ORIGINAL ARTICLE

Optimization of Fenton Oxidation Process for the Palm Oil Mill Effluent (POME) Treatment and Its Phytotoxicity Effect

Syuhaini Binti Ramli[1], Mohd Yusmaidie Aziz[2], Farah Ayuni Shafie[1], Ahmad Razali Ishak[1]

[1] Centre of Environmental Health and Safety, Faculty of Health Sciences, Universiti Teknologi MARA Selangor, Malaysia
[2] Integrative Medicine Cluster, Advanced Medical and Dental Institute, SAINS@Bertam, Universiti Sains Malaysia 13200 Kepala Batas, Penang, Malaysia

ABSTRACT

Introduction: : High incidence of surface water pollution contributed by palm oil mill effluent (POME) is implacable and proper treatment of the effluent is necessary. **Methods:** Thus, the feasibility of Fenton treatment for turbidity reduction of POME was investigated to obtain the optimum operating conditions such as reaction time, pH, H_2O_2 dosage and H_2O_2: Fe^{2+} ratio followed by the phytotoxicity study of the treated POME. **Results:** A fast reaction of Fenton was achieved within 10 minutes of treatment, which successfully removed ~87% of the turbidity. The Fenton reaction was favorable in acidic condition whereby 87% of turbidity were successfully removed at pH 3. The highest percentage of turbidity removal at 86% was obtained and optimized at 25 mM of H_2O_2 with 1:1 ratio of H_2O_2: Fe^{2+}. On the other hand, the phytotoxicity of treated POME that was evaluated based on the germination index of mung beans and lady finger showed a decline of the relative toxicity from 70% and 80% of mung beans and lady finger to 40% and 70%, respectively. The final chemical oxygen demand (COD) concentration of treated POME at 127 mg/L was compliant with Malaysian discharge standard. **Conclusion:** These findings indicate that Fenton reaction is effective to be utilized for POME treatment.

Keywords: POME, Turbidity, Fenton oxidation, Phytotoxicity

Corresponding Author:
Ahmad Razali Ishak PhD
Email: ahmadr2772@uitm.edu.my
Tel: +603-32584509

INTRODUCTION

The palm oil industry is crucial to Malaysia's economy, as it helps to meet the country's rising population demand. There are 453 operating mills throughout Malaysia with the total production of 19.5 million tonnes of crude palm oil every year (1). Despite its economic value and massive development of palm oil plantations, this industry undeniably generates some environmental problems such as deforestation and habitat degradation. In addition, it also contributes to surface water pollution due to the generation of palm oil mill effluent (POME) (2). Since no chemicals are used in the oil extraction process, POME is a non-toxic greasy waste water generated from palm oil processing mills. However, this wastewater contains high levels of organic compounds such as chemical oxygen demand (COD) and biological oxygen demand (BOD), which raise environmental concerns due to their ability to deplete oxygen in aquatic environments. To handle POME, a few typical methods have been used, including an open decomposing tank, an advanced ventilation system, a closed anaerobic decomposition tank, and organic fertiliser composting. However, all these methods require longer retention time and a larger space of treatment facility (3). In addition, most of the treated POME from conventional treatment methods do not comply with Malaysian discharge standards which require COD and BOD values not exceeding 1000 mg/L and 100 mg/L, respectively (4).

Advanced oxidation processes (AOPs) are gaining traction as a promising new approach for treating industrial wastewater, such as POME. AOPs have a quick reaction time and non-selective oxidation, allowing several contaminants to be treated at the same time (5). Fenton is one of the AOP that has been used in the full-scale treatment of wastewater from various industries such as pulp & paper, food, textile and pharmaceutical (6). To produce hydroxyl radicals, hydrogen peroxide (H_2O_2) was used as an oxidizing reagent, and iron (II) (Fe^{2+}) was used as a catalyst (7). The radicals immediately react with numerous species of organic matter with the rate constants of 10^8 - 10^{10} $M^{-1} s^{-1}$ (8). The radicals break down and convert the organic pollutant into less dangerous compounds, providing the ultimate wastewater treatment solution (8). Fenton-based reactions do not require high costs because the chemical reaction could perform under ambient temperature and no illumination is required. Furthermore, the reagents are available, easy to store, safe and non-toxic to the environment (9). The goals of this study were to (1) optimize the Fenton treatment parameters for removing turbidity, COD, colour, and NH_3N from POME, and (2) assess the phytotoxicity of the treated POME using mung beans and lady fingers.

