Removal of ammonia by palm oil clinker (POC) as submerged fixed media in sequence batch reactor (SBR) mode

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Abstract. Currently, utilization of waste by-products or waste materials have received attention globally as it brings significant economic and environmental impacts. In this study, palm oil clinker (POC) which is one of the waste by-products generated in the processing of palm oil was utilized as submerged fixed media in Sequence Batch Reactor (SBR). By using POC as filter media for wastewater treatment, it is able to extend the useful life of POC and reduce the demand manufacturing new media. SBR is a fill-and-draw type reactor system which allow all activated sludge process to occur over a series of time in a single complete-mix reactor. During the operational steps of SBR, the combined attached growth/activated sludge system will promote the growth microorganism that attached on the media in the activated sludge process to remove pollutants such as organic matters and nutrients passes through the media. Laboratory-scale of two Sequence Batch Reactors (SBR) was fabricated with one of the reactors filled up with POC submerged fixed media. Influent of domestic wastewater from Universiti Teknologi Petronas (UTP) ’s Sewage Treatment Plant (STP) was adopted for wastewater treatment. Based on the result obtained, SBR reactor with POC submerged fixed media has higher ammonia removal efficiency, which approximately 90% than the SBR reactor without POC submerged fixed media, which approximately 85%.

1. Introduction
Since late 1950s, expansion of agriculture-based industry due to government’s diversified cautious policy has make Malaysia become world ‘s leading palm oil producer and exporter. According to the statistic, the total crude palm oil (CPO) production in 2017 was 19.92 million tonnes which recorded double digit growth 15.0 % from 17.32 million tonnes in 2016 [1]. As higher CPO produced, higher waste by-products is produced such as palm oil fuel ash (POFA), oil palm shell (OPS), palm oil mill effluent (POME) and palm oil clinker (POC). These waste by-products are mostly disposing to landfills. Therefore, utilization of waste by-products as an input to new industry should be promoted in order to decrease the demand for raw materials extraction, carbon footprint and energy consumption.

Palm Oil Clinker (POC), one of the waste by-products produced from incineration process of oil palm shell (OPS) and fibres in the palm oil mill boilers. The incineration of oil palm shell (OPS) and fibres also generates POC which can bring pollution to the environment if not handle properly [5]. POC is lightweight, irregularly shaped and can be obtained in large chunks. It possesses a surface area with immense number of pores due to the pyrolysis process. The study reported that POC has some good hardened properties, economic and eco-friendly. POC can be used to fill up the potholes on the road. There is also a previous study that used POC as a replacement for sand in self-compacting mortar (SCM) mix to enhance the finishing and architectural output of the mortar [1].
SBR is a fill-and-draw type reactor system which allow all activated sludge process to occur over a series of time in a single complete-mix reactor community [2]. Submerged attached growth processes bring advantages such as no activated sludge settling concerns and its ability to handle dilute wastewaters. An integrated fixed-film activated sludge (IFAS) reactor which operated is Sequence Batch Reactor (SBR) mode was fabricated to study the impact of ammonium concentration on the establishment of partial nitrification microbial community [4]. Besides, A previous study on 4 treatment plant which utilize submerged attached growth treatment system has been carried out. The treatment system comprises anoxic/equalization tank submerged attached growth bioreactor (SAGB) and clear well tank. To allow the continues feeding of wastewater through the filter, the system was operated in sequencing batch reactor (SBR) mode [3].

In addition, submerged attached growth treatment system required less area which a proportion of is (1/5 to 1/3) of the area required for activated sludge treatment. Filter media acts as a structure for the attachment and growth of a biofilm. To develop an ideal filter packing media, a material with high specific surface area, high void ratio, high durability must be used [2]. Therefore, POC with high specific surface area and void ratio is suitable attachment of biomass due to the porous surface. In this study, the performance of POC as submerged fixed media will be systematically evaluated. A Sequence Batch Reactor (SBR) without POC as submerged fixed media was fabricated for comparison purposes. In addition, testing on ammonia and nitrate concentration will also be conducted to understand about the ammonia removal efficiency of POC as submerged fixed media for Sequence Batch Reactor. This paper also investigates the application of POC as filter media as submerged fixed media in a Sequence Batch Reactor (SBR) to treat domestic wastewater.

