Production and Characterization of Activated Carbon from Baobab Fruit Shells by Chemical Activation Using ZnCl₂, H₃PO₄ and KOH

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Abstract. Chemical agents have a good influence on the formation of activated carbons, surface characteristic, and its adsorption properties. In this study, the effect of activating agents (ZnCl₂, KOH, and H₃PO₄) on baobab fruit shell (BFS) were evaluated. The characteristics of the baobab fruit shell based activated carbon (BF-ACs) were evaluated through the yield and iodine number. BF-ACs were also characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), and nitrogen (N₂) adsorption. SEM analysis illustrates those porous structures formed on the surface of BF-ACs were with different sizes. The XRD analysis show that the main structures of BF-ACs are amorphous. FT-IR data demonstrates the presence of different surface groups on the produced BF-ACs. Among activating agent, the KOH was observed to the most appropriate for the production of activated carbon with a large surface area (1029.44 m²/g) from baobab fruit shell.

1. Introduction
Activated Carbon is unique and a versatile adsorbent due to its microporous structures, extended surface areas, high adsorption capacities, universal adsorption effects, and high degree of surface reactivity [1,2]. It has been widely used to purify, dechlorinate, decolorize, separate, and concentrate for recovery and filtration. Furthermore, it has been used to remove the unfavourable constituents from gases and liquid solutions. Therefore, it is utilized in a variety of domains, such as pharmaceutical, chemical, nuclear, naphtha, and for the drinking water treatment and wastewater and so on [1]. This is a result of its relatively high mechanical strength, adequate pore size distribution, and high adsorption capacity [3].

The two basic techniques for producing activated carbon are physical and chemical activation methods. Comparing both methods, chemical activation has shown several advantages over physical method, such as low energy and operating cost, higher carbon yields and larger surface areas and it is usually a one-step process at a temperature range around 450–900 °C [4]. In chemical activation, the raw material is impregnated with activating agents such as ZnCl₂, H₃PO₄, KOH, H₂SO₄ and NaOH, followed by carbonization [5]. The activation agent functions as dehydration agent which, during this process, inhibits the formation of tar and refuses volatile compounds, which helps improve the AC yield and reduce the temperature of carbonization compared to the physical activation method [6].

The broad use of activated carbons is limited by the availability of low-cost and high-quality materials which may meet unique consumer criteria. Therefore, in the last years, lignocellulosic biomass has become one of the most important starting materials to produce activated carbon due to its benefits,
especially for the environment [7]. Many studies have proposed the use of lignocellulosic wastes as suitable raw materials to prepare AC, such as coconut shells [8,9], peanut shell [10,11], sunflower seed [10], baobab fruit shell [12], gelatine, starch [13], palm kernel shell [14], empty fruit bunch [14], pistachio nut shells [15], neem husk [16], almond shell [15], fox nutshell [17], rice husk [18], and rubber seed shell [19].

Baobab fruit shell (BFS) is a lignocellulosic residue of the baobab fruit. The baobab tree belongs to the genus *Adansonia* and the family of *Malvaceae*, which includes about 30 genera [20]. The potential average yield of whole baobab fruit of 673,000 tonnes per year and the average of the mature fruiting produces approximately 200 kg of fruit per season [21,22]. The creation of a huge amount of baobab fruit shells (BFS) as waste from the treatment of baobab fruits, which represent major environmental and economic challenges together, could be processed more into value-added by-products [23]. However, there has been a recent interest to utilize this massive baobab biomass as an alternative source to produce the activated carbon due to its beneficial features, which are cheap, abundant, renewable, non-toxic, environmentally friendly, and has no economic benefits.

The aim of the present work was to study the characteristics of activated carbons prepared from baobab fruit shell by chemical activation method using H$_3$PO$_4$, KOH and ZnCl$_2$ as activating agents. The morphological structure and chemical properties of raw BFS and its derived ACs have also been investigated. The surface morphology and surface chemistry components were analysed by SEM, FT-IR, and XRD. The BET surface areas were also determined using N$_2$ adsorption.

2. Materials and Methods

2.1 Materials

Baobab fruit has been collected from the Kordofan State in North Sudan. Phosphoric acid (H$_3$PO$_4$) was obtained from Macron Fine Chemicals, USA. Potassium hydroxide (KOH), zinc chloride (ZnCl$_2$), and sodium thiosulfate (Na$_2$S$_2$O$_3$) were purchased from Sigma-Aldrich and R&M Chemicals, Malaysia. Hydrochloric acid 37% was purchased from Friendemann Schmidt Chemical, Malaysia. Iodine (I) was obtained from UNIVAR, UK, while potassium iodide (KI) from Duchefa biochemie, Malaysia. High-purity nitrogen gas was obtained from Fuelink Marketing Sdn. Bhd., Selangor, Malaysia. All other chemicals of analytical grade were utilized during the experiments.

