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Pre-treatments Anaerobic Palm Oil Mill Effluent (POME) for Microalgae Treatment

Mohd Sobri Takriff[1, 2*], Muhamad Zuhairi Zakaria[2], Mohd Shaiful Sajab[2] and Yeit Haan Teow[2]

[1]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia; sobritakriff@ukm.edu.my
[2]Research Center for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia; mohdshaiful@ukm.edu.my, yh_teow@ukm.edu.my

Abstract

Background/Objectives: Pre-treatments Palm Oil Mill Effluent (POME) by coagulation process and adsorption have been done to enhance light penetration during culturing microalgae process for POME anaerobic treatment. **Methods/Statistical Analysis:** Coagulation process was done by using rice starch and tapioca starch and the adsorption process was done using activated carbon from Palm Kernel Shell (PKS). In this pre-treatments study, several parameter for pre-treatments study (dosages, pH, stirring speed, particles sizes) were done in order to optimize the suitable method for POME treatment using microalgae. In microalgae treatment, optimum pre-treatment condition of POME was used for culturing *Scenedesmus dimorphus, Chlorella vulgaris and Dunaliella salina.* **Findings:** Pre-treatment by coagulation process using rice starch and tapioca starch as a coagulant showed optimum levels for dosages, the pH of anaerobic POME, settling time and slow stirring speed is 2.5g/L, pH 3, 60 min and 10 rpm and 2.5 g/L, pH 3, 80 min and 10rpm, respectively. While, pre-treatment by adsorption process using activated carbon Palm Kernel Shell (PKS) shows optimum levels for dosages, the pH of anaerobic POME, reaction time and the size of the activated palm kernel shell is 25g, pH 5, 120 hours and 0.5mm, respectively. Adsorption process was fixed at the optimum reduction in turbidity, COD and suspended solids at 83.33, 83.91 and 92.30%, respectively, which are higher than the coagulation process using tapioca and rice starch. In microalgae treatment, *Scenedesmus dimorphus* and *Chlorella vulgaris* were suitable for culturing microalgae in synthetic and anaerobic POME as growth medium with rate growth of microalgae are 0.1721 and 0.1699/day, respectively.

Keywords: Activated Carbon, Adsorption, Coagulation, Microalgae, POME

1 Introduction

Environmental issues are always been the top priority in the national concern due to the negative impact on ecological balance, health and life of local community. Expeditious agricultural activity is one of many causes of wastewater pollution in developing country. As example, Malaysia is one of the world largest palm oil producers, second exporter after Indonesia. Although palm oil industry has been a larger contribution on Malaysia's gross domestic product every year, but the increasing of oil palm by-products especially palm oil mill effluent (POME) has become the major sources of wastewater pollution in Malaysia[1,2]. In the palm oil mill process, approximately 5-7.5 tonne of water was used in obtaining a tonne of crude palm oil[3]. The POME generated was viscous, dark brownish colour with 80–90 ˚C and pH between 4-5. While, similar with others agricultural industry effluent, POME was rich with organics matter, nitrogen and phosphorus which can be hazardous on environment such as eutrophication on water resources, pollution on water soil and air pollution with the releasing of ammonia gas[4].

Nowadays, POME has been treated with conventional method of combination several stages with pond and digestion system of biological method. This process usually takes a longer retention time up to 90 days before it

*Author for correspondence

been released to water resources[5]. Therefore, microalgae for POME treatment has been introduce as alternative of wastewater treatment. Microalgae use organic and inorganic as food resources for reproduction and light source for photosynthesis[6]. Microalgae treatment digested most of the contamination on wastewater effluent and maintains the aquatic ecosystem. Besides, microalgae reproduction is efficient for producing high value added product which is use for industrial in food, health, and the top of it is biodiesel production[7]. However, POME known of its characteristic of dark and cloudy haves limit the light penetration, which is necessary for microalgae growth. In order to solve this issue, pre-treatments for POME are unavoidable before microalgae can be applied in wastewater treatment.

In this study, pre-treatments POME of coagulation and adsorption have been done to enhance light penetration during culturing microalgae process for POME anaerobic treatment. Coagulation process was done by using rice starch and tapioca starch and the adsorption process was done using activated carbon from Palm Kernel Shell (PKS). In this pre-treatments study, the optimum parameter for pre-treatments study was used for POME treatment using microalgae.

