An enhanced treatment efficiency for diluted palm oil mill effluent using a photo-electro-Fenton hybrid system

NORALISYA ALI¹, CHEE BENG YEOH², SENG LAU¹ and MENG GUAN TAY¹*

¹Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia and ²Malaysian Palm Oil Board, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia

(Received 16 October, accepted 29 November 2018)

Abstract: Photocatalysis, electrolysis and Fenton process are three important advanced oxidation processes (AOPs) which produce hydroxyl radical in order to degrade organic matter in wastewater within 4-6 hours under ambient conditions. A photocatalysis, electrolysis and Fenton (photo-electro-Fenton) process hybrid system has been carried out to treat the diluted palm oil mill effluent (POME) in this study. An electrolytic cell was set up with a stainless steel anode and a platinum wire cathode with the applied cell voltage of 1.5 V. The diluted POME was then treated in the cell with the mixture of titanium oxide as the photocatalyst, sodium sulfate solution as the electrolyte, hydrogen peroxide and iron sulfate as the Fenton reagents. The effects on the duration, pH, concentration of TiO₂ and different light conditions on the removal efficiency of the chemical oxygen demand (COD) of the diluted POME were studied. The optimal conditions for the photo-electro-Fenton hybrid system were found to be 4 hr contact time at pH 4 with 60 mg/L TiO₂ under sunlight. With such conditions, the COD removal efficiency was able to achieve 97%. On the other hand, the photo-electro-Fenton hybrid system gave the highest COD removal efficiency, compared to the electro-Fenton hybrid system, Fenton and photocatalyst, respectively.

Keywords: photo-electro-Fenton hybrid system; advanced oxidation process (AOP); Fenton; palm oil mill effluent (POME).

INTRODUCTION

Advanced oxidation processes (AOPs) are defined as the processes that generate hydroxyl radicals (·OH) in sufficient quantities to degrade organic matter and nutrients present in the wastewater effluents. Among the AOPs, photocatalysis, electrolysis and Fenton process, in particular, were widely studied and used in various industries because of their low costs, ease of operation, highly

* Corresponding author. E-mail: mgtay@unimas.my
https://doi.org/10.2298/JSC181016103A

517
efficient and rapid treatment.\textsuperscript{1,2} In general, the principle of \({}^{\bullet}\text{OH}\) formation in the three AOPs are summarized in Eqs. (1)–(4).\textsuperscript{3–5}

**Photocatalysis:**
\[
\text{TiO}_2 \rightarrow \text{TiO}_2 (e^-_{\text{BC}} + h^+_{\text{BV}}) 
\]
\[
h^+ + \text{H}_2\text{O} \rightarrow {}^{\bullet}\text{OH} + \text{H}^+ \quad (2)
\]
where \(e^-\) is electron and \(h^+\) is hole.

**Electrolysis:**
\[
\text{H}_2\text{O} \rightarrow {}^{\bullet}\text{OH} + \text{H}^+ + e^- \quad (3)
\]

**Fenton process:**
\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + {}^{\bullet}\text{OH} + \text{OH}^- \quad (4)
\]

Despite the ability of each of the AOP above to generate the \({}^{\bullet}\text{OH}\) in their own way, each of them produces \({}^{\bullet}\text{OH}\) at different rates and it is subjected to various inhibitions. For example, the Fe(II) catalyst in Fenton process could form Fe(OH)\(_3\) brown precipitate, which is no longer active in the catalytic cycle in Fenton process. In the case of photocatalysis, the light source and its intensity are important to activate the TiO\(_2\) to produce hole in the reaction; whereas for electrolysis, the electrolyte, redox potential and electrodes play vital roles in generating a sufficient amount of \({}^{\bullet}\text{OH}\).

Palm oil mill effluent (POME) has been classified as highly pollutant containing wastewater due to its high amount of nutrient (i.e., ammoniacal nitrogen = 220 mg/L) and organic matter (i.e., COD value = 50000 mg/L).\textsuperscript{6–8} Thus, POME requires an extremely efficient treatment technology to ensure the effluent complies with the discharge requirements set by the Department of Environment (DoE), Malaysia. In 2017, we reported the hybridization of electrolysis and Fenton process for the diluted POME treatment, and a maximum of 94 \% of COD removal efficiency was recorded in the previous study.\textsuperscript{9} It is worth to note that the hybridization of electrolysis and Fenton process improved the COD removal efficiency by 48 \%, when compared to the Fenton process alone. Align to this improvement, we extended the study to hybridize three AOPs, namely, photocatalysis, electrolysis and Fenton processes for the treatment of diluted POME with the aim to further improve the treatment efficiency.

