Oxidation of Palm Oil Mill Effluent Using Hydrogen Peroxide and Catalysed by UV Light/Zinc Oxide

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Abstract. The amount of palm oil mill effluent produced annually in Malaysia has been on the increase increasing and causing degradation of the environment due to poor disposal owing to incomplete treatment. Various studies have been carried out in order to study ways to improve the condition of the wastewater characteristics before discharging into any water body. This study determined the efficacy of photocatalytic treatment method using hydrogen peroxide, zinc oxide and ultraviolet light. A variety of operating conditions were investigated such as the effect of pH, hydrogen peroxide dosage, amount zinc oxide, ultraviolet light irradiation and contact time in order to determine the optimum condition for the treatment method. Kinetics of degradation was also conducted. For UV/H$_2$O$_2$ treatment process, under optimum conditions, it was found that the highest COD and colour removal efficiency was 41.9% and 38.3%, respectively. For UV/ZnO treatment process, under optimum conditions, the highest COD and colour removal efficiency was 37% and 85%, respectively. For UV/H$_2$O$_2$/ZnO treatment process, under optimum conditions, the highest COD and removal efficiency was 60.2% and 91.6%, respectively. This study found pH 11, H$_2$O$_2$/COD molar ratio of 5, 0.4 g of zinc oxide, 200 rpm at 4 h reaction time as the desirable operating condition for removal of COD and colour from the palm oil mill effluent.

1. Introduction

Palm oil mill effluent (POME) is a thick liquid, brownish in colour, rich in organic matter and unpleasant odour [1]. This causes considerable damage to the environment because of its characteristics. Hydrogen peroxide is a reactive chemical compound with the formula H$_2$O$_2$. It may appear to be colourless in a dilute solution and has a pale blue colour when it is saturated [2]. Zinc oxide is a reactive chemical compound with the formula ZnO. It has a white to yellowish-white crystalline colour in powder form and nearly soluble in water. Its crystal structures are made up from wurtzite (hexagonal) and zinc blend [3]. This chemical compound is a cheap alternative to titanium dioxide and it is also able to induce photocatalytic degradation of organic compounds [4]. Photocatalytic process used with ZnO to degrade organic compounds and also remove high purity of noble/heavy metals from water [5]. Ultraviolet (UV) light is an electromagnetic radiation [6] which is not visible to the human eye. It has a wavelength of 10 to 400 nm, longer than X-rays but shorter than that of visible light [7]. This electromagnetic radiation may be artificially generated or may come from the sun and produces electric arcs and specialized lights. UV light is effective in treatment of wastewater and it is safe for those who work with it. It helps to disinfect the wastewater by damaging the DNA and RNA of microorganisms [8].

POME produces huge amount of methane gas from its anaerobic processes and has 21 times Global Warming Potential (GWP) compared to other gasses [9]. Igwe and Onyegbado [10], stated in their
findings that POME contains soluble materials that are harmful to the environment, either in the form of soluble gaseous, soluble liquids or solids, with concentrations above the threshold limit values. This highly polluting wastewater can, therefore, cause pollution of waterways due to oxygen depletion and other related effects as studied by Ahmad et al. [11]. Raw POME should be treated before discharge into any medium to avoid serious environmental pollution as it has an extremely high content of degradable organic matter, which is due in part to the presence of unrecovered palm oil [12]. According to Maheswaran and Singam [13], raw POME has BOD values averaging around 25,000 mg/l, making it about 100 times more polluting than domestic sewage. With respect to population equivalent (PE), the palm oil industry generates BOD value that is equivalent to that generated by 38 million people [14]. Since there is a huge amount of POME produced, a response by the Malaysian government was given to show concern towards the social and environmental impact of palm oil by pledging to limit palm oil plantation expansion through retention of at least half of the nation’s land as forest cover [15]. Even with the new pledge, this may not necessarily be enough to minimize the damages that may have been done by the palm oil industry. The main problem is that POME after biological treatment still has high concentration of organics which are more than the stipulated discharge requirements by the EQA 1974. This is because most palm oil industries ignore the proper treatment for POME which has caused problems to the environment. A number of studies have been reported for treatment of POME including moving-bed biofilm reactor technology [16], nano-composite membrane [17], catalysis [18], electro-coagulation-peroxidation method [19] amongst others. Several methods have been reported for treatment of POME. However, no study has reported UV/H₂O₂ for treatment of biologically treated POME. Thus in this work, we investigated the process in order to obtain desirable discharge standards according to the Environmental Quality Assessment (EQA, 1974), Malaysia for biologically treated palm oil mill effluent.

