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Electrocoagulation for Treatment of Industrial Effluents and Hydrogen Production

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1. Introduction

World has entered into a new era where sustainability is the main factor to encounter the challenges of depletion of our reserves and environmental upsets. Wastewater is not only one of the main causes of irreversible damages to the environmental balances but also contributing to the depletion of fresh water reserves at this planet, generating threats to the next generation. A lot of industrial processes are conducted at the expense of plenty of fresh water which is exhausted as a wastewater, and need to be treated properly to reduce or eradicate the pollutants and achieve the purity level for its reutilization in the industrial process to promote sustainability. A number of wastewater treatment methods are prevailing associated with subsequent advantages and disadvantages. Most commonly wastewater treatments involve biological treatment[1], chemical treatment [2] and Electrocoagulation [3]. Biological and chemical treatments of wastewater are usually associated with the production of green house gases and activated sludge along with some other limitations regarding required area and removal of residual chemicals respectively. On the other hand, Electrocoagulation is an extremely effective wastewater treatment system, removing pollutants and producing hydrogen gas simultaneously as revenue to compensate the operational cost[3]. Electrocoagulation has been documented positively to treat the wastewater from steam cleaners, pressure washers, textile manufacturing, metal platers, meat and poultry processors, commercial laundry, mining operations, municipal sewage system plants and palm oil industrial effluents.

Around the world, 45 million metric tons of palm oil has been produced in 2009 [5]. Approximately 0.65 tons of raw palm oil mill effluent (POME) is produced for every ton of processed fresh fruit bunches (FFB). A large quantity of water is necessary to process the palm fruit for oil production [6]. Furthermore, POME contributes 83% of the industrial organic pollution load in Malaysia (Vigneswaran *et al*, 1999). The POME is rich in organic

carbon with a chemical oxygen demand (COD) higher than 40 g/L and nitrogen content around 0.2 to 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 [7]. Conventionally, POME is usually treated with open lagoon technology by subjecting it to anaerobic treatment in open pond system to reduce the COD & BOD, this pretreatment method is associated with the risks of production of green house gases i.e. methane as a pollutant to the environment [8]. Usually the existing conventional methods for the pretreatment of POME are expensive or taking long retention time and require a vast pond area.

Parameter	Concentration (mg/L)	Element	Concentration (mg/L)
Oil and grease	4000–6000	Potassium	2,270
Biochemical oxygen demand	25,000	Magnesium	615
Chemical oxygen demand	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

Table 1. Characteristics of palm oil mill effluent [4]

This chapter emphasizes on the use of Electrocoagulation technique as a tool to promote the trends of sustainability in the existing industrialized world. Electrocoagulation technology was used successfully to pre-treat the Palm oil mill effluent (POME) as an electrolyte for the removal of polluting factors as a result of coagulation and precipitation of suspended solids followed by sedimentation under gravity. Aluminium and iron electrodes were used as sacrificing anodes to be used up in electrolytic oxidation for the production of $\text{Al(OH)}_3\text{XH}_2\text{O}$ and $\text{Fe(OH)}_3\text{XH}_2\text{O}$ respectively in different batch experiments. This study was also partially focused 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 during Electrocoagulation (EC). The metal (anode) based coagulants were found enough efficient to reduce the chemical oxygen demand (COD) and turbidity of POME. The remarkable pollutants removal was also associated with the hydrogen production as revenue to contribute the operational cost of wastewater treatment. Hydrogen production was also found helpful to remove the lighter suspended solids towards surface. The electrical inputs and findings were subjected to determine the Energy Efficiencies of POME treatment in comparison with water to highlight the associated advantages with EC of POME. This chapter is encompassing a detailed study of the related topics in general linked

with experimental findings. Experimental findings have also been discussed in depth with reference to the published articles by other researchers. Concepts and mechanisms of coagulation and Electrocoagulation have been elaborated covering the maximum applications and gains in the industrial sector in context with the literature. Chemical composition of the wastewater and associated risks to the environment and health has been included for the better understanding of the readers. A précised approach was used to make the methodology reproducible and effective by supporting it with diagrammatic representation of the experimental set up. Process description is made conceivable and discussed in context to the general information in the literature. A separate discussion is made to understand the advantageous hydrogen production in addition to the removal of contaminants from the wastewater. Mathematical derivations and graphic representations are frequently used to represent the Energy Efficiency of the Electrocoagulation of the wastewater in comparison with the tap water at different pH. This chapter is presenting a real image of conceptual Electrocoagulation in the light of experimental verification in relation to previous studies.