**EXPERIMENTAL**

**Chemicals**

All the chemicals such as hydrogen peroxide, titanium dioxide, sodium sulfate, iron(II) sulfate and reagents for COD determination were purchased from either Sigma-Aldrich, Merck or Acros, and used without further purification. Distilled water was used for dilution purposes and COD reagents’ preparation.

**Sampling of POME**

The POME samples were obtained in Oct 2017 from the cooling pond of the Bau Palm Oil Mill as previously described in Lim \textit{et al.}\textsuperscript{9} The samples were then transported to Universiti Malaysia Sarawak, Malaysia, and kept in a refrigerator at 4 °C.
COD analysis

COD analysis was performed according to the Standard Method (5220B) APHA (1992). The samples were analyzed under the same procedures as described in literature Lim et al. also.9

Electrolysis with H₂O₂

An electrochemical cell with 500 mL capacity was set up for the electrolysis treatment. A platinum wire electrode was used as the cathode while a stainless steel electrode was acted as the anode. Both electrodes were immersed into 250 mL of the mixture solution containing 75 mL of 0.25 M Na₂SO₄, 75 mL of 35 % H₂O₂, 50 mL of 0.05 M FeSO₄ and 50 mL of diluted POME solutions. A 1.5 V of DC voltage was applied to the cell. All the experiments were conducted at room temperature (22±2 °C).

Optimization of photo-electro-Fenton for diluted POME degradation

Contact time. The experiments were performed on the reaction mixtures as aforementioned in Electrolysis with H₂O₂. The set up was placed under UV light (Ultraviolet A lamp, Philips, 15 W, 315–400 nm) as shown in Fig. 1. The experiments were conducted over 5 h with sample withdrawal at 1 h interval for COD analysis. Each test was repeated three times. The COD removal efficiency in % was calculated based on Eq. (5). The highest efficiency represented the optimal condition of the test. Thus, the optimal conditions were used in the subsequent experiments:

\[
\text{COD removal efficiency, \%} = 100 \left( \frac{\text{Initial COD} - \text{Final COD}}{\text{Initial COD}} \right) \tag{5}
\]

Fig. 1. Set up of photo-electro-Fenton cell.

pH. The experiments were performed under the same conditions as described in the Section of contact time, the optimal contact time used was same as found in the previous section. In this experiment, the pH values of the cell were adjusted to pH 2, 4 and 6 by adding either 0.1 M of H₂SO₄ or 0.1 M of NaOH solution.

Light sources. The experiments were conducted under three different light sources namely dark room, UV light and under sunlight by using the same conditions as described in previous sections. However, the contact time and pH value were based on the optimal conditions as found in the respective section before. The light intensity of UV light and sunlight was recorded using lux meter (Sunche Digital Light Meter HS1010, 0-200,000 lux, China).
The UV light intensity for the distance of 30 cm between light source and reaction flask was about 50–55 lux.

*Photocatalyst concentration.* The concentration of photocatalyst (TiO$_2$) added into the cell were varied from 20, 40, 60 and 80 mg/L. The contact time, pH and light source were based on the optimal conditions found in previous sections.

*Comparison between Fenton, electro-Fenton, photocatalysis and photo-electro-Fenton treatments*

The experiments were conducted under the optimal conditions as found in previous optimization sections. Four treatments namely Fenton, electro-Fenton, photocatalysis and photo-electro-Fenton were set up to treat diluted POME.

For Fenton reaction, 50 mL of 0.05 M FeSO$_4$ and 75 mL of 35 % H$_2$O$_2$ solution were added into 50 mL diluted POME. The contact time was 4 h at pH 4 without any voltage applied.

