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Application of Chemical and Biological Coupled Treatment Technology in POME and Petroleum Waste Water as Biodegradation Alternative

N.I. Siddique and Z. Abdul Wahid

Faculty of Civil and Environmental Engineering, University Malaysia Pahang (UMP), Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia

Corresponding Author: Nurul Islam Siddique, Faculty of Civil and Environmental Engineering, University Malaysia Pahang (UMP), Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia Tel: 0105167968 Fax: +6095492998

ABSTRACT

The current experiment was aimed at investigating the efficiency of Hydrogen peroxide and activated sludge biomass to enhance Biodegradable Dissolved Organic Carbon (BDOC) and Catalase Activity (CA) activation for proficient biological degradation of Palm Oil Mill Effluent (POME) and Crude Petroleum Wastes (CPW). Batch test experiments were carried out, with the applied H_2O_2 doses of 0.5, 1 and 1.5% for contact times of 5, 10 and 15 min in the POME and CPW and subsequently by the Activated Sludge Biomass (ASB) of the same. Results of the combined effect revealed that 1% H_2O_2 dose (1.0 Mm Fe^{3+}) for 5 min exposure was found most effective for the reduction of 98.60% COD, 92.61% TOC, 70.13% TN, 85% VSS from POME and similarly, 75% COD, 71% TOC, 54.86% TN, 71% VSS from CPW and BOD_5/COD ratio indicating fatty acid removal was enhanced from 0.50 to 0.79 and 0.51 to 0.65 for POME and CPW, respectively. BDOC enhancement 59 and 35% were realized, with 58 and 29% activation of catalase activity in ASB for POME and CPW respectively. Superoxide radicals were scavenged by SOD activity. Experiment disclosed that BDOC formation and catalase activity activation were significantly related with H_2O_2 dose and exposure time both and coupled technology might enhance treatment efficiency of industrial waste rendering economical feasibility.

Key words: H_2O_2 , biodegradation, BDOC, ASB, catalase

INTRODUCTION

Hydrogen Peroxide, a versatile, vigorous oxidative agent, react via a hydroxyl radical mechanism having oxidizing potential 2.8 V, plays remarkable reduction of COD producing H_2O and CO_2 with enhancement of biodegradability of organic compounds (Siedlecka and Stepnowski, 2005; Saif-Ur-Rehman *et al.*, 2008; Khan *et al.*, 2009; Ghosh *et al.*, 2011). Moreover, application of H_2O_2 as an oxidizing auto catalyst is already proved treating halogenated hydrocarbon endures in waste water treatment (Muganlinskii and Adeyinka, 1987; Aboulhassan *et al.*, 2008). To degrade various variety of hazardous wastes *in situ* chemical oxidation (ISCO) has been used as an encouraging inventive technology (ITRC, 2001; ITRC, 2005). Catalase, an antioxidant can break down of H_2O_2 into water and oxygen (Milton, 2008). In combination of biological treatment, make Oxidation by Hydrogen Peroxide (OHP) an innovative alternative for advanced waste water treatment (Jeworski and Heinzle, 2000).

Habitually, in the industrial effluents, proportion of biodegradable COD which can be indicated by BDOC is relatively low (Tripathi *et al.*, 2011). Hence, in order to enhance the treatment efficiency, an evocative oxidant which increases the BDOC of the influent is obligatory. H_2O_2 can transubstantiate some refractory organic matters to biodegradable organic ones, that is, BDOC, which can be removed easily through biodegradation process. Primitive researchers reported that H_2O_2 may increase biodegradability of organic pollutants producing most effective intermediates like OH^\cdot radicals in presence of Fe^{2+} (Tengrui *et al.*, 2007; Babu *et al.*, 2010). These researchers studied that hydroxyl radicals generated through Fenton-like reaction are capable of oxidative degradation of numerous organic pollutant, including diesel (Kong *et al.*, 1998; Ferguson *et al.*, 2004; Yeh *et al.*, 2008; Ghosh *et al.*, 2011), chlorinated ethylenes (Yeh *et al.*, 2003), aromatic hydrocarbons (Yeh *et al.*, 2008; Ahad and Slater, 2008), 2,4-dichlorophenol (Zhou *et al.*, 2008a) and 4-chlorophenol (Zhou *et al.*, 2008b). To split H_2O_2 into molecular oxygen and water, catalases (H_2O_2 : H_2O_2 -oxidoreductase, EC 1.11.1.6.) use a two-electron transfer mechanism (Guwy *et al.*, 1999). One unit of catalase activity corresponds to the breakdown of 1 μ mole of H_2O_2 per minute under specified conditions, giving a gas flow of 11.2 μ L of O_2 /min at STP (Guwy *et al.*, 1999).