Hydrogen is considered as an energy carrier like electricity and produces no green house gas or carbon dioxide when burnt in the presence of oxygen in related appliances including fuel cell or combustion engines. Hydrogen can be produced from different feedstock using a variety of techniques. Hydrogen is currently produced in large quantities from natural gas. Although, it is the cheapest way at present to produce hydrogen but the presence of carbon in methane is contributing to increase the global warming. A challenging problem in establishing H_2 as a source of energy for the future is to establish the procedures to produce hydrogen in abundance without creating any environmental threats. This chapter will emphasize on the treatment of wastewater and simultaneous hydrogen production using Electrocoagulation.

2. Technology description

2.1. Mechanism of coagulation and electrocoagulation

Industrial wastewater is in possession of impurities including colloidal particles and dissolved organic substances. The finely dispersed colloids or suspended solids are usually repelled by their outer layer of negative electrical charges and maintain the colloidal nature until treated by flocculants/coagulants for their removal. The process of flocculation and coagulation can be defined as *“the ionic bridging between the finely divided particles to make flocs followed by their grouping into larger aggregates to be settled under gravity”*. The terms; flocculation and coagulation can separately be restricted to the preparation of flocs and grouping of flocs into aggregates respectively. The mechanism involved is the neutralization of the charges on the suspended solids or compression of the double layer of charges on the suspended solids. Overdose of coagulants may reverse the charge at the outer layer of the colloidal particles to re-stabilize them in a reverse mode. The wastewater treatment and down streaming of industrial fluids can be performed by using a number of flocculating/coagulating agents based on chemical salts and organic polymers.

Figure 1. Gradual decrease in COD & turbidity during Electrocoagulation

A wide variety of chemicals and organic compounds have been recognized as efficient agents to remove the suspended solids from the wastewater. Wastewater is a very general term and can be designated to any water after being utilized by the human activities. A range of industrial processes are involved to exhaust a variety of effluents with different nature of pollutants. The treatment by the chemicals as well as organic molecules depends on the nature of pollutants and pH conditions. Because of the different nature of pollutants, no specific strategy can be recognized as versatile treatment to all types of wastewaters. Organic polymers are considerably preferred as coagulating/flocculating agents because of their biodegradable nature as compared to the chemicals causing to produce activated sludge. Coagulation is in routine practice for the treatment of drinking water[9], wastewater and industrial effluents [10].

Treatment of water using electricity was first proposed in UK in 1889 [11]. The application of electrolysis in mineral beneficiation was patented by Elmore in 1904 [11]. Electrocoagulation, precipitation of ions (heavy metals) and colloids (organic and inorganic) using electricity has been known as an ideal technology to upgrade water quality for a long time and successfully applied to a wide range of pollutants in even wider range of reactor designs [12-14]. Electrocoagulation is the technique to create conglomerates of the suspended, dissolved or emulsified particles in aqueous medium using electrical current causing production of metal ions at the expense of sacrificing electrodes and hydroxyl ions as a result of water splitting. Metal hydroxides are produced as a result of EC and acts as coagulant/flocculant for the suspended solids to convert them into flocs of enough density to be sediment under gravity. The electrical current provides the electromotive force to drive the chemical reactions to produce metal hydroxides.

Following reactions are carried out at different electrodes:

Anode:

Alkaline condition:

Acidic condition:

Cathode:

Dissociation of water by EC generate hydroxide ions which are known as one of the most reactive aqueous radical specie and this radical has the ability to oxidize organic compounds because of its high affinity value of 136 kcal [15]. The generated hydroxides or polyhydroxides have strong attractions towards dispersed particles as well as counter ions to cause coagulation. The gases evolved at the electrodes are also helpful to remove the suspended solids in upward direction [16].

