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A Comparative Study Using Aluminum and Iron Electrodes for the Electrocoagulation of Palm Oil Mill Effluent to Reduce its Polluting Nature and Hydrogen Production Simultaneously

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Abstract.- This study was designed to compare the effectiveness of Aluminium (Al) and Iron (Fe) as electrodes to reduce the polluting nature of Palm Oil Mill Effluent (POME) and simultaneous hydrogen production using electrocoagulation (EC). Electrocoagulation of raw POME and anaerobically pretreated POME was performed using Direct Current (DC) electricity of 2.0, 3.0, and 4.0 volts in a reactor volume of 20 liters. The results of raw POME treatment reveal that the chemical oxygen demand (COD) and turbidity was decreased around 57.66% and 62.5%, respectively, using Al electrode. However, the use of iron electrodes could reduce the COD and turbidity of raw POME about 35.3% and 43.10%, respectively. The reduction in polluting factors of the raw POME was accompanied with the production of 42% and 22.8% of hydrogen gas concentration using Al and Fe electrodes, respectively. On the other hand, the results of Electrocoagulation of POME which was pretreated in anaerobic pond show that the COD was decreased around 62.35% and 59.41% using Al and Fe respectively, and turbidity was reduced up to 90.55% and 76.96% using Al and Fe respectively. The concentration of hydrogen gas yielded as a result of EC of anaerobically pretreated POME was around 31.37% and 25.6% using Al and Fe respectively as electrodes. Removal of pollutants from POME using Electrocoagulation is faster than some other existing processes and requires a relatively small area as compared to the conventional anaerobic treatment in pond system which is potential source of green house gases.

Keywords: Palm oil mill effluent, electrocoagulation, hydrogen gas, COD, aluminium electrode, iron electrode.

INTRODUCTION

Electrolysis is a branch of electrochemistry science. Electrolysis is the method for the production of hydrogen also an alternative treatment for waste water treatment (Stojic *et al*., 2003). Moreover, it was also mentioned that electrolysis is a very simple method to produce Hydrogen gas by splitting water into its elements – hydrogen and oxygen – by running a direct current between two electrodes in the water. Electrolytic hydrogen production offers the potential to produce hydrogen with almost no pollution or greenhouse gas production (Barbir, 2005).

Increasing oil palm plantation and palm oil mill processing is seriously responsible to generate wastes as environmental threats. Around the world, 45 million metric tons of palm oil has been produced in 2009 (Stichnothe and Schuchardt, 2010). Approximately 0.65 tons of raw palm oil mill effluent POME) is produced for every ton of fresh fruit bunches (FFB) processed. A large quantity of water is necessary to process the palm fruit for oil production (Ahmad *et al*., 2003). The POME is rich in organic carbon with a chemical oxygen demand (COD) value higher than 40 g/L and nitrogen content around 0.2 and 0.5 g/L as ammonia nitrogen and total nitrogen. POME can also be described as a colloidal suspension of 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids (Ahmad *et al*., 2009). Table I shows a chemical analysis of a typical POME which comprise of a number of potential ingredients including carbohydrates, proteins, fats and minerals (Sumathi *et al*., 2008, Yacob *et al*., 2005).

Nowadays, POME is usually treated with open lagoon technology. Usually POME is subjected to anaerobic treatment in open pond

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system for pretreatment to reduce the COD and BOD. However this system will produce methane as a pollutant to the environment (Wulfert *et al*., 2002). Currently, a combination of open lagoon technology and land application is developed and employed to minimize the polluting nature of POME and utilize the potential ingredients for cultivation purposes (Wulfert *et al*., 2000, Pamin *et al*., 1996). Usually the existing conventional methods for the pretreatment of POME are time consuming and require vast pond area.

Table I.- Characteristics of palm oil mill effluent.

Parameter	Conc. (mg/L)	Element	Conc. (mg/L)
Oil and grease	4000–6000	Potassium	2,270
Biochemical oxygen demand (BOD)	25,000	Magnesium	615
Chemical oxygen demand (COD)	50,000	Calcium	439
Total solid	40,500	Phosphorus	180
Suspended solids	18,000	Iron	46.5
Total volatile solids	34,000	Boron	7.6
Total Nitrogen	750	Zinc	2.3
Ammonicals nitrogen	35	Manganese	2.0
		Copper	0.89

Some other techniques have also been introduced to replace the open anaerobic fermentation system, these include the conventional anaerobic digester, anaerobic contact process, up-flow anaerobic sludge blanket (UASB) reactor, close tank digester, trickling filter, aerobic rotating bio-logical contactor and evaporation process (Ahmad *et al*., 2009).