The conventional treatments include gravitational separation, centrifugation, ozonation and wet oxidation, application of coagulants, flocculants, flotation, ultra filtration or sorption on organic minerals, advanced treatment process (Parilti, 2010; Dutta and Basu, 2012). The anaerobic digestion of POME and industrial waste water can achieve 62-98% of COD reduction and 39-84% of methane production depending upon system operation, feed rate and substrate concentration as reported by recent researches investigation (Najafpour *et al.*, 2006; Jafarzadeh *et al.*, 2006; Choorit and Wisarnwan, 2007; Magram and Abdel-Azeem, 2008; Baharuddin *et al.*, 2009). However, the hydrolysis reaction is the rate-limiting step in the overall anaerobic digestion process (Kim and Tanaka, 2010; Park *et al.*, 2005). All that study suggested that conventional treatments are time consuming having less economical feasibility (Rajendran *et al.*, 2011). Subsequently, application of microbial consortium could be a better solution to solve this problem (Rajendran *et al.*, 2011; Durai and Rajasimman, 2011).

Though oxidation by hydrogen per oxide (OHP) is becoming popular for wastewater treatment, however, more studies are required to establish couple treatment method utilizing catalase activity as bio-decomposers. Therefore, present study was performed with the aim to investigate biodegradability of POME and CPW through removal of physico-chemical parameters as well as activation of catalase activity using H_2O_2 as proficient oxidizing agent followed by biological oxidation.

MATERIALS AND METHODS

Sample collection and characterization: A hundred liter POME and CPW sample was collected in plastic containers at the point of discharge in to the main stream and from the receiving stream. Then, transported to the laboratory, preserved and stored in cold room at 4°C for further study were physicochemical analysis and treatment. The pH of the effluent was adjusted to 6.5, using 6 N sodium hydroxide solution. The alkalinity was adjusted to 1500-1700 mg $CaCO_3$ /l using sodium bicarbonate. Supplementary nutrients like nitrogen (NH_4Cl) and phosphorous (KH_2PO_4) were added to yield a COD: N: P ratio of 250:5:1. Table 1 explains composition and characteristics of POME and CPW.

Sludge and seed formation: Activated sludge biomass (ASB) formation was executed according to the procedure of Ahmad *et al.* (2010). For ASB cultivation, a composite medium was used as an energy source: 3.0 g L^{-1} K_2HPO_4 , 0.1 g L^{-1} $MgSO_4 \cdot 7H_2O$, 0.3 g L^{-1} $CaCl_2 \cdot 2H_2O$, 0.01 g L^{-1} $FeSO_4$.

Table 1: Composition and characteristics of the POME and CPW

Parameters	POME	CPW
pH	4.15-5.5	6.5-8.5
BOD	21-29	8-32
COD	22-73	15-60
TOC	7- 15	6-9
Total solids	21-42	0.02-0.30
Acetic acid	52.62	46.60
Phenol	0.20-0.40	0.36
Total nitrogen	0.7-1.0	0.05-0.212
Total phosphate	0.473	0.102-0.227
Volatile fatty acids	1.21-2.55	93-95

Except pH and acetic acid, all parameters in (g L⁻¹)

