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ELECTROLYTIC TREATMENT OF PALM OIL MILL EFFLUENT

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ABSTRACT: *An innovative method of palm oil mill effluent treatment was developed based on electrochemical oxidation process. The hypochlorous acid was generated in an undivided electrolytic cell consisting of two sets of graphite as anode and stainless sheets as cathode. The generated hypochlorous acid served as an oxidizing agent to destroy the organic present in the palm oil mill effluent. The electrochemical oxidations were carried out for varying influent COD concentrations namely 7,000; 10,000 and 15,000 mg/L. For an influent COD concentration of 7,000 mg/L at an initial pH of 3.6 ± 0.1; current density of 37.6 mA/cm2; sodium chloride content of 3% and at an electrolysis period of 240 min, resulted in the following residual concentrations of pH 6.9; COD 114 mg/L; BOD5 73 mg/L; TOC 56 mg/L; residual total chlorine 172 mg/L; turbidity 24 NTU and temperature 62°C respectively. In the case of influent COD concentration of 15,000 mg/L for the above said operating condition resulted in a residual concentrations of pH 6.5; COD 2,680 mg/L; BOD5 1,265 mg/L; TOC 1,024 mg/L; residual total chlorine 86 mg/L; turbidity 1,157 NTU and temperature 61°C respectively. The energy requirement were also investigated for an influent COD concentration of 7,000 mg/L at 2 and 3% sodium chloride concentration at a fixed current density of 37.6 mA/cm2. The results showed that at 2 and 3% sodium chloride content for achieving a COD removal efficiency of 90%, the energy requirement were found to be 32 and 17 Wh/L respectively. The observed energy difference was due to the improved conductivity at 3% sodium chloride content.*

Keywords: *Electrolytic treatment; palm oil mill effluent; hypochlorous acid; chlorine, electrochemical treatment.*

1. INTRODUCTION

Oil palm (*Eleasis guineensis jacq*) is an important crop in Malaysia, and palm oil industry is one of its major agro-industry. The commercial palm oil production is mainly located in Peninsular Malaysia and dates back to the 1960s (1). Malaysia is the current world largest producer and exporter of palm oil, accounting for about 48 and 58% respectively (2). In the processing of palm oil fruit large quantities of wastewater are generated from sterilizer condensate, hydrocyclone waste and separator sludge (3). On an average 0.9 to 1.5 m^3 of palm oil mill effluent is generated for each ton of crude palm oil produced (4). Palm oil mill effluent is rich in organic carbon with a biochemical oxygen demand (BOD) higher than 20 g/L and nitrogen content around 0.2 g/L as ammonia nitrogen and 0.5 g/L total nitrogen (5).

Currently the Malaysian palm oil industry adopts the following effluent treatment schemes in the descending order namely

(*a*) Anaerobic/facultative ponds;
(*b*) Tank digestion and mechanical aeration;
(*c*) Tank digestion and facultative ponds;
(*d*) Decanter and facultative pond (5, 6, 7) and
(*e*) Physico-chemical and biological treatment (8). The viability of evaporation technology was also tested using palm oil mill effluent (9).

As the conventional methods of palm oil mill effluent treatment are based on biological system, it naturally leads to longer hydraulic retention time; moreover they are subjected to failures due to shock loading and improper maintenance of biological process. The electrochemical methods of treatment are favored as they are neither subjected to failures due to variation in wastewater strength or due to the presence of toxic substance and require less hydraulic retention time. The most promising way to carry out electrolytic treatment in a convenient and cost effective method is to generate chlorine or hypochlorous acid as and when required using sea water or brine liquor. The electrochemical method of waste treatment came into existence when it was first employed to treat sewage generated by ship onboard by mixing sewage and seawater in the ratio 3:1 and subjecting them to electrolysis (10).

The electrochemical method of treatment was widely received in treating industrial wastewaters rich in refractory organics and chloride content. Earlier researchers have successfully proved the viability of electrochemical oxidation method to treat effluents originating from textile (11, 12, 13, 14, 15); olive mill (16, 17); tannery (18, 19, 20); distillery (21); syntan (22) and azo dye (23). The electrochemical oxidation of swine manure resulted in simultaneous removal of COD and ammonia nitrogen (24). Numerous works on electrochemical oxidation of phenol and chlorinated phenol were carried out using porous carbon felt (25); boron-doped diamond (26); ruthenium mixed oxide (27); DSA and graphite felt as electrode (28).