2.2 Methods

An amount of chemical reagent (ZnCl$_2$, KOH, or H$_3$PO$_4$) was added to 15 g of the raw material (BFS) at an impregnation ratio of 1:1. Next, distilled water was added which was equal to four times the total mixture mass and then agitated for 1 h utilizing the rotary shaker at 50°C. The mixture was placed to oven-dried overnight at 100 °C to get a thick paste. The sample was placed in a reactor, which was continuously purged with high-purity nitrogen gas (99.95%), and later was inserted into an electric furnace for 1 hour at 10 °C/min at 500 °C. The produced BF-AC was moved to the desiccator for cooling and later washed with 50 ml of 0.5 M HCl to remove any ash in the sample and any residual of the dehydrating agents. The product was frequently rinsed with warm distilled water until a constant pH was attained [24]. BF-AC was inserted in a vacuum oven to dry for 24 hours at 110°C. The yield of BF-ACs was calculated based on the following equation:

\[ \text{Yield} \ (\%) = \frac{M_d}{M_o} \times 100 \]

Where $M_d$: the dry mass of final BF-AC (g), which is measured after the BF-AC is prepared. Whereas $M_o$ is the dry mass of baobab fruit shells (g), which is measured at the beginning of the experiment [25]. Iodine Number was determined following Vunain et al., [12] procedure.

The morphological structure of the raw material (BFS) and the produced BF-ACs were observed using a JEOL-IT 100 SEM instrument. Fourier transform infrared (FT-IR) spectroscopic was utilized to

![Image](image_url)
analysis the surface chemistry of raw BFS and produced BF-ACs utilizing a Perkin Elmer Frontier model FTIR-spectrometer. X-ray diffraction patterns of precursor and prepared BF-AC were carried out using a Bruker D2 Phaser at 30 kV and 10 mA Cu Ka radiation source ($k = 1.54184$ Å). The specific surface area and porosity of BF-AC were measured by N$_2$ adsorption–desorption isotherms (Brunauer–Emmett–Teller analysis, BET) at 77 K using a Quantachrome, Autosorb-1C and a surface area analyser.

3. Results and Discussions

3.1 Effects of Activating Agents on The Yield of BF-ACs And Iodine Number

The yields of BF-ACs are presented in figure 1. The findings show that phosphoric acid (H$_3$PO$_4$) produced the highest yield of 43.9 %, whereas potassium hydroxide (KOH) produced the lowest yield of 38 %. The H$_3$PO$_4$ yield is higher due to the involvement of H$_3$PO$_4$ during activation, which facilitates the transition of aliphatic to aromatic compounds, and promotes depolymerization, dehydration, and redistribution of constituent biopolymers, thereby increasing the output of activated carbon [25]. Iodine number is a good method utilized for the determination of the adsorption capacity and the quality of activated carbon, also known as iodine adsorption. It is often used due to its simplicity and rapidity [12]. The higher iodine number means there is a high surface area for adsorption to take place and a great probability that the activated carbon has a very large micropore structure [26]. Figure 2 illustrates that the iodine number achieved for the three produced activated carbons ranging from 1213.451 to 1248.357 mg/g. Furthermore, these results disclosed that activated carbon produced with H$_3$PO$_4$ presented the highest iodine number of 1248.357 mg/g compared to the AC samples produced by KOH and ZnCl$_2$, which were of 1227.413 mg/g and 1213.451 mg/g, respectively.

Figure 1. Yield of AC produced from different chemicals (%) (Temperature: 500 °C, time: 60 min, impregnation ration: 1:1).

Figure 2. Iodine Number of Produced BF-ACs (Temperature: 500 °C, time: 60 min, impregnation ration: 1:1).