METHODS AND MATERIALS

Palm Oil Mill Effluent (POME)

POME was obtained from an oil palm mill from Sime Darby plantations, Selangor, Malaysia. The sample was kept in a 15 L plastic container at 4 °C before further analysis.

Reagents and Instrumental analysis

The turbidity, pH, NH3N and COD of POME were measured using APHA-approved methods (10). Hydrogen peroxide (H_2O_2), ferrous sulphate (Fe_2SO_4), sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4) were purchased from Merck (Darmstadt, Germany). Ammonia salicylate and ammonia cyanurate were obtained from HACH (Colorado, USA).

Fenton Treatment

The experiment began with 40 ml of POME in a vial, accompanied by addition of oxidants and Fe_2SO_4 to achieve a total volume of 50 ml. The mixtures were shaken at 150 rpm with an orbital shaker. The treatments were carried out at room temperature. Four optimum operating conditions of the Fenton process; reaction time, ratio H_2O_2 to Fe^{2+} (H_2O_2:Fe^{2+}), H_2O_2 dosage and pH were obtained based on the turbidity removal efficiency. The efficiency of the removal was calculated based on the Equation 1:

$$\text{Removal Efficiency } (\%) = \frac{\text{Raw POME - Treated POME}}{\text{Raw POME}} \times 100 \quad (1)$$

Phytotoxicity Test

The phytotoxic effect of untreated and treated POME was investigated based on the seed germination of mung beans (*Vigna radiata*) and lady fingers (*Abelmoschus esculentus)*. The procedure was modified from the method published by Noel et al. (11). Twenty sterilized seeds were placed in the petri dishes containing untreated or treated POME. The germination % was recorded after 48 hours and the relative toxicity was calculated using the following equation;

$$\text{Germination Index } (\%) = \frac{\text{Number of Seed Generation}}{\text{Number of Total Seed}} \times 100 \quad (2)$$

$$\text{Relative Toxicity} = \frac{\text{(GP Contol - GP Test)}}{\text{GP Control}} \times 100 \quad (3)$$

RESULTS

POME Characterization

The collected POME in this study was initially screened for the physicochemical characteristics. Table I shows the physicochemical results of the untreated POME which consists of 1080 mg/L COD, 399 NTU turbidity, pH 5.5 and 8.0 mg/L of NH_3N.

Table I : Physicochemical characteristics of untreated POME

Parameter	Mean ± SD
pH	5.5 ± 0.1
COD (mg/L)	1080 ± 8
NH_3N (mg/L)	8.0 ± 0.1
Turbidity (NTU)	399 ± 12
Colour (Pt/Co)	9586 ± 15

Fenton Optimisation

Variations in reaction time (5, 10, 15, 20, 25 and 30 min), pH (3, 5, 7, 9 and 11), H_2O_2 dosage (20, 25, 30, 35, and 40 mM), and the H_2O_2 to Fe^{2+} ratio (H_2O_2:Fe^{2+}) (1:.05, 1:1, 1:2, 1:3, 1:4) were used to improve the Fenton process's operating conditions. The experiment began with an analysis of turbidity removal as a function of reaction time, whereby POME turbidity was removed, up to 87% for the first 10 minutes of reaction (Figure 1a). After 15 to 30 minutes, the turbidity was gradually removed but the reaction occurred slowly at approximately an average 4% increase. As a result, 10 minutes of reaction time was chosen for further research due to its faster reaction rate, high performance, and short duration. After that, the effect of pH on turbidity removal was tested at pH levels ranging from 3 to 11. As shown in Figure 1b, pH has an important impact on the efficiency of the Fenton reaction in removing turbidity. At pH 3, the turbidity removal had reached its peak efficiency of 87%. When the pH was raised to 7, however, the turbidity removal rate steadily decreased to 64%.