For electro-Fenton, 50 mL of 0.05 M FeSO$_4$, 75 mL of 35 % H$_2$O$_2$ solution and 75 mL of 0.25 M Na$_2$SO$_4$ solution were added into 50 mL diluted POME. The contact time was 4 h at pH 4 with 1.5 V applied.

In photocatalysis treatment, the experiment was conducted at pH 4 with the optimal light source and the amount of TiO$_2$ found in the previous respective experiments.

For photo-electro-Fenton experiment, 50 mL of 0.05M FeSO$_4$ and 75 mL of 35 % H$_2$O$_2$ solutions were added into 50 mL of diluted POME with the optimal amount of TiO$_2$, pH value and the contact time of 4 h.

**RESULTS AND DISCUSSION**

*Effect of contact time in treatment efficiency*

Fig. 2 shows the result of the optimal contact time to the COD removal efficiency in POME using photo-electro-Fenton system.

![Fig. 2. COD removal efficiency in different contact times.](image)

The result showed that the highest efficiency at about 84 % was achieved at the 4$^{th}$ hour. The efficiency decreased slightly after the 1$^{st}$ hour, but gradually increased from the 2$^{nd}$ to the 4$^{th}$ hour. It decreased sharply at the 5$^{th}$ hour. This
result was in agreement with our previous finding, whereby we also noticed that the 4th hour was the optimal contact time of electro-Fenton system. In general, the longer the contact time, the higher is the efficiency, because of the greater amount of $\cdot OH$ formation. However, the COD removal efficiency decreased to 55% at 5th hour due to the finishing of H$_2$O$_2$ in the solution, thus, the $\cdot OH$ generation at the 5th hour was basically relied on the electrolysis and photolysis processes. It is important to highlight that the amount of H$_2$O$_2$ in the solution has to remain in optimal concentration because the increase of H$_2$O$_2$ amount in the solution can result lower removal efficiency.

**pH effect in treatment efficiency**

pH value plays an important role in the organic matter degradation especially for Fenton process. By using the optimal contact hour that we obtained in the previous experiment, the effect of pH was studied under the conditions of 50 mL of diluted POME, 75 mL of 0.25 M Na$_2$SO$_4$, 75 mL of 35% H$_2$O$_2$, 50 mL of 0.05 M FeSO$_4$ with DC voltage of 1.5 V under UV light radiation. The pH values studied were pH 2, 4 and 6, and the results obtained are shown in Fig. 3.

![COD removal efficiency at different pH](image)

**Fig. 3. COD removal efficiency at different pH.**

The highest COD removal efficiency was achieved at pH 4 (i.e., 84.7%), whereas the COD removal efficiencies at pH 2 and 6 were at 79.5 and 69.9%, respectively. The Fenton process actually requires acidic condition to keep the Fe$^{2+}$ catalyst actively produce $\cdot OH$. In addition, Fe$^{2+}$ is often oxidized in high pH conditions to produce iron(III) hydroxide, Fe(OH)$_3$, which is no longer active in Fenton process. The COD removal efficiency decreased at pH 6 is likely to be due to the radical scavenging activity by H$^+$ ion as shown in Eq. (6) and the decomposition of H$_2$O$_2$ to oxygen and water molecule in pH 6,11,12

$$\cdot OH + H^+ + e^- \rightarrow H_2O$$  (6)
In a review by Gogate and Pandit, the optimal pH for photo-Fenton process was in strong acidic condition, in which most studies used pH 2.5–3.5. Despite the intrinsic rate of UV/H₂O₂ was not much affected when pH value is low, the effect of the radical scavengers could be the main reason for promoting the organic matter degradation in low pH condition. In addition, Mota and co-workers also found that the formation of electron–hole pairs in photocatalysis is more favourable in acidic conditions (i.e., pH 3). The group also mentioned that, for pH values below 3, the presence of anions from the dissociation of sulfuric acid could reduce the contact of organic matter on the surface of catalysts and this will eventually reduce the degradation rate of organic matter. Due to this reason, the COD removal efficiency at pH 2 was lower than the one at pH 4.

**Effect of light source**

The effect of the light source was studied under UV light, sunlight and dark room. By using the optimal contact time and pH value, the experiments were set up under the same reaction mixture as aforementioned. The light intensity of the sunlight was recorded in the range of 140–780 lux, and the COD removal efficiencies in different light source are shown in Fig. 4.