2. Materials and methods

2.1 Wastewater

POME was collected from a nearby palm oil mill in Sibu, Sarawak Malaysia and was stored at 4°C until it was needed.

2.2 Chemicals and Equipment

The zinc oxide and hydrogen peroxide used were of analytical grade and were purchased from Fisher Scientific International, Inc. The UV light used was supplied by a specialist in Malaysia.

2.3 Analytical methods

The COD (Standard Methods 5220 D) and colour was measured by standard methods using the photo spectrometer [20]. In order to stop interference and obtain accurate COD readings, the solution was made above pH 10 to enable H₂O₂ decompose into water and oxygen according to previous studies [21-22], pH meter produced by HACH was employed to measure pH during treatment. All sampling and testing were in duplicates.

2.4 Experimental Procedure

Batch treatment process was adopted in this work. The POME wastewater was treated using a stand-alone orbital shaker unit. Addition of zinc oxide and hydrogen peroxide were as required. The zinc oxide and hydrogen peroxide were added to the flask containing POME. Specifically, hydrogen peroxide was added last and the time was monitored thereafter. A flask was withdrawn from the
orbital shaker and the sample was filtered using 0.45 µm membrane diameter filter size. Thereafter, COD and colour was measured in the treated sample.

3 Results and discussion

3.1 Effect of pH

To study the effect of pH, treatment of POME was conducted at various pH values between 3 and 11. The pH of POME sample was adjusted by using 0.5 M HCl or NaOH solutions [3, 23]. Figure 1 shows the results of the experiment that was conducted. Other varying operating conditions was the contact time of 10 to 90 min with shaking speed of 200 rpm on an orbital shaker. The highest COD removal of 27% was at pH 11 with a 20 min reaction time. It was observed that the colour removal had the highest colour removal of 51.7% at pH 11. According to Andreozzi et al. [24] the rate of photolysis in the presence of H.O. was pH dependent. They found that the rate of photolysis increases when more alkaline conditions are used. The pH value directly affected the generation of hydroxyl radicals and hence the oxidation efficiency [3].

Figure 1: Effect of pH in terms of COD and Colour removal
3.2 Effect of Hydrogen Peroxide Concentration

To determine the effect of H$_2$O$_2$ concentration in the treatment of POME, various H$_2$O$_2$ concentrations were prepared. Elmolla et al. [3] stated that molar ratio H$_2$O$_2$/COD of 3 was optimum in their experiment. From our study, it can be observed that the molar ratio H$_2$O$_2$/COD of 5 was the optimum for treatment and removal of 30% COD removal from the POME. Other operating conditions included, contact time 10-60 min, pH 11 and various H$_2$O$_2$ concentrations, with an orbital shaker speed of 200 rpm. The COD value increased to a certain extent and then reduced as shown in Figure 2. As the COD removal decreased, the hydroxyl radicals with other inorganic species form oxidizable materials which will then increase the value of COD [4][5]. This trend can be seen for most of the pH values (Figure 2). The higher hydroxyl radicals that can be produced, the easier the organic compounds are converted into inorganic substances [25]. For colour removal, H$_2$O$_2$ also helps in the reduction of the murkiness of the wastewater (Figure 2). The Molar ratio H$_2$O$_2$/COD 5 was optimum in reduction of the COD and colour in the POME sample at 30 and 53%, respectively. This was used in the further treatments.