To the best of our knowledge there are no published scientific reports based on in-situ hypochlorous oxidation for palm oil mill effluent treatment. Hence, in this article electrolytic oxidation based on in-situ hypochlorous acid generation is being proposed as a method of treatment for palm oil mill effluent. The hypochlorous acid is generated using graphite anode and stainless sheet as cathode in an undivided electrolytic reactor. The palm oil mill effluent was collected from Golden Hope Plantation, Banting, Malaysia.

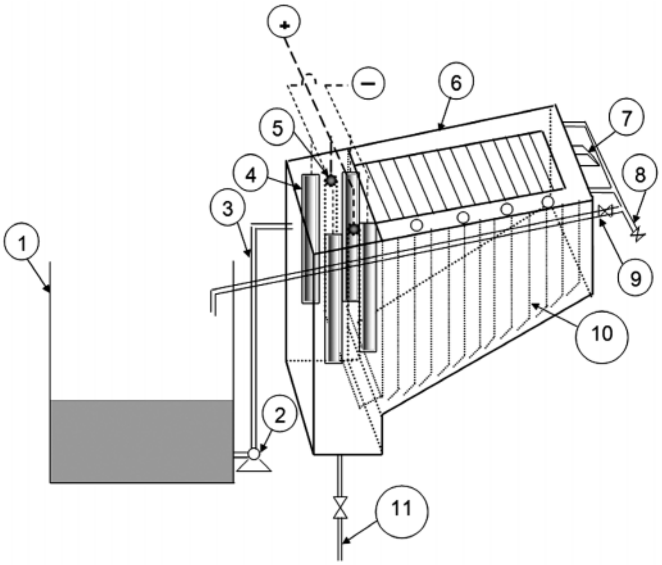
2. MATERIAL AND METHODS

2.1. Palm Oil Mill Effluent Characteristics

The raw palm oil mill effluent was collected from the collection pit of Golden Hope Plantation, Banting, Malaysia, whose characteristics are presented in Table 1. The POME was preserved at a temperature less than 4ºC, but above freezing point in order to prevent the wastewater from undergoing biodegradation due to microbial action (29). The raw palm oil mill effluent was preserved for a maximum of 30-45 days thereafter fresh sample were collected for further analysis.

2.2. Electrolytic Reactor Setup

The schematic diagram of the pilot plant electrolytic reactor set-up is as shown in Fig. 1. A total liquid volume of 100 L were taken in order to achieve recirculation. One-third of the reactor area is used for housing the electrode, while the two-third served as a clarifier zone. A graphite rod of 550 mm in length and 60 mm in diameter was used as an anode. Perforated stainless steel sheets 550 mm long, 50 mm wide and having a thickness of 0.8 mm were used as cathodes. Two sets of anode and cathode were employed during the electrolysis. Each set of graphite anode was surrounded by two cathode sheets. The distance between anode and cathode was 20 mm. A rectifier having an input of 230 V and variable output of 0-20 V with a maximum current of 100 A was used as a direct current source. The electrochemical reactor was operated in a batch mode with continuous recirculation. The floating sludge was removed from the top outlet zone while the settled sludge was removed from the bottom sludge line.



1. Feed tank	7. Floating sludge outlet
2. Feed pump	8. Treated effluent outlet line
3. Inlet line	9. Recirculation line
4. Stainless sheet -Cathode	10. Parallel plate settler
5. Graphite-Anode	11. Settled sludge outlet
6. Electrolytic reactor	

Figure 1. Diagram of Electrolytic Reactor

2.3. Analytical Method

The organic strength of the wastewater was determined by COD and TOC method (30), while its biodegradability was measured based on BOD5. The total chlorine concentration in the sample was determined by iodometric method. The clarity of the wastewater was determined with by Nephelometric method. The ammonia-nitrogen was determined by titrimetric method. The color of the wastewater was determined based on Platinum scale measured in Hazen units. The suspended solids were determined by drying the sample at 105ºC (29).

