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OPTIMIZATION OF SOLAR FENTON OXIDATION AND COMPARISON OF RECYCLE WET AND DRIED FENTON SLUDGE IN TREATING PALM OIL MILL SECONDARY EFFLUENT

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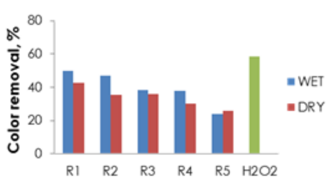
Graphical abstract



Abstract

This paper reports on the potential use of wet and dried Fenton sludge in replacement of the ferrous salt in treating Palm Oil Mill Secondary Effluent (POMSE) sample. The aims of this study were to characterize the Fenton sludge and to compare the performances of wet and dried Fenton sludge as iron sources in treating POMSE. The Fenton sludge were used to replace the Ferrous salt in R1- R5 and the results were compared with treatment used only H_2O_2 (non-catalyze). The optimum condition was run prior to tests and was found to be pH 3, H_2O_2/COD 1.59 (weight ratio) and Fe/COD 1.0 (weight ratio). Findings showed the removal of COD, color, turbidity and TSS in recycle wet Fenton sludge were ranging from 62% - 79%, 24% - 50%, 46% -74% and 62% - 73% respectively, while dried Fenton sludge treatment were ranging from 34% - 40%, 26% - 43%, 39% - 45% and 54% - 57% respectively. On the other hand, treatment with H_2O_2 showed approximately 60% removal for both COD and color while approximately 79% for both turbidity and TSS respectively. In conclusion recycled wet Fenton sludge treatment demonstrated higher removal of contaminant compared to the recycle dried Fenton sludge treatment.

Keywords: Recycle sludge, Fenton Sludge, Advance Oxidation Process, Fenton Oxidation, Optimization of Fenton, Palm Oil Mill Secondary Effluent

1.0 INTRODUCTION

Sludge production is the major problem in wastewater treatment. Currently, there are many technology built up to overcome the massive sludge, including carbonization [1], activated sludge [2], increase flow-aeration pattern [3], reuse of sludge cake for irrigation and fertilizer purposes [4], reuse bio-sludge in paper industry to produce paper [5], burning and ashing the sludge for disposal purposes, and many more.

The Solar Fenton process is one of the Advance Oxidation Process (AOP) that has been proven as an alternative treatment in wastewater treatment [6], [7] as well as in sludge treatment technology since it can reduce the sludge production [8], [9]. The utilization of UV solar either from natural solar sources or UV lamp shows the best ability to induce the catalytic photo-reduction of ferric ion, Fe^{3+} to ferrous ion, Fe^{2+} [10], [11], [12], thus making Solar Fenton continuously occurs as the Fe^{2+} will continuously reproduced from Fe^{3+}. According to [13], light / solar plays two different roles, which 1) it produces additional hydroxyl radicals and speeds up the reaction, and 2) it drives ligand to metal

charge transfer in the potentially photo liable complexes formed by Fe^{3+} and organic compounds.
The performance of solar Fenton process is fast and economic as the process with fresh catalyst can be replace with the sludge generating in the wastewater treatment and the light can be replace with sunlight/solar. The Fenton process starts with the combination of H_2O_2 with Fe^{2+} as portrayed below [14].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO. \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}OOH_2^{+} + H^{+} \quad (2)$$

However, the process faces a plunge of degradation as all Fe^{2+} is converted to Fe^{3+} and less hydroxyl radical is being produced. According to [15], the Fenton process accumulates Fe^{3+} ions in the system and retards the process until all the Fe^{2+} ions are consumed. Hence, the presence of solar irradiation speeds up and accelerates the reactions as it enhances the production of hydroxyl radicals [16], [17]. The reaction is simplified, as in equation (3) as shown below.