![Figure 2: Effect of H$_2$O$_2$ concentration in terms of COD and Colour removal](image)

3.3 Effect of UV light
In order to study the effect of UV light, the experiment was carried out with the obtained optimum pH 5, and molar ratio of H$_2$O$_2$/COD molar ratio Emolla et al. [3] for 1 to 5 h with a constant UV light exposure while rotated at 200 rpm on an orbital shaker. Hydrogen peroxide is only considered as an AOP if combined with other agents like UV, solar light or in the presence of other catalyst such as ZnO or TiO$_2$ [26]. Since it requires the other agents in order to generate hydroxyl radicals. The highest COD and colour removal were 41.9% and 38.3%, respectively after 5 hours of reaction. Figure 3 shows the COD removal efficiency value increased every hour showing consistency in the COD removal efficiency. This indicates that the UV light enables COD reduction. Two different studies were carried out and in both of the studies an increase in their percentage of degradation through the use of UV [27-28] has been reported.

![Figure 3: Effect of UV light in terms of COD and Colour removal](image)

3.4 **Effect of Zinc Oxide and UV light**

To study the effects of zinc oxide with the exposure of UV light, different amounts of ZnO ranging from 0.1 g to 0.5 g were used to carry out the experiments. The time of UV light exposure ranging from 2 hr to 5 hr with the intensity wavelength of 254 nm has been recommended by Bertelli et al. [29]. The tests were carried out at 200 rpm speed and pH 11. As shown in Figure 4, the optimum value of ZnO was 0.5 g with the COD removal efficiency at 37%. The trend of the results seemed to be indicative of the fact that additional ZnO would improve the COD removal efficiency consistently. However, as more time elapsed, the removal efficiency decreased after 3 hours. Zhao and Zhang [30] reported in their investigation that ZnO degradation can be increased with an increasing amount of ZnO dosage. Another report also stated that the higher concentration of catalyst would lead to a decrease in the passage of irradiation through the sample leading to poor light utilization which means lower COD removal efficiency in terms of the use of UV light [31].

The colour removal efficiency results obtained is shown in Figure 4. The result shows that the highest colour removal efficiency was 85 % at 0.5 g of ZnO and at a reaction time of 5 h. An increase in time allows more degradation to occur. The presence of ZnO in the POME irradiated by UV light causes degradation of colour [32]. This is due to the produced hydroxyl radicals that were extremely strong and non-selective oxidants which provided the degradation of the organic pollutant existing in the
POME [33] and can only happen when the catalyst and UV light irradiation were used concurrently in one setup [32].

![Graph showing COD and Colour removal efficiency over time with different zinc oxide concentrations.

Figure 4: Effect of zinc oxide in terms of COD and Colour removal

3.5 Effects of Photocatalysis Treatment using UV light /H₂O₂/Zinc Oxide

The combination of the photolysis treatment and the addition of ZnO was studied. Photolysis treatment is the UV/H₂O₂ treatment and the results of the experiments results were shown in Figure 5. The operations that were carried out for this treatment was the addition of ZnO of different amounts ranging from 0.1 to 0.5 g, pH 11, constant UV light exposure (254 nm wavelength) and 1 mL H₂O₂/COD molar ratio 5. The treatment was also carried out in 1 to 5 hr time duration and rotated on an orbital shaker at a speed of 200 rpm.
From the data obtained, it showed that the addition of 0.4 g ZnO had the highest COD removal efficiency of 60.2% at the 4th hour and starts to decline in the last hour. In relation with H$_2$O$_2$, further additional amount of H$_2$O$_2$ may increase the value of COD instead of decreasing it. This is due to the additional H$_2$O$_2$ which would react with potassium dichromate. This would further react as another oxidant which will increase the value of COD. This has been reported by Oliveira and Leão [34]. They stated that H$_2$O$_2$ gathered with the effluent under chemical reaction might be an influence in the investigations based on oxidation processes, such as COD test, which may utilize potassium dichromate that works as an ideal oxidant. In this experiment, the amount of H$_2$O$_2$ used were the optimal amount which were obtained in the earlier experiments and the data obtained also showed that the additional amount of H$_2$O$_2$ will only reduce the COD removal efficiency [5, 28]. The operating conditions for the optimum colour removal efficiency is the addition of 0.5 g ZnO, COD/H$_2$O$_2$ molar ratio 5 and 5 h of UV light exposure. A study investigated the effect of pH for photolytic dye treatment and determined that the decolourization happens to have higher value at alkaline pH and less at acidic pH [35]. It was also reported that the higher decolourization occurs in basic conditions and this is most likely due to the alkalinity of the sample, where more peroxide anions (HO$_2$) are generated in the sample through UV irradiation which can produce more HO$_2$ [35].
3.6 Effects of POME Concentration

