fixed carbon increased. This was expected as devolatilisation leads to the loss of oxygen and hydrogen in the form of water during carbonisation and activation resulted in sample containing predominantly carbon. Furthermore, ash content increased from starting material while moisture content decreased. These results were similar to that reported in the work of Ahmad et al. 12. Low amounts of moisture, volatile matter and ash contents indicate that the activated carbon should be a good raw material for adsorbents 6. Ash content reduces the activity of activated carbon the lower the ash content; the better activated carbon will be for adsorption 6.

**CONCLUSION**

In this preliminary study, the production of activated carbon from *Dipterocarpus alatus* fruit using the chemical activation method with ZnCl₂, FeCl₃ and KOH, has been investigated. The maximum BET surface area obtained by ZnCl₂ activation was 447, 312 and 278 m²/g for mesocarp, wing and endocarp, respectively. In the case of FeCl₃ activation, activated

| Table 1: Proximate analysis (wt%) of each part of *Dipterocarpus alatus* fruit |
|--------------------------|--------------------------|--------------------------|
|                         | Endocarp                 | Mesocarp                 | Wing                     |
| Moisture                | 8.26                     | 8.74                     | 8.12                     |
| Volatile Matter         | 73.02                    | 72.35                    | 72.08                    |
| Ash                     | 2.70                     | 2.21                     | 2.54                     |
| Fixed carbon            | 16.02                    | 16.70                    | 17.26                    |
carbon with surface area of 199 and 122 m²/g were produced from the mesocarp and endocarp, respectively, but no porosity was formed for the wing part of the fruit. Regarding the activation with KOH, surface area of activated carbon from mesocarp was 256 m²/g. However, KOH activation of the endocarp and wing parts could not develop porosity in activated carbon structure. The activated carbon prepared under the described experimental conditions demonstrates the potentiality of Dipterocarpus alatus fruit as low cost material for the preparation of activated carbon, resulting a surface area higher than that of activated carbons obtained from some biomass wastes.

Future studies will utilise Dipterocarpus alatus fruit activated carbons for adsorption of dye or heavy metal molecules. The preparation conditions such as activator ratio, impregnation time, carbonization temperature and carbonization time should also be investigated.

ACKNOWLEDGEMENT

This study was supported by Research and Academic Services Affairs of Khon Kaen University under Yang Na Scholarship for fiscal year 2019.

AUTHOR CONTRIBUTIONS

All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Table 2: Yield and porous texture of the prepared activated carbon

| Sample  | Yield (wt%) | SBET (m²/g) | Vmic (cm³/g) | Vmeso (cm³/g) | VT (cm³/g) | DP (nm) |
|---------|------------|-------------|--------------|---------------|------------|--------|
| Endocarp |            |             |              |               |            |        |
| ZnCl₂   | 35         | 278         | 0.101 (66%)  | 0.053 (34%)   | 0.154      | 2.22   |
| FeCl₃   | 51         | 122         | 0.045 (58%)  | 0.033 (42%)   | 0.078      | 2.55   |
| KOH     | 16         | 2           | 0.001 (25%)  | 0.003 (75%)   | 0.004      | 13.84  |
| Mesocarp |            |             |              |               |            |        |
| ZnCl₂   | 32         | 447         | 0.117 (44%)  | 0.148 (56%)   | 0.265      | 2.37   |
| FeCl₃   | 45         | 199         | 0.080 (74%)  | 0.028 (26%)   | 0.108      | 2.18   |
| KOH     | 25         | 256         | 0.096 (64%)  | 0.053 (36%)   | 0.149      | 2.33   |
| Wing    |            |             |              |               |            |        |
| ZnCl₂   | 38         | 312         | 0.112 (62%)  | 0.070 (38%)   | 0.182      | 2.33   |
| FeCl₃   | 43         | 6           | 0.002 (15%)  | 0.011 (85%)   | 0.013      | 8.84   |
| KOH     | 19         | 24          | 0.009 (30%)  | 0.021 (70%)   | 0.030      | 4.95   |

Table 3: Proximate analysis (wt%) of activated carbon prepared by ZnCl₂ activation

|          | Endocarp | Mesocarp | Wing |
|----------|----------|----------|------|
| Moisture | 7.00     | 6.50     | 7.14 |
| Volatile Matter | 25.71 | 26.36 | 27.77 |
| Ash      | 8.53     | 7.32     | 8.29 |
| Fixed carbon | 58.76 | 59.82 | 56.88 |
CONFLICT OF INTEREST

We declare that there is no conflict of whatsoever involved in publishing this research.

REFERENCES

1. Matos M, Barreiro MF, Gandini A. Olive stone as a renewable source biopolyols. Ind. Crop. Prod. 2010;32:7–12. Available from: https://doi.org/10.1016/j.indcrop.2010.02.010.

2. Sangon S, et al. Valorization of waste rice straw for the production of highly effective carbon based adsorbents for dyes removal. J. Clean. Prod. 2018;172:1128–1139. Available from: https://doi.org/10.1016/j.jclepro.2017.10.210.

3. El-Sayed GO, Yehia MM, Asaad AA. Assessment of activated carbon prepared from corncob by chemical activation with phosphoric acid. Water Resources and Industry. 2014;7:866–75. Available from: https://doi.org/10.1016/j.wri.2014.10.001.