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + .OH \quad (3)$$

The use of sunlight as the source of light give a better performance than the conventional Fenton process as it can also reduce the sludge production [8], [18], [19]. As stated by [15], [16], [17] and [18] the iron species will accumulate in the sludge from the Fenton reaction, thus, the sludge can be recover and reuse in the other Fenton treatment although the percentage reduction of contaminant were lower compared to the non-recycle treatment [18], [19], [20], [21]. Several studies on recycling sludge has been well presented in [18] and [22].

Study done by [23] found that the increase of the organic contents in the sludge was the factor that affecting the efficiency of Fenton treatment (in recycle batch). Thus, the used of wet and dried Fenton sludge in Fenton process were conducted, after considering dried sludge may contained less organic content than the wet sludge. The aims of this study were to characterize the Fenton sludge and to compare the performances of wet and dried Fenton sludge as iron sources in treating POMSE.

2.0 EXPERIMENTAL

2.1 Chemicals and Materials

Sulfuric acid, H_2SO_4, 96% (J.T Baker) and sodium hydroxide, NaOH 50% (Macron) were used for pH adjustment. Hydrogen peroxide (Bendosen) and ferrous salt, $FeSO_4$.7H2O (Bendosen) were used as Fenton reagent in F1. Palm Oil Mill Secondary Effluent, POMSE was obtained from the Palm Oil Mill at Selangor, stored at 4°C prior to use.

2.2 Experimental procedure

2.2.1 Optimization

The mass ratio of H_2O_2/COD and H_2O_2/Fe was based on the stoichiometric ratio as mentioned below [24]:

1g COD = 1g O_2 = 0.03125 mol O_2
= 0.0625 mol H_2O_2 = 2.125 g H_2O_2

The variables and design conducted to the treatment were as shown as Table 1 below:

Table 1 Experimental factors and ratio/levels

Factor	Ratio / level				
H_2O_2/COD	1.06	1.59	2.12	2.65	3.18
Fe / COD	0.5	1.0	1.5	2.0	-
pH	2.5	3.0	3.5	-	-

2.2.2 Solar Fenton Oxidation

As the pretreatment, the sulfuric acid was added until the pH reached 3.0 and was stirred for 20 minutes to remove all carbonate species (HCO^{3-}/CO_3^{2-}), which are known to be hydroxyl radical scavengers [25]. The temperature was kept at 20-30°C and the reaction of the mixture inside the cell was continuously maintained by magnetic stirring and left under solar irradiation (>100 W/ m^2). The F1 was run in 4L of samples of Palm Oil Mill Secondary Effluent (POMSE) according to the mass optimization results. After treatment, the solutions were left for 4 hours retention time so that the liquid-solid mixture of sludge and the effluent were well separated.

2.2.3 Sludge Preparation

Sludge was prepared in two phases a) wet Fenton sludge b) dried Fenton sludge. The wet Fenton sludge from F1 was decanted and thickens with 3000rpm centrifuge for 5 minutes. While the dried Fenton sludge was decanted, thicken and undergo drying process. The sludge is placed in 105°C oven for 1 hour to remove the organic content before undergo calcination process in furnace to remove the carbonate at 550°C for 15minutes [23].

2.2.4 Solar Fenton Oxidation using Fenton Sludge As Iron Sources/Catalyst

The Fenton sludge from F1 was recovered and reuse for the next Fenton process in the new wastewater sample, and produce R1. The efficiency of using the recycle sludge in treating the POMSE were determined by five times recycle (producing R1-R5) and compared with the POMSE treated with only hydrogen peroxide, H_2O_2 (non-catalyst). The procedure were as same as the Solar Fenton Oxidation process, just the ferrous salt were replace by recovered wet Fenton sludge / dried Fenton sludge.

2.3 Analytical Method

COD were digested by COD reactor and determined using HACH DR2800 Spectrometry according to Method 8000-Reactor Digestion Method. Color and TSS were determined by using a HACH DRB280 Spectrometry based on 10048-ADMI Weighted Ordinate Method and 8006, respectively. Meanwhile, the turbidity was determined with a turbidity meter, Digimed DM-TU. Centrifugation process was run using the Centurion Scientific K3 Series Centrifuge (UK) (model K241R) and the solar irradiation was recorded by Solar Meter (EKO, MS-02).