7H₂O. Initially, pH of the medium was found 4. Thereafter, 150 mL POME was added in to a 250 mL Erlenmeyer flask containing 100 mL of energy medium and was pre-cultured with aeration at 30°C and 120 rpm in incubator for three weeks. Subsequently, pH at 6.5 was maintained using 1 N H₂SO₄ and 1 N NaOH during incubation period. The culture was finally planted in an agar medium and ameliorated bacterial medium was developed, after 20 successive cultures. Eventually, the bacterial medium was cultivated in 500 mL Erlenmeyer flask containing 200 mL of medium and POME at 30°C and 120 rpm in incubator for five days. The ultimate bacterial medium was used as ASB for biological degradation of waste. The same procedure was followed in case of CPW.

Batch test studies: Four waste water samples of equal volume (150 mL) were placed in conical flasks. Thereafter, each of the three volume of waste water was treated with 50 mL of standard volume of H₂O₂ solution of 30% concentration and 1.0 Mm Fe³⁺. To find the optimal dose of H₂O₂ solution for better degradation, percentage of H₂O₂ addition was gradually increased (i.e., 0.5, 1, 1.5%). The liquid content of effluent with H₂O₂ was agitated for 30 min with a mechanical device. The residual H₂O₂ was scavenged by Catalase activity. Finally, the pretreated POME and CPW was further degraded by activated sludge for 15 days at 37°C through anaerobic digestion. The pre-treated sample and post-treated sample analysis of certain properties will determine the optimal dose of H₂O₂.

Catalase activity, OH⁻, superoxide free radical measurements: Catalase is an enzyme that decomposes H₂O₂ into oxygen and water. Chance *et al.* (1979) reported the H₂O₂ is a normal metabolic in living cells. As excess of H₂O₂ may oxidize cellular components, so removal of H₂O₂ is necessary (Gaetani *et al.*, 1989). Following the Worthington enzyme manual the catalase (units mg⁻¹) activity test was done in the lab with the help of UV Spectrophotometer of Perkin Elmer Lambda 25. The maximum wave length 245 nm was fixed through Scan. Hence, spectrophotometer was adjusted at 245 nm and 25°C. Reagent grade water of 1.9 mL and 0.059 M of 1 mL H₂O₂ was pipette in to cuvette. Incubation in spectrophotometer for 4-5 min was done to achieve temperature equilibration and to establish blank rate. Adding 0.1 mL of diluted enzyme decrease in absorbance at 245 nm for 2-3 min was recorded. Alkalinity OH⁻ was measured through titration method. Spectrophotometric assay of SOD activity was carried out by following the procedure of Oberley and Spitz (1985).

Instrumental analysis: Raw effluent and treated effluent samples were subjected to certain common analytical determinations, including pH, Biochemical Oxygen Demand (BOD), Chemical

Oxygen Demand (COD), Total Organic Carbon (TOC) and Biodegradable Dissolved Organic Carbon (BDOC). pH was measured with EcoScan pH meter. BOD was monitored with YSI 5100 DO meter. COD was monitored with apparatus HACH/DR5000. TOC and TN were analyzed with Shimadzu TOC-V_{CPN} (220 V). Calibration both for TC and IC was performed properly. The TOC analyzer calculates TOC in terms of TC and IC i.e., subtracting IC from TC. For TOC determination samples were filtered through 0.45 µm membrane. The difference between initial and final values of TOC was considered as the BDOC of the water.

RESULTS AND DISCUSSION

Effect of H₂O₂ on physicochemical characteristics of POME and CPW: Table 2 represents biological fermentation of POME with different applied doses of H₂O₂ under Sami Batch test operation. The implemented H₂O₂ doses varied between 0.5 to 1.5% and while the oxidation process lasted from 2 to 30 min. The efficiency of per-oxidation to promote the effluent quality was strongly depended upon the applied H₂O₂ dose. In the present study 5 min OHP time was found most significant period for maximum removal of pollutants, higher OHP period did not significantly affect the physicochemical properties of the effluent. Volk *et al.* (1996) and Kim and Tanaka (2010) reported 6.5 mg L⁻¹ ozone and H₂O₂ doses (ratio 0.35 mg H₂O₂/mg O₃) for contact time of 10 min was found to be effective for higher removal of pollutants in waste. The effect of H₂O₂ dose on the effluent properties at 5 min exposure was depicted in Fig. 1 (a-b). COD and TOC removal was 40 and 32% at 1% H₂O₂ dose. Similarly from Table 3, 31 and 28% COD and TOC removal was realized