2. Materials and Method

2.1 Materials

POME in this study was collected from Sime Darby East Palm Oil Mill located at Carrey Island, Klang, Selangor. POME was collected from anaerobic pond and kept into polyvinyl chloride container at 4°C to maintain it element composition of Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and nutrient from POME. Rice starch and tapioca starch was obtained from Sigma-Aldrich without modification and kept into air tight container at room temperature. Activated carbon from Palm Kernel Shell (PKS) was obtained from pilot plant Malaysian Palm Oil Board (MPOB). Synthetic medium of Bold Basal Medium was prepared for cultivating microalgae biomass of *Scenedesmus dimorphus* and *Chlorella vulgaris*, and Modified Johnsons for *Dunaliella salina*.

2.2 Preparation of Starch Solution

Starch solutions were prepared by added 6 g of starch in bottle of 200 mL distilled water. Each bottle was stirred several times to ensure the homogeneity of the mixture and dissolving starch. Next, mixtures were heat using autoclave method at 121°C and pressurized at 117 kPa for 20 minutes. After heated, starch solutions were leaved at 80°C and stirred at 400 rpm using magnetic stirrer. Starch solutions were prepared fresh before experiment done to avoid biodegradation on starch.

2.3 Coagulation Process

Coagulation process was done by conventional flocculator (Flocculator VELP Scientifica JLT4) which allows four beakers simultaneously stir. In each coagulation experiment, 300mL of POME was used in 500mL of beaker. Initial pH effluent was measured and adjusted at pH desired (pH 3-8) by using acid and base. Starch dosage was controlled between 0-3 g/L and mixed with POME. Mixture was stirred at high speed stirring of 150 rpm for 5 minutes and follow by low speed stirring of 10 rpm for 15 minutes. Lowering speed was controlled at different time taken between 0-50 rpm. After low speed stirring, beaker was removed from flocculator and leave between 0-100 minutes for time retention for precipitation occurs.

2.4 Adsorption Study

Briefly, activated carbon PKS was immersed in distilled water for 1 hour or until all fibres was sediment. Activated carbon PKS was washed by distilled water for several times and dry in the oven for 3 hour at

100˚C. The activated carbon PKS was mixed with POME in the conical flask at different adsorbent dosage (5, 10, 15, 20, 25 and 30 g) in the 200 mL of POME. The mixtures was stirred using shaker and adequate sample of POME was taken at distinctive time (24, 48, 72, 96 and 120 hours). The efficiency of the adsorbent was study at different parameter of pH (pH 3-7) and sizes particle of activated carbon PKS (0.5, 1.0 and 2.0 mm).

2.5 Characterization

After pre-treatment, sample of POME was taken from 2 cm of it surface. COD was analysed by Reactor Digestion Method using COD Test Tube Heater HI 839800 and Multiparameter Bench Photometer. Suspended solid of sample was measured by Gravimetric Method involving vacuum filtration and filter paper (0.45μm). Turbidity test was done using Absorptometric Method using turbidity analysis (HACH method 8237). Percentages of COD, suspended solid and turbidity were calculated using formula below:

Reduction percentage analysis (%):

$$1-\frac{C_f}{C_0}\times 100 \quad (1)$$

where, C_0 and C_f are initial and final concentrations of COD, suspended solid and turbidity of samples. While, the cell density was measured by using Haemocytometer method. Microalgae biomass was collected using vacuum filtration with filter paper (Whatman Paper C) and the sample collected was dried overnight in the oven and the dry weight microalgae biomass was measured accordingly.

