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ORIGINAL ARTICLE

Aluminum Modified Biochar for Chemical Oxygen Demand Removal in Palm Oil Mill Effluent

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ABSTRACT - This study has carbonized the palm kernel shell (PKS) and modified with aluminium (Al) to produce aluminium–biochar (Al-biochar). The PKS biochar was steam activated for further Al impregnation process to improve the adsorption efficiency for palm oil mill efluent (POME) treatment. Al-biochar was characterised by SEM-EDX and tested for COD removal of POME in fixed bed columns treatment. The column adsorption study was carried out to investigate the efficiency of Al-biochar to reduce the POME's COD in a continuous flow. The column adsorption study demonstrated that the flow rate of the POME sample is significant on the exhaustion time of the designed column system, showing the maximum exhaustion time of 140 minutes and 105 minutes at the flow rate of 10 ml/min and 15 ml/min respectively. Al-biochar also exhibited the total adsorption of 29 mg/g. The outcome of the research provides an alternative way to improve POME treatment with Al modified AC.

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INTRODUCTION

Malaysia has accounting 28% of global production become the second largest palm oil producer, and is expected to increase the production to 6.5 million tonnes by the year 2023 with 3.31 million hectares of palm oil cultivation [1]. The income generated from palm oil industry has a significant impact on the country's GDP and economy, but at the same time, it has posed severe threats to the surrounding environments. Dealing with a large amount of wastes generated by palm oil mills such as solid biomass (i.e. palm kernel shell, palm fibre, empty fruit bunches) and wastewater, known as palm oil mill effluent (POME), has become the main challenge and priority of the current palm oil industry .

Fresh POME is the hot and acidic wastewater discharged during the palm oil processing. About 5 to 7.5 tonnes of water is needed to extract 1 tonne of crude palm oil (CPO) and more than 50% of this water eventually ends up as the POME [2]. There are three main operations that contribute to the POME - sterilization of fresh fruit bunch (FFB), clarification of the extracted CPO and hydrocyclone separation of the cracked mixture of kernel and shell. The POME itself is non-toxic wastewater, but due to the extremely high level of biochemical oxygen demand (BOD) (25,000mg/L - 65,714mg/ L) and chemical oxygen demand (COD) (44,300 - 102,696 mg/ L), the direct discharge of POME results in oxygen depletion of the water [3]. The high BOD and COD of POME are mainly contributed by the high concentration of biodegradable matters in the POME, which serve as food sources for microorganisms. This promotes the bacterial growth and results in large consumption of dissolved oxygen in the water that may leads to the death of aquatic life.

In Malaysia, about 85% of palm oil mills have employed the ponding system to treat the POME via aerobic digestion [4]. However, ponding system occupies huge land area (10-12 acres) and long retention time (7-14 days) is needed for the decomposition of organic matter in POME. Moreover, biogas released to

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the surrounding from the digestion process has triggered the greenhouse effect [5]. The ponding system with aerobic digestion, in fact, can hardly reduce the BOD and COD levels to meet the Department of Environment's requirement. Alternative treatments by reacting hydrogen peroxide and ozone with POME were conducted but it incurred higher cost and may form toxic by-products. Therefore, the adsorption technique was proposed in this study to reduce the COD of POME.

The adsorption method is commonly used in the wastewater treatment. The adsorption mechanism is initiated via the attachment of the multi-components fluid mixture to the surface of the adsorbent, either through physical or chemical bonding. This study utilised the palm kernel shell (PKS) as the feedstock for aluminum modified Biochar (Al-biochar) production to treat POME in fixed bed column. The Al-biochar was characterised and COD removal efficiency was evaluated with different flow rates. The performance of the designed column system was determined from the breakthrough and exhaustion time.

MATERIALS AND METHODOLOGY

POME Sample and COD Analysis

The POME sample (last pond before discharge) was collected from the palm oil mill in Sibu, Sarawak. The POME was stored in the chiller at the temperature of 4˚C. The COD reagent was prepared by mixing 2.5 ml of silver sulfate-sulfuric acid and 1 ml of potassium dichromate solution. The silver sulfate-sulfuric acid solution was prepared by mixing 5.5 g of silver sulfate powder with 1 L of concentrated sulfuric acid. On the other hand, the potassium dichromate solution was prepared by mixing 12.25 g of potassium dichromate powder in 1 L of distilled water. The COD reagent was kept for 24 hours before the test was started. 2 mL of POME sample was added into the COD reagent. The mixture was shaken manually prior to heating at 150^0C for 2 hours in the Digital Reactor Block 200 (DBR 200). The mixture was then cooled down to room temperature. The COD analysis was set to zero with distilled water and reagent first before further analysis with POME samples

Al-biochar Preparation and Characterization

PKS was collected from the local palm oil mill in Sibu, Sarawak. The PKS was washed thoroughly to remove the impurities before oven-dried at 105˚C for 24 hours to remove the moisture. The PKS was placed inside the clay pot and carbonized at 600 ˚C in a furnace. The PKS biochar was further activated with steam before impregnating with aluminum (Al) at ratio 1:1. Aluminum nitrate solution was prepared by dissolving 77.2 g of aluminum nitrate powder in 150 ml distilled water. Biochar was then added into the solution and the mixture was agitated by using thermo shaker for 24 hours. Next, the Al-biochar was recovered from the solution by vacuum filtering and heated to 500˚C for 2 hours in the furnace. The Al-biochar was washed with distilled water to get rid of the residual metal ions and to neutralize the pH of Al-biochar.