A number of electrochemical reactions are involved within the electrocoagulation reactor. Reduction of metal anodes is responsible to produce hydroxide complexes causing flocculation of suspended solids into stable agglomerates. Production of oxygen and hydrogen as a result of electrolytic dissociation of water molecules cause emulsified oil droplets to be freed from water molecules making a separate layer on the surface. The same mechanism is involved in case of dyes, inks and other type of emulsions. In the presence of chlorine, metal ions can make chlorides which are also helpful in flocculation/coagulation of the wastewater. The production of oxygen in the electrocoagulation chamber can oxidize or bleach the chemicals like dyes.

System components and functions

An Electrocoagulation reactor consists of anode and cathode like a battery cell, metal plates of specific dimensions are used as electrodes and supplied with adequate direct current using power supply. The metal plates known as sacrificial electrodes are usually connected in parallel connection with a specified inter electrode distance (1.5-3.5cm) and supplied electric current is distributed on all the electrodes depending on the resistance of the individual electrodes. Distance of the electrodes has a direct relationship with the consumption of electricity. An electrode is an electrical conductor used to make contact with a nonmetallic part of a circuit. In case of EC, electrodes are known to be sacrificed for the release of metal ions at the anode, and cathode is responsible to produce hydroxyl ions. Metallic electrodes sacrificed to produce ions in the water which ultimately neutralized the charges of suspended particles leading to coagulation. The released ions remove suspended solids by precipitation or flotation. Water molecules are usually in bonding with colloidal particles, oils, or other contaminants in the wastewater leading to stable suspension, EC caused ionization of the water molecules adhering the contaminants to convert them into insoluble moieties to be sediment under gravity or float depending on density.

Experimental data to be presented in this chapter was generated by using the reactor with essential components as below:

Electrocoagulation cell was operated using rectifier, power supply with working range of electric current and voltage 0-60 amp and 0-15 volts respectively, ampere meter with digital working range 0-20 ampere and voltmeter with digital working range of 0-300 volt DC. Electrocoagulation was performed at different voltage (2, 3 and 4 volts). A reactor containing volume 20 liters of POME or water was used to conduct EC experiments (Fig. 1). The twelve aluminum plates were connected to a low voltage power supply. Six alternate plates were connected to the positive pole and the other six were connected to negative pole of the battery, thus acting as anode and cathode respectively. The weight of the plates was measured before and after the electrocoagulation. Aluminium plates were cut from commercial grade sheet (95%-99%) of 3 mm thickness as anode and cathode. POME samples were collected from Sri Ulu Langat Palm Oil Mill with COD, turbidity and pH around 50,000 mg/L, 2800 NTU and 4 respectively. Water samples were collected from usual tap water in the laboratory, the pH of tap water was 6 to 8.5. The pH of the water was adjusted to pH 4 by using 1N HCl.

2.2. Applications for different wastes

Coagulation and precipitation of contaminants can be induced by electrocoagulation technology and addition of coagulation-inducing chemicals. As a result of EC, the liberated hydrogen also took part to remove the lighter suspended solids in upward direction. Electrocoagulation has been employed in treating wastewaters from textile, catering, petroleum, tar sand, and oil shale. It is also used to treat the carpet wastewater, municipal sewage, chemical fiber wastewater, oil–water emulsion, oily wastewater clay suspension, nitrite, and dye stuff from wastewater.

Treatment of wastewater by EC has been practiced from pulp and paper industries[17], vegetable oil industries[18], textile industries [19-20], mining and metal-processing industries[21-22]. In addition, EC has been applied to treat water containing food waste, oily wastes, waste dyes, domestic wastewater etc. Copper reduction, coagulation and separation were also found by a direct current electrolytic process followed by sedimentation of the flocs by using EC [11]. This chapter is encompassing the details of Electrocoagulation of industrial effluent for the pretreatment and hydrogen production as an advantage. It has been explained that how the hydrogen production from industrial effluent may contribute to the cost effectiveness of the treatment process by producing extra revenue.