3. Result and Discussion

3.1 Coagulation Study

In this experiment, the effect of coagulator dosage of rice starch and tapioca starch were done to study the reduction percentages of COD, suspended solid and turbidity of the sample with several parameters controlled of stirring speed (150 rpm for 5 minutes and 10 rpm for 15 minutes), temperature (37 °C), pH (pH 3) and coagulation time was 1 hour. Figure 1 shows the optimum dosages for rice starch and tapioca starch at 2.5 g/L with higher percentages reduction of COD, suspended solid and turbidity. Rice starch show the higher percentages reduction of sample analysis to be compare with tapioca starch due to the higher amylopectin[8,9,10]. As a main component of starch, branch chain of amylopectin highly contribute on characterizations of the starch (temperature gelatinization of starch, enthalpy changes and others)[8]. The increment of coagulator dosage will increase the reduction percentages of COD, suspended solid and turbidity of POME due to the higher interaction between polymer and colloid particles of POME which form the particle-polymer-particle aggregation. However, the higher dosage which are exceed optimum level dosage will stabilize particle as a result of saturation sorption on surface of excess polymer. This resulted of no changes by increasing the dosage of coagulators on reduction percentages of COD, suspended solid and turbidity[11].

In this study, the natural pH of anaerobic POME is recorded between 7.2[6]. The effect of pH desired on anaerobic POME was measured to identify the efficiency of the coagulation process on reduction of COD, suspended solid and turbidity of the samples. Figure 2 shows the optimum pH of anaerobic POME for coagulation process using rice starch and tapioca starch was measured at

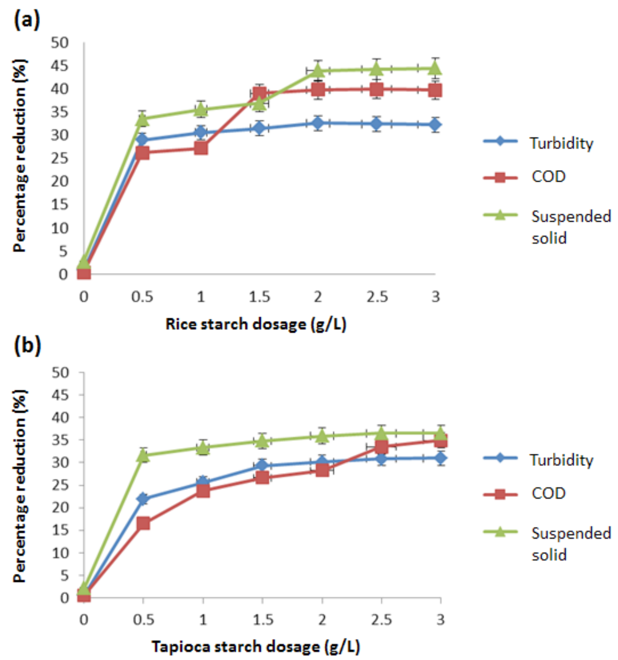

Figure 1. Effect of (a) rice starch and (b) tapioca starch dosages on percentages reduction of turbidity, COD and suspended solid of anaerobic POME at controlled parameters of stirring speed (150 rpm for 5 minutes and 10 rpm for 15 minutes), temperature (37 °C), pH (pH 3) and coagulation time was 1 hour.

pH 3. This results explained that the coagulation process was higher at acid condition to be compare with neutral and alkaline condition[12]. Rice starch and tapioca starch are not ionic polymer, which interpret that the interaction mechanism of polymer and particles are dominantly cause by hydrogen bonding[1,13]. Moreover, the coagulation process was dependable on zeta potential (ζ) of the starch. Zeta potential represent the stability of the colloid in the system, which are repelling each other at higher positivity and negativity of zeta potential. In the acidic condition, lone electron pair of nitrogen was protonated and shift to positively charged ($-NH_3^+$), and the carboxyl groups of protein became neutral (–COOH). While in the higher pH of basic condition, most of the protein retained at negatively charged, which involved the negativity of carboxyl groups ($-COO^-$) and in part of amino groups became neutral ($-NH_2$)[14].

The coagulation process was observe at the precipitation time between 20-100 minutes. Figure 3 shows the