2.4. Experimental Method

During electrolysis, chlorine was produced at the anode and hydrogen gas at the cathode. As the anode and cathode were kept in undivided electrolytic reactor the generated chlorine undergoes disproportionation reaction resulting in hypochlorous acid ($Cl_2 + H_2O \rightarrow HOCl + HCl$). Further disproportion of OCl^- to ClO_3^- was favoured at high temperature (approximately 75ºC) and under alkaline conditions ($3OCl^- \rightarrow ClO_3^- + 2Cl^-$). At 20ºC the hypochlorous acid dissociates to the extent of 3% at pH 6; 30% at pH 7 and 80% at pH 8 (31). The floating sludge rose to the top of the reactor zone and was removed through the floating sludge outlet. Samples of effluent were drawn periodically and were analyzed to assess the performance of the electrolytic system. Experimental variables such as current densities; pH and sodium chloride concentration were evaluated systematically. The initial experiments were carried out using potable water at 3% sodium chloride concentration for a pH range 4.5 to 7.5 in steps of 0.5, in order to determine the amount of total chlorine generated.

3. RESULTS AND DISCUSSION

The electrochemical oxidation of palm oil mill effluent was carried out in a pilot plant reactor with a liquid volume of 100 L (Fig. 1). The Fig. 2 shows the residual COD concentration during the electrolysis period for an initial COD concentration of 7,000; 10,000 and 15,000 mg/L at a fixed current density of 37.6 mA/cm^2 with an electrolyte concentration of 3% NaCl respectively. For the above said influent COD concentration and current density at an electrolysis period of 60 min resulted in a residual COD concentrations of 4,270; 6,700 and 10,250 mg/L respectively. Further increase in electrolysis period showed a decrease in residual COD concentration. At the end of 240 min of electrolysis the residual COD concentrations were found to be 114; 629 and 2680 mg/L respectively. The decrease in COD concentration was due to the oxidation of organics by the generated hypochlorous acid. During the electrochemical oxidation process apart from oxidation, inherent floatation also aids in the removal of organics in the form of scum.

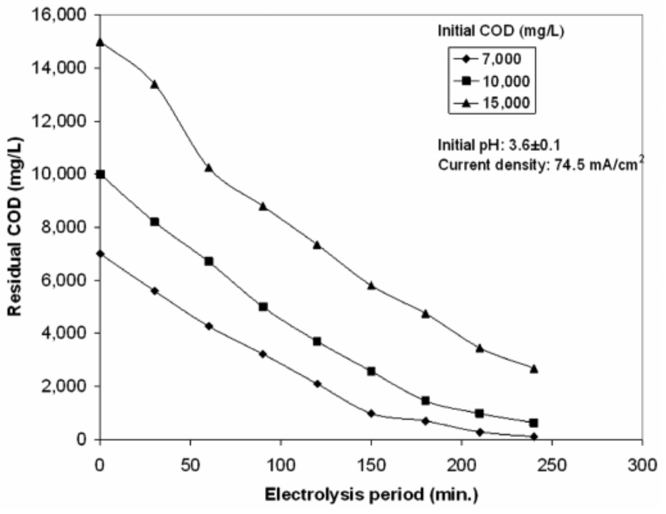


Figure 2: Residual COD Concentration Versus Electrolysis Period

The residual BOD5 concentration versus the electrolysis period is shown in Fig. 3 for varying influent BOD concentrations of 3,385; 4,860 and 7,410 mg/L at a fixed current density of 37.6 mA/cm^2 with an electrolyte concentration of 3% NaCl. As shown in Fig. 3 with the increase in electrolysis period the residual BOD5 also decreased. For example at the end of 60 min of electrolysis for the above said condition resulted in residual BOD5 values of 2,340; 3,252; and 5,911 mg/L respectively. In the case of 240 min of electrolysis period the residual BOD5 values were found to be 73; 386 and 1,265 mg/L respectively. The decrease in BOD5 was due to the destruction of organics by the generated hypochlorous acid.