2.3. Advantages of technology

Electrocoagulation requires simple equipment and small area as compared to the conventional pond system which causes increase in the green house gases. Electrocoagulation is an alternative wastewater treatment that dissolves metal anode using electricity and provide active cations required for coagulation without increasing the salinity of the water [23]. Electrocoagulation has the capability to remove a large number of pollutants under a variety of conditions ranging from: suspended solids, heavy metals, petroleum products, colour from dye-containing solution, aquatic humus and defluoridation of water [23]. Electrocoagulation is usually recognized by ease of operation

and reduced production of sludge [24]. Aluminium and iron are suitable electrode materials for the treatment using electrocoagulation [25]. The removal efficiency of electrocoagulation using Aluminium electrodes was higher than that of using Iron electrodes [26]. Electrocoagulation process consists of two stages: (i) electro generation of the metal cations and their physical action on the pollutant, (ii) formation of the flocs, flocculation and settling upon addition of flocculating agents and under low stirring [27].

Figure 2. Electrocoagulation of Palm Oil Mill effluent as Wastewater Treatment and Hydrogen Production using Electrode Aluminium

Figure 3. Electrocoagulation of Palm Oil Mill effluent as Wastewater Treatment and Hydrogen Production using Electrode Aluminium

3. Experimental procedures

Palm oil mill effluent (POME) was used as an electrolyte without any additive or pretreatment to perform electrocoagulation (EC) using electricity (Direct current) ranging from 2-4 volts in the presence of aluminum electrodes in a reactor volume of 20 liters. Investigations were made on the removal of pollutant like chemical oxygen demand (COD) and turbidity as a result of electrocoagulation of palm oil mill effluent (POME), and production of hydrogen gas as an advantageous step to meet the energy challenges. The results show that EC was responsible to reduce the COD and turbidity of POME 57% and 62% respectively in addition to the 42% hydrogen production during electrocoagulation. Hydrogen production was also helpful to remove the lighter solids towards surface. The anode reaction was responsible to produce $\text{Al}(\text{OH})_3 \cdot \text{XH}_2\text{O}$ at aluminium electrode (anode) which is a very reactive agent for flocculation/coagulation of suspended solids. The production of hydrogen gas from POME during electrocoagulation was also compared with hydrogen gas production from tap water at pH 4 and tap water without pH adjustment under the same conditions to highlight the advantageous aspects hydrogen production and wastewater treatment simultaneously. The main advantage of this study was to produce hydrogen gas while treating POME with EC to reduce COD and turbidity effectively. A number of experiments were designed and findings are discussed in different sections.

Figure 4. Electrocoagulation of Palm Oil Mill effluent as Wastewater Treatment and Hydrogen Production using Electrode Aluminium

3.1. Methodology

Materials and equipments

Electrocoagulation cell was operated using rectifier, power supply with working range of electric current and voltage 0-60 amp and 0-15 volts respectively, ampere meter with digital

working range 0-20 ampere and voltmeter with digital working range of 0-300 volt DC. Electrocoagulation was performed at different voltage (2, 3 and 4 volts). A reactor containing volume 20 liters of POME or water was used to conduct EC experiments (Fig. 1). The twelve aluminum plates were connected to a low voltage power supply. Six alternate plates were connected to the positive pole and the other six were connected to negative pole of the battery, thus acting as anode and cathode respectively. The weight of the plates was measured before and after the electrocoagulation. Aluminium plates were cut from commercial grade sheet (95%-99%) of 3 mm thickness as anode and cathode. POME samples were collected from Sri Ulu Langat Palm Oil Mill with COD, turbidity and pH around 50,000 mg/L, 2800 NTU and 4 respectively. Water samples were collected from usual tap water in the laboratory, the pH of tap water was 6 to 8.5. The pH of the water was adjusted to pH 4 by using 1N HCl.

Figure 5. Electrocoagulation of Palm Oil Mill effluent as Wastewater Treatment and Hydrogen Production using Electrode Aluminium

3.2. Removal of pollutants from industrial effluent

Cell operation

A comparative study was conducted by using the POME, tap water at pH 4 (pH was adjusted with acid) and tap water without pH adjustment as electrolyte during different run, each electrolyte was analyzed for pH, COD and turbidity before and after the run. The

pH of tap water was found in the range of pH 6.5-8.5 during different runs depending on the source of supply. The experiments were conducted in batch system. Electrodes were put in the reactor as multiple channels; with inter-electrode distance of 3 cm [28]. To perform EC, direct current (DC) was used throughout the experiment which was being converted from alternating current by using power supply and rectifier. POME, tap water at pH 4 and tap water (without pH adjustment) samples were analyzed before and after electrolysis for pH, COD and turbidity using standard techniques and Equipments. Hydrogen concentration was also analyzed using gas chromatography. The electrode surface was mechanically rubbed with 400 grade abrasive paper to remove the rusting or deposits before each run. The experiments were carried out at different voltage values: 2, 3 and 4 volt, and the current were measured during each run. Standard deviations were calculated and plotted to facilitate the reproducibility of the data regarding measurements.