3.0 RESULTS AND DISCUSSION

3.1 Optimization

3.1.1 Effect of Different pH

pH plays a very important factor in Fenton process as iron will present as iron oxohydroxides in the form of ferric precipitation at higher pH [6]. Thus, it will slow the Fenton reaction as less iron free ion will produced less hydroxyl radical [26]. Besides that, hydrogen peroxide will automatically decompose to H_2O and O_2 as the pH is increase. This explains why the pH is raised up to 10 to ensure there are no more excess H_2O_2 that may interfere the COD reading. In the other hand, at lower pH, iron will be present as $Fe(H_2O)_6$ and this complex will react slowly with H_2O_2 [27]. Figure 1 shows the percentage removals of COD and color in different pH.

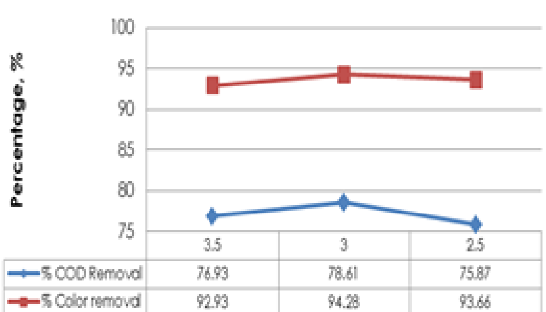


Figure 1 Percentage removals of COD and Color in different pH

3.1.2 Effect of Different Time Contact

Figure 2 shows the percentage removal of COD and color in 5 different time exposes, 15, 30, 60, 120, and 180min. The rapid removal was achieved during the first 15 minutes, and then reached plateau until 180 minutes. At 180 minutes, the removal for COD and color were only 87.14% and 96.92% compared to 83.14 and 96.3% in first 15 minutes. The results showed that the reaction occurs after 15 minutes are the slow reaction. This result was similar to [24] and [26].

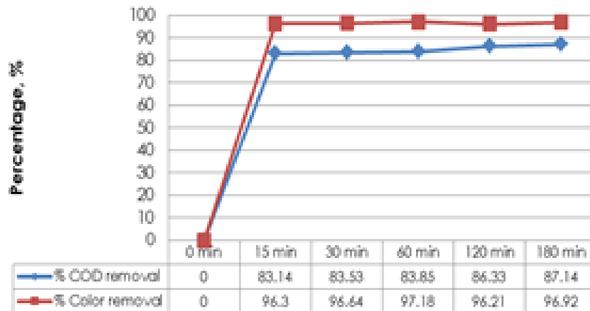


Figure 2 Percentage removals of COD and Color in different time contact

3.1.3 Effect of Different H_2O_2 Dosage and Fe Dosage

In order to find out the optimum condition (mass ratio of H_2O_2/COD and H_2O_2/Fe) in Fenton reaction, the total of 60 sets of experiment (triplicate) with different operating condition were conducted. All experiments were conducted in 60 minutes time, pH 3. In Figure 3 and 4, it is clearly observed that the H_2O_2/Fe is directly proportional to the COD and color removal. However, excessive of H_2O_2 may cause unutilized of hydroxyl radical whereas the abundant of iron may cause increase in sludge production. The excess of H_2O_2 influenced the settling time, TSS and turbidity. The percentage of COD and color removal in different H_2O_2/COD and Fe/COD mass ratio were presented in Figure 3 and 4.