The optimal Fenton treatment dosage for turbidity removal was determined by varying the H_2O_2 dosage from 15 to 40 mM while keeping the H_2O_2:Fe^{2+} ratio constant at 1:1. (Figure 1c). Turbidity removal efficiency was observed to spike from 28 to 86% by increasing H_2O_2 dosage from 15 to 25 mM. However, the turbidity removal efficiency for 30, 35 and 40 mM of H_2O_2 were declined to 43, 60 and 57%, respectively. The effect of the H_2O_2:Fe^{2+} ratio on turbidity removal was investigated by changing the Fe^{2+} concentration from 12.5 to 100 mM while keeping the H_2O_2 concentration constant at 25 mM. At pH 3, the turbidity removal was controlled after 10 minutes of reaction time. When the ratio of H_2O_2 to Fe^{2+} was adjusted from 1:0.5 to 1:1, turbidity removal increased from 63% to 86% (Figure 1d).

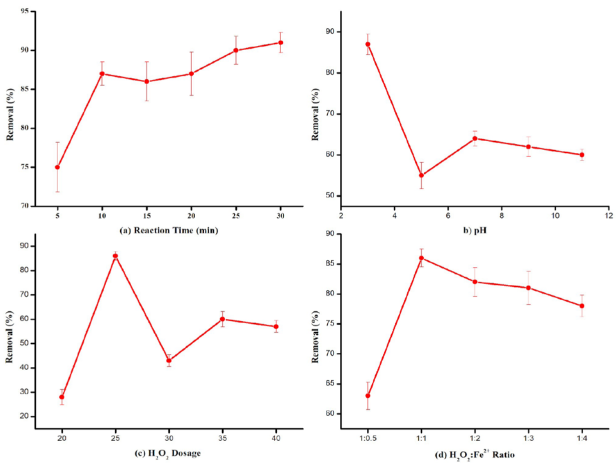

Figure 1: Effect of operating parameter on turbidity removal; (a) reaction time, (b) pH, (c) H_2O_2 Dosage and (d) H_2O_2:Fe^{2+} ratio.

Toxicity Analysis

Seed germination test of mung beans (*Vigna radiata*) and lady finger (*Abelmoschus esculentus*) was evaluated to assess POME phytotoxicity. Germination index of both plants was improved in treated POME compared to untreated POME (Table II). The relative toxicity for both plants were reduced from 70% and 80% in the untreated POME to 40% for mung beans and 70% for lady fingers after the Fenton treatment.

Table II: Treated POME after Fenton treatment

Parameter	Mean ± SD	% of Removal
COD (mg/L)	127 ±12	88
NH_3N (mg/L)	1.4 ± 0.5	82
Turbidity (NTU)	23.5 ± 5.5	94
Colour (Pt/Co)	341± 10	96

DISCUSSION

Based on Table III, a typical POME is normally characterized by high concentration of COD, acidic pH in the range of 3.4 – 5.5 and NH_3N in the range of 4-80 mg/L (12). High COD levels observed in the untreated POME samples indicate high concentration of organic compounds, which can accelerate the bacterial growth in the water bodies. This may result in the competition between microorganisms and aquatic life for the oxygen uptake. Massive growth of microorganism and lack of oxygen for aquatic livings may lead to extinction of certain species (3). Thus, proper treatment of POME before being discharged into the environment was necessary.

The Fenton oxidation process is one of the most efficient and appropriate methods for reducing organic contaminants such as POME (13). Operating parameters such as reaction times, pH, oxidants dosage and oxidants-catalyst ratio were amongst the factors that determine the effectiveness of Fenton treatment. The highest turbidity removal of POME was observed in this study after only 10 minutes of Fenton reaction. The rate of reaction is extremely fast, and it is influenced by a variety of factors such as the pH of the solution, the concentration of iron salts, and the amount of H_2O_2 supplied (14). This finding was in agreement with Deng and Engelhardt (14), stating that Fenton treatment usually demonstrated faster reaction rate compared to other biological and physicochemical treatments.

