

PALM SHELL-DERIVED ACTIVATED CARBON ADSORBENT IS BETTER THAN THAT OF COCONUT SHELL: COMPARATIVE STUDIES OF COD ADSORPTION FROM PALM OIL MILL EFFLUENT

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ABSTRACT

Palm and coconut shells are among the most common feed materials for activated carbon manufacturing. Activated carbon is an excellent adsorbent for palm oil mill effluent (POME), especially for the removal of chemical oxygen demand (COD). Palm shell-based activated carbon (PAC) and coconut shell-based activated carbon (CAC) have been prepared through carbonization and followed by an activation process using H₂SO₄ 2.5 M. Both PAC and CAC have lower contents of moisture, fly ash, and ash than that of Indonesian national standard thresholds. The COD removal from POME was performed with the batch adsorption method, where it reached adsorption saturation after 45 minutes of stirring time and optimum removal at pH 3. Isotherm studies suggest that the COD removal using PAC and CAC fit the theoretical data from the Langmuir isotherm model ($R^2 > 0.99$) with Q_m of 854.701 and 826.446 mg/g, respectively. The investigation also indicates that PAC has a better performance in COD removal, which has been justified by the elucidation using Fourier Transform-Infrared (FT-IR) and Scanning Electron Microscopy – Electron Dispersive Spectroscopy (SEM-EDS) technique.

Keywords: COD, POME, FT-IR, SEM-EDS, Langmuir, Activated Carbon, Adsorption

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INTRODUCTION

The biggest world's palm oil producer country, Indonesia, occupies 54% (33.5 million tons) of the total production in 2016.¹ The wastewater produced from the palm oil milling activities is a major environmental consequence of the palm oil industry. The palm oil milling effluent (POME) is generated as much as 2.5–3.0 m³ for each ton production of crude palm oil. It comprises 0.6–0.7% oil, 4–5% total solids, 2–4% suspended solids, and 95–96% water.² Some of the identified organic compounds in the effluent include trioxymethylene; docosane; tricosane; 3-nitroalkene, 3-methyl-; heptacosane, 1-chloro-; and so on.³ The number of organic pollutants in the wastewater can be expressed in chemical oxygen demand (COD). The COD of POME can reach 15,000 to 100,000 mg/L⁴ and needs a reduction to be below the Indonesian national maximum threshold (25 mg/L). Adsorptive COD removal using carbonaceous materials can be an effective and low-cost solution.

Activated carbon can be obtained from the carbonization of various precursors that yielded different active site intensities and porous architectures.⁵ For POME treatment, there have been some reported studies that prepared activated carbon from different feed materials and activation methods. The feed materials or precursors, for the most part, are agricultural solid waste including date palm shell⁶, coconut shell^{7,8}, walnut shell⁹, jujube shell¹⁰, crypress cones¹¹, palm shell or oil palm empty fruit bunch (OPEFB)¹², sugarcane bagasse¹³, rice husk¹⁴, foxtail palm fruit¹⁵, cabbage³, and oil palm frond.¹⁶ In this research, we used palm shell (or OPEFB) and coconut shell because they are still categorized as economically invaluable solid waste whilst numerously abundant; thus, can offer a low-cost property. More importantly, palm shell and coconut shell are rich in cellulose, hemicellulose, and lignin^{17,18}, making them good candidates for activated

carbon precursors. Based on the studies, acid activating agents such as HNO_3^{15} and $\text{H}_3\text{PO}_4^{9,11}$ can facilitate well-developed pores in the activated carbon. Herein, we tried to employ H_2SO_4 as the activating agent which we expect can also provide a desirable porous architecture. The performance of the produced activated carbon from each precursor will be studied comparatively based on the COD uptake using POME collected from the palm oil industry itself.

EXPERIMENTAL

Materials

Palm shell and palm oil mill effluent (POME) were collected from PT. Nafasindon Aceh Singkil, Aceh Province, Indonesia. The POME had pH of 6.5 and COD concentration of 23,520 mg/L. Coconut shells were collected from the local traditional market in Banda Aceh, Aceh Province, Indonesia. Analytical grade H_2SO_4 , KMnO_4 , KI, $\text{Na}_2\text{S}_2\text{O}_3$, and KNO_3 were purchased from Sigma-Aldrich (Selangor, Malaysia).

Preparation of Activated Carbon

Palm shells and coconut shells were washed, dried, and ground before being carbonized with a furnace at 300°C for 2 h. The products were crushed and sieved (mesh 100) to obtain palm shell-based activated carbon (PAC) and coconut shell-based activated carbon (CAC). The activated carbon was activated using H_2SO_4 2.5 M and neutralized by washing with distilled water, then oven-dried (105°C ; 3 hours).

Determination of Moisture, Fly Ash, and Ash Contents

To determine the moisture content, fly ash, and ash contents, the prepared PAC and CAC were treated using an oven (105°C ; 3 h for the moisture) and furnace (900°C ; 20 min and 600°C ; 7 h for the fly ash and ash, respectively).

Batch Adsorption

The adsorption studies were conducted in batch method, where the activated carbon was poured onto an Erlenmeyer with 20 mL POME and stirred for a certain contact time at 250 rpm. To study the influence of contact time, the settings were 30 – 50 min stirring time, pH of 6.5, and 0.5 g activated carbon. For the effect of pH, they were 45 min stirring time, initial pH of 3 – 8, and 0.5 g activated carbon. As for the isotherm studies, the activated carbon weight was varied (0.1-0.5) and used for the adsorption with optimum pH and contact time. Thereafter, the activated carbon was removed and the filtrate was determined for COD concentration. The adsorption capacity at t contact time (q_t), adsorption capacity at equilibrium (q_e), and removal (%) were calculated based on our previous works.^{19,20}

For the determination of COD level, the 10 mL filtrate was inserted into a test tube and subsequently added with 0.5 mL H_2SO_4 4M and 2 mL KMnO_4 0.002 M. The test tube was heated on the boiling water bath for 20 minutes, and then left cold. Next, as much as 1 mL KI 0.1 M and 0.25 mL starch solution were added into the test tube. The mixture was titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.01 M, where the endpoint was observed by the change of blue color into colorless. Concentration was obtained based on the following Eqn.-1⁶:

$$\text{COD} = \frac{(A-B) \times M \times 8000 \times \text{dissolution factor}}{V_{\text{filtrate}}} \quad (1)$$

Where:

A = Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for blank

B = Volume of $\text{Na}_2\text{S}_2\text{O}_3$ used for sample

M = Molarity of $\text{Na}_2\text{S}_2\text{O}_3$

8000 is milliequivalent weight of oxygen $\times 1000$ mL/L

Functional Group and Surface Morphology Studies

Identification of the functional groups in both PAC and CAC employed Shimadzu 8400 Fourier Transform Infrared (FTIR) (Kyoto, Japan) using a transmittance mode. Prior to the analysis, samples were oven-dried (60°C) and ground with KNO_3 . The surface morphology was observed using JEOL JSM 6510 LA Scanning Electron Microscopy – Electron Dispersive Spectroscopy (SEM-EDS) (Tokyo, Japan) at 20,000 kV with 20 kx magnification.

RESULTS AND DISCUSSION

Moisture, Fly Ash, and Ash Contents

The moisture, fly ash, and ash content of PAC and CAC had been determined and presented in Table-1. CAC was found to have lower moisture content than PAC, while the other values (fly ash and ash contents) are higher in PAC. Significantly, ash content was 79.76% lower in PAC in comparison with CAC. Higher fly ash and ash may contribute to the hindrance of the adsorption process due to the blockage of the pore structure. However, both PAC and CAC had moisture, fly ash, and ash contents lower than the Indonesian National Standard (SNI), suggesting our prepared activated carbons could satisfy the commercial use.

Table-1: Water, Fly Ash, and Ash Contents of the prepared Activated Carbon

Sample	Moisture Content (%)	Fly Ash (%)	Ash (%)
PAC	7.4	44.26	0.85
CAC	6.8	49.05	4.20
SNI	10	25	10

Effect of Contact Time on COD Adsorption

To gain the optimum parameter for batch adsorption studies, contact time is the most important parameter as it explains the diffusion of the adsorbate onto the adsorbent. In this research, we observed the adsorption capacity at t contact time (qt) within the range of 30 to 50 minutes (Fig.-1). It revealed that during the observation time, the increase of adsorption capacity of PAC and CAC was no longer significant indicating the phase is dominated by chemical interaction. At the 30th minute, the adsorption capacity reached 639.32 mg/g with 76.09% removal and 501.53 mg/g with 59.69% for PAC and CAC, respectively. The adsorption equilibrium was observed after 45 minutes where the adsorption capacities for PAC and CAC were 670.16 (79.76% removal) and 563.23 mg/g (67.03% removal), respectively. Similar optimum contact time has been obtained by several studies, where the equilibrium was achieved after 30^{9,10}, 50¹⁶, and 60^{3,12} minutes. The differences might be attributed to the difference in feed materials, yielding activated carbon with different structures and functional groups. Hydrophilic functional groups, especially OH and COOH, can increase the water absorbing ability of the material and, as a consequence, faster diffusion.^{21,22} Pore structure also contributes to the diffusion rate of the adsorbate.²³

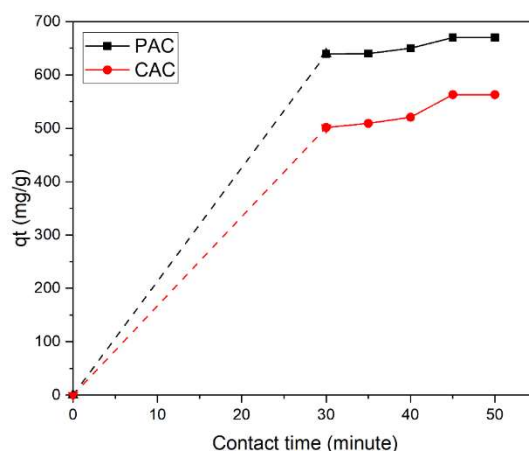


Fig.-1: Effect of Contact Time on the COD Adsorption onto PAC and CAC.

Influence of pH on COD Adsorption

The performance of batch adsorption can be dependent on the adsorbent-adsorbate interaction driven by electrostatic force. The adsorbent surface may be charged negatively or positively, depending on the initial pH of the solution. We have studied the influence of pH on the removal of COD using PAC and CAC (Fig.-2). As can be seen, the adsorption capacity reached its highest value at pH 3 for either PAC (814.86 mg/g) or CAC (751.13 mg/g). At low pH, the functional groups might be protonated causing the surface to be positively charged.²⁴ It is then beneficial to augment the electrostatic interaction for the adsorbates with

strong electronegative affinity. Some studies reported the optimum COD adsorption using activated carbon at a close pH range to ours.^{9,10,14}

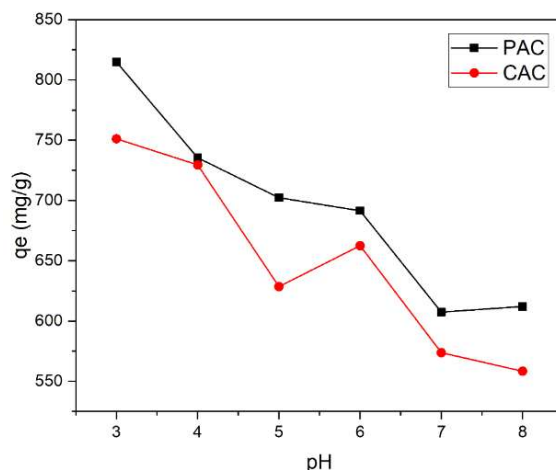


Fig.-2. Influence of pH on the COD Adsorption onto PAC and CAC

Isotherm of COD Adsorption

In this research, we employed the two mostly employed isotherm models; Langmuir and Freundlich (Fig.-3). We used the linearized equations as presented in our previous works^{19,20}, and obtained the parameters as presented in Table-2. Both modelings yielded high R^2 and low Root-Mean-Square-Errors (RMSE) indicating that the adsorption fit both adsorption isotherm models. However, the R^2 is higher in Langmuir compared to that in Freundlich. Thus, the COD adsorption either onto the PAC or CAC is Langmuir-dependent.

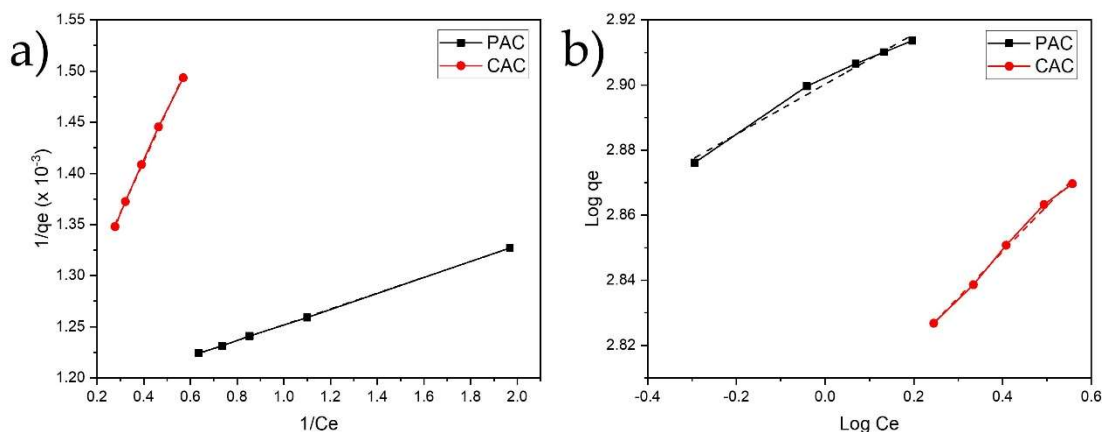


Fig.-3: (a) Langmuir and (b) Freundlich Isotherm Modelings of COD Adsorption onto PAC and CAC. Solid Lines are the Experimental Data and Dashed Lines are the Theoretical Data.

Table-2: Langmuir and Freundlich Parameters

Isotherm Model	Parameters	PAC	CAC
Langmuir	R^2	0.99984	0.99807
	RMSE	5.31×10^{-7}	2.54×10^{-6}
	K_L (L/mg)	15.1	2.43
	q_m (mg/g)	854.701	826.446
Freundlich	R^2	0.98061	0.99466
	RMSE	2.08×10^{-3}	1.28×10^{-3}
	K_F (mg/g)	794.786	619.998
	n	12.99	7.09

Based on the obtained values of maximum adsorption (q_m), PAC (854.701 mg/g) has a better performance in COD uptake than that of CAC (826.446 mg/g). These values are higher in comparison with the reported studies who only achieved $q_m = 41.30^6$, 46.18^7 , 272.75^9 , and 15.87^{12} mg/g. Another study that prepared the activated carbon from oil palm frond with $ZnCl_2$ activating agent had 146.93 mg/g adsorption capacity at optimum parameter, meanwhile, we had achieved 814.86 mg/g with 89.39% removal (45 minutes; pH 3). To understand what factors contribute to this high uptake of COD, we had conducted structural, elemental quantitative, and morphological analyses.

FT-IR and SEM-EDS

Functional groups contained in PAC and CAC have been identified using FT-IR analysis (Fig.-4a). A broad spectral band at $2800-3750\text{ cm}^{-1}$ is associated with the overlapping of C-H aromatic, O-H, and C-H aliphatic stretching vibrations. Meanwhile, transmittance peaks at 1708 and 1589 cm^{-1} are assigned to C=O (carboxylic acid and lactone) and C=C functional groups.²⁵ An overlapping band of C-O and O-H stretching vibration is observed at $1250-1550\text{ cm}^{-1}$. Another transmittance band is found at $730-850\text{ cm}^{-1}$ and assigned to C-H aromatic and aliphatic. These functional groups are commonly observed in activated carbon.^{9,11,15,16} The carboxylic and carbonyl functional groups can donate their electron during the adsorption via electrostatic interaction.¹² Moreover, it has been widely reported that O-containing functional groups contribute to the attachment of organic pollutants.^{21,26,27} Besides, the presence of C=C double bond can induce COD adsorption via π - π interaction.^{21,28} These contributing functional groups are higher in PAC, indicated by a higher transmittance percentage.

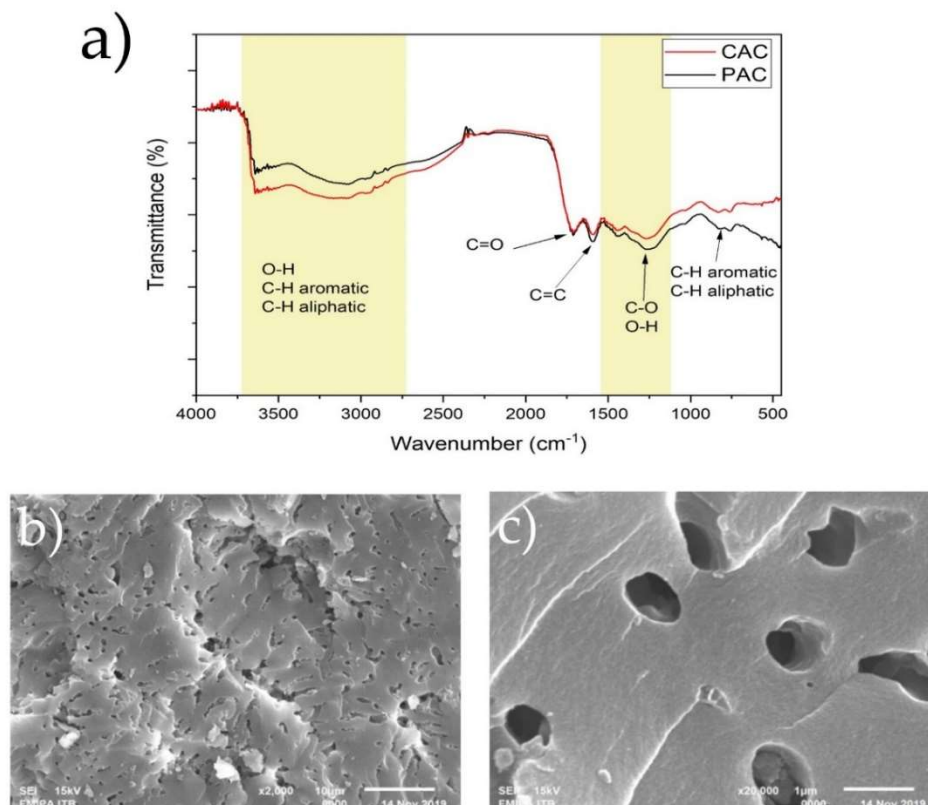


Fig.-4: (a) FT-IR Spectra of PAC and CAC; SEM Images of (b) PAC and (c) CAC

The elemental compositions, obtained from EDS analysis (Table-3), show that PAC has a higher O/C ratio (0.25) than CAC (0.22). It further corroborates the claim that PAC has a higher O-containing functional group which generates more COD uptake. Other significant differences in elemental composition between PAC and CAC are the contents of Al and K, where they are higher in CAC. Uniquely, Si and Na are only found in CAC which can be attributed to the coconut habitat – coastal area. The presence of these metals can facilitate adsorption via an ion exchange mechanism, which in the case of COD is less likely.⁶

Table-3: Elemental Composition of PAC and CAC Obtained from EDS Analysis

Element	PAC (%)	CAC (%)
C	80.06	81.47
O	19.66	18.10
Na	ND	0.01
Mg	0.06	0.03
Al	0.04	0.13
Si	ND	0.11
K	0.06	0.15
Ca	0.08	ND
Cr	0.03	ND

*ND = not detected

From the SEM images of PAC (Fig.-4b) and CAC (Fig.-c), we can observe the formation of pore structure. Both PAC and CAC have heterogeneous sizes and shapes of pores. CAC has a smooth surface with a big porous diameter, meanwhile, PAC has a relatively rougher surface with a small porous diameter. It can be observed that the pore structure in PAC is rather rudimentary with a flake-like structure. Higher adsorption performance in PAC is ascribed to the rougher surface and smaller porous diameter that can facilitate more adsorbate diffusion.^{23,29,30}

CONCLUSION

Activated carbon adsorbents derived from palm-shell and coconut-shell have been successfully prepared by means of carbonization and acidic chemical activation. The moisture, fly ash, and ash contents of PAC and CAC have satisfied the SNI, suggesting their commercial functionality. From the adsorption parameters studies, COD adsorptive removal using PAC and CAC was facilitated by rapid diffusion and electrostatic attraction. O-containing functional groups, as well as C=C double bond, are responsible for the rich active site on the adsorbent surface. Rough surface morphology and small porous diameter are among the important factors that contribute to the high COD uptake. The COD adsorption, either onto PAC or CAC, is categorized as Langmuir-dependent due to high R^2 and low RMSE values. Overall, based on the maximum adsorption constant from the Langmuir isotherm model, PAC performed better COD removal from POME.

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