Decolorization of Anaerobically Treated Palm Oil Mill Wastewater Using Combined Coagulation and Vacuum Ultraviolet-Hydrogen Peroxide

Thunyalux Ratpukdi

***Abstract*—The removal of color in anaerobically treated palm oil mill wastewater was investigated. The experiment consisted of two processes including coagulation and advanced oxidation processes. The first process is alum coagulation which was used as a pretreatment. The second process is vacuum ultraviolet (VUV) with hydrogen peroxide (H_2O_2) which was conducted in comparison with ultraviolet (UV)-H_2O_2. For the coagulation process, the optimum dose of alum and optimum pH were 5 g/L and 5.67, respectively. This condition reduced color (ADMI unit) by 94.88%. For VUV-H_2O_2 and UV-H_2O_2 experiments, the effect of H_2O_2 concentrations (H_2O_2:COD; 0.5:1, 1:1, 2:1, and 3:1) and VUV/UV power (30W and 60W) were studied. Increasing of H_2O_2 and VUV/UV power generally resulted in higher reduction of color. This is due to more hydroxyl radical generation. However, in some conditions, increasing of H_2O_2 acted as hydroxyl radical scavengers that reduced the color removal efficiency. At the end of experiment (180 min), VUV (30W) -H_2O_2 (H_2O_2:COD of 2:1) could remove 95.5% of color in ADMI unit.**

***Index Terms*—Anaerobically treated palm oil mill effluent, vacuum ultraviolet, color, hydroxyl radicals.**

I. Introduction

Palm oil mill is one of important industries in South East Asia. The oil extraction processes generates considerable amount of wastewater (2-3.5 m^3/ton of crude palm oil) [1]. It was reported that 40.2 million tons of palm oil mill effluent (POME) was generated in Malaysia in 2004 [1]. The POME, typically, has high organic content that can be used to produce energy from ethanol or biogas by anaerobic treatment process [1], [2]. Although this seems to be successful practice, the anaerobically treated POME (ATPOME) still has high organic content, turbidity, and especially dark brown color [2]. This color is refractory compounds of natural organic matter, tannins, phenolic compounds, and melanoidin (generated from heating of organic in oil extraction process) [1]. Discharging brownish color wastewater to water bodies could cause adverse effect to aquatic lives by filtering the light passing through. As a result, there will be less photosynthesis activity and less dissolved oxygen. To prevent the impact to environment, the reuse of ATPOME is one of alternatives. Nevertheless, its dark color makes the ATPOME unattractive for reuse application. Nowadays, the current technology that used for ATPOME wastewater reclamation is such as membrane filtration [3]. However, this technology could suffer from fouling problem. To the best of our knowledge, the use of vacuum ultraviolet (VUV) which is one of advanced oxidation processes for color removal of ATPOME has never been investigated. VUV has a unique feature that can produce $OH^{\bullet}$, strong oxidizing agent, by water homolysis as presented in (1) [4].

$$H_2O + h\nu\ (< 190\ \text{nm}) \rightarrow H^{\bullet} + OH^{\bullet} \quad (1)$$

Also additional of H_2O_2 which is a catalyst to the system could produce more $OH^{\bullet}$. This study investigated removal of color of ATPOME wastewater using combination of coagulation and VUV-H_2O_2 process. Coagulation was used a pre-treatment step since ATPOME has relatively high organic content and turbidity. UV-H_2O_2, VUV alone and H_2O_2 alone were also conducted for comparison purpose.

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II. Materials and Methods

A. Wastewater Sample

Wastewater sample used in the experiment was collected from a palm oil mill plant in Chonburi, Thailand on October 2011. The wastewater was the effluent of anaerobic treatment plant that still has dark brown color. Table I shows the characteristic of wastewater used in the experiment.