Table III: Germination index and relative toxicity of mung beans (Vigna radiata) and lady finger (Abelmoschus esculentus).

Treatments	Germination Index (Relative Toxicity)	
	Mung beans (*Vigna Radiata*)	Lady finger (*Abelmoschus esculentus*)
Untreated POME	30 (70± 5)	20 (80± 5)
Treated POME	60 (40± 5)	30 (70± 5)

The chemistry of Fenton treatment requires the reaction to be carried out in acidic condition. According to the previous research, pH 3-4 is the most preferable condition of Fenton due to higher catalytic activity (8, 14). The pH higher than 4 contributes to the formation of hydroxide precipitation, thus preventing the activation of hydroxyl radical (15). In addition, self-decomposition of H_2O_2 into O_2 and H_2O limits the availability of hydroxyl radicals for destruction of organic matters (16). Since it removes the highest turbidity with 87% removal, pH 3 was chosen as the optimum pH condition for the treatment.

The amount of H_2O_2 in the treatment system is critical in determining the overall efficiency of the Fenton process. The increased amount of H_2O_2 will increase the hydroxyl radical production as depicted in equation 4 (17). However, the formation of hydroxyl radicals only limited to certain dosages since the excess oxidants amount will also scavenges the hydroxyl radical production as illustrated in the Equation 5.

$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$ (4)

$H_2O_2 + \cdot OH \rightarrow H_20 + \cdot H_2O$ (5)

Another important parameter in Fenton treatment is the ratio between the oxidant and catalyst. It was noted that sufficient catalyst (Fe^{2+}) is compulsory to generate an adequate amount of hydroxyl radical. An increase of catalyst dosage in the Fenton reaction generates more hydroxyl radicals from H_2O_2 as illustrated in Equation 6 (14). The inadequate amount of Fe2+ to trigger the Fenton reaction resulted in lower turbidity removal at a lower ratio (1:0.5), which decreased the amount of hydroxyl radical production (17). The turbidity removal was also significantly reduced in the higher ratio of H_2O_2:Fe^{2+} (1:2–1:5) due to the excess amount of Fe^{2+} ions that scavenge the hydroxyl radical, as shown in Equation 7.

$Fe^{2+} + H_20_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O$ (6)

$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$ (7)

The treated POME toxicity was evaluated using Seed germination test of mung beans *(Vigna radiata)* and lady finger *(Abelmoschus esculentus)*. So far, no proper standard has been set up for the toxicity of POME before discharge into the environment. Most of the standards are developed based on the physicochemical parameters such as COD, BOD, heavy metals, NH_3N etc. Besides, high concentration of organic pollutant removal efficiency may not always reflect the toxicity reduction. Seed germination test has been widely used as short-term phytotoxicity test to provide valuable information about root growth inhibition, plant enzymes activation, cell expansion and other parameters (18). The test is fast, simple, cost-effective and sensitive with minimal operational cost. With all the advantages, germination test is ideally suitable as a rapid toxicity test and cost-effective tool to evaluate the toxicological risk of different pollutants including POME.

CONCLUSION

In this study, the efficiency of Fenton reaction for the treatment of POME was successfully evaluated. Optimization of Fenton treatment conditions was obtained at 10 minutes reaction times, acidic medium at pH 3, 25 mM of H_2O_2 dosage and 1:1 H_2O_2:Fe^{2+} ratio to remove the COD, NH_3N, colour, and ~ 80% turbidity. The treated POME also demonstrated reduction of phytotoxicity. Based on the observed findings in this study, the treated POME is considered in compliance to Malaysian Environmental Quality (Prescribed Premises) (Crude Palm-Oil) Regulations 1977.