3.3. Hydrogen production

Hydrogen production

A closed container was used to conduct the electrocoagulation; the container was connected to the peristaltic pump to collect the total gas (Fig. 1). The gas was collected at the rate of 900 ml/minute at room temperature in the gas bags equipped with one way valves. The composition of the total gas was analyzed using gas chromatography (SRI 8610C, USA), equipped with a helium ionization detector (15 m length). The temperatures of the oven, injector and detector were 50, 100 and 200 °C respectively.

Cumulative hydrogen gas (Fig. 9) was calculated using the following equation:

$$V_n = (QxX_{H_2}) + V_{n-1} \quad (1)$$

Where V_n is the volume of hydrogen gas at n hours; Q is the flow rate of total gas; X_{H_2} is the concentration of hydrogen gas in total gas; V_{n-1} is the volume of hydrogen gas in total gas.

The electrical energy supplied to the system was calculated using the following equation

$$E_e = VIt \quad (2)$$

Where E_e is the electrical energy supplied by the DC power supply (J); V is the DC voltage applied; I is the current (A) and t (hour) is the duration of the DC voltage applied to the system.

The amount of produced hydrogen gas was calculated using the following equation:

$$PV_{H_2} = \left(\frac{m}{M}\right) RT \quad (3)$$

Where P denotes pressure in atm; V_{H_2} denotes volume of the cumulative hydrogen calculated from equation (1); m denotes the mass of the cumulative hydrogen (g); M is the molar mass of hydrogen (2 g /mol); R is the gas constant (0.082 L atm. mol⁻¹ K⁻¹), T is denoting the room temperature (298 K).

The energy contents of the hydrogen gas were calculated using the equation

$$EH_2 = m \left(122 \frac{\text{kJ}}{\text{g}} \right) \quad (4)$$

where m denotes the mass of the cumulative hydrogen produced within a specified time period.

Energy efficiency of the system was calculated by using the following equation

$$EEf = \frac{EH_2}{E_e} \quad (5)$$

Energy efficiencies were determined by using electrolytes like water at pH 4, tap water, and POME at the expense of electrical inputs of 2, 3 and 4 volts.

4. Results and discussion

Electrocoagulation of POME was performed to reduce its polluting nature as well as hydrogen gas production. It was observed that the POME before electrocoagulation process was brown in color and after electrocoagulation became whitish in color. A remarkable reduction in the turbidity of POME can be visualized after electrocoagulation (Fig.2).

Dynamic response of pH during electrocoagulation

Kılıc M.G. and C. Hosten (2010) has mentioned that the optimum effectiveness of EC can be achieved at pH 9. Chen and Hung (2007) have described pH as an important factor in EC and variation in pH is usually caused by the solubility of metal hydroxides. They further reported that the pH of the effluent after electrocoagulation would increase for acidic influent, however pH would decrease for alkaline effluent [12]. Hydroxides, which are produced as a result of dissociation of water are known as one of the most reactive aqueous radical specie and this radical has the ability to oxidize almost all of the organic compounds because of its high affinity value of 136 kcal [15]. Figure 3 has shown the dynamic response of pH of POME at pH 4, water at pH 4 and tap water (pH 6.6 to 8.2) using electricity at 2, 3 and 4 volt inputs. The pH of the POME under the influence of 2 volts was found near about constant, however a slight increase in pH was found using 3 and 4 volts of electricity with POME. Agustin et al (2008) has performed the EC of de-oiled POME in the presence of additional sodium chloride as electrolyte aid and reported the increase in pH value from 4.3 to 7.63. In our case, the study was performed by using raw POME as it was obtained from palm oil mill and no additional salts were added to enhance the conductivity. It was assumed that the formation of aluminium hydroxide at aluminium electrodes was leading to a simultaneous coagulation of the suspended solids followed by effective sedimentation under gravity. In case of EC of water (pH 4), the 2 volt input was able to increase the pH (4.23 to 6.18) as compared to the 3 volts input (4.34 to 5.76). However the use of 4 volts input was responsible to increase the pH value up to more than 6.5. Tap water at pH (6.6 to 8.2) was also investigated but there was no remarkable change in the pH of tap water after EC. EC of water at pH 4 and water at pH 6.5-8.5 was conducted to compare the efficiency of hydrogen production at different pH of water

