A review on palm oil mill biogas plant wastewater treatment using coagulation-ozonation

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Abstract. Palm oil mill effluent (POME) generated from the palm oil industry is highly polluted and requires urgent attention for treatment due to its high organic content. Biogas plant containing anaerobic digester is capable to treat the high organic content of the POME while generating valuable biogas at the same time. This green energy from POME is environmental-friendly but the wastewater produced is still highly polluted and blackish in colour. Therefore a novel concept of combining coagulation with ozonation treatment is proposed to treat pollution of this nature. Several parameters should be taken under consideration in order to ensure the effectiveness of the hybrid treatment including ozone dosage, ozone contact time, pH of the water or wastewater, coagulant dosage, and mixing and settling time. This review paper will elucidate the importance of hybrid coagulation-ozonation treatment in producing a clear treated wastewater which is known as the main challenge in palm oil industry

1. Introduction
Palm oil industry gives rise to highly polluting wastewater, known as Palm Oil Mill Effluent (POME). In general appearance, POME is an oily wastewater which is brownish in colour and consists of fine suspended solid at pH of between 4 and 5. The POME wastewater has high biological oxygen demand (BOD) and chemical oxygen demand (COD) [2, 21, 29]. Therefore the discharge of POME without proper treatment will certainly damage the environment including causing aesthetic damaged such as foul smell in the surrounding area. To meet the discharge limit of BOD < 20 ppm as proposed by the Department of Environment (DOE), the POME must be treated effectively before being released into the receiving watercourse. Anaerobic digestion in a closed tank is the most suitable method for the treatment of wastewater containing high concentration of organic carbon such as COD and BOD while releasing biogas [1, 7]. This biogas can be used in the mills to generate electricity and steam for the mill processes. Palm oil industry has adopted the anaerobic digestion system known as biogas plant to support the government effort in preserving the sustainable environment towards zero discharge.

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Generally, the biogas plant is unable to produce wastewater that can be discharged directly into the watercourse because the treated water still could not comply with the discharge standard limit set by DOE. Some researchers reported that the wastewater can be reuse in other applications including composting [31] and land application. However, these applications seem impracticable since only less amount of wastewater is required. Thus, large amount of wastewater still need to be discharged in the watercourse without complying with the standard limit. The wastewater colour turned from brownish (POME) to blackish after POME was digested. This extremely coloured wastewater is because of the presence of lignin and its by-product, tannins, humic acids, lipids, fatty acids, melanoidin and phenolic compounds [32, 46, 30]. Consequently, it will create aesthetic problem, reduce the sunlight penetration thus affecting the photosynthesis activity, and the humic substances reaction with chlorine may produces trihalomethanes which is carcinogenic; if large amount of the wastewater are discharged into the watercourse [43, 27, 17, 30]. Figure 1 shows the simplified diagram in palm oil wastewater treatment containing biogas plant.

![Simplified diagram in palm oil wastewater treatment containing biogas plant](image)

**Figure 1.** Simplified diagram in palm oil wastewater treatment containing biogas plant in Sabah, Malaysia.

Many studies have used the hybrid technology that combines a conventional physico-chemical treatment and Advanced Oxidation Process (AOP) to treat various kinds of water and wastewater [18, 33, 38]. The biogas plant wastewater characteristics may vary significantly from industry to industry. Due to this variation, the value will be stated in a range to give a brief view regarding the characteristics. Table 1 shows the summary of biogas wastewater characteristics from various places [46, 47, 49].

| Characteristic                        | Value          |
|--------------------------------------|----------------|
| pH                                   | 7.2 – 8.3      |
| Chemical Oxygen Demand (mg/L)        | 1003 – 13532   |
| Biological Oxygen Demand (mg/L)      | 440 – 1355     |
| Suspended Solid (mg/L)               | 290 – 12750    |
| Total Nitrogen (mg/L)                | 26 – 310       |
| Ammoniacal Nitrogen (mg/L)           | 45 – 100       |
| Total Phosphate (mg/L)               | 28 – 85        |
| Colour (PtCo)                        | 1633 – 54200   |

**Table 1. Summary of Biogas Plant Wastewater Characteristic [46]**

2. **Engineering Parameters for Coagulation-Ozonation Process**

Coagulation is one of the most important physico-chemical treatment that commonly used to treat water and wastewater. Every coagulant has their optimum pH, where it is most likely related to the
minimum solubility of the coagulant at this point, the coagulation mechanism changes from charge neutralization to sweep coagulation. Metal hydroxides can be produced when the metal coagulants (iron or aluminium salts) are hydrolyzed with water [9]. Hydrolysis and precipitation of ferric salts are less sensitive to pH than aluminium salts, since ferric hydroxide is much less soluble than aluminium salts and precipitates over a wide range of pH [3]. The Fe(OH)$_3$ dominates between a pH of 6 and 10, whereas the Al(OH)$_3$ is present between a pH of 5.5 and 7.5. It means that at a pH above 7.5, some aluminium is resolubilised in the water and no sweep coagulation occurs anymore [9]. Inorganic coagulants such as aluminium salts and iron salts are commonly used in water and wastewater treatment. Both coagulants were found to change the particle size of organic matter in the wastewater towards larger fractions [13]. Usage of inorganic coagulants as a sole treatment is less effective especially for highly concentrated dyes [20]. Therefore, selection of coagulants must be considered carefully by understanding the type of wastewater that has to be dealt with. Increasing coagulant dosage may alter the zeta potential of wastewater towards less negative values. Zeta potential for wastewater is negatively charged and it is also depends on the pH. Aluminium and iron salts which are positively charged will neutralize the wastewater by increasing the particle size, hence increasing the zeta potential to be near zero. However, overdosing will lead to restabilization of particles where the ions will repel each other and produce breakage of flocs. Proper mixing promotes uniform distribution in the coagulation process. When coagulant is added into the water or wastewater, charge neutralization will take place during the first second [9]. Therefore, it is important to distribute the coagulant quickly via rapid mixing so that the coagulant and particles can stick together. Over rapid mixing can cause the restabilization of the colloids. For the slow mixing, it should be sufficient enough to ensure homogenization and not to break the aggregation of flocs [40]. Over mixing might not have effect on the coagulation, however insufficient time for mixing will deteriorate the performance of the coagulant. Recently, a study on single stirring scheme shows that it is possible for the coagulation and flocculation process to take place together in a simpler process [48].

