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

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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.

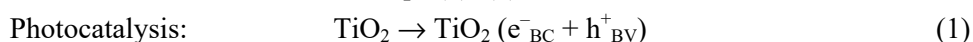
Keywords: photo-electro-Fenton hybrid system; advanced oxidation process (AOP); Fenton; palm oil mill effluent (POME).

INTRODUCTION

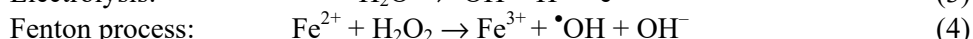
Advanced oxidation processes (AOPs) are defined as the processes that generate hydroxyl radicals ($\cdot\text{OH}$) in sufficient quantities to degrade organic matter and nutrients present in the wastewater effluents. Among the AOPs, photocatalysis, electrolysis and Fenton process, in particular, were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

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



where e^- is electron and h^+ is hole.



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 $\text{Fe}(\text{OH})_3$ 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 \approx 50000 mg/L).^{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.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 *et al.*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 Fe₂SO₄ 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:

$$\text{COD removal efficiency, \%} = 100(\text{Initial COD} - \text{Final COD}) / \text{Initial COD} \quad (5)$$

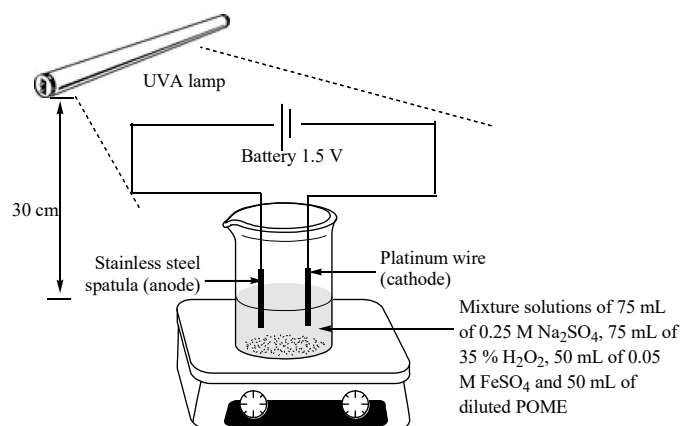


Fig. 1. Set up of photo-electro-Fenton cell.

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_2O_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_2O_2 solution and 75 mL of 0.25 M Na_2SO_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_2O_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.

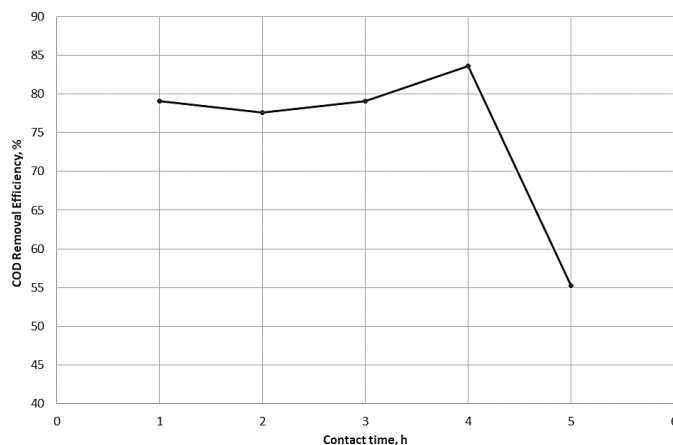


Fig. 2. COD removal efficiency in different contact times.

The result showed that the highest efficiency at about 84 % was achieved at the 4th hour. The efficiency decreased slightly after the 1st hour, but gradually increased from the 2nd to the 4th hour. It decreased sharply at the 5th hour. This

result was in agreement with our previous finding,⁹ 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 $\bullet\text{OH}$ formation. However, the *COD* removal efficiency decreased to 55 % at 5th hour due to the finishing of H_2O_2 in the solution, thus, the $\bullet\text{OH}$ generation at the 5th hour was basically relied on the electrolysis and photolysis processes. It is important to highlight that the amount of H_2O_2 in the solution has to remain in optimal concentration because the increase of H_2O_2 amount in the solution can result lower removal efficiency.⁹

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_2SO_4 , 75 mL of 35 % H_2O_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.

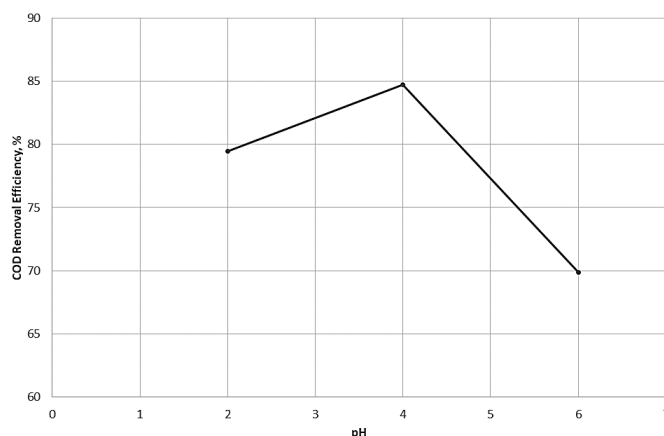


Fig. 3. *COD* removal efficiency at different pH.