3.2 Morphological structure of BF-ACs

The SEM technique was applied to observe the morphological surface of the raw BFS, and the resulting prepared BF-ACs with chemical activation methods using ZnCl$_2$, KOH, H$_3$PO$_4$. The SEM micrographs of the BF-ACs samples show the existence of abundant pores produced by activating agents during carbonization, which demonstrated a significant variance in the morphological surface of the raw material (Figure 3a) and BF-ACs (Figure 3b, c, d). These results revealed that chemicals influenced the topographical characteristics of the surfaces of the carbon. Figure 3 shows that the morphology of prepared activated carbons with distinct pores of various sizes refers to the appearance of various mechanisms of reaction. KOH mechanism is more complex and involves (almost explosive) disintegration after intercalation of the structure, and even some gasification by hydroxide oxygen molecules. While, ZnCl$_2$ promoting the elimination of H$_2$O molecules from the lignocellulosic structure of raw material, and H$_3$PO$_4$ chemically incorporates inside the lignocellulosic structures. Consequently,
during activation process, there is no selective carbon removal that increases the yields [27]. H$_3$PO$_4$-AC and ZnCl$_2$-AC (Figure 3c and d) evidently presented developed honeycomb as highly determined pores and cavities compared with precursor (BFS). Furthermore, the number of pores present in the KOH micrograph is highest than those present in H$_3$PO$_4$ and ZnCl$_2$. The KOH-AC micrograph has a high number of pores than H$_3$PO$_4$-AC and ZnCl$_2$-AC. In the case of large pores, there is a high chance of pollutant trapping and absorption.

**Figure 3.** SEM image of BFS (a) and of prepared BF-ACs (KOH (b); H$_3$PO$_4$ (c); ZnCl$_2$ (d)) (magnification scale ×1000).

### 3.3 Surface Chemistry

The FT-IR spectrum of un-activated baobab fruit shells and activated carbons generated by BFS is shown in figure 4. There were more absorbent bands on the raw BFS spectrum than the BF-ACs spectrum. For the case of raw BFS, the broadband at 3285 cm$^{-1}$ was assigned to the presence of hydrogen bound (O–H) groups of cellulose, pectin, and lignin [28]. The peak appearing at around 2889 cm$^{-1}$ was ascribed to (C–H) symmetric stretching and (–CH$_2$) alkyl groups. The weak bands observed at around 2160 cm$^{-1}$ and 2031 cm$^{-1}$ were owing to the presence of (C≡N) stretching. The peak at 1613 cm$^{-1}$ is the aromatic ring or the olefinic (C=C) stretching vibration due to ketones, aldehyde, lactone, and carboxyl [12,25,28], which is disappeared after the activation process. A relatively low-intensity band at around 1367 cm$^{-1}$ was due to the presence of (C–O–C) stretching or C–C stretching that can be attributed to the existence of ester, ether and phenol. The major functional groups in BFS are hydroxyl groups, carbonyl groups and carboxyl groups. A comparable FT-IR spectrum exists in KOH-AC and H$_3$PO$_4$-AC which shows the identical type of surface functional groups. All of activated carbons spectra display broad weak peaks around 3900–3600 cm$^{-1}$. The bands at around 3333 cm$^{-1}$, 2886 cm$^{-1}$, 2161 cm$^{-1}$, 1575 cm$^{-1}$, 1255.5 cm$^{-1}$ were the characteristics of O–H (hydroxyls), C–H (alkyls), C=C (alkyne), C–O–C (ester, ether and phenol) and C–O (anhydrides), respectively. H$_3$PO$_4$-AC displays more intensive bands than KOH, which also reveals greater amounts of functional groups in H$_3$PO$_4$-AC. The brand acquired by H$_3$PO$_4$ at 1179 cm$^{-1}$ might be designated for the phosphorous-containing group P–O, O–C stretching vibrations in P–O–C linkage, and P=OOH [29]. For ZnCl$_2$-AC, very weak peaks around 2358 and 1087 cm$^{-1}$ ascribed to the presence of alkyls groups (C–H), and hydroxyls (O–H).
3.4 X-ray Diffraction (XRD)

Figure 5 presented the X-ray patterns of raw BFS and BF-ACs. It can be seen that a diffraction profile of the raw material and prepared BF-ACs exhibits a strong Bragg diffraction peak in $2\theta = 20–30^\circ$ regions. The appearance of these extraordinary humps was illustrative of the presence of carbonaceous materials. Furthermore, in all areas of the diffraction profile, there was no strongly defined peak indicating that the samples were not exposed to any mineral peaks. Other researches have produced similar findings and conclusions [28,30–32].

3.5 Pore Structure Analysis

One of the most common and efficient means of determining the surface area and pore structure of ACs is the physisorption with inert nitrogen gas (N$_2$). The nitrogen adsorption–desorption isotherms of the prepared BFS activated carbons with different activating agents are shown in Figure 6. The pore structural parameters deduced from the isotherms are presented in Table 2.

All adsorption isotherms are classified into Type IV isotherm (ZnCl$_2$-AC and H$_3$PO$_4$-AC) and Type I isotherm (KOH-AC), which is described for mesoporous (containing pores 2-50nm) and microporous adsorbents (containing pores < 2nm), as per the IUPAC classification approach [33]. These results were compatible with the pore size distribution curve and demonstrated the micro porosity (1.68 nm) of KOH-AC and mesoporosity (3.06-4.13nm) of H$_3$PO$_4$-AC and ZnCl$_2$-AC. The hysteresis loop constituted for each sample of BF-ACs by the adsorption and desorption branches was also detected. In accordance with the IUPAC classification approach of Hysteresis Loops, the hysteresis loop of ZnCl$_2$-AC exhibited the Type H1 (the narrow range of uniform mesopores where net-working effects are minimal). While the hysteresis loop of H$_3$PO$_4$ showed Type H4, which is associated with narrow slit-like pores. The complex pore structures exist and networking effects are important and the desorption branch is delayed owing to various phenomena such as pore blocking or cavitation, associated with pore evaporation in networked structures [33].

The surface area was calculated by the Brunauer, Emmett, and Teller (BET) equation [34] utilizing the N$_2$ adsorption data. According to the results shown in Table 2, ZnCl$_2$-AC, H$_3$PO$_4$-AC, and KOH-AC presented high surface areas of 559.54 m$^2$/g, 904.49 m$^2$/g, and 1029.44 m$^2$/g, respectively. The average size of the pores determines adsorbate molecules' ability to penetrate inside the AC, the adsorbed molecules penetrate the adsorbent only if pores have a diameter that is greater than the effective molecular diameter of the adsorbate [35]. From Table 2, it can be seen that the KOH-AC is a highly developed micropore area of 940.88 m$^2$/g, micropore volume of 0.37 cm$^3$/g, a smaller external surface area 88.56 m$^2$/g, and a smaller pore diameter of 1.676 nm in comparison with ZnCl$_2$-AC and H$_3$PO$_4$-AC samples. Table 3 presents a comparison of the $S_{BET}$ of BF-ACs with other stated values from various precursors in the literature. It can be observed that the $S_{BET}$ surface area of the KOH-AC prepared from
BFS was found 1029.44 m$^2$/g. These findings were agreed with the preceding study [30], which reported that after impregnated the BFS with H$_3$PO$_4$ with IR of 1:1.75, and activation temperature of 700 °C for 2.5 h, the BET surface is greater than 1089 m$^2$/g. Moreover, KOH-AC has surface areas consistent with other precursors such as tomato solid waste and corkboard, which makes it a suitable candidate for utilizing as a precursor in the preparation of AC. Furthermore, the raw material utilized in this study, which is the BFS, could be utilized at lower activation temperatures and shorter pyrolysis times in comparison with activated carbons produced from other raw materials.

Figure 6. Nitrogen adsorption–desorption isotherms of (a) ZnCl$_2$-AC, (b) H$_3$PO$_4$- AC, and (c) KOH-AC at 77K.

| Absorbent   | $S_{BET}$ (m$^2$/g) | $S_{Micro}$ (m$^2$/g) | $S_{External}$ (m$^2$/g) | $D_{pore}$ (nm) | $V_{t}$ (cm$^3$/g) | $V_{Micro}$ (cm$^3$/g) |
|-------------|---------------------|-----------------------|--------------------------|-----------------|-------------------|------------------------|
| ZnCl$_2$-AC | 559.54              | 261.83                | 297.70                   | 4.13            | 0.58              | 0.11                   |
| H$_3$PO$_4$-AC | 904.49          | 413.32                | 491.17                   | 3.06            | 0.69              | 0.18                   |
| KOH-AC      | 1029.44             | 940.88                | 88.56                    | 1.68            | 0.43              | 0.37                   |

$^a$ BET specific surface area, $^b$ t-Plot Micropore Area, $^c$ t-Plot External Surface Area, $^d$ Adsorption average pore diameter, $^e$ Single point adsorption total pore volume of pores, $^f$ t-Plot micropore volume

Table 2. BET Surface Area, Pore Diameter sizes, and Pore Volume of Various Activated Carbons

| Precursor             | Activating Agent | $S_{BET}$ (m$^2$/g) | Pore diameter (nm) | References |
|-----------------------|------------------|---------------------|--------------------|------------|
| Peanut shell          | KOH              | 393.8               | 2.26               | [36]       |
| Durian seed           | KOH              | 980.62              | 3.40               | [37]       |
| Periwinkle shell      | ZnCl$_2$         | 7.79                | -                  | [38]       |
| Grape industrial waste| ZnCl$_2$         | 1455                | 6.81               | [39]       |
4. Conclusion
In this study, the effect of chemical activating agents (ZnCl$_2$, KOH, and H$_3$PO$_4$) on baobab fruit shell (BFS) were evaluated. The characteristics of the baobab fruit shell based activated carbon (BF-ACs) have been from the above results it may be concluded that:

- The highest yield and iodine number of BF-AC were produced by H$_3$PO$_4$.
- SEM micrographs showed porous structures formed on the surface of BF-ACs were with different shapes and sizes.
- The XRD Data showed that the main structures of prepared BF-ACs were amorphous.
- FTIR spectra results indicate the presence of different surface groups on the produced BF-ACs.
- The KOH-AC has found 1029.44 m$^2$/g of highest BET surface area, which indicated that KOH to the most appropriate for the production of activated carbon from BFS.

| Tomato processing solid waste          | ZnCl$_2$ | 1093 | 5.92 | [40] |
|----------------------------------------|----------|------|------|------|
| Corkboard                              | KOH      | 1065 | -    |      |
| Grape stalk                            | ZnCl$_2$ | 1411 | 2.0491 | [42] |
| Palm Kernel Shell                      | KOH      | 217  | -    | [43] |
| Baobab fruit shell                     | H$_3$PO$_4$ | 1089 | 1.45 | [30] |
| Baobab fruit Shell                     | ZnCl$_2$ | 559.54 | 4.127 |      |
|                                        | H$_3$PO$_4$ | 904.49 | 3.061 |      |
|                                        | KOH      | 1029.44 | 1.68 | This study |

References
[1] Bansal R C and Goyal M 2005 Activated Carbon Adsorption (Boca Raton: CRC press)
[2] L B Khalil, Girgis B S and Tawfik T A M 2000 Adsorpt. Sci. Technol. pp 18373–18383
[3] Guo J and Lua A. C. 1998 Appl. Pyrolysis. 46 pp 113–125
[4] Salas-Enriquez B G, Torres-Huerta A M, Conde-Barajas E, Dominguez-Crespo M A, Díaz-Garcia L and de la Negrete-Rodriguez M L X 2016 J. Therm. Anal. Calorim. 124 pp 1383-1398
[5] Mamaní A, Sardella M F, Giménez M and Deiana C 2019 J. Environ. Chem. Eng. 7 P 102830
[6] Idris-Hermann K T, Raoul T T D, Giscard D and Gabche A S 2018 Chem. Sci. Int. J. 23 pp 1-15
[7] González-Garcia P 2018 Renew. Sustain. Energy Rev. 82 pp 1393–1414
[8] Mohammed J, Nasri N S, Ahmad Zaini M A, Hamza U D and Ani F N 2015 Int. Biodeterior. Biodegrad. 102 pp 245–255
[9] Kosha S and Parmar A 2018 Int. J. Latest Eng. Res. Appl. 3 pp 27–31
[10] Deng S, Hu B, Chen T, Wang B, Huang J, Wang Y and Yu G 2015 Adsorption. 21 pp 125-133
[11] Al-Othman Z A, Ali R and Naushad M 2012 Chem. Eng. J. 184 pp 238–247
[12] Vunain E, Kenneth D and Timothy B 2017 Appl. Water Sci. 7 pp 4301–4319
[13] Alabadi A, Razzaque S, Yang Y, Chen S and Tan B 2015 Chem. Eng. J. 281 pp 606–612
[14] García J R, Sedran U, Zaini M A A and Zakaria Z A 2018 Environ. Sci. Pollut. Res. 25 pp 5076-5085
[15] Nabais J M V, Laginhas C E C, Carrott P J M 2011 Fuel Process. Technol. 92 pp 234–240
[16] Alau K K, Gimba C E and Kagbu J A 2010 Arch. Appl. Sci. Res. 2 pp 451–455
[17] Kumar A and Jena H M 2016 J. Clean. Prod. 137 pp 1246–1259
[18] Daffalla S B, Mukhtar H and Shaharun M S 2012 Int. J. Glob. Environ. Issues. 12 pp 107–129
[19] Yan K Z, Zaini M A A, Arsad A and Nasri N S 2019 Chem. Eng. Trans. 72 pp 151–156
[20] Rahul J, Jain M K, Singh S P, Kamal R K, Naz A, Gupta A K and Kumar K 2015 Asian Pac. J.
Engineering, International Islamic University Malaysia. Special thanks to those who contributed to this project directly or indirectly.

Acknowledgments

The authors express their thankfulness to Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia. Special thanks to those who contributed to this project directly or indirectly.

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