![Fig. 4. COD removal efficiency under different light sources.](image-url)

In general, the presence of light in photo-Fenton process assists the regeneration of Fe²⁺ and •OH from hydroxo iron(III) ion, [Fe(OH)]²⁺ (Eq. (7)). The process is dominant in the acidic conditions at the wavelengths of 290 and 400 nm:

\[
[\text{Fe(OH)}]^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} \tag{7}
\]

In addition to that, Gogate and Pandit also highlighted that the oxalate ion (C₂O₄²⁻) which is present in organic matter rich wastewater can lead to the formation of trioxalato iron(III) complex ion, [Fe(C₂O₄)₃]³⁻ and subsequently give a
higher yield of Fe(II) ion formation (Eqs. (8) and (9)) than [Fe(OH)]^{2+}. Another advantage of [Fe(C_2O_4)_3]^{3−} is that it can absorb at a longer wavelength at 570 nm which allows the treatment to be in sunlight and there the highest efficiency at 94% in this study was recorded. This efficiency was about 10% higher than the one under UV radiation, and 30% higher than the dark room treatment:

\[
[\text{Fe(C}_2\text{O}_4)_3]^{3−} \rightarrow \text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2−} + \text{C}_2\text{O}_4^{−} \quad (8)
\]

\[
\text{C}_2\text{O}_4^{−} + [\text{Fe(C}_2\text{O}_4)_3]^{3−} \rightarrow \text{Fe}^{2+} + 3\text{C}_2\text{O}_4^{2−} + 2\text{CO}_2^{∗} \quad (9)
\]

Contrary to that, it has also been reported that UV radiation can make the removal rate higher than the sunlight, but another factor that could affect the removal efficiency is the light intensity. The stronger the light intensity, the higher is the removal efficiency. Due to this reason, the efficiency under sunlight was the highest in this study because the sunlight intensity (i.e., 13900–78200 lux) was much stronger than UV light (i.e., 50–55 lux).

**Effect of photocatalyst loading**

In our previous electro-Fenton hybrid study, the COD removal efficiency was not in direct proportional to the loadings of Fe^{2+} catalyst and H_2O_2. In fact, many researches’ outcome was that the increase of TiO_2 loading in their photocatalytic degradation did not help to increase the degradation rate. Since the loading of TiO_2 also plays an important role in the photocatalysis, the TiO_2 loadings at 20, 40, 60 and 80 mg/L were investigated and reported herein. It is worth to note that the sunlight intensity was monitored throughout the study in order to ensure the COD removal efficiency was kept constant with respect to light intensity. The sunlight intensity throughout the study was in the range of 3000–99000 lux and the result obtained is shown in Fig. 5.

![Fig. 5. COD removal efficiency in different TiO_2 concentration.](available online at www.shd.org.rs/JSCS/)
The result showed that the loading of 60 mg/L TiO₂ was the optimal concentration as the COD removal efficiency reached its maximum at 97 %. Similar to the iron catalyst in the Fenton process, the increase of TiO₂ loading to 80 mg/L did not show a better performance in the photo-electro-Fenton hybrid system but rather decreased to 86 %. The high photocatalyst loading could lead to the light scattering and low light penetration in the treatment system, which eventually resulted in a lower treatment efficiency.18–20

Comparison between Fenton, electro-Fenton, photocatalysis and photo-electro-Fenton treatments

Based on the optimal conditions of photo-electro-Fenton process, the other three AOP systems namely Fenton process, electro-Fenton and photocatalysis were used in the diluted POME treatment for the removal of COD. For Fenton process, the experiment was performed in the presence of FeSO₄ and H₂O₂ without applying any voltage to the system, whereas for electro-Fenton hybrid system, in addition to the Fenton reagents, a D.C. voltage of 1.5 V was also applied to the system with the presence of Na₂SO₄ as the electrolyte. For photocatalysis, the experiment was performed in the presence of TiO₂ under sunlight radiation only.

The hybridized AOP systems apparently have higher COD removal efficiency than the individual AOP. As shown in Table I, the photocatalysis treatment has the lowest efficiency (50 %), whereas the photo-electro-Fenton hybrid system recorded the highest efficiency (97 %).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Conditions</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{\text{FeSO}_4}$</td>
<td>$V_{\text{TiO}_2}$</td>
</tr>
<tr>
<td>Fenton</td>
<td>0.05</td>
<td>75</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Electro-Fenton</td>
<td>0.05</td>
<td>75</td>
</tr>
<tr>
<td>Photo-electro-Fenton</td>
<td>0.05</td>
<td>75</td>
</tr>
</tbody>
</table>

The lowest COD removal efficiency in photocatalysis treatment was due to the source of *OH formation and was only depended on the hole (h⁺) formation when TiO₂ was being excited, which limited the organic matter degradation in the system. Therefore, the advantage of hybridizing AOPs is enhancing the *OH formation in the system from different AOPs, and importantly the reagents in each AOP do not interfere with each other during the treatment process. As a result, the degradation increased in the photo-electro-Fenton hybrid system due
to the highest \(^\circ\)OH production in the system. However, the photo-electro-Fenton hybrid system did not display the synergetic effect to the organic matter degradation, but merely a small linear increment compared to the Fenton process alone (87\%).

**CONCLUSION**

Four parameters of the photo-electro-Fenton hybrid system have been studied, namely the contact time, pH, the light source and the photocatalyst concentration in this work. A maximum efficiency of 97\% has been achieved under the optimal conditions of pH 4 with 60 mg/L TiO\(_2\) for 4 h contact time under sunlight radiation. Hybridizing AOPs has proven to have higher degradation ability as compared to any AOP alone. However, no synergetic effect was observed when the three AOPs were hybridized in this study.

**Acknowledgements.** The financial support from Malaysian Ministry of Education under Exploratory Research Grant Scheme [ERGS/STG01(01)/1021/2013(01)] is gratefully acknowledged. The authors also would like to thank Bau Palm Oil Mill Sdn. Bhd., Sarawak, for the long-term research collaboration in POME research.

**ИЗВОД**

ПОБОЉШАЊЕ ЕФИКАСНОСТИ ТРЕТМАНА РАЗРЕЂЕНОГ ЕФЛУЕНТА ИЗ МЛИНОВА ЗА ДОБИЈАЊЕ ПАЛМИНОГ УЉА КОРИШЋЕЊЕМ ФОТО-ЕЛЕКТРО-ФЕНТОН ХИБРИДНОГ СИСТЕМА

**NORALISYA ALI**\(^1\), CHEE BENG YEOH\(^2\), SENG LAU\(^1\) и MENG GUAN TAY\(^1\)

\(^1\)Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia \(^2\)Malaysian Palm Oil Board, Bandar Baru Bangi, 43000 Kajang, Selangor, Malaysia

Фотокатализма, електролиза и Фентон процес су три важна напредна процеса оксидације (AOPs) која произведе хидроксили радикал за разградњу органских материја у отпадним водама, током 4–6 сати у амбијенталним условима. Током ове студије извршена је фото-катализа, електролиза и Фентон (фото-електро-Фентон) процес хибридног система за третирање разблаженог ефлуента млинова за добијање палминистог уља (POME). Електролитичка ћелија са анодом од нерђајућег челика и платинском жицом као катодом, уз применени напон од 3 V. Разређени POME је затим третиран у ћелији користећи раствор натријум-суфата као електролит, титан(IV)-оксид као фотокатализатор, водоник-пероксид и гвожђе(II)-суфат као Фентон реагент. Испитивани су ефекти дужине процеса, pH, концентрације TiO\(_2\) и различитих светлосних услова на ефикасност смањења хемијске потрошње кисеоника (COD) разређеног POME. Утврђене су оптималне услови за фото-електро-Фентон хибридни систем: дужина процеса од 4 h, pH 4, садржај TiO\(_2\) 60 mg/L, под сунчевом светлошћу. Под таквим условима, ефикасност смањења COD успела је да достигне 97\%. Са друге стране, фото-електро-Фентон хибридни систем даје највећу ефикасност смањења COD у поређењу са електро-Фентон хибридним системом, Фентон и фотокатализичким процесом.

(Примљено 16. октобра, прихваћено 29. новембра 2018)

**REFERENCES**