Table 2: Biological fermentation of POME with applied various doses hydrogen peroxide

		Applied H ₂ O ₂ doses									
		0.5 (%)			1 (%)			1.5 (%)			
		5	10	15	5	10	15	5	10	15	
Parameters	Effluent 0 H ₂ O ₂	(min)									ASB
pH	5.3	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50
TOC	9500	7695	7394	7193	6460	6145	6034	5795	5700	5700	703
COD	32150	23791	23469	23148	19290	18968	18647	17682	17680	17678	450
TN	750	615	595	574	562	545	540	532	520	519	224
VSS	15542	10102	10084	10042	9836	9800	9782	8548	8512	8510	2331
BOD ₅ /COD	0.50	0.54	0.54	0.54	0.61	0.61	0.61	0.80	0.80	0.80	0.75

Table 3: Biological fermentation of CPW with applied various doses hydrogen peroxide

		Applied H ₂ O ₂ doses									
		0.5 (%)			1 (%)			1.5 (%)			
		5	10	15	5	10	15	5	10	15	
Parameters	Effluent 0 H ₂ O ₂	(min)									ASB
pH	7.3	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50	6.50
T OC	3840	3148	3047	2998	2764	2660	2601	2534	2489	2482	1114
COD	15012	12009	11708	11498	10358	10257	10156	9457	9357	9351	3002
TN	350	287	284	282	262	260	259	248	245	244	158
VSS	6118	4587	4563	4546	3916	3892	3864	3790	3785	3781	1774
BOD ₅ /COD	0.51	0.51	0.51	0.51	0.57	0.57	0.57	0.65	0.65	0.65	0.59

ASB: Activated sludge biomass

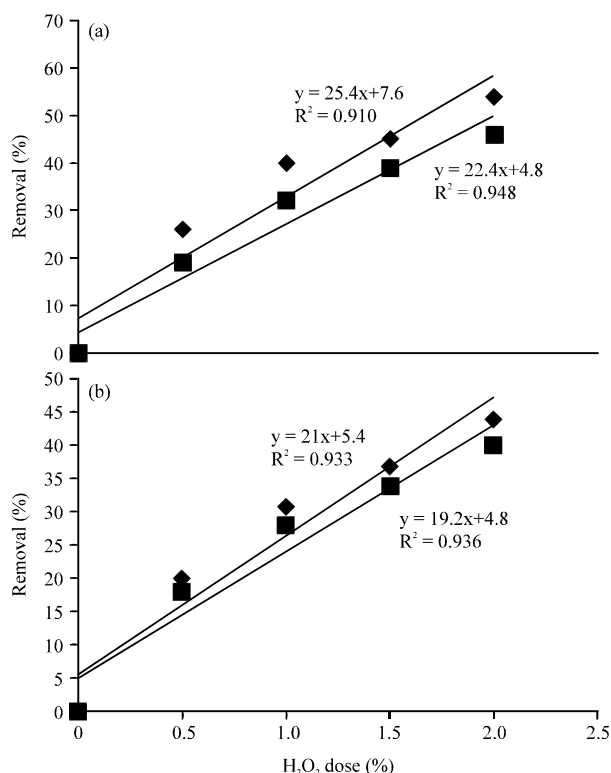


Fig. 1(a-b): (a) Effect of oxidation by hydrogen per oxide (OHP) on COD and TOC removal in POME at different H_2O_2 dose and (b) Effect of OHP on COD and TOC removal in CPW at different H_2O_2 dose (◆: COD, ■: TOC removal%