2. Methodology

2.1 Material collection
Palm Oil Clinker (POC) was collected from Felcra Berhad’s palm oil mill that located at Seberang Perak. POC was obtained in large chunks after the final stage of combustion of palm oil shells and fibres in boilers. Usually, these POC is used as cover for the roads at oil palm estates or landfilled. The raw POC was then crushed and sieved to exclude the unwanted small particle size of sand and leaves. The POC passed through #37 (37 mm) sieve size and retained on #28 (28 mm) was utilized as packing filter media. A portion of POC after sieve analysis was used to immersed into domestic wastewater to observe the reaction of POC with domestic wastewater. Bulk weight, density of POC is determined before immersed into the wastewater. This to test the difference in bulk weight of POC after immersed into the wastewater for a certain time interval.

![Figure 1. Raw Palm Oil Clinker collected.](image1)

![Figure 2. Sieve analysis of POC.](image2)

2.2. Experimental Set-Up
The Sequence Batch Reactor (SBR) system consists of 3 components which are a feed tank, a pump and 2 reactors. Both reactors were fabricated by using Perspex to allow for better visibility. One of the
reactors consists of filter unit and aeration equipment (air diffuser) while another one only consists of aeration equipment (air diffuser) for comparison purposes. The air diffuser was located at the bottom of the reactor uniformly operate by a pump to distribute the air evenly.

2.3. Sampling Method
The influent sample was obtained from Universiti Teknologi PETRONAS Sewage Treatment Plant before allowed to flow into the reactor. During the fill phase, 1.6 litre of influent was pumped into each reactor with an operating flowrate of 1.6 litre/hour. The filling time will be 1 hour. The solid retention time (SRT) was set to be 2 days which allows nitrification to occur. Aeration and mixing were provided throughout the operation. After 2 days, sludge in the reactor was allowed to settle for 1 hours to separate the solids from the liquid under quiescent condition and obtain the clarified supernatant as effluent. Then, the 1.6 litre of clarified supernatant was decanted as effluent sample for determination of concentration of ammonia and nitrate. The remaining effluent and settled sludge in the reactor was mixed and 100 ml of mixed sludge was taken for sludge settle-ability test and Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) test. After the testing, the 100 ml of mixed sludge was used for subsequent tests.

Figure 3. Cycle time for each phase of an SBR system.

2.4. Testing Method
2.4.1. Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) Test. Mixed Liquor Suspended Solids (MLSS) is a test for the total suspended solids in a sample of mixed liquor. MLVSS, or Mixed Liquor Volatile Suspended Solids, is a test to determine the amount of volatile suspended solids found in a sample of mixed liquor. In this project, USEPA Standard Method 2540 D was used to determine the concentration of MLSS and MLVSS. Most of the volatile solids in a sample of mixed liquor will consist of microorganisms and organic matter. As a result, the volatile solids concentration of mixed liquor is approximately equal to the number of microorganisms in the water and can be used to determine whether there are enough microorganisms present to digest the sludge.

Microfiber filters were prepared a day before sampling day. The effluent with sludge sample was diluted with dilution factor of 1:10. 10 mL of wastewater sample was pipetted immediately into a flask. 90 mL of distilled water is then added to the sample and the flask shaken properly. The aluminium pans were labelled to ease the identification of sample. The initial weight of pans with filter paper were measured and recorded as [A]. Distilled water was used to clean up the filter pump and filter papers were placed on top of the filter holder. 25mL of diluted sample was measured by using measuring cylinder and poured into the filter. Rinsed the measuring cylinder using distilled water. The pump was
switched on to pump out the wastewater sample. During the pumping, distilled water was added to ensure that there are no suspended solids sticking on the side of the filter. After pumping out of water, the watch glass was removed and the filter papers containing the solids were placed on the pan. The pan with the filter paper was placed in the drying oven at 105°C for 1 hour. The pan with the filter was removed from the drying oven and placed in a desiccator for 10 minutes to cool down to room temperature. The weight of pans together with the filter paper and solids were measured and recorded as [B].