Using electricity to treat wastewater was first proposed in UK in 1889 (Chen, 2004). The application of electrolysis in mineral beneficiation was patented by Elmore in 1904 (Chen, 2004). Electrocoagulation (EC) with aluminum and iron electrodes was patented in the US in 1909. EC was found particularly useful in wastewater treatment. It has been employed in treating textile wastewater, catering wastewater, petroleum wastewater, tar sand wastewater, oil shale wastewater, carpet wastewater, municipal sewage, chemical fiber wastewater, oil–water emulsion, oily wastewater, clay suspension, nitrite, and dye (Chen, 2004). Results show that the EC of POME as pretreatment and hydrogen production can minimize the maintenance cost as well as contribute to the efforts for the management of fuel crisis and pollution problems. This is the first report regarding POME treatment using EC with hydrogen gas captured as a beneficial side product.

EC process is based on electrolysis principle. An EC system consists of a rectifier, EC cell, and electrodes. Oxidation reactions occur at anode electrodes and reduction reactions occur in cathodes. Reactions occurred using ferum electrodes and aluminium electrodes are slightly different. Reactions occurred in EC cell can be summarized as previously reported (Chen and Hung, 2007): Electrolytic reaction at different electrodes in acidic and alkaline conditions have been summarized below;

Reaction at anode while using Aluminium electrode

$$Al \rightarrow Al^{3+} + 3e$$

At alkaline condition: $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$

At acidic condition: $Al^{3+} + 3H_2O \rightarrow AlOH_3 + 3H^+$

In addition, oxygen evolution reaction $2H_2O + 4e \rightarrow O_2 + 4H^+$

At cathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

Ferum electrode:

At anode: $Fe \rightarrow Fe^{2+} + 2e$

At alkaline condition: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

At acidic condition: $4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^-$

In addition, oxygen evolution reaction

$$2H_2O + 4e \rightarrow O_2 + 4H^+$$

At cathode: $2H_2O + 2e \rightarrow H_2 + 2OH^-$

The hydroxide formed by either ferum or aluminium possess the characteristics of a coagulant. The role of the coagulant produced during EC is the same as coagulant derived from the chemicals for wastewater treatment. However, using EC, no extra chemical is needed, and hydrogen gas is produced simultaneously.

MATERIALS AND EQUIPMENT

POME from two different sources was compared in this research. One of these was a raw POME sample from Sri Ulu Langat Palm Oil Mill with COD 50,000 ppm, turbidity 12,800 NTU and pH 4. The second sample of POME was collected from the outlet of anaerobic pond at Sime Darby palm oil mill with COD 22,000 ppm, turbidity 2,900 NTU and pH 4.

EC cell used in this experiment has a capacity of 20L. Twelve electrodes used whereby six act as cathode and other six as anode in parallel connection. Aluminium and ferum used were cut from commercial grade sheet with 95-99% purity. The total effective surface area of electrode was 0.33 m^2. For every batch of run, only aluminium or ferum was used as anode and cathode. Ampere meter and voltmeter used for electricity measuring have a working range of 0-20 ampere and 0-300 volt DC respectively. The schematic diagram of the EC system is shown in Figure 1.

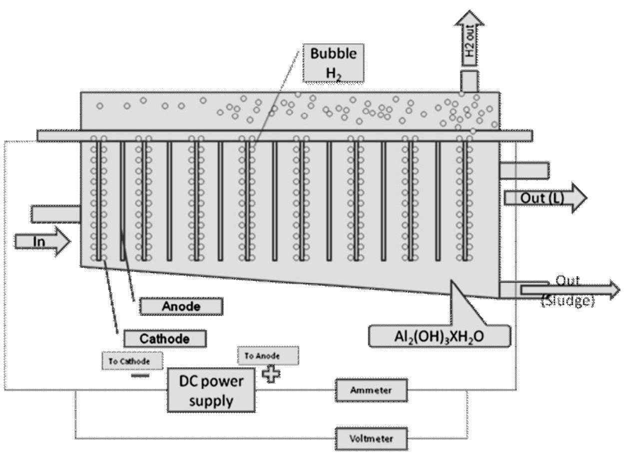

Fig. 1. Schematic view of experimental set up.