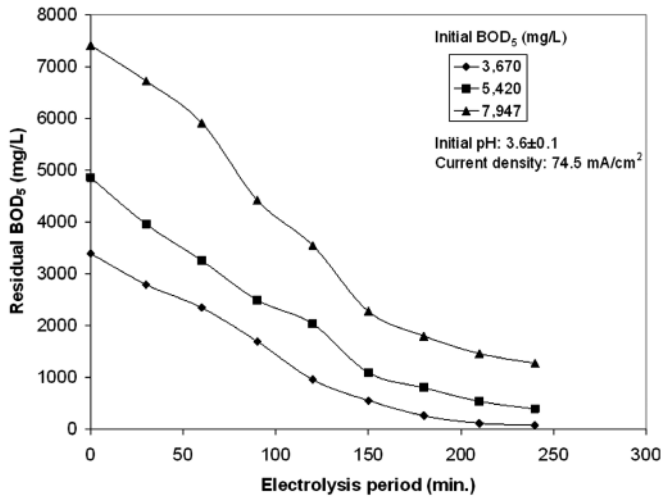


Figure 3: Residual BOD5 Concentration Versus Electrolysis Period

Fig. 4 shows the residual total organic carbon (TOC) concentration for a varying influent TOC concentration of 2,210; 3,123 and 4,820 mg/L respectively. The electrochemical oxidation was carried out with 3% NaCl as electrolyte at a fixed current density of 37.6 mA/cm^2. For example at the end of 60 min of electrolysis the residual TOC were found to be 1,504; 2,176 and 3,612 45 mg/L respectively. In the case of 240 min of electrolysis period, the residual TOC were found to be 56; 297 and 1,024 mg/L respectively. For an influent TOC concentration of 2,210 mg/L the COD/TOC ratio decreased from 3.1 to 1.5. In the case of influent TOC of 3,123 mg/L the COD/TOC ratio decreased from 3.2 to 2.1, whereas for an influent TOC of 4,820 mg/L the COD/TOC ratio decreased from 3.2 to 2.2 respectively. The decrease in COD/TOC ratio clearly states that carbon was oxidized by the generated hypochlorous acid. The observed decrease in COD/TOC ratio was in corroboration with earlier researcher who stated that hypochlorous oxidation of phenol formaldehyde resin wastewater resulted in a decrease in COD/TOC ratio from 4.3 to 1.3 (32). Whereas in the case of electrochemical oxidation of effluents originated from flavor manufacturing facility showed a decrease in COD/TOC ratio from 3.3 to 1.7 (33).

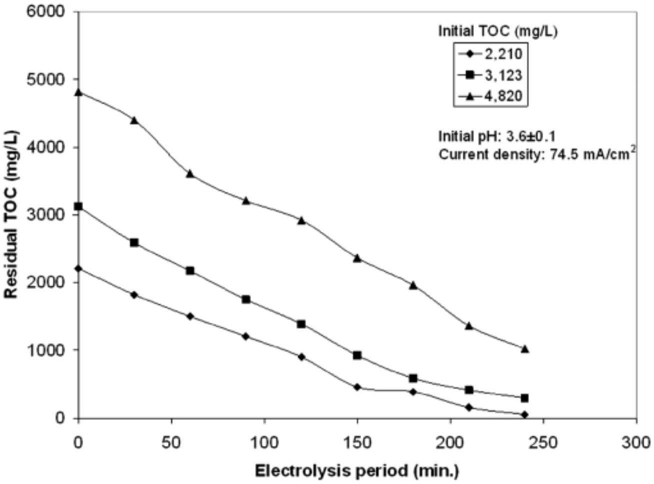


Figure 4: Residual TOC Concentration Versus Electrolysis Period

The total residual chlorine concentration during the electrolysis period is shown in Fig. 5, for an initial COD concentration of 7,000; 10,000 and 15,000 mg/L at a fixed current density of 37.6 mA/cm^2 with an electrolyte concentration of 3% NaCl. During the initial period of electrolysis period the residual chlorine level was low, thereafter the chlorine level in the electrolyte showed a gradual rise. For example at an initial COD concentration of 7,000; 10,000 and 15,000 mg/L for an electrolysis period of 60 min resulted in a total residual chlorine concentrations of 27; 15 and 4 mg/L respectively. Further increase in electrolysis period to 240 min resulted in a total residual chlorine concentrations of 188; 136 and 107 mg/L respectively. The accumulation of hypochorous acid was relative low as it has been utilized to destroy the organic content of the palm oil mill effluent as shown in Fig. 2. During electrolysis the chloride was converted into chlorine gas at the graphite anode. As a result of disproportionation reaction the generated chlorine was converted into hypochlorous which oxidizes the organic matter and reduces to chloride. In the absence of organic substance the accumulation of residual chorine was remarkable as the same was illustrated when electrolysis was conducted using potable water.