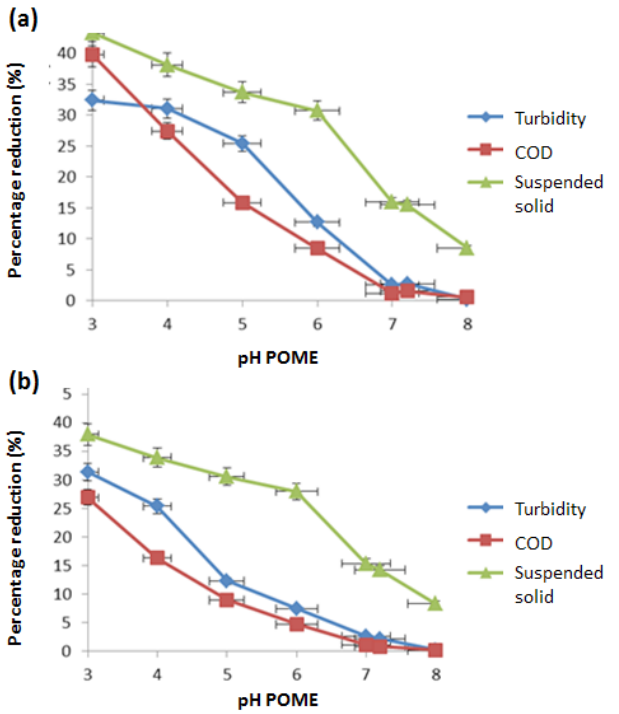

Figure 2. Effect of POME pH on percentage of turbidity, COD and suspended solid of anaerobic POME by coagulating with (a) rich starch and (b) tapioca starch at controlled parameters of stirring speed (150 rpm for 5 minutes and 10 rpm for 15 minutes), temperature (37 °C) and coagulation time was 1 hour.

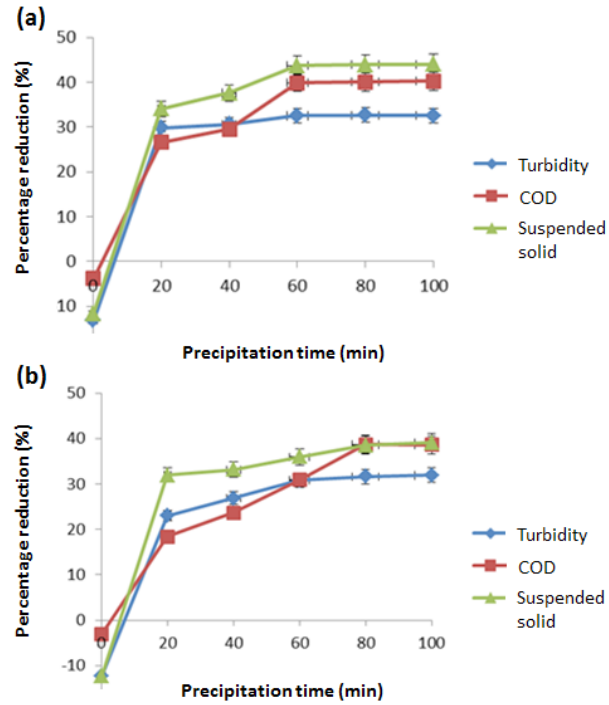

Figure 3. Precipitation time retention on percentage of turbidity, COD and suspended solid of anaerobic POME using (a) rice starch and (b) tapioca starch at controlled parameters of stirring speed (150 rpm for 5 minutes and 10 rpm for 15 minutes), temperature (37 °C) and pH (pH 3).

optimum precipitation time of coagulation process by using rice starch and tapioca starch are at 60 and 80 minutes, respectively. The precipitation using rice starch was much faster than tapioca starch is due to the formation of large aggregation which is easier to precipitate[15]. The increase of aggregation sizes and density of coagulation process due to polymer and particles in anaerobic POME interaction will rapid the precipitation process.

In the beginning of coagulation process, the high speed stirring was to increase the homogeneity of the starch dispersion on the anaerobic POME. Afterward, the low speed stirring was taken controlled, which allow particle-polymer-particle to form aggregate and increase the coagulation density size before precipitation[16]. The effect of low stirring speed on coagulation process shows in Figure 4 shows the increment of stirring speed more than optimum state, 10 rpm have decreased the reduction percentages on turbidity, COD and suspended solid of anaerobic POME. The higher stirring speed may disrupt formation of coagulating process[17].