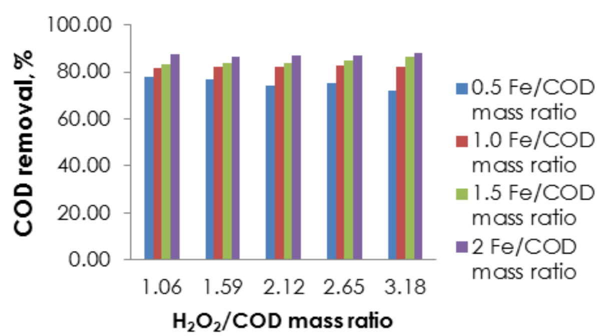


Figure 3 Percentage of COD removals in different H_2O_2 /COD mass ratio and different Fe/COD mass ratio

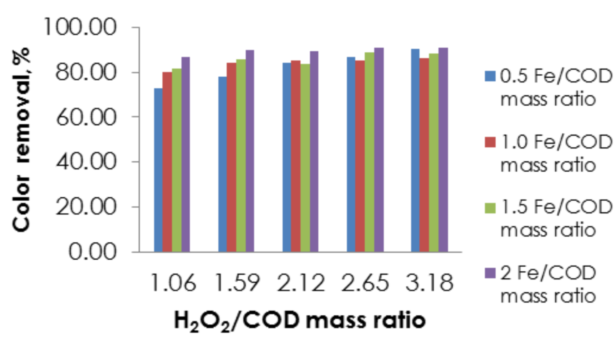


Figure 4 Percentage of Color removals in different H_2O_2/COD mass ratio and different Fe/COD mass ratio

[26] stated that unutilized H_2O_2 will decompose into oxygen bubbles, causing the difficulty during sludge settling. Besides, the ratio of H_2O_2/COD should not be more than 2.0 as it could give detrimental effect [13] since these species can react with other intermediates like OH**.** as depicted below:

$$H_2O_2 + OH. \rightarrow HO._2 + H_2O \quad (4)$$

$$Fe^{2+} + OH. \rightarrow OH^- + Fe^{3+} \quad (5)$$

$$Fe^{2+} + HO._2 \rightarrow HO_2^- + Fe^{3+} \quad (6)$$

$$Fe^{3+} + HO._2 \rightarrow O_2 + Fe^{2+} + H^+ \quad (7)$$

The removal of COD, color, TSS and turbidity is direct proportional to $FeSO_4$/COD ratio. However, higher ratio of $FeSO_4$/COD might lead several problems: 1) additional of treatment steps for Fe removal / sludge removal 2) darker the color solution, thus reduced the solar penetration to the solution during treatment process [13] and 3) cause hydroperoxyl radicals scavenger [28]. In addition, [29] suggested that the ratio of H_2O_2 to $FeSO_4$ should be as small as possible to avoid the recombination of free radical and reduce the sludge production from iron complex. Figure 5 and 6 show removal percentage of turbidity and total suspended solid, TSS.

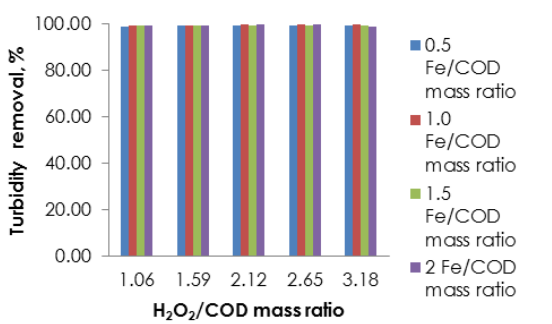


Figure 5 Percentage of turbidity reduction in different H_2O_2/COD mass ratio and different Fe/COD mass ratio

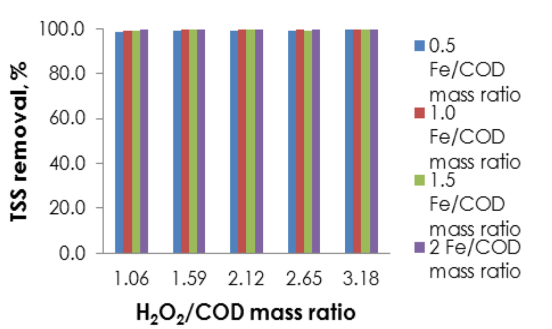


Figure 6 Percentage of TSS reductions in different H_2O_2/COD mass ratio and different Fe/COD mass ratio

Almost 100% of turbidity and TSS removal were achieved at the lowest H_2O_2/COD and Fe/COD ratio. This is expected as Fenton reaction is proved to have good settling and compaction properties [30]. According to [30], Fenton treatment have high sludge settling rates(V_S), approximately 0.16cm s^{-1} and low sludge volume index (SVI) (<100mLg^{-1})and volumes of settled sludge (SSV) < 50 min s^{-1}.