4. Nsami JN, Mbudcam JK. The adsorption efficiency of chemically prepared activated carbon from cola nut shell by ZnCl2 on methylene blue. Journal of Chemistry. Article ID 469170. 2013;Available from: https://doi.org/10.1155/2013/469170.

5. Pathania D, Sharma S, Singh P. Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. Arab. J. Chem. 2017;p. S1445–S1451. Available from: https://doi.org/10.1016/j.arabjc.2013.04.021.

6. Ekpete OA, Marcus AC, Osi V. Preparation and characterization of activated carbon obtained from plantain (Musa paradisaca) fruit stem. Journal of Chemistry. 2017;Available from: https://doi.org/10.1155/2017/9635615.

7. Aboua KN, Yobouet YA, et al. Investigation of dye adsorption onto activated carbon from the shells of Macoré fruit. J. Environ. Manage. 2015;156:10–14. PMID: 25791232. Available from: https://doi.org/10.1016/j.jenvman.2015.03.006.

8. Ogumbenro AE, Quang DV, Al-Ki KA, Vega LF, Abu-Zahra MRM. Physical synthesis and characterization of activated carbon from date seeds for CO2 capture. J. Environ. Chem. Eng. 2018;6:4245–4252. Available from: https://doi.org/10.1016/j.jtecce.2018.06.030.

9. Heidari A, Younesi H. Adsorptive removal of CO2 on highly microporous activated carbons prepared from Eucalyptus camaldulensis wood: Effect of chemical activation. J. Taiwan Inst. Chem. Eng. 2014;45:579–588. Available from: https://doi.org/10.1016/j.tice.2013.06.007.

10. Dąbrowski A, Podkościelny P, Hubicki Z, Barczak M. Adsorption of phenolic compounds by activated carbon - a critical review. Chemosphere. 2005;58:1049–1070. PMID: 15664613. Available from: https://doi.org/10.1016/j.chemosphere.2004.09.067.

11. Aygün A, Yenisoy-Karakas S, Duman I. Production of granular activated carbon from fruit stones and nutsHELLS and evaluation of their physical, chemical and adsorption properties. Micropor Mesop. Mat. 2003;66:189–195. Available from: https://doi.org/10.1016/S1387-3806(03)00227-4.

12. Ahmad AL, Loh MM, Aazj JA. Preparation and characterization of activated carbon from oil palm wood and its evaluation on methylene blue adsorption. Dyes and Pigments. 2007;75:263–272. Available from: https://doi.org/10.1016/j.dyepig.2006.05.034.

13. Shamsuddin MS, Yusoff SRN, Sulaiman MA. Synthesis and characterization of activated carbon produced from kenaf core fiber using H3PO4 activation. Procedia Chem. 2016;19:558–565. Available from: https://doi.org/10.1016/j.proche.2016.03.053.

14. Kan Y, Yue Q, Li D, Wu Y, Gao B. Preparation and characterization of activated carbons from waste tea by H3PO4 activation in different atmospheres for oxytetracycline removal. J. Taiwan Inst. Chem. Eng. 2017;71:494–500. Available from: https://doi.org/10.1016/j.jtice.2016.12.012.

15. Darmstadt H, García-Perez M, Chaala A, Cao NZ, Roy C. Co-pyrolysis under vacuum of sugar cane bagasse and petroleum residue properties of the char and activated char products. Carbon. 2001;39:815–825. Available from: https://doi.org/10.1016/S0008-6223(00)00204-5.

16. Pallarés J, González-Cencerrado A, Arauzo I. Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam. Biomass Bioenerg. 2018;115:64–73. Available from: https://doi.org/10.1016/j.biombioe.2018.04.015.

17. Oh GH, Park CR. Preparation and characteristics of rice-straw-based porous carbons with high adsorption capacity. Fuel. 2002;81:327–336. Available from: https://doi.org/10.1016/S0016-2361(01)00171-5.

18. Yakout SM, El-Deen GS. Characterization of activated carbon prepared by phosphoric acid activation of olive stones. Arab. J. Chem. 2016;9:5155–5162. Available from: https://doi.org/10.1016/j.arabjc.2011.12.002.

19. Nethaji S, Sivasamy A. Adsorptive removal of an acid dye by lignocellulosic waste biomass activated carbon: equilibrium and kinetic studies. Chemosphere. 2011;82:1367–1372. PMID: 21176940. Available from: https://doi.org/10.1016/j.chemosphere.2010.11.080.

20. Ghaedi M, Mazaheri H, Khodadoust S, Hajati S, Purkait MK. Application of central composite design for simultaneous removal of methylene blue and Pb2+ ions by walnut wood activated carbon. Spectrochim Acta A. 2015;135:479–490. PMID: 25113736. Available from: https://doi.org/10.1016/j.saa.2014.06.138.

21. Hajati S, Ghaedi M, Yaghoubi S. Local, cheap and nontoxic activated carbon as efficient adsorbent for the simultaneous removal of cadmium ions and malachite green: optimization by surface response methodology. J. Ind. Eng. Chem. 2015;21:760–767. Available from: https://doi.org/10.1016/j.jiec.2014.04.009.

22. Al-Othman ZA, Ali R, Naushad M. Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies. Chem. Eng. J. 2012;184:238–247. Available from: https://doi.org/10.1016/j.cej.2012.01.048.

23. Lacerda VS, et al. Rhodamine B removal with activated carbon prepared from lignocellulosic waste biomass. Bioenerg. 2018;115:64–73. Available from: https://doi.org/10.1016/j.biombioe.2018.04.015.