TABLE I: Characteristics of Anaerobically Treated Palm Oil Mill Effluent (ATPOME) Wastewater and Coagulated ATPOME

Parameter (Unit)	ATPOME	Coagulated* ATPOME
pH	8.27	5.67
Turbidity (NTU)	1,667	28
Color (ADMI)	6,450	400
BOD (mg/L)	201	160
COD (mg/L)	1,958	336

*5 g/L of alum

B. Experimental Setup and Procedure

The experiment consists of two parts. In the first part, ATPOME was pretreated by coagulation (jar test) using alum at different pH and alum dosages in order to find the optimum pH and dosage. The second part was the advanced oxidation

processes including VUV-H_2O_2, and UV-H_2O_2. VUV alone and H_2O_2 alone were conducted for comparison purpose.

The reactor of the advanced oxidation process was a 2-L glass cylinder reactor which has a diameter of 8 cm and a height of 54 cm. The volume of coagulated ATPOME wastewater used for experiment was 2 L. The reactor was equipped with a VUV lamp (model GPS383T5/VH/HO, Universal Light Source, Inc., USA) or UV lamp (model GPH383T5/L/HO universal Light Source, Inc., USA) at the center of the reactor. The wastewater was mixed using a magnetic stirring system. A Glass tube was set in the reactor for drawing water sample. The lamp had a power input of 30 W per lamp. The VUV lamp has major emission spectra at 254 nm with relative emission of 10% at 185 nm. The UV lamp has emission spectra only 254 nm.

For the VUV-H_2O_2 and UV-H_2O_2 experiments, the amount of H_2O_2 added to the reactor was expressed as mg H_2O_2: mg COD of 0.5, 1, 2 and 3. Sample of 50 mL was taken from reactor at 30, 60, 90, 120 and 180 min to measure color (ADMI) and turbidity.

III. Results and Discussion

A. Effect of Alum Coagulation (Jar test)

Alum coagulation of ATPOME was conducted as a pre-treatment step prior to VUV-H_2O_2 and UV-H_2O_2 processes. This is because ATPOME has relatively high color and large colloidal particulate matter that could filter VUV or UV (Table I). From Fig. 1, the increasing of alum dose caused decrease of color. At alum dose of 5 g/L, 86 % color removal was achieved. It is noticed that further increase of alum dose higher than 5 g/L resulting in minimum improvement of color removal. Therefore, the optimum dose of alum for color removal for ATPOME was 5 g/L. The optimum pH was found at 5.6 (data not shown). The optimum alum dose and pH obtained from this step were used to pre-treat the ATPOME before undergo the VUV-H_2O_2 and UV-H_2O_2 processes. The characteristics of coagulated ATPOME are shown in Table I.

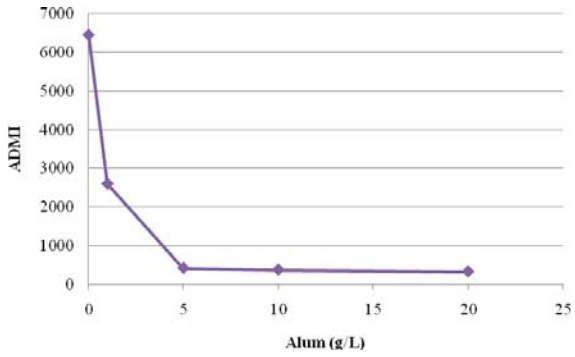

Fig. 1. Effect of alum dosage on color removal for ATPOME wastewater (pH = 5.7).

B. Effect of VUV-$H_2O_2$and UV-H_2O_2

Fig. 2, 3, 4 and 5 illustrates the change of color with time for the systems with VUV-H_2O_2 (30W), VUV-H_2O_2 (60W), UV-H_2O_2 (30W), and UV-H_2O_2 (60W), respectively. Initial color removal rate constants are presented in Table II. In this study, VUV alone and H_2O_2 alone experiments were also conducted. However, VUV alone caused the increasing of color by 60% while H_2O_2 (at H_2O_2:COD =3) reduced color only 7% (data not shown). From Fig. 2-5, the decreasing of color occurred rapidly during the first 60 min for most of experimental conditions and slowly decreased thereafter. Fast reduction indicated that color molecules comprised in ATPOME are susceptible to $OH^{\bullet}$. In later period, the slow reduction of color could suggest that there was less amount of H_2O_2 available for $OH^{\bullet}$ formation or the oxidation byproducts generated were not oxidized well with $OH^{\bullet}$.