3.2 Adsorption Study

In the adsorption study, the adsorbent dosage was observed to identify the optimum uptake of anaerobic POME pre-treatment. Figure 5(a) show the optimum dosage of activated carbon PKS was obtained at 25 g with reduction turbidity, COD and suspended solid of anaerobic POME are 78.39, 79.87 and 70.55%, respectively. Concisely, the addition of adsorbent dosages will be significantly increase the reduction percentages of controlled parameter due to the increment of the active sites of the adsorbent[18,19,20]. However, the efficiency of the higher adsorbent dosage is reduce when the adsorption equilibrium is achieved[21,22]. The optimum dosage was use as controlled parameter on pH, time and particle sized adsorption studies.

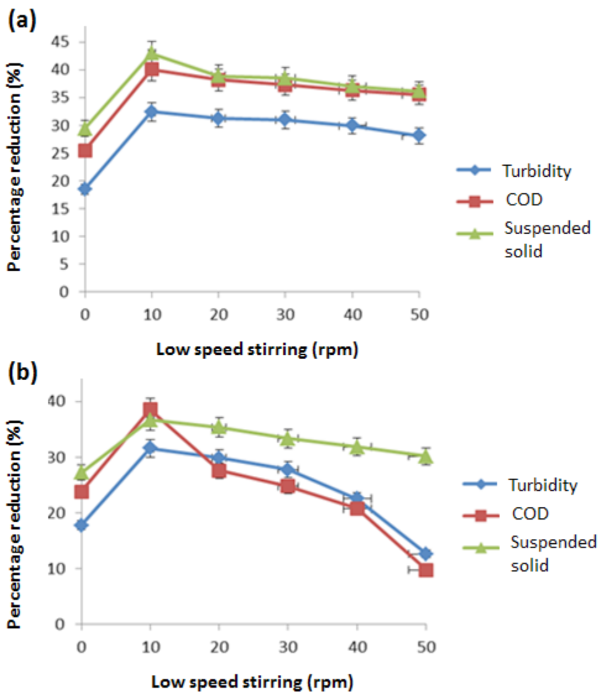

Figure 4. Effect on stirring speed on percentage of turbidity, COD and suspended solid of anaerobic POME using (a) rice starch and (b) tapioca starch at controlled parameters of temperature (37 °C), pH (pH 3) and coagulation time was 1 hour.

The effect of pH anaerobic POME on the adsorption capacity was show in the Figure 5(b). The optimum pH for the adsorption resulted at pH 5, which are reduced the percentages of turbidity, COD and suspended solid of anaerobic POME up to 75.46, 71.10 and 75.55 %, respectively. While the lower pH shows the reduction performance of the activated carbon PKS considering the active sites of the adsorbent was weak and the competition between OH^- and adsorbate in the anaerobic POME at acid condition[23].

Figure 5(c) show adsorption time of activated carbon PKS to reach the adsorption equilibrium. The adsorption equilibrium was reach after 120 hours of the adsorption process with reduction percentages of turbidity, COD and suspended solid of anaerobic POME are 78.83, 80.45 and 75.55 %, respectively. The time taken to achieve adsorption equilibrium was correspond to the time required for active site to attach with the adsorbate particles of anaero-