For the MLVSS sample, the pans together with the filter paper and solids were placed into another oven at 550°C for 1 hour after the first drying oven. Then, placed in the desiccator for 10 minutes to cool down to room temperature. The weight of pans together with the filter paper and solids were measured and recorded as [C]. This gives the MLFSS value. Calculate MLVSS and MLSS using the formula given:

\[
\text{MLSS} = \text{Weight at 105°C (B)} - \text{Initial weight (A)}
\]

\[
\text{MLVSS} = \text{Weight at 105°C (B)} - \text{Weight at 550°C (C)} \times \text{Dilution Factor} \times 50\text{mL or 100mL}
\]

2.4.2. Nessler Ammonia Test. USEPA Nessler Method by Hach company was used to determine the concentration of ammonia nitrogen. The experimental procedure is applying the Standard Methods for the Examination of Water and Wastewater, 4500-NH3 B & C, 15th Edition. In this experiment, polyvinyl alcohol and mineral stabilizer will be used to add into the sample. The Mineral Stabilizer complexes hardness in the sample. The Polyvinyl Alcohol Dispersing Agent helps the colour formation in the reaction of ammonia with Nessler Reagent with certain other amines. The ammonia concentration is proportional to the yellow colour formed. Higher intensity of the colour indicates the higher concentration of ammonia. The wavelength of the light emitted by spectrophotometer is 425 nm. The measurement wavelength of the light emitted by spectrophotometer will determine the intensity of the colour. For the experimental procedure, it will first start with the dilution of the sample as the range of concentration that spectrophotometer able to determine is only around 0.02 mg/L \(NH_3-N\) to 2.5 mg/L \(NH_3-N\). The wastewater sample will be diluted with dilution factor of 1:10 using volumetric flask. 25 mL of diluted sample will be measured by using measuring cylinder. Then, 3 drops of mineral stabilizer and 3 drops of polyvinyl alcohol will be added to the sample. Mix the sample. 1 mL of Nessler reagent will be added to the sample. Mix the sample for 1 minute. Place the 10 mL of the sample into the cuvette. Step 2 to step 7 is repeat using distilled water for zero calibration. Insert the cuvette with distilled water sample into spectrophotometer for zero calibration. Insert the cuvette filled with sample into spectrophotometer. Before the measurement, make sure that there are no fingerprints or liquid on the external surface of the sample cells. The cuvette must be wiped clearly to prevent the inaccuracy of data. Observe and take the reading.

3. Results and discussion

3.1. Reactor Fabrication

The Perspex reactor for Sequence Batch Reactor (SBR) system had been fabricated with the total volume of 0.016 m\(^3\) (16L). The dimension of the reactor are as in Table 1.

| Table 1. Dimension of reactor |
|-----------------------------|
| **Value (cm)**              |
| Length                      | 37.5 |
| Width                       | 17.0 |
| Height                      | 25.0 |

The system has been fabricated as shown as Figure 4 with total volume of 0.016 m\(^3\). It can be divided in to 3 components which are a feed tank, a pump and 2 reactors. Reactor A is the SBR Bioreactor without POC as submerged fixed media while Reactor B is the SBR Bioreactor with POC as submerged
fixed media. Oxygen was provided by air diffuser for microorganism in the reactor to perform biological treatment. The influent was allowed to fill up 75% of the maximum liquid volume. The wastewater in both reactors are brown in colour which indicates the presence of microorganisms in the reactor. Pipeline are connected properly to prevent leakage of wastewater and low pumping efficiency. The maximum storage capacity of feed tank is about 60 L. Based on Figure 6, it shows the attachment of biomass on POC ‘s porous surface. POC with higher void ratio able to allow more biomass attach on it.

![Figure 4. Front view of reactor system.](image)

![Figure 5. Palm Oil Clinker with attached biomass.](image)

3.2. Experimental Testing

3.2.1. Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) Test. MLSS indicates the total suspended solids in a sample of mixed liquor as shown in Figure 6. The values of MLVSS for both reactors vary around 650 mg/L to 1050 mg/L as shown in Figure 7. MLVSS indicates the number of microorganisms in the water that can be used for ammonia removal. The values of MLVSS for both reactors vary around 500 mg/L to 700 mg/L.
3.2.2. Nessler Ammonia Test. The concentration of ammonia nitrogen was determined using Nessler method which utilize spectrophotometer. Spectrophotometer is an optical equipment to measure the intensity of light relative to wavelength which usually use determine the concentration of an aqueous solution. Therefore, higher intensity of colour of wastewater sample represent higher concentration of ammonia nitrogen.