and ultimately to compare with POME at pH 4.0. It was observed that the EC of POME at pH 4.0 is presenting better results as compared to the water at different pH. Electrolysis/electrocoagulation is closely associated with the variation of the pH and its effects on the experimental solutions. Different aluminium species are formed at the aluminium cathode (electrode) by the combination of the electro-dissolved Al^{3+} ions with hydroxyl ions to affect the pH [29]. The influence of the pH while studying the EC has also been reported by some other researcher's e.g. Kobya et al (2003), has reported the pH increase from 3 to 11 while conducting the EC using aluminium electrode with textile wastewater. A like trend was also achieved by some other researchers [30]. Hence, it has been concluded that the effect of pH is an important parameter influencing the performance of the EC process.

Electrocoagulation for the removal of COD and turbidity from POME

Reduction in the chemical oxygen demand (COD) is a key factor in waste water treatment. EC was performed to investigate the effects of electrochemical treatment of POME. The electrical inputs of 2, 3 and 4 volts were used to proceed the EC of POME to remove the COD and turbidity as well as hydrogen production. As a result of electrocoagulation, a gradual reduction in the color intensity and turbidity of the POME can be visualized with respect to time (Fig. 3). EC is responsible for the electrolytic dissociation of water to produce reactive specie (OH^-) which facilitate the process of flocculation/coagulation of the potential pollutants in the POME. The reactivity of the (OH^-) ions and zeta potential has been described by Wang et al, Li, et al (2003). According to figure 4, a higher reduction in COD of POME was observed while proceeding electrocoagulation at 4 volts rather than at 2 and 3 volts. Electrocoagulation was efficiently responsible to decrease the COD to 57.66% at 4 volts in 8 hours, on the other hand COD reduction at 2 and 3 volts were 42.8% and 56.16% respectively under same conditions. The combination of the Al^{3+} ions and highly reactive specie (OH^-) is effectively known as flocculating/coagulating agent to remove the suspended solids from the waste water [12]. However the total reduction of the COD and turbidity was also contributed by the upward flow of the hydrogen gas during electrocoagulation. Agustin et al (2008) have reported the removal of 30% COD as a result of EC of POME in six hours of operation time but our study has shown a greater reduction in the COD of POME as compared to their study [31].

In this study, neither any additive was used to enhance the electrolytic efficiency of the electrolyte nor was the POME subjected to the extraction of oil or pH adjustment. This study was designed to treat the POME at the industrial level as an effective and primary treatment without any extra treatment or addition of chemicals. Agustin et al (2008) have reported a 100% reduction in turbidity and only 30% reduction in COD after electrocoagulation of POME in the presence of sodium chloride, the high residual COD value in the transparent fluid might be attributed to the presence of some soluble salts due to sodium chloride. The efficiency of EC is also depending on the nature of effluent and processing time. Ugurlu et al (2008) has reported 75% removal of COD with paper mill effluent treatment but the initial COD of this effluent was 86 times lower than initial COD of POME [31]. O.T. Can has also reported 50% COD removal by conducting EC of textile wastewater with 10 minute operating time [32].

Turbidity and COD have straight relation as caused by the presence of suspended solids. Removal of the COD might automatically reduce the turbidity to the lower level accordingly. According to Fig. 5, the maximum removal of turbidity achieved at electrical inputs of 4 volt in 8 hours operating time was 62%. The operating time and value of electrical input have a direct influence on the removal of COD and turbidity. Agustin et al (2008) has reported a transparent fluid after six hours EC operating time but the experimental solution was still in possession of 70% residual COD. In our study removal of 57.66% of COD and 62% turbidity was not able to create the transparency; apparently a remarkable decrease in the color intensity was observed (Fig. 2). It was also observed during the experiments that long operating times, high voltage values, bubbling of hydrogen gas at cathode were supporting factors to remove the turbidity and COD from the electrolyte (POME), as it was previously reported by Kilic et al. [33]. Kilic and Hosten has also reported the removal of 90% turbidity while conducting EC of aqueous suspensions of kaolinite powders with concentration of 0.2 g/L using electrical input of 40 volts, 20 minute operating time and NaCl as additive [34].