3.2 Potential Use of Wet and Dried Sludge in Removal COD, Color, Turbidity and TSS.

After optimization, this works use the mass ratio of $FeSO_4$/COD and H_2O_2/COD, 1:1 and 1.59 after considering the fact that mention that the ratio of H_2O_2/COD should not be more than 2.0 as it could give detrimental effect. [13] and [29] stated that the ratio of H_2O_2 to $FeSO_4$ should be as small as possible to avoid scavengers of radicals and to reduce formation of iron complex.

3.2.1 COD Removal

Results showed wet Fenton sludge has better capability in reducing the contaminant compared to the dried Fenton sludge. Figure 7 shows the percentage removal of COD using wet, dried and also the comparison with the treatment using only H_2O_2 (non-catalyze). The removal of COD is decreased in every next cycle in the wet treatment, parallel with [20]. Compared to the dry treatment, COD removal in wet treatment is almost 40% better than dried treatment. However, the removal is not much different than the blank, 60%.

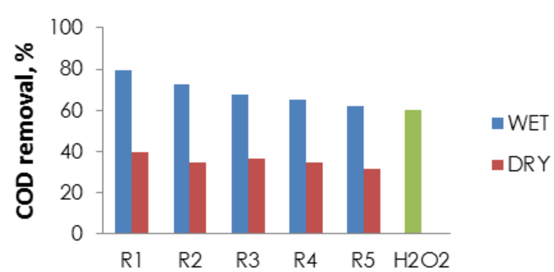


Figure 7 Percentage of COD removals for wet and dry sludge as compared with blank

This indicated that the remaining of iron content in the wet sludge only helps a small percentage in removing the COD (in the recycle batch), the rest, the reaction were depending on the hydrogen peroxide, H_2O_2 itself. Low removal recorded in dry sludge compared to others. This might due to the iron leaching during calcination process. In addition, high temperature during treatment not only helps in removing carbonate and organic, but may cause leaching of iron in sludge that eventually affected the catalyst effectiveness [31].

3.2.2 Color Removal

Removal of color in treated POMSE using wet and dry sludge was showed in Figure 8. The results were also compared with the treatment using H_2O_2 (non-catalyst).

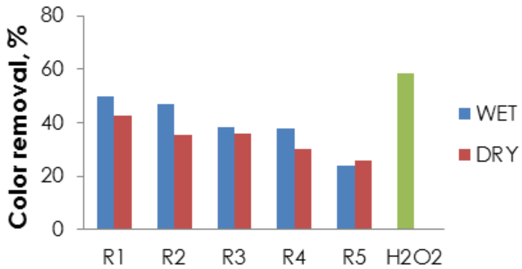


Figure 8 Percentage of Color removals for wet and dry sludge as compared with blank

In color removal, both the recycle sludge showed lower removal compared to the blank that only use H_2O_2 (without ferrous salt). From the observation, it is clear that the use of recycle wet /dried sludge has contributed to the increase of COD, color, turbidity and TSS to the next batch of recycle. This explains why the percentage removal decreased in every recycle batch. On the other hand, the use of only H_2O_2 (non-catalyst) do not include the adding of any particle inside the batch, thus, it can remove color better than the recycle batch.

3.2.3 Turbidity and TSS Reduction

Reduction of turbidity and TSS for wet and dry sludge together with blank was plotted in graph Figure 9 and 10.