To study the effect of POME concentration, different ratios of POME were added to the distilled water produced. Wastewater ratios in mL of 500:500, 250:750 and 100:900 were used to carry out the experiment. Other operating conditions of the wastewater were pH 11, concentration of H$_2$O$_2$ with molar ratio H$_2$O$_2$/COD of 5 and contact time between 10 and 60 min. It can be observed that the ratio of POME to distilled water 100:900 had the best colour and COD removal as shown (Figure 6). The colour removal efficiency for one hour reaction, whereas the highest colour removal took place at 60 min. The trend seemed to show consistent increasing of both COD and colour removal efficiency. With respect to the results obtained, the dilution factor of the wastewater plays an important role in the removal of COD and might be related to the presence of high concentration of the substrate in the treatment system. In terms of comparison the performance of the three process were UV/H$_2$O$_2$/ZnO> UV/H$_2$O$_2$> UV/ZnO.
3.7 Kinetics of degradation

The pseudo-first-order (Eqn. 1) and pseudo-second-order (Eqn. 2) were applied to the available data from the experiments.

\[
\ln \left( \frac{C_0}{C_t} \right) = K_t t 
\]  \hspace{1cm} \text{(1)}

\[
\left( \frac{1}{C_t} \right) = K_t t 
\]  \hspace{1cm} \text{(2)}

These models were used to describe the relation between the amount of pollutants and its uptake rate and its equilibrium concentration in solution [20-21]. Where \( C_0 \), \( C_t \), \( K \) expresses pollutant initial concentration, pollutant concentration at time \( t \) and the pseudo first-order rate constant of pollutant degradation, respectively.

The kinetics of degradation of the POME pollutants were obtained for UV/H\(_2\)O\(_2\), UV/ZnO and UV/H\(_2\)O\(_2\)/ZnO, and are presented in Figure 7 - 12. The values of \( R^2 \) for UV/H\(_2\)O\(_2\), UV/ZnO and UV/H\(_2\)O\(_2\)/ZnO were 0.9303, 0.9964 and 0.9653, respectively. All three \( R^2 \) values were higher values during the pseudo-first order reaction than the pseudo-second order reaction. Thus, describes the process as pseudo-first order reaction. The kinetics of degradation was carried out to investigate the rate of photocatalysis occurring during the treatment process.
Figure 7: Pseudo-first order reaction for UV/H$_2$O$_2$

Figure 8: Pseudo-second order reaction for UV/H$_2$O$_2$
Figure 9: Pseudo-first order reaction for UV/ZnO

Figure 10: Pseudo-second order reaction for UV/ZnO
Two different treatment of POME processes were determined namely; UV/H$_2$O$_2$ and UV/ZnO. From our study, both treatment processes could be used to treat the POME in order to reduce the COD and colour concentrations. The combined UV/ H$_2$O$_2$/ZnO process was also applied in the POME treatment. To study and compare the results for each phase of the process, experiments were performed with different operating conditions while trying to determine the optimum conditions in each case in order to achieve high degradation rates in the photocatalytic process. For UV/H$_2$O$_2$ treatment under optimum conditions (pH 11, 200 rpm, molar ratio COD/H$_2$O$_2$ 5, time: 1-5 hr), it was found that the highest COD and colour removal efficiency were 41.9% and 38.3%, respectively. For UV/ZnO
treatment process under optimum conditions (pH 11, 200 rpm, 0.1-0.5 g ZnO, time: 2-5 hr), the highest COD and colour removal efficiency was recorded at 37% and 85% respectively. For UV/H$_2$O$_2$/ZnO treatment under optimum conditions (pH 11, 200 rpm, molar ratio COD/H$_2$O$_2$ 5.0, 0.1-0.5 g ZnO, and time of 1 to 5 h), the highest COD and colour removal efficiency recorded was 60.2% and 91.6%, respectively.

Acknowledgement
This work was supported by University College of Technology Sarawak (UCTS) Research Grant No. UCTS/RESEARCH/3/2018/08(01) and UCTS/RESEARCH/3/2018/09(01)

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