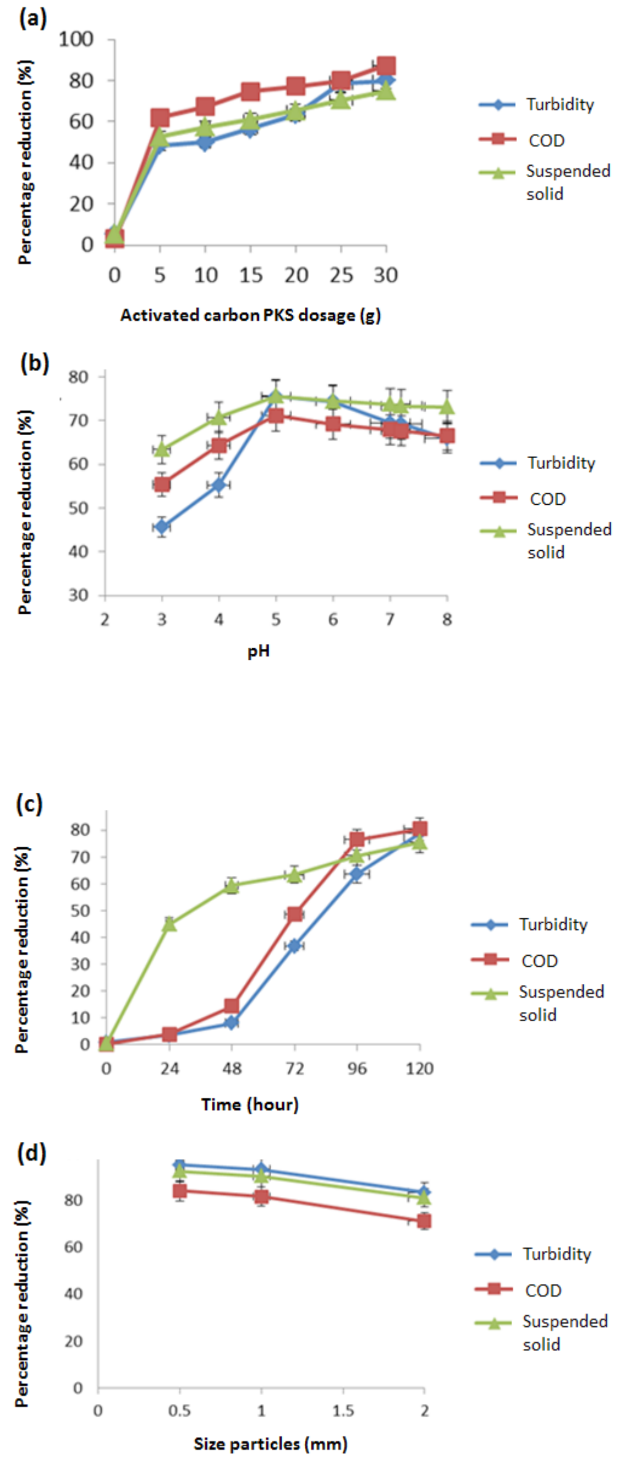

Figure 5. Effect on (a) activated carbon PKS dosage, (b) pH adsorption, (c) adsorption time retention and (d) size particles on percentage of turbidity, COD and suspended solid of anaerobic POME.

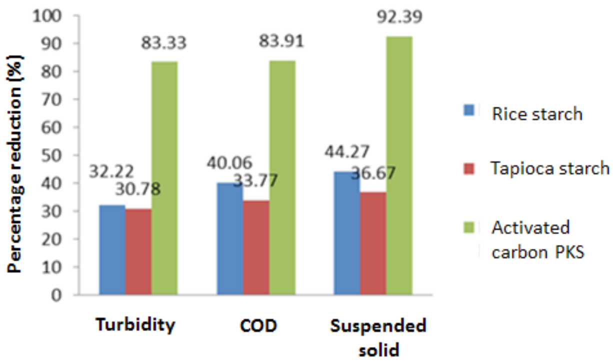

Figure 6. Reduction percentages of COD, suspended solid and turbidity of anaerobic POME using coagulation process (rice starch and tapioca starch) and adsorption process (activated carbon PKS).

bic POME[18]. In the reduction of turbidity and COD, the time taken for adsorbent to reach equilibrium is much longer due to small particles of activated carbon PKS were float at the upper level of the adsorption system and gave low interaction between adsorbent-adsorbate before all the adsorbent homogeneously stable.

Not withstanding the effect of the particle sizes of the activated carbon PKS on the reduction of turbidity and COD, Figure 5(d) show the effect of various particle sizes of the adsorbent (0.5, 1, 1.5 and 2 mm). The result obtain show the smaller size of the adsorbent of 0.5 mm gave the maximum performance in reduction percentages of turbidity, COD and suspended solid of anaerobic POME are 95.14, 84.06 and 92.38 %, respectively. Briefly, the smaller size of the adsorbent gave the higher surface area and active surface sites to interact with adsorbate particles of anaerobic POME[24]. As shown in Figure 6, although the adsorption process can take up to six days of treatment process to be compare with one day of coagulation process, but the optimum turbidity of adsorption process is more suitable for secondary treatment of microalgae treatment[6].