A comparative study was conducted by using aluminium and iron as electrode, raw POME and POME from anaerobic pond, with different voltage supply. Twelve experiments were run as summarized in the Table II. Research conducted with voltage variation of 2, 3 and 4 volts, using two sources of wastewater and two electrodes. Wastewater sources used are raw POME and POME output anaerobic pond, while the electrodes used are aluminium and iron metals. The electrodes' surface and connecter were mechanically rubbed with 400 grade abrasive paper before each run. Experiments were run in batch system and each run took 8 hours. POME samples before and after EC process were analyzed for pH, COD, and turbidity. Concentration and composition of the hydrogen gas was analyzed using gas chromatography (SRI 8610C, USA), equipped with a helium ionization detector and packed column (15 m length). The temperatures of the oven, injector, and detector were 50°C, 100°C and 200°C, respectively. Turbidity meter model "Portable Microprocessor Turbidity Meter" branded "Hanna Instrument" was used to measure the turbidity of the samples before and after EC.

Table II.- Experimental design of EC at different voltage using raw POME and POME from anaerobic pond and two different electrodes (Aluminum and iron or ferum).

Raw POME		POME from anaerobic pond	
Aluminium	**Ferum**	**Aluminium**	**Ferum**
2V	2V	2V	2V
3V	3V	3V	3V
4V	4V	4V	4V

RESULTS AND DISCUSSION

Removal of COD and turbidity

The calculation of COD removal efficiency after EC was performed using the formula (Tezcan *et al*., 2009):

$$RE\ (\%) = \frac{C_0 - C}{C} X100$$

Where C_0 and C are the concentrations of COD before and after EC in mgL^{-1}, respectively.

Figures 2 and 3 presents that aluminium electrode has some higher potential to remove the COD as compared to ferum electrode while using raw POME and POME from the outlet of anaerobic pond. For both aluminium and ferum electrode, COD removal efficiency was increased with the increase in voltage supply. However, comparing Figure 2 and Figure 3, an enhanced removal of COD was observed using POME from the outlet of anaerobic pond than the raw POME. Turbidity also decreased while COD decreased. According Figures 4 and 5, the maximum decreases of turbidity is at 4 volt at 8 hours retention time using POME from anaerobic pond and aluminium electrode, which is 90.55%. Figures 2 and 4 also illustrate that efficiency of POME treatment using EC was increased with the increase in retention time.

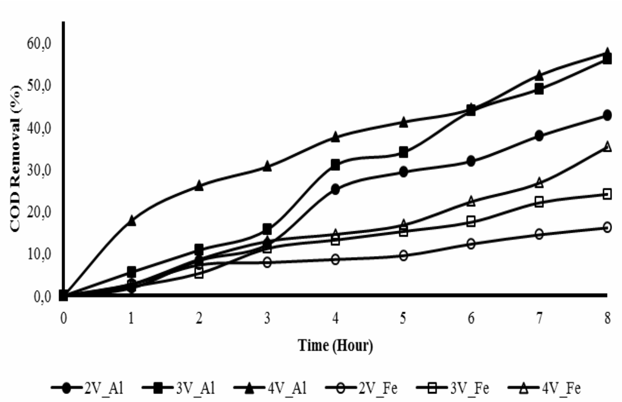

Fig. 2. Percentage removal of COD from raw POME.

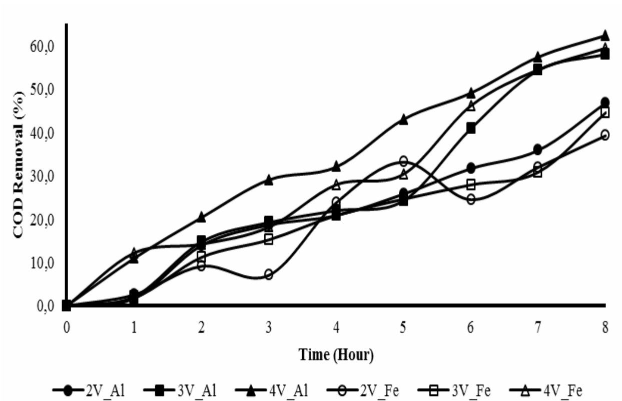

Fig. 3. Percentage removal of COD of POME from outlet of anaerobic pond.