The Al-biochar was then oven-dried at 105˚C for 24 hours, sieved to different sizes and stored in an airtight container. The Al-biochar with the size between 0.9 mm to 2 mm was selected for the column adsorption experiment. The surface morphology and elemental analysis of the Al-biochar were investigated by the scanning electron microscope coupled with energy dispersive X-ray (SEM-EDX). The sample was coated with thin layer of platinum to eliminate the charging effect for a clearer image. The presence of Al metal ions on the Al-biochar was quantified by SEM-EDX.

Experimental Setup for Fixed Bed Column Treatment

Figure 1 shows the fixed-bed column experiment with an acrylic tube (3 cm of internal diameter x 20 cm of height) packed with Al-biochar. A total 20 g of Al-biochar was supported by the glass wool at the upper and lower part to prevent any loss of adsorbent during the experiment. The distilled water flowed through the entire column system to remove the impurities and air gap within the column system. The control valve and water pump were installed to inject the POME from the bottom of the column with uniform flow rates of 10 ml/min and 15 ml/min. The POME samples were taken every 15 minutes for the COD test. The column adsorption was stopped when the adsorbent capacity was exhausted. The effect of the flow rate was investigated to determine the efficiency of column treatment process.

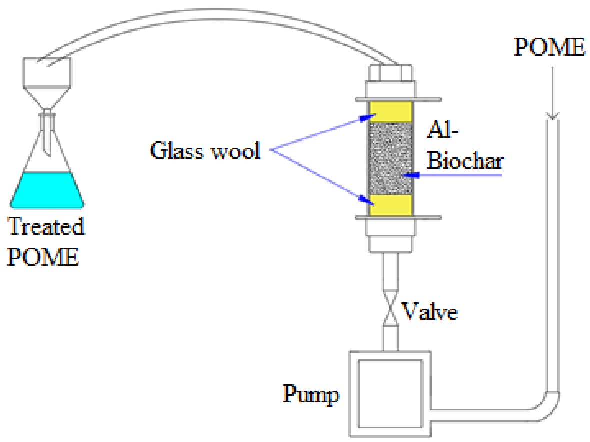
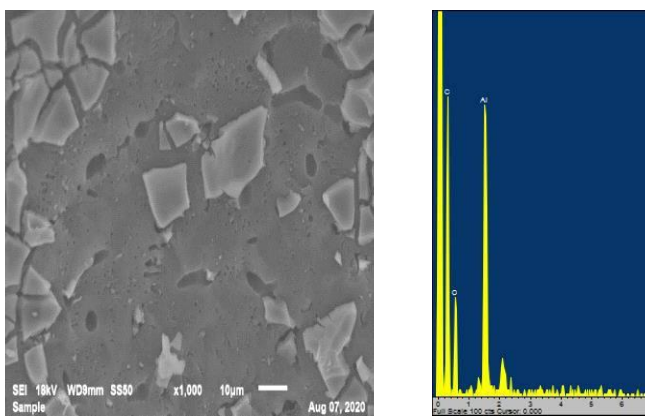


Figure 1. Schematic Diagram of Fixed Bed Column Setup

RESULTS AND DISCUSSION

SEM-EDX Analysis

Figure 2 (a,b) and Table 1 shows the surface morphology and elemental analysis of Al-biochar, respectively. The EDX analysis showed the weight percentage of C, O and Al were 62.4%, 30.9% and 6.7% respectively [6, 7], which indicated that Al was successfully impregnated on the AC [8].



(a) (b)

Figure 1. (a) Surface Morphology of Al-biochar and (b) Spectrum for Aluminum (Al)

Table 1. Elemental analysis of SEM-EDX

Adsorbate	Initial COD (mg/L)	Bed height (cm)	Flow rate (ml/min)	Exhaustion time (min)	Adsorption efficiency (mg/g)	Removal (%)
POME	1590	5	10	140	24	47
	1590	5	15	105	18	36