ACKNOWLEDGEMENTS

We thanked to the Faculty of Health Sciences, Universiti Teknologi MARA (UiTM) for the technical assistances rendered.

REFERENCES

1. Azman I. The impact of palm oil mills' capacity on technical efficiency of palm oil millers in Malaysia. Oil palm industry economic journal. 2014;14(1):34-41.
2. Choong YY, Chou KW, Norli I. Strategies for improving biogas production of palm oil mill effluent (POME) anaerobic digestion: A critical review. Renewable and Sustainable Energy Reviews. 2018 Feb 1;82:2993-3006.
3. Iskandar MJ, Baharum A, Anuar FH, Othaman R. Palm oil industry in South East Asia and the effluent treatment technology—A review. Environmental technology & innovation. 2018 Feb 1;9:169-85.
4. Environmental Quality (Prescribes Premises) (Crude Palm-Oil) Regulations. Malaysia; 1977.
5. Krishnan S, Singh L, Sakinah M, Thakur S, Wahid ZA, Ghrayeb OA. Role of organic loading rate in bioenergy generation from palm oil mill effluent in a two-stage up-flow anaerobic sludge blanket continuous-stirred tank reactor. Journal of cleaner production. 2017 Jan 20;142:3044-9.
6. Ishak AR, Hamid FS, Mohamad S, Tay KS. Stabilized landfill leachate treatment by coagulation-flocculation coupled with UV-based sulfate radical oxidation process. Waste Manag. 2018 Jun 1;76:575–81.
7. Ghanbari F, Moradi M, Manshouri M. Textile wastewater decolorization by zero valent iron activated peroxymonosulfate: compared with zero valent copper. Journal of Environmental Chemical Engineering. 2014 Sep 1;2(3):1846-51.
8. Deng Y, Zhao R. Advanced Oxidation Processes (AOPs) in Wastewater Treatment. Vol. 1, Current Pollution Reports. Springer; 2015. p. 167–76.
9. Mirzaei A, Chen Z, Haghighat F, Yerushalmi L. Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes–A review. Chemosphere. 2017 May 1;174:665-88.
10. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Water Environment Federation. Standard methods for the examination of water and wastewater. American Public Health Association.; 1912.
11. David Noel S, Rajan MR. Phytotoxic effect of dyeing industry effluent on seed germination and early growth of lady's finger. J. Pollut. Eff. Contr. 2015;2(126):10-4172.
12. Nahrul HZ, Nor FJ, Ropandi M, Astimar AA. A review on the development of palm oil mill effluent

(POME) final discharge polishing treatments. Journal of Oil Palm Research. 2017;29(4):528-40.
13. Zhang MH, Dong H, Zhao L, Wang DX, Meng D. A review on Fenton process for organic wastewater treatment based on optimization perspective. Science of the total environment. 2019 Jun 20;670:110-21.
14. Deng Y, Englehardt JD. Treatment of landfill leachate by the Fenton process. Water research. 2006 Dec 1;40(20):3683-94.
15. Ishak AR, Hamid FS, Mohamad S, Tay KS. Removal of organic matter from stabilized landfill leachate using Coagulation-Flocculation-Fenton coupled with activated charcoal adsorption. Waste Management & Research. 2017 Jul;35(7):739-46.
16. Vasquez-Medrano R, Prato-Garcia D, Vedrenne M. Ferrioxalate-mediated processes. InAdvanced Oxidation Processes for Waste Water Treatment 2018 Jan 1 (pp. 89-113). Academic press.
17. Babuponnusami A, Muthukumar K. A review on Fenton and improvements to the Fenton process for wastewater treatment. Journal of Environmental Chemical Engineering. 2014 Mar 1;2(1):557-72.
18. Wang X, Sun C, Wang Y, Wang L. Quantitative structure-activity relationships for the inhibition toxicity to root elongation of Cucumis sativus of selected phenols and interspecies correlation with Tetrahymena pyriformis. Chemosphere. 2002 Jan 1;46(2):153-61.