Specific electrical energy consumed (SEEC)

It has been documented earlier that cost of operation is the main parameter which can greatly affect the application of any method regarding wastewater treatment (Tezcan *et al.*, 2009). Using electrocoagulation for wastewater treatment, the major operating cost is the consumption of electrical energy and metal electrodes. SEEC is defined as the amount of electrical energy consumed per unit mass of organic load removed and was calculated by:

$$SEEC = \frac{V.i.t.}{C0 - C) Q}$$

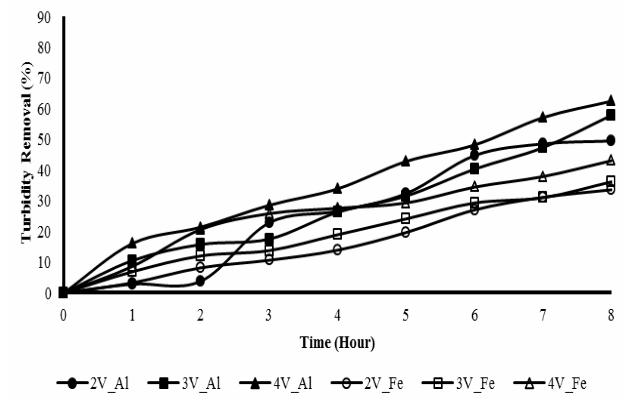

Fig. 4. Percentage decrease of turbidity of raw POME.

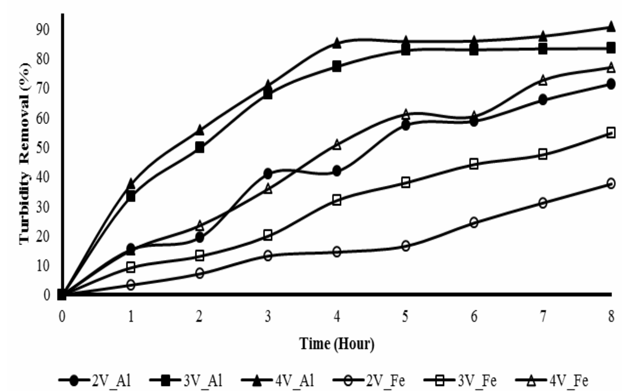

Fig. 5. Percentage decrease of turbidity at POME from outlet of anaerobic pond

Where V is voltage in volts; I is current in amperes; t is time in hours and Q is volume of wastewater in liters. In this research, voltage was kept constant and current density was performed with average of current electricity during 8 h operation. Table III is presenting the values of conducted current density for each voltage and electrode.

According to Figures 6 and 7, the enhanced percentage of COD removal was carried out at the expense of considerably reduced SEEC. In addition, increasing the SEEC will predict the reduced cost of operation. As show in Figures 6 and 7, the SEEC value during EC to treat raw POME using aluminium electrode was generally lower than SEEC, while using iron electrode for the same purpose. While comparing the Figures 6 and 7, it can be demonstrated that average SEEC achieved during EC treatment of raw POME was higher than POME sampled from the outlet of anaerobic pond using aluminium as electrode. Average SEEC at raw POME was 0.3 kWh/kg $COD_{removed}$ and average SEEC for POME from outlet of anaerobic pond was 0.23 kWh/kg $COD_{removed}$. The SEEC values in this research were found lower as compared values by some other researchers. Tezcan *et al* (2009) have reported achieved SEEC values as 131 kWh/(kg $COD_{removed}$) at 350 A/m^2 in EC of vegetable oil refinery wastewater using aluminium as electrode (Un *et al*., 2009).

Table III.- Electrocoagulation showing current density at each variable voltage and electrode

Current Density (A/m^2)	Raw POME	POME from anaerobic fond
2V_Al*	10.3	6.7
3V_Al	20.0	17.6
4V_Al	35.8	26.4
2V_Fe**	17.9	16.1
3V_Fe	27	22.7
4V_Fe	42.4	39.1

*Aluminum, ** Iron

Hydrogen production during EC

EC is generally used for wastewater treatment but this study is contributing an advantageous revenue generating rare reported aspects of hydrogen production simultaneously. In this research, EC was used as wastewater treatment unit and also as hydrogen gas generator as a result of electrolytic dissociation of water. Figures 8 and 9 showed percentage hydrogen production during EC process and present that the yield of hydrogen using electrode aluminium is generally greater than the hydrogen produced using electrode iron. Moreover, increased voltage supply caused enhanced electrolytic dissociation of water leading to increased hydrogen production and metal hydroxides to be utilized for the removal of suspended solids in the electrolytes (POME).