Ozone is a molecule that consists of three negatively charged oxygen atoms. The ozone molecule is very unstable and has a short half-life, causing it to fall back to its original form after a while, according to the following reaction mechanism; 2O$_3$ → 3O$_2$ [41]. Several researchers have found that pre-ozonation can improve the effectiveness of the coagulation process [12, 4, 28, 44]. Sometimes ozone can act as an oxidant or/and as a coagulant-aid [12]. As a coagulant aid, besides reducing coagulant dosage, it might enhance the surface charge of the complex pollutant to become more negatively charge [14]. Due to its strong oxidizing nature, ozone can oxidize the mostly organic and inorganic compounds [15]. Ozone oxidizes the compounds into insoluble oxides that can precipitate or settle out (normally all are filterable), and occasionally some are foamy (so can be skimmed) [14]. When ozone react with natural organic matter (NOM), the oxidation leads to the formation of aldehydes, organic acids, and aldo- and ketoacids [15]. A study compares the ozone point of application in the several of sources of water samples to remove the disinfection by-product formation potential (DBPFP). Both pre- and post-ozonation processes were better choices to reduce the DBPFP than the conventional methods which by using coagulation process. However, the result showed that pre-ozonation gave better reduction than the post-ozonation process in term of UV$_{254}$/DOC. 73% and 53% of UV$_{254}$/DOC percentage removal for pre- and post-ozonation processes respectively [12]. This can be concluded that the overall removal depends on which pre-treatment is used. The post-treatment can act as a “back-up” for the overall process.

Another studies from the same researcher reported that pre-ozonation can enhance the efficiency of coagulation. Aluminium sulphate (alum) is better choice than PAC when reducing the level of TOC and also less total trihalomethane formation potential (THMFP) when combining with ozone. In contrast, total haloacetic acid formation potential (THAAPFP) increased after each coagulation, ozonation and their combination. Results also indicated that coagulation after pre-ozonation is not applicable for bromate removal in water [37, 36]. Even though many studies have been conducted on the effect of ozone on coagulation, there still some contradiction among different researchers. Some studies have reported that pre-ozonation can reduce the consumption of coagulant in the treatment
process [16, 26, 19, 11]. In contrast, the effect of pre-ozonation does not reduce the coagulation dosage [39, 5]. As mentioned earlier, pre-ozonation can act as a coagulant aid in the treatment process. However, several researchers mentioned that when high dosage is applied, the coagulant efficiency will be impaired thus can affect the removal of organic matter [22, 5, 25, 8]. This is due to the ozonation process which breaks down the long chain molecular weight of organic matter into smaller one in which coagulation is less effective [23, 6, 44, 24, 34, 10, 45, 35]. Increasing in pH makes the ozone decomposition to occur faster. The OH-radical was produced in alkaline solution as per mentioned in the previous chapter. Thus, increasing the pH will increase the removal efficiency. However, very high pH will cause less removal. This is due to there is an increase of OH-radical scavenging by the carbonate ion which is a predominant species as higher pH [42].

Generally, increasing the ozone concentration causes faster oxidation rate, and increase in removal. However, at greater ozone doses, more extensive degradation of organic matter occurs in which the resulting molecules no longer behave as colloidal particles [16]. Pre-ozonation has shifted the molecular weight distribution of organic matter towards lower average molecular weight values [34, 24] and thus affecting the behaviour of the colloidal. Ozonation contact time may also influence the removal efficiency of organic matter. As the contact time increases, the decolourization rate and COD removal may also increase. Decolourization may occur when the ozone molecule reacts with unsaturated bond of phenolic lignin compound as per mentioned in the previous chapter. However, other substances that are more hydrophilic and polar might be produced during that period. Thus, COD removal may not be significantly increased.

3. Conclusions
Anaerobic digestion is capable in treating POME and at the same time producing biogas which is beneficial to the mills. However, the treated wastewater is highly polluted with blackish in colour and unable to be discharged to surface water. From past experiences, hybrid coagulation-ozonation could treat biogas plant wastewater effectively. In the future, several parameters should be studied in order to ensure the effectiveness of the hybrid treatment such as flocculant dosage, type of metal and polymer flocculants, effect of wastewater pH, settling time as well as sludge generation. The sludge potential to be converted as a fertiliser/soil conditioner would be an interesting topic to be explored. In addition, a study on biological treatment for the chemically treated wastewater also can be carried out.

4. References
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