1) Effect of H_2O_2 dosage

Color removal efficiencies and initial removal rate constants of VUV-H_2O_2 and UV-H_2O_2 processes tended to increase as H_2O_2 dosage increased (Table II). This is due to more hydroxyl radical generation. For VUV-H_2O_2 (30W), the H_2O_2:COD of 2 provided the highest removal efficiency (95.5%) and removal rate constant of 10.47 ADMI/s. Interestingly, the initial rate constant dropped by half at the H_2O_2:COD dosage of 3 (Fig. 2). This phenomenon could be attributed from the excess H_2O_2 that acts as $OH^{\bullet}$ scavenger as shown in (2). Previous studies also observed the reduction of removal efficiencies of humic acid and natural organic matter when H_2O_2 was excess [5]-[6].

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \text{ , } k = 2.7\ 10^{-7}\ M^{-1}s^{-1} \quad (2)$$

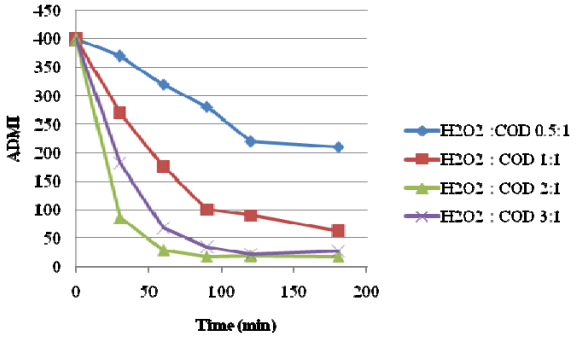

Fig. 2. Effect of VUV-H_2O_2 on color removal for alum treated ATPOME wastewater (VUV 30 W).

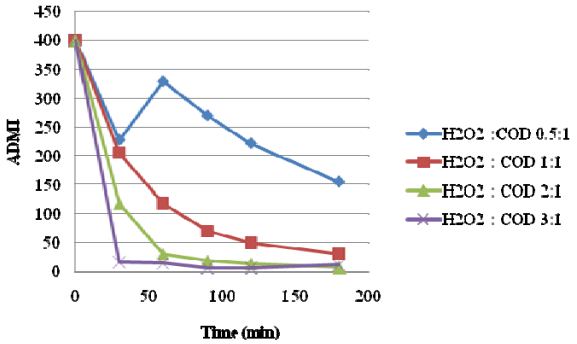

Fig. 3. Effect of VUV-H_2O_2 on color removal for alum treated ATPOME wastewater (VUV 60 W).

2) Effect of VUV and UV intensity

An increase of VUV and UV intensity was found to increase the color removal efficiencies and initial color removal rate constant in most conditions (Table II). No

improvement of removal efficiencies and rate constants was observed at H_2O_2: COD of 0.5, and 2. Note that as VUV or UV intensities changed from 30W to 60W, the ratio of H_2O_2: COD that yielded the highest efficiencies changed to H_2O_2:COD of 3. The results from previous and current sections suggested that the amount of H_2O_2 added and energy input by VUV or UV had to be matched in order to achieve maximum $OH^{\bullet}$ formation and also degradation of contaminant.

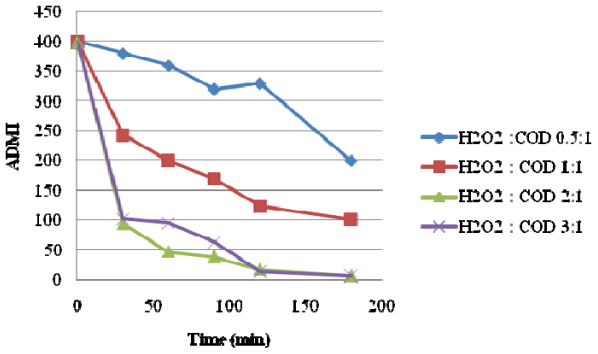

Fig. 4. Effect of UV-H_2O_2 on color removal for alum treated ATPOME wastewater (UV 30 W).