EC of wastewater is presenting dual advantages of wastewater treatment and hydrogen production in a minimum operating area without producing any environmental hazards which are associated with the microbial treatment of wastewater as greenhouse gases and chemical treatment as activated sludge. Chong *et al*. (2009)

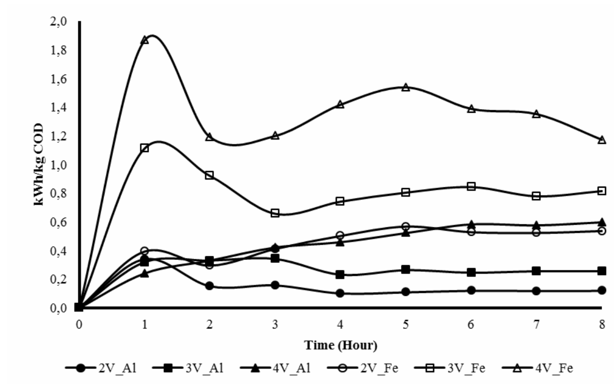

Fig. 6. Specific electrical energy consumed (SEEC) for 2, 3 and 4 volts with electrodes of iron and aluminium of raw POME.

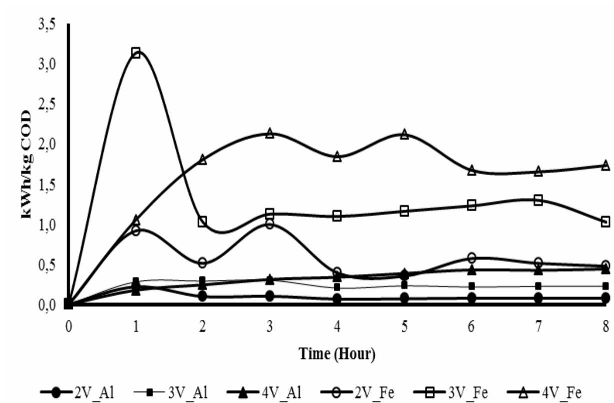

Fig. 7. Specific electrical energy consumed (SEEC) for 2, 3 and 4 volt with electrode iron and aluminium of POME from the outlet of anaerobic pond

have reported 60-70% of hydrogen content in total gas by fermentation using bacteria. Ismail *et al*. (2010) have reported that hydrogen constitutes the total gas up to 52% by fermentation of POME (Ismail *et al*., 2010). Take *et al*. (2007) have reported 95.5-97.2 mol% hydrogen production in cathode exhaust by electrolysis of methanol-water solution separated by a membrane making anode and cathode chambers (Take *et al*., 2007). In our study, the flow rate of hydrogen gas outlet was around 0.9 liter/min, the maximum hydrogen gas produced was about 22.68 liters/h.

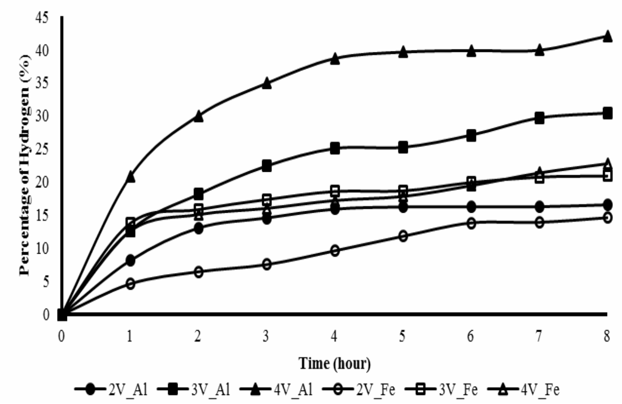

Fig. 8. Hydrogen yield from raw POME.

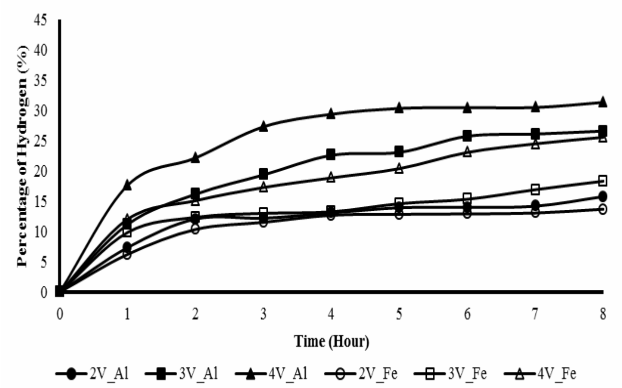

Fig. 9. Hydrogen yield from POME obtained from the outlet of anaerobic pond.