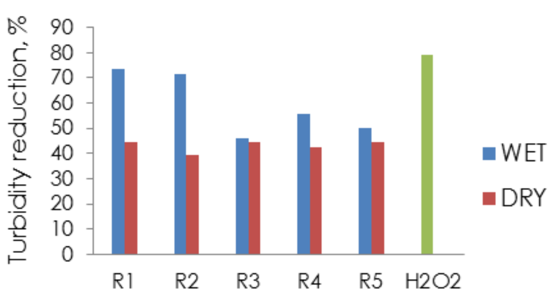


Figure 9 Percentage of turbidity reduction for wet and dry sludge as compared with blank

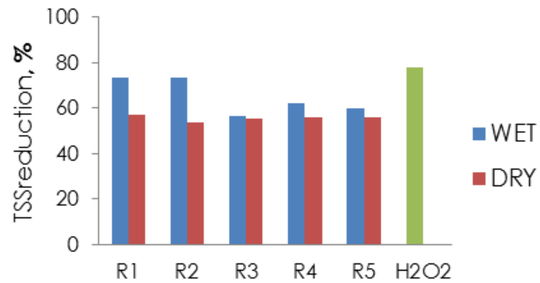


Figure 10 Percentage of TSS reductions for wet and dry sludge as compared with blank

Wet Fenton sludge showed high capability for turbidity and TSS removal compared to dried Fenton sludge. In conducting Fenton process using wet sludge, the amount of the sludge produced depends on the initial untreated POMSE that been used. The suspended solids presences in the untreated POMSE contribute to the amount of sludge produced after the end of each treatment. However, it is noticed that the amount of sludge were reduced up to 80% from the first treatment (F1) to the fifth recycle (R5). In contrast, for dried sludge experiment, a total amount of 200ml sludge (from F1) has been dried and this made up to 5.16g of dry sludge. This amount is slightly decreased from R1 (5.16g) to R5 (3.46g). Thus, the percentage removal is slightly same from R1 to R5.

In addition, iron levels in the sludge reduced as the sludge lessen. Decomposition of extra and unutilized H_2O_2 into H_2O and O_2 caused inefficient during settling process, resulting the increasing of TSS and turbidity level. Bubbles produced from decomposition of unutilized H_2O_2 into O_2 interfered the sludge settling process, and eventually causing inefficient in TSS and turbidity removal [26].

3.3 Characterization of Sludge and Reduction of Sludge Amount During Treatment

Recycling the Fenton sludge in Fenton treatment without adding any additional catalyst could reduce the sludge amount. Table 2 summarized the characteristic of Fenton sludge.

Table 2 Characteristic of Sludge

Parameters	
Color	Brownish.
Specific gravity	2.4 - 2.5
Moisture %	91.9%
TSS,mg/L	4050
VSS,mg/L	2760
VSS,%	68.15%

In this experiment, the initial sludge that produced in the first treatment (4L POMSE) built up a 200ml thick sludge. After 5 times recycling of this sludge and without adding extra ferrous salt in the batch, the amount of the sludge could reduce to 35ml. The reduction is almost 82.5%. However, it is worth to mention that the reuse of sludge had reduce the iron contained, thus the consistent amount of H_2O_2 that inserted to the solution were unutilized. This excess of H_2O_2 will produce hydroxyl radical that eventually will act as scavengers to each other. Thus, it is suggested to add a lower amount of Fe in the recycle sludge to help in balancing the amount of H_2O_2 inserted

4.0 CONCLUSION

It is justifiable to recycle the Fenton sludge, however, the use of recycle wet sludge / dried sludge had caused the solution to be cloudy and reduced the irradiation penetration to the solution. The separation of the sludge and effluent is inefficient and took longer time. The difficulties in settling process caused increase in TSS and turbidity. Thus, it is assumed that the sludge mix from early treatment has added up the suspended solid, thus increase the color, TSS and turbidity.

In conclusion, the percentage reduction using wet sludge as iron sources in removing COD, color, turbidity and TSS is higher than the percentage of using dry sludge. The utilization of recycle sludge repeatedly has caused increase in TSS and turbidity whereas the high temperature in calcination process is expected to cause iron leaching in Fenton sludge. Thus, it is recommended to add a small amount of Fe salt so that the reaction could react in optimum condition as the H_2O_2 is introduced in the system or addition for some coagulant and to reduce the time in calcination process.

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