Hydrogen production using electrocoagulation

Production of hydrogen by the electrolytic dissociation of water is a usual practice but the production cost is considerably high [35-36]. It was assumed that any advantage accompanying with the electrolysis of water to produce hydrogen may compensate the actual operational cost partially. This study was launched with a specific objective to produce hydrogen gas as well as the pretreatment of palm oil mill effluent simultaneously to maintain the cost effectiveness of the process. The EC was designed to make pretreatment of POME in a closed container specially equipped with a gas collection system Fig. 1. Tap water at pH 4, tap water at pH 6.5-8.5 and POME were used as an electrolyte to conduct the EC with electrical inputs of 2, 3 and 4 volts separately. The pH of the POME was not adjusted but the pH of tap water was adjusted nearer to POME (pH 4) to compare the hydrogen production under the same conditions. Tap water pH (6.5-8.2) was found varied at different times but not subjected to any adjustment of pH (Fig.7). The tap water was used to compare the efficiency of hydrogen production from water at different pH and ultimately to compare this hydrogen production efficiency from POME while simultaneous removal of pollutants. The above mentioned EC experiments have generated the data which is clearly representing a difference in hydrogen production from water and POME. The gas was collected at the rate of 900 ml/minute at room temperature in the plastic gas bags. The rate of total gas production was 54 L/h. The overall hydrogen production from tap water at pH 4 and pH 6.5-8.5 was found below than 5% (v/v) of the total gas. In case of POME as an electrolyte, the maximum hydrogen production was estimated as 15% (v/v), 30% (v/v) and 42% (v/v) at different electrical inputs of 2, 3 and 4 volts respectively. Phalakornkule et al have reported $0.521 \times 10^3 \text{ m}^3$ (6.252×10^6 liter/hour) hydrogen gas production using EC in five minutes from waste water containing dyes [37]. Take et al have investigated hydrogen production by using methanol-water solution as an electrolyte keeping cathode and anode separate from each other by a membrane and reported that the hydrogen in cathode exhaust gas was 95.5-97.2 mol% [38]. In our study, the maximum hydrogen gas produced was about

22.68 liters/hour and an efficient reduction of COD and turbidity of POME by as much as 57% and 62% was achieved respectively.

To determine energy efficiency

Energy efficiency (EEf) can be defined as the output obtained in the form of hydrogen gas on the expense of electrical energy provided to the reactor for a certain time period. The energy efficiency was calculated as described in material and equipments using equations (1-5). The EEf showed some variations while using water at pH 4, water at pH (6.5-8.5) and POME during electrolysis/electrocoagulation. The highest energy efficiencies were determined while using water at pH 4.0, water at pH (6.5-8.5) and POME with electrical inputs of 2 volts (Fig. 8). Energy efficiency for the treatment of POME as well as hydrogen production was also determined and plotted separately (Fig. 9). Although, energy efficiency was not so high while using POME as an electrolyte but can be further improved by standardizing the conditions regarding inter-electrode distance, nature of electrodes and proper dilution of POME. EEf was found increasing with the passage of time while using water at pH 4 and water at pH (6.5-8.5), however the EEf of POME was not subjected to any remarkable increment with respect to time (hours). Kargi et al (2001) have reported the hydrogen production by using electrolysis of anaerobic sludge with EEf of 74%, but they have used the serum bottles containing 1L sludge [39]. The low EEf values in our study might be due to the large volume of the electrolyte and can be improved further by standardizing the conditions regarding inter-electrode distance, nature of electrodes and proper dilution of POME.

Palm oil mill effluent can be treated by using environment friendly electrocoagulation, and hydrogen gas can be obtained as revenue to compensate the treatment cost of POME. EC of POME can be performed by using small area as compared to the conventional aerobic/anaerobic pond system. Hydrogen gas was also found helpful to remove the suspended solids towards surface. This study is presenting an approach towards environment friendly treatment of POME and hydrogen production as an alternative energy.

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