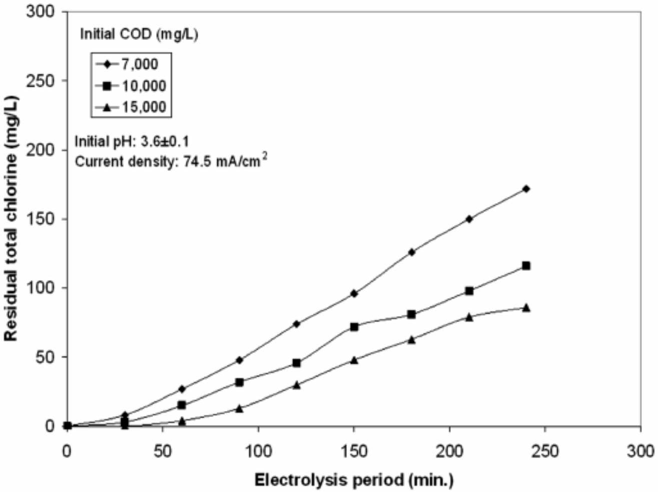


Figure 5: Residual Total Chlorine Concentration Versus Electrolysis Perio

The Fig. 6 shows the residual turbidity level during the electrolysis period for an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at a fixed current density of 37.6 mA/cm^2 with 3% NaCl as electrolyte. The initial turbidity values for the above said influent COD concentrations were found to be 1,630; 2,490 and 3,947 NTU respectively. At the end of 60 min of electrolysis period for a current density of 37.6 mA/cm^2, the residual turbidity values were found to be 1,164; 1,967 and 2,789 NTU respectively. In the case of 240 min of electrolysis the residual turbidity values were found to be 24; 257 and 1157 NTU respectively. The clarity of the treated palm oil mill effluent was also correlated with respect to residual color. The color of the treated palm oil mill effluent was evaluated for an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at a current density of 37.6 mA/cm^2 with 3% NaCl as electrolyte. The results showed that at the end of 240 min of electrolysis for the above said condition the residual color were found to be 5; 18 and 47 Hazen units respectively. The decrease in color was due to the beaching action of the generated hypochlorous acid.

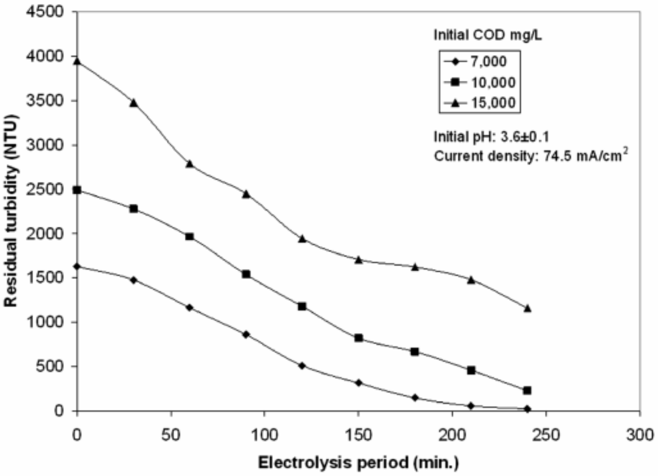


Figure 6: Residual Turbidity Versus Electrolysis Period

Fig. 7 shows the effluent temperature during the electrolysis of palm oil mill effluent having an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at a fixed current density of 37.6 mA/cm^2 with 3% NaCl as electrolyte. For example at the above said operating condition for an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at the end of 60 min of electrolysis the effluent temperatures were found to be 29; 27 and 26°C respectively. In the case of 240 min of electrolysis, for the above said condition resulted in an effluent temperature of 62; 60 and 61°C respectively.