Based on Figure 8, it shows that the ammonia nitrogen concentration of influent varies from time to time. This could be due to dilution of rainwater and variation of sewerage generation as the influent of both reactors are taken directly from UTP’s Sewage Treatment Plant. The ammonia nitrogen concentration from Reactor A is higher than Reactor B. For Reactor A effluent ammonia concentration vary around 0.6 mg/L to 1.3 mg/L while Reactor B effluent ammonia concentration vary around 0.4 mg/L to 0.9 mg/L. This indicates that SBR with POC as submerged fixed media greater efficiency of nitrogen removal. The ammonia removal efficiency of Reactor A is approximately 85% while Reactor B is approximately 90%. However, no significant difference in ammonia nitrogen concentration between Reactor A effluent and Reactor B effluent. The difference in ammonia nitrogen concentration is only within the range of 0.5 mg/L to 0.1 mg/L. This is because of the limitation of the reactor and small amount of POC was placed in the reactor. More POC will results in more attachment of biomass on POC and will leads to better removal of ammonia nitrogen.
3.2.3. Microbial Analysis. The removal efficiency of ammonia is dependent on the quantity and quality of Mixed Liquor Suspended Solids (MLSS) population and strength. The microscopic analysis has been carried out to determine the microorganisms present and microbial activity in the activated sludge of Reactor A and Reactor B. Based on the analysis, presence of Spirogyra, Rotifers and Nematodes has been found and classified accordingly to their microscopic morphology (Figure 10). Based on the analysis, it has been proved that the Reactor A and Reactor B are in the pin floc zone due to the predominance of Nematodes and Rotifers. From the Figure 11, it showed the relationships between predominance microorganism versus solid retention time (SRT) and food to microorganism (F/M) ratio. For influent that taken from UTP sewage treatment plant, the concentration of suspended solid is slightly lower compared to another typical domestic wastewater. Therefore, it leads to lower F/M ratio and poor settling process which is in pin floc region of microorganism.

![Influent Ammonia concentration versus time graph.](image1)

**Figure 8.** Influent Ammonia concentration versus time graph.

![Effluent Ammonia concentration versus time graph for Reactor A and Reactor B.](image2)

**Figure 9.** Effluent Ammonia concentration versus time graph for Reactor A and Reactor B.

![Microscopic morphology.](image3)

**Figure 10.** Microscopic morphology.
4. Conclusion and recommendations

This study investigated on the potential of Palm Oil Clinker (POC) as filter media for submerged attached growth system. Sequence Batch Reactor with POC as submerged fixed media is an effective treatment system in removing pollutants. This system has a simple operation, required relatively small spaces and no activated sludge settling concerns. Utilization of waste by-products or waste materials have received attention globally as it brings significant economic and environmental impacts. However, there is currently there are lack of study on utilization of waste by-products in wastewater treatment. In addition, excessive nutrient in wastewater discharge to natural water body will cause serious environmental impact such as eutrophication. Hence, this study is to determine the efficiency in removing nutrients by using Palm Oil Clinker (POC) as filter media for submerged attached growth system.

During the preliminary stage of this study, extensive literature review has been conducted on submerged attached growth system and palm oil clinker. Besides, experimental methodology is also proposed. The reactor had also been fabricated. In the next semester, the experiments proposed will be carried out accordingly. As a conclusion, the proposed Sequence Batch Reactor system with utilization of POC as submerged fixed media was fabricated based on the research methodology and literature review that had been done to achieve the objectives of the project.

As the reactor system is a scale down treatment system, difficulties in design calculation has been faced. For example, the design of trickling filter is unable to achieve ammonia removal due to the limitation of dimension of reactor. Therefore, more intensive study should be carried out in early phase of the project to determine the most suitable treatment system that able to utilize Palm Oil Clinker (POC) as filter media. Besides, the fabrication of reactor system became time-consuming due to availability of material. Thus, planning on alternative materials should be done before the procurement of materials.

The operational steps of Sequence Batch Reactor (SBR) requires monitoring over a series of time. Thus, it has caused the sampling to be time consuming. As this study was carried out in a limited time, only few parameters of wastewater are able to determine. Besides, problem such as sludge stagnant at the bottom of reactor has been faced. This could be due to inefficiency of aeration equipment to provide mixing and aeration. Modification on filter unit that enclosed the POC submerged fixed media and higher aeration should be done to prevent the stagnation of sludge in reactor.

5. References

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