3.3 Microalgae Biomass Growth

In this study, cultivating microalgae biomass of *Scenedesmus dimorphus*, *Chlorella vulgaris* and *Dunaliella salina* were performed in synthetic and anaerobic POME culture medium. The growth of microalgae biomass in synthetic medium was investigated shows in Figure 7. In synthetic medium, *Scenedesmus dimorphus* resulted the higher growth rate of 0.2862/day to be compare to *Chlorella vulgaris* and *Dunaliella salina* which achieved growth rate at 0.2648 and 0.1525/day, respectively. The higher growth rates of both of *Scenedesmus dimorphus* and *Chlorella vulgaris* are due to the suitability medium culture at optimum pH of 7. While, the optimum growth rates for *Dunaliella salina* in previous study is at pH 9 [25].

Figure 8 shows the growth rates of culturing microalgae biomass in anaerobic POME. The growth rates of both *Scenedesmus dimorphus* and *Chlorella vulgaris* are much higher to compare with *Dunaliella salina* which are cultivate at 0.1721, 0.1699 and 0.1056/day, respectively. The growth rates microalgae are lower compare than the synthetic culturing medium due to slightly acidic and salinity of anaerobic POME culture medium.

4. Conclusion

In this study, both pre-treatments POME of coagulation and adsorption processes was investigated for better effluent in further process of microalgae treatment. These processes have been working on reducing the turbidity, COD and suspended solid of POME, accordingly.

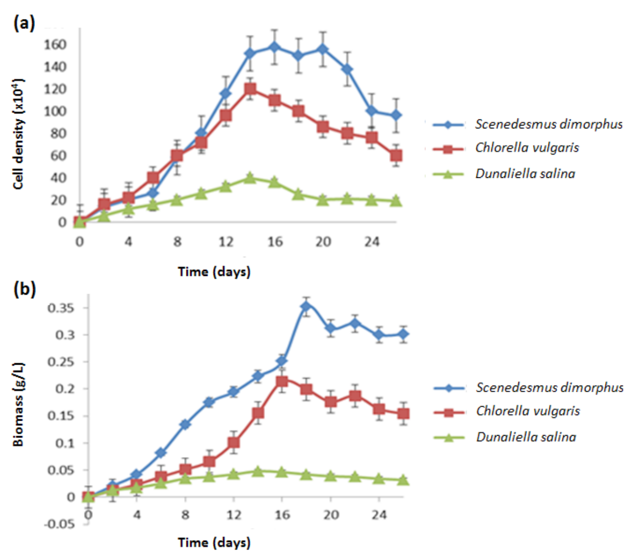

Figure 7. Results of culturing microalgae using synthetic medium for (a) cell density and (b) growth profile of Scenedesmus dimorphus, Chlorella vulgaris and Dunaliella salina.

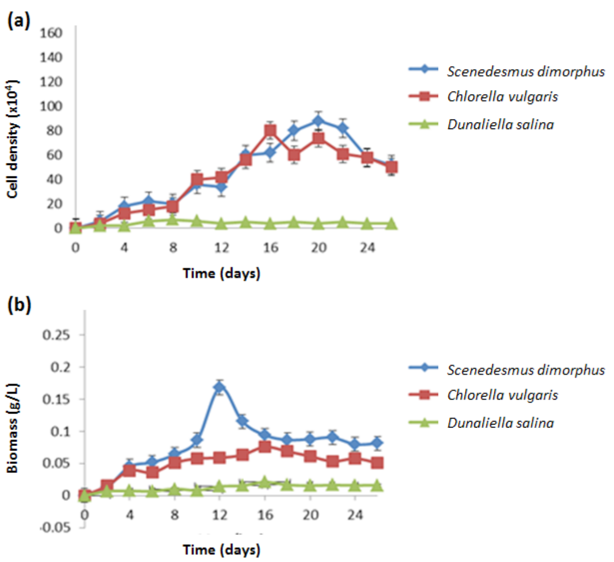

Figure 8. Results of culturing microalgae using anaerobic POME for (a) cell density and (b) growth profile of *Scenedesmus dimorphus, Chlorella vulgaris and Dunaliella salina.*

Activated carbon PKS was chosen as favourable treatment process, indicating the better clarity of effluent which contribute on culturing microalgae when compare to coagulation process. While in the culturing microalgae in the POME medium, *Scenedesmus dimorphus* and *Chlorella vulgaris* show better growth rate compare with *Dunaliella salina*.

5. Acknowledgement

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