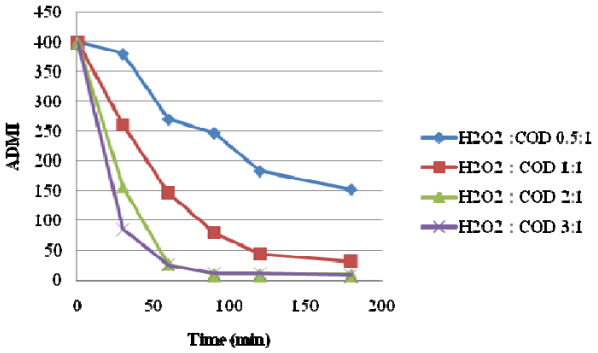

Fig. 5. Effect of UV-H_2O_2 on color removal for alum treated ATPOME wastewater (UV 60 W).

TABLE II: COLOR REMOVAL EFFICIENCIES AND INITIAL REMOVAL RATE CONSTANTS OF COAGULATED ATPOME WASTEWATER

Condition		% Removal (at 180 min)	Initial removal rate constant (ADMI/min)	R^2
H_2O_2:COD	VUV (W)			
0.5	30	47.50	1.50	0.9888
1.0	30	84.50	3.31	0.9851
2.0	30	95.50	10.47	1.0000
3.0	30	93.00	5.53	0.9683
H_2O_2:COD	VUV (W)			
0.5	60	61.25	1.41	0.9902
1.0	60	92.50	6.50	1.0000
2.0	60	98.00	9.40	1.0000
3.0	60	97.00	12.77	1.0000
H_2O_2:COD	UV (W)			
0.5	30	50.00	1.04	0.8957
1.0	30	74.75	3.00	0.9023
2.0	30	98.25	10.20	1.0000
3.0	30	98.50	9.93	1.0000
H_2O_2:COD	VUV (W)			
0.5	60	62.00	1.49	0.9212
1.0	60	92.25	4.23	0.9965
2.0	60	97.75	6.23	0.9700
3.0	60	98.00	10.50	1.0000

C. Comparison between VUV-H_2O_2 and UV-H_2O_2

In this study, VUV-H_2O_2 and UV-H_2O_2 processes were compared. In general VUV-H_2O_2 was expected to have higher efficiency than UV-H_2O_2. This is due to VUV can emit the wavelength of 185 nm that could have additional $OH^{\bullet}$ formation. From the results (Fig. 2 to 5 and Table II), several conditions of VUV-H_2O_2 were slightly better than UV-H_2O_2. This might be because of too high H_2O_2 concentration that caused the competitive adsorption with water to form $OH^{\bullet}$. Thomson et al. [7] also reported this phenomenon when studied the removal of NOM using VUV-H_2O_2 and UV-H_2O_2. They found that once concentration of H_2O_2 was greater than 24 mg/L the efficiencies of VUV-H_2O_2 and UV-H_2O_2 processes were comparable.

IV. CONCLUSION

In this study, the combined alum coagulation with VUV-H_2O_2 or UV-H_2O_2 was found to be effective to remove color from ATPOME wastewater. The optimum dose of alum was 5 g/L which result in 93.7% removal. Consequent advanced oxidation processes of VUV-H_2O_2 or UV-H_2O_2 remove color down to single digit of ADMI unit which yield 99.8% color reduction in total. The H_2O_2 dosage and VUV or UV intensity played important roles to color removal efficiencies and removal rates. At VUV or UV of 30W, the optimum dosage of H_2O_2:COD was 2 while at VUV or UV of 60W, the optimum H_2O_2:COD was 3. Both processes provided comparable results. Further study needs to investigate the mineralization and biodegradability of ATPOME for possible reuse ATPOME wastewater.

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