CONCLUSIONS

EC is an economical wastewater treatment with revenue generating hydrogen to be used for fuel cell or other combustion applications. Aluminum electrodes exhibit a higher efficiency as compared to iron electrodes. Palm oil mill effluent can be treated by using EC and the cost of treatment can be compensated to some extent by producing hydrogen gas. EC of POME can be performed by using smaller area without producing environmental hazards associated with aerobic/anaerobic pond system producing greenhouse gases and chemical treatment producing activated sludge. Hydrogen gas production is considered as additional revenue while using EC for the removal of pollutants from highly polluted wastewater.

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REFERENCES

AHMAD, A. L., CHONG, M. F. AND BHATIA, S., 2009. A comparative study on the membrane based palm oil mill effluent (POME) treatment plant. *J. Hazard. Mat.,* **171:** 166–174.

AHMAD, A. L., ISMAIL, S. AND BHATIA, S., 2003. Water recycling from palm oil mill effluent (POME) using membrane technology. *Desalination,* **157**: 87-95.

BARBIR, F., 2005. PEM electrolysis for production of hydrogen from renewable energy sources. *Solar Energy,* **78:** 661–669.

CHEN, G., 2004. Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.,* **38:** 11-41.

CHEN, G. AND HUNG, Y.-T., 2007. Electrochemical Wastewater Treatment Processes. In: *Handbook of environmental engineering* (eds. L.K. Wang, Y.-T. Hung and N.K. Shammas), Volume 5: Advanced physicochemical treatment technologies. The Humana Press Inc., Totowa, NJ:

CHONG, M.-L., RAHIM, R. A., SHIRAI, Y. AND HASSAN, M.A., 2009. Biohydrogen production by Clostridium butyricum EB6 from palm oil mill effluent. *Int. J. Hydrog. Ener.,* **34:** 764-771.

ISMAIL, I., HASSAN, M.A., RAHMAN, N.A.A. AND SOON, C.S., 2010. Thermophilic biohydrogen production from palm oil mill effluent (POME) using suspended mixed culture. *Biomass Bioener.,* **34:** 42-47.

PAMIN, K., SIAHAAN, M. M. AND TOBING, P. L., 1996. Pemanfaatan Limbah Cair PKS pada Perkebunan Kelapa Sawit di Indonesia. *Lokakarya Nasional Pemanfaatan Limbah Cair cara Land Application.* Jakarta.

STICHNOTHE, H. AND SCHUCHARDT, F., 2010. Comparison of different treatment options for palm oil production waste on a life cycle basis. *Int. J. Life Cycle Assess.*, 15: 907-915.

STOJIC, D.L., MARCETA, M.P., SOVILJ, S.P. AND MILJANIC, S.S., 2003. Hydrogen generation from water electrolysis—possibilities of energy saving. *J. Pow. Sourc.,* **118:** 315–319.

SUMATHI, S., CHAI, S.P. AND MOHAMED, A. R., 2008. Utilization of oil palm as a source of renewable energy in Malaysia. *Renew. Sustain. Ener. Rev.,* **12**: 2404–2421.

TAKE, T., TSURUTANI, K. AND UMEDA, M., 2007. Hydrogen production by methanol–water solution electrolysis. *J. Pow. Sourc.*, **164:** 9–16.

TEZCAN, U.U., KOPARAL, A.S. AND OGUTVEREN, U.B., 2009. Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes. *J. environ. Manage.*, **90:** 428-433.

UN, U. T., KOPARAL, A. S. AND OGUTVEREN, U. B., 2009. Electrocoagulation of vegetable oil refinery wastewater using aluminum electrodes. *J. environ. Manage.*, **90:** 428-433.

WULFERT, K., DARNOKO, TOBING, P. L., YULIASARI, R. AND GURITNO, P., 2002. *Treatment of POME in anaerobic fixed bed digesters.* International Oil Palm Conference.

WULFERT, K., GINDULIS, W., KOHLER, M., DARNOKO, D., TOBING, P. L. AND YULIASARI, R., 2000. Pengolahan Limbah Cair Pabrik Kelapa Sawit Secara Anaerobik. Prosiding Pertemuan Teknis Kelapa Sawit, 2000. Pusat Penelitian Kelapa Sawit.

YACOB, S., HASSAN, M. A., SHIRAI, Y., WAKISAKA, M. AND SUBASH, S. 2005. Baseline study of methane emission from open digesting tanks of palm oil mill effluent treatment. *Chemosphere*, **59:** 1575–1581.

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