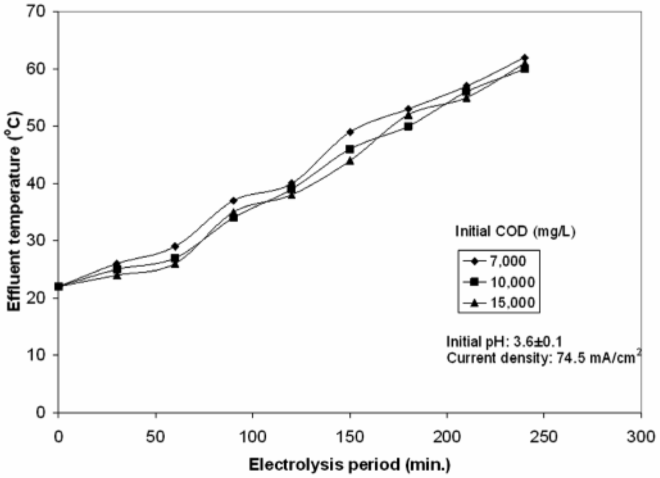


Figure 7: Effluent Temperature Versus Electrolysis Period

Fig. 8 shows the residual pH during the electrochemical oxidation of palm oil mill effluent for an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at a current density of 37.6 mA/cm^2 with 3% NaCl as electrolyte. During the increase in electrolysis period the residual pH showed a gradual increase. The rise in pH could be due to loss of hydrogen at the cathode. For the above said influent COD concentration and operating condition at the end of 60 min of electrolysis, the residual pH values were found to be 4.2; 4 and 4.1 respectively. Further increase in electrolysis period showed an increase in residual pH. In the case of 240 min of electrolysis the residual pH values were found to be 6.9; 6.7 and 6.5 respectively. As the electrolyte pH and temperature was below 7.5 and 75°C respectively, the formation of ClO_3^- was negligible in the present investigation (34).

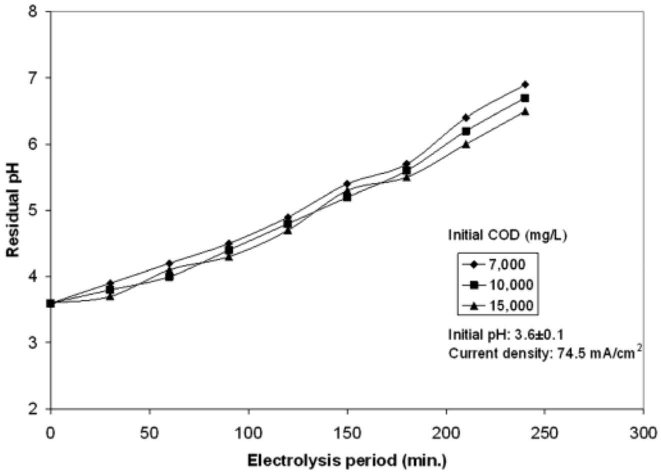


Figure 8: Residual pH Versus Electrolysis Period

The residual ammonia-nitrogen concentration was investigated during the electrolysis period for a current density of 37.6 mA/cm^2 at 3% NaCl. For an influent COD concentration of 7,000; 10,000 and 15,000 mg/L at the end of 30 min of electrolysis period the residual ammonia-nitrogen was found be below detectable limit. The possible mechanism for the destruction of ammonia nitrogen could be due to conversion into to chloramines by the generated hypochlorous acid.

The energy requirement for treating palm oil mill effluent was investigated at an influent COD concentration of 7,000 mg/L, for a fixed current density of 37.6 mA/cm^2 and at a sodium chloride content of 2 and 3% respectively. For the above said operating condition with 2 and 3% NaCl at an electrolysis period of 180 min resulted in a COD removal efficiency of 78 and 90% respectively. In order to achieve a same COD removal efficiency of 90% for an influent COD concentration of 7,000 mg/L at 2 and 3% NaCl content, the electrolysis period were found to be 240 and 180 min respectively. Hence the corresponding energy requirements were found to be

32 and 17 Wh/L respectively. The observed low energy requirement at 3% electrolyte was due to the improved conductivity, in comparison to the 2% electrolyte addition.

5. CONCLUSION

The foregoing investigation revealed that in-situ generation of hypochlorous acid could be adopted as a treatment scheme for treating palm oil mill effluent. Due to the acidic nature of the palm oil mill effluent it's advantageous to carry out electrolysis without pH adjustment. The electrochemical oxidations were carried out for varying influent COD concentrations namely 7,000; 10,000 and 15,000 mg/L in order to determine the efficiency of the oxidation process due to the generated hypochlorous acid. The results showed that it's feasible to remove the organics and color below the discharge limit provided the electrolytic reactors are scaled up to handle the given organic strength. During the electrochemical oxidation process the palm oil mill effluent undergoes in-situ disinfection due to generated hypochlorous acid. Moreover the excess chlorine concentration can be reduced by the addition of bisulfite. The chlorinated organics formed during the electrolytic treatment can be removed by passing through activated carbon before the discharge of the treated effluent. The reuse of treated effluent can be achieved by subjecting it to reverse osmosis, whereby the total dissolved solids level can be brought down in order to meet the reuse standard.

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