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 $\bullet\text{OH}$. In addition, Fe^{2+} is often oxidized in high pH conditions to produce iron(III) hydroxide, $\text{Fe}(\text{OH})_3$, which is no longer active in Fenton process.¹⁰ 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_2O_2 to oxygen and water molecule in pH 6:^{11,12}



In a review by Gogate and Pandit,¹³ 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.¹³ 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).⁴ 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.⁴ 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.

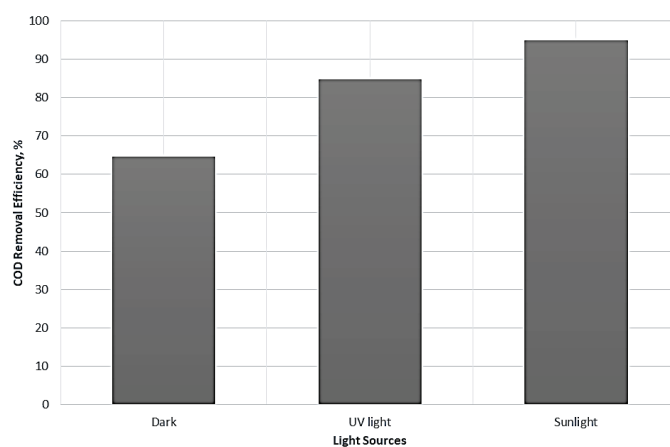
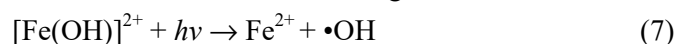


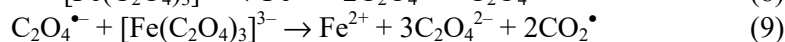
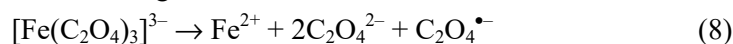
Fig. 4. COD removal efficiency under different light sources.

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:



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 $[\text{Fe}(\text{OH})]^{2+}$.¹³ Another advantage of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ 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:



Contrary to that, it has also been reported that UV radiation can make the removal rate higher than the sunlight,¹³ but another factor that could affect the removal efficiency is the light intensity.^{14,15} 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 .⁹ 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.^{16–18} 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.

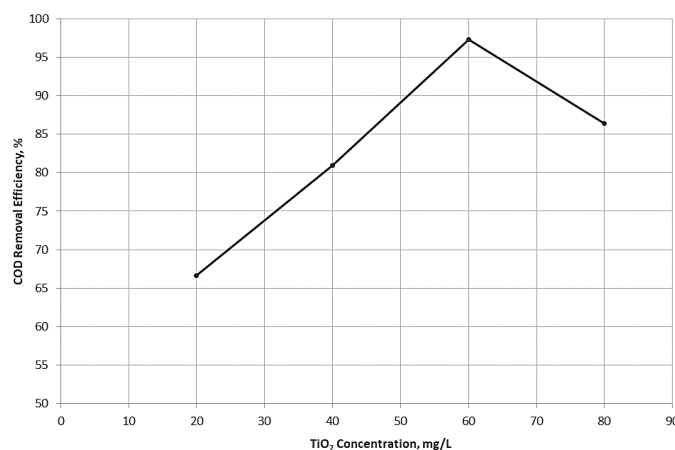


Fig. 5. *COD* removal efficiency in different TiO_2 concentration.

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 I. Comparison COD removal efficiencies under different AOP treatment systems; $V - V_{\text{Diluted POME}}$

Treatment	Conditions									Efficiency %
	C_{FeSO_4} M	$V_{\text{H}_2\text{O}_2}$ mL	U V	Retention time, h	pH	V mL	$C_{\text{Na}_2\text{SO}_4}$ M	C_{TiO_2} mg/L	Lighting source	
Fenton	0.05	75	–	4	4	50	–	–	ambient	87
Photocatalysis	–	–	–	4	4	50	–	60	UV	50
Electro-Fenton	0.05	75	1.5	4	4	50	0.25	–	UV	90
Photo-electro-Fenton	0.05	75	1.5	4	4	50	0.25	60	Sunlight	97

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 $\cdot\text{OH}$ 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.

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ИЗВОД

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

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Фотокатализа, електролиза и Фентон процес су три важна напредна процеса оксидације (AOPs) која производе хидроксилни радикал за разградњу органских материја у отпадним водама, током 4–6 сати у амбијенталним условима. Током ове студије извршена је фотокатализа, електролиза и Фентон (фото-електро-Фентон) процес хибридног система за третирање разблаженог ефлуента млинова за добијање палминог уља (РОМЕ). Електролитичка ћелија са анодом од нерђајућег челика и платинском жицом као катодом, уз примењени напон од 3 V. Разређени РОМЕ је затим третиран у ћелији користећи раствор натријум-сулфата као електролит, титан(IV)-оксид као фотокатализатор, водоник-пероксид и гвожђе(II)-сулфат као Фентон реагенс. Испитивани су ефекти дужине процеса, pH, концентрације TiO_2 и различитих светлосних услова на ефикасност смањења хемијске потрошње кисеоника (COD) разређеног РОМЕ. Утврђени су оптимални 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 хибридном системом, Фентон и фотокаталитичким процесом.

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