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Comparative analysis of physiochemical properties of physically activated carbon from palm bio-waste

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ABSTRACT

Conversion of palm waste to activated carbon have attracted significant attention due to their lignocellulose chemistry and abundance. In the past, several palm waste has been converted to activated carbon for various applications. The highly porous material is efficient for application in gas, heavy metals, and pesticide adsorption, water purification, and as the active material of electrochemical double layer capacitor. Due to variation in the preparatory conditions, there is no adequate comparison in the electrochemical properties of palm waste derived activated carbons. In this study, palm kernel shell (PKS), oil palm fiber (OPF), and empty fruit bunch (EFB) were used to produce activated carbon by one step physical carbonization and activation at 700 °C and 1 h hold time. A comparative analysis of the physiochemical characteristics of the activated carbon is presented. XRD results reflect the amorphous nature of all the samples and BET surface area of 823 m²/g, 700 m²/g, and 592 m²/g were recorded for EFB, PKS, and OPF, respectively.

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1. Introduction

The demand for novel, efficient, and economic materials for gas sensing and adsorption, energy storage devices, and water treatment have received serial attention from researchers. Metallic oxides and carbon-based materials including graphene [1,2], carbon nanotubes (CNTs) [3], carbon aerogels and their composites are the conventional materials explored for these purpose [4,5]. The efficiency of these materials is well established in literature traceable to their large surface area and porosity. However, the extensive commercialization of these materials has been greatly challenged by (i) material agglomeration; (ii) commercial quantity upscale; (iii) eco-friendliness; and (iv) expensive production cost. Hence, the search for a cheap, stable, and commercially feasible material is unavoidable for researchers [6–9].

Activated carbon derived from agricultural wastes has become a sustainable alternative for gas adsorption, water treatment, and active material for electrodes of double layer capacitor. The excellent physiochemical properties of the amorphous material such as high surface area, tunable pore size, stable thermal and mechanical strength made it a suitable alternative to the expensive graphene-based materials.

Numerous promising biowastes have been converted to activated carbon for specific applications. Some of the agricultural waste recently converted to activated carbon include but not limited to pistachio plant [10], paper mill sludge [11],
soapstock [12], orange peel [13], olive oil [14], hazelnut [15], coconut husk [16], winemaking waste [17], cassava stem [18], palm kernel shell [19]. However, the chemistry of the starting material, optimization and activation techniques have great influence on the efficiency of the activated char.

Recently, palm waste conversion to activated carbon has attracted significant attention from researchers. Palm tree is scientifically called Areaceae belong to kingdom Plantae, division Magnoliophyta, class Lilia, and order Aracales. There are more than 2600 species of palm trees grown in temperate, tropical and subtropical climates. With respect to the world’s growing demand for palm oil, concerted effort are continuously being made by palm oil producing countries to respond to this demand. South-East Asian countries and some part of West-Africa are responsible for most of the world palm oil production. In a recent study by United States Department of Agriculture (USDA) in 2018 [20], Indonesia leads the world palm oil production with 55% of the world’s total palm supply amounting to seventy-three thousand four hundred million tonnes, Malaysia produced 28%, Thailand, Colombia and Nigeria produced 4%, 2% and 1%, respectively. While the other countries have an accumulated production of 10% of the total supply. The active palm milling process has continuously generated huge amount of waste such as palm kernel shell (PKS), palm empty fruit bunch (EFB), palm tree frond, palm mesocarp fiber, and palm trunk.

The use of palm waste has attracted attention due to its lignocellulosic composition and the will to mitigate the abundant waste into valuable and economic material for potential applications. Table 1 present the potential application of activated carbon with their specific desirable properties for optimum performance. Large surface area and high pore volume are important characteristics for water treatment, as active material in supercapacitor electrodes, and in gas adsorption.

| Table 1 – Desirable factors of activated carbon for specific applications. |
|----------------------------------|------------------|
| **Application**                  | **Properties**   |
| Water treatment                  | • Large surface area, Fast adsorption rate, Wide and stable pores |
| Gas/pollutant adsorption         | • Specific gas compatibility, large surface area, high reactivity with target gas/pollutant. |
| Energy storage                   | • Large surface area, wide and stable micropores and mesopores, high electrolyte wettability, high thermal stability, high reactivity. |

PKS was also activated with ZnCl at 550 °C using different impregnation ratio (1:1 and 2:1). The equal mass impregnated ratio sample produced the highest surface area of 1058 m²/g and show an adsorption uptake of 225 mg of methylene blue per gram [23]. In another study by Yek et al. [24], activated carbon was prepared using microwave steam activation at 500 °C for 15 min, and a BET surface area of 570 m²/g was recorded.

In literature, different researches have explored varying preparatory conditions and optimization techniques in the synthesis of activated carbon. However, the variation in the activation conditions did not allow adequate comparison of the efficiency of waste. In this study, EFB, PKS, and OPF were physically activated using furnace using the same pretreatment and activation condition to allow adequate comparison.

2. **Experiment**

2.1. **Precursor pretreatment**

Empty fruit bunch (EFB), oil palm fiber (OPF), and palm kernel shell (PKS) were soaked from Kilang Sawit FELCRA Berhad Bota, Perak, Malaysia. The collected samples were soaked separately in 1 L/100 g of distill water for 24 h. The samples were then washed with 0.5 L/100 g acetone and dried at 110 °C for 24 h in an oven. Fig. 1 shows the image of all the starting materials after the pretreatment processes.

After drying, sample sizing was first done using a mechanical granulator to reduce the size to 3–5 mm. Then, Fritsch ball milling machine was used to grind the PKS to 75 μm powder, while the electric wheel grinder was used to grind EFB and OPF to 75 μm powder.

2.2. **Carbonization and activation**

30 g of EFB, PKS, and OPF pretreated samples were carbonized and activated by a one-step process at 700 °C with a heat rate of 10 °C/min under argon flow using a tube furnace. When the set temperature of 700 °C was reached the argon flow was substituted for N₂ at 5 L/min flow rate for activation for 1 h hold time. Fig. 2 presents the schematic diagram of the experimental setup of one step physical activation. The samples were then allowed to cool down and stored in a closed container to avoid pore blockage from the adsorption of atmospheric gasses.

2.3. **Characterization techniques**

The physiochemical characteristics of EFB, PKS, and OPF derived activated carbon were studied using Carbon, Hydrogen, Nitrogen, and Sulphur (CHNS) analyzer, Brunauer Emmett and Teller (BET) surface and pore analyzer, Fourier Transform Infrared (FTIR) Spectroscopy, Field Effect Scanning Electron Microscopy (FESEM), X-ray Diffractometer (XRD), and X-ray Photoelectron Spectroscopy (XPS).

Micrometrics ASAP 2020 was used for the BET analysis at 77K. Before the analysis, the samples were degassed at 400 °C for 8 h to remove the unwanted gasses deposited on the surface of the samples. The BET technique uses the adsorption and desorption of N₂ gas on the surface of the samples to
estimate their surface area. The volume of N\textsubscript{2} gas adsorbed in relation to the relative pressure (P/P\textsubscript{o}) was also used to determine the pore characteristics while the hysteresis curve of the generated isotherm graph gives information about the nature of the pores in the samples according to IUPAC.

FTIR spectroscopy was used to study the surface chemistry of the samples using approximately 1 g of the samples for the analysis. The percentage transmittance over the spectra wave number range 500 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1} is used to identify the functional groups present on the samples.

The surface morphology is also studied using FESEM. The XRD gives information about the crystallinity or amorphous nature of the samples while the XPS provides information about the elemental composition of the samples.

3. Results and discussion

3.1. CHNS analysis

The elemental composition of pretreated EFB, PKS, and OPF was analyzed before carbonization and activation. Fig. 3 presents the graphical representation of the quantitative elemental analysis of the pretreated samples. Carbon is the most prominent element in all the samples with 48.55%, 47.78%, and 47.05% in PKS, EFB, and OPF, respectively. EFB has 7.03% hydrogen, and 1.36% of nitrogen. OPF contains 6.58% hydrogen, 1.73% nitrogen while PKS contains 6.26% hydrogen and 1.05% nitrogen. For all the samples, the sulphur content is less significant as they contain less than 1%.

3.2. BET surface area and pore size distribution

The adsorbate employed in the physisorption process is nitrogen (N\textsubscript{2}) gas. The adsorption and desorption isotherms were used to estimate the surface area and pore distribution of each of the samples. Fig. 4 shows the isotherm plot of EFB\textsubscript{AC}, PKS\textsubscript{AC}, and OPF\textsubscript{AC}. Open-ended type II hysteresis curves are observed on all the samples at low relative pressure. This openness and low adsorption at low relative pressure which increases with increasing relative pressure is said to occur when there is incomplete combustion during precursor carbonization resulting into pore shrinkage \[22,25\].

Table 2 presents the adsorption and desorption parameters of the prepared activated carbon. EFB\textsubscript{AC} show the highest surface area of 823 m\textsuperscript{2}/g followed by PKS\textsubscript{AC} with 700 m\textsuperscript{2}/g and OPF\textsubscript{AC} with 592 m\textsuperscript{2}/g. The high surface area of in EFB\textsubscript{AC} is traceable to the well-developed network of honeycomb pores on the sample. The data shows that both micropores and mesopores are present in the prepared activated carbon. The
average pore distribution in all the samples is in the mesopore range (>2 nm) as recommended by International Union of Pure and Applied Chemistry (IUPAC) [26].

3.3. XRD analysis

The XRD pattern of EFB_AC, OPF_AC, and PKS_AC is presented in Fig. 5. The broad pattern clearly depicts the amorphous nature of activated carbon. At 2θ = 23° and 43° peaks corresponding to (002) and (101) are noticed on all the samples, respectively.

3.4. FESEM

The micrograph images of EFB activated carbon (EFB_AC), OPF activated carbon (OPF_AC), and PKS activated carbon (PKS_AC) at different magnifications are shown in Fig. 6. EFB_AC sample produced pore networks of honeycomb pattern similar to that found on optimized carbon nanotubes (CNTs) [27]. The pores on the OPF_AC are also similar to the EFB_AC honeycomb pattern. However, the pore network in EFB_AC is more prominent and develop as compared to both OPF_AC and PKS_AC. The PKS_AC samples show scantly tunneling pores and contain visible micro lumps blocking the pores. The well-developed porous network is an indication of high surface area on which Adsorbate or ions can be deposited.

3.5. FTIR analysis

Fig. 7 shows the infrared spectra of OPF_AC, EFB_AC, and PKS_AC. The transmittance pattern of infrared light in the three samples are used to determine the functional group present in the diagnostic domain. The spectra have similar peaks for all the samples. A broad and strong peak is noticed on the three spectra at 3441 cm\(^{-1}\) corresponds to the polar
3.6. XPS analysis

XPS is an efficient tool in the determination of the surface element and functional groups present on the samples. The three samples were characterized and the C1, O1 and N1 spectra of the PKS, OPF, and EFB are presented in Fig. 8. The C1 spectra of the three samples have similar sharp and narrow peaks with binding energies 284.7 eV corresponding to graphitic carbon (C), 286.2 eV showing the presence of phenolic or alcoholic group (C–O) [29]. It also shows 288.2 eV corresponding to the carboxylic/ester functional group and low peak in the range of 290.1–290.6 eV indicating carbonates or π electron in an aromatic ring. Only EFB shows a narrow and slightly broad peak at 293.3 eV corresponding to π–π transition [30].

The O1 spectra show a narrow and sharp peak at 531.9 eV corresponding to oxygen double bond to carbon (C=O) for all the samples. They also show 533.2 eV which indicate the presence of oxygen single bond to aromatic carbon (C=O–) [30,31].

Finally, the N1 spectra show about four nitrogen groups on the surface of the three samples. A sharp and narrow peak in the range 400.2–400.9 eV corresponding to pyrrolic nitrogen, pyridine, or a mixture of both (C–N–C). The EFB sample also indicates a visible peak at 403.7 which shows the presence...
Fig. 8 – XPS spectra of [(a) PKS AC (b) OPF AC (c) EFB AC] C1 scan [(d) PKS AC (e) OPF AC (f) EFB AC] O1 scan [(g) PKS AC (h) OPF AC (i) EFB AC] N1 scan.
of oxidized nitrogen functionalities (C–N+H–C) or nitrogen dioxide (NO₃) [32]

XPS survey also gives the elemental composition of the three samples as shown in Table 3. Primary carbon predominantly dominates all the samples with more than 80 At% in all the samples. They contain graphitic carbon, Sp2 and Sp3 hybridized carbons. Oxygen is highest in EFB AC with 14.44 At% while there is no significant difference in the nitrogen content of PKS AC and OFF AC.

| Table 3 – XPS elemental analysis of PKS AC, OFF AC, and EFB AC. |
|-----------------|-----------------|-----------------|
| Samples        | At% carbon      | At% nitrogen    | At% oxygen     |
| PKS AC         | 81.29           | 0.81            | 12.41          |
| OFF AC         | 80.46           | 1.47            | 12.01          |
| EFB AC         | 80.43           | NA              | 14.44          |

NA, not available.

4. Conclusion

Activated carbon was produced by one-step physical activation technique from abundant palm kernel shell (PKS), oil palm fiber (OFF), and empty fruit bunch (EFB) at 700 °C for 1 h. The result shows that all the starting materials have a high percentage of fixed carbon which aid conversion into activated carbon. The physicochemical properties of the amorphous activated carbon derived from these starting materials including the elemental composition, wide honeycomb network of pores, high surface areas, and surface functional group. These properties make the materials suitable for gas, heavy metal, and pesticide adsorption, wastewater treatment, and active material of electrochemical double layer capacitors (EDLC). Accordingly, economic advantages can be derived from the abandoned and environmentally challenging waste by utilizing them as starting materials for activated carbon production for different applications.

Conflicts of interest

The authors declare no conflicts of interest.

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References


electrode application. Waste Biomass Valorization 2018;0(0):1–10.