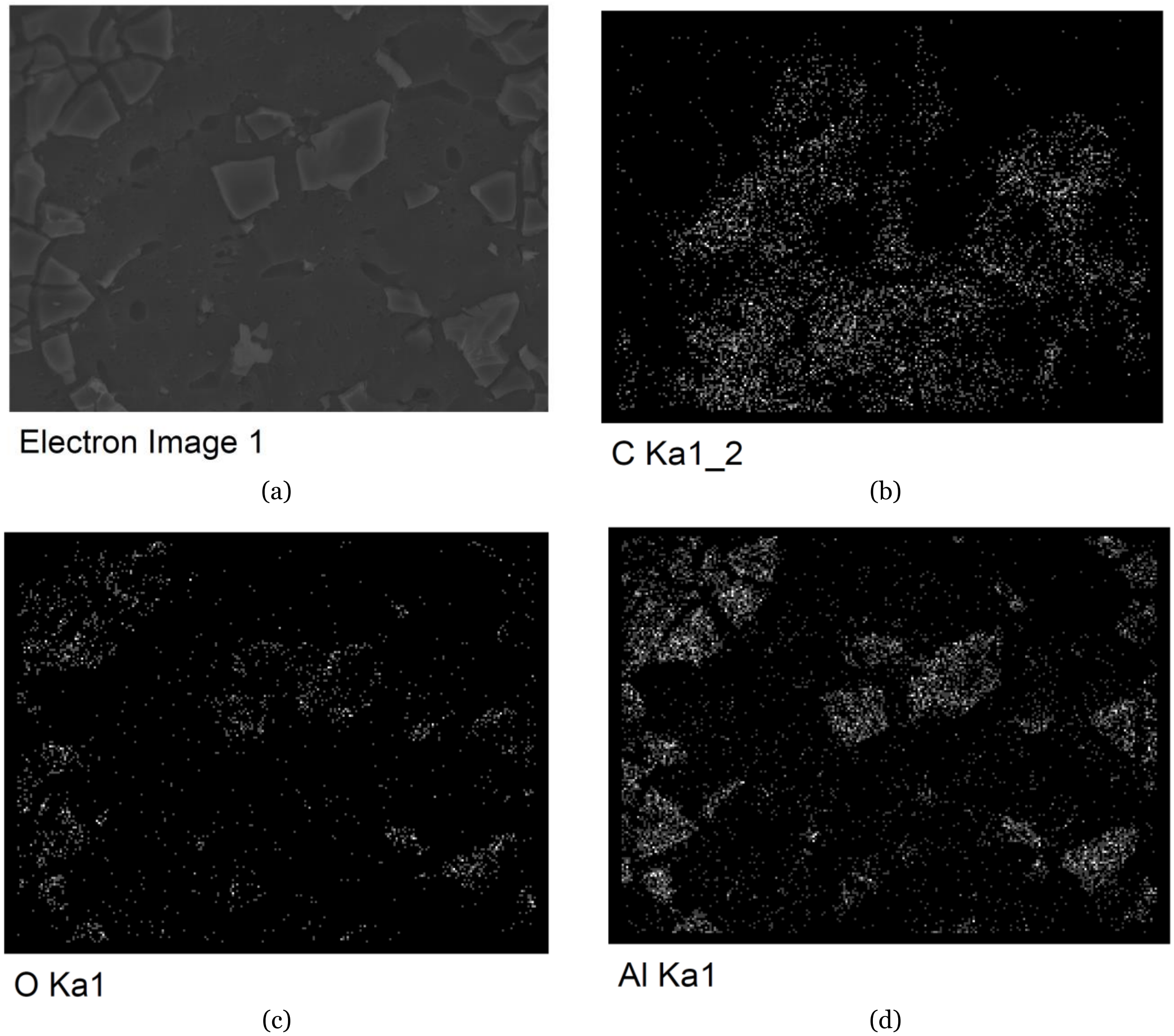


Figure 3. Elemental Mapping of Al-biochar (a) photo of AL-biochar (b) Carbon (c) Oxygen and (d) Aluminum

Table 2: Fixed Bed Column Adsorption of POME by Al-AC

Element (wt%)	Weight ratio (wt%)
C	62.4
O	30.9
Al	6.7
Total	100.0

POME Treatment in Fixed Bed Column

The granular size (1-2 mm) of Al-biochar was used as adsorbent for POME treatment in fixed bed column. Table 2 reveals the exhaustion time and bed capacity increased with lower flow rate of the POME sample. The exhaustion time of 140 and 105 minutes were achieved when the flow rate of POME were 10 and 15 ml/min respectively. Moreover, higher adsorption efficiency of 24 mg/g and 47% of COD removal were achieved at lower flow rate of 10 ml/min compared to 18 mg/g and 36% of COD removal at higher flow rate. Higher flow rate of POME sample shortened the contact time between the sample and adsorbent's surface, thus the adsorption efficiency of Al-biochar in column system was reduced. However, the presence of Al on the surface of Al-biochar increased the tendency of adsorbent to bind with negatively charged particles in the POME sample [9]. The Al on the biochar surface aided in adsorption of substances such as microorganism and chemical residues towards the Al-AC.

CONCLUSION

The column adsorption study showed that the flow rate of the POME sample had a significant effect on the exhaustion time. The exhaustion time increased with decreasing flow rate. The Al-biochar demonstrated the maximum exhaustion time of 140 minutes and 105 minutes at the flow rate of 10 ml/min and 15 ml/min respectively. The column study also showed that Al-biochar had a higher bed capacity (29 mg/g). Overall, this study suggests that the biochar modified by Al is suitable to be used as the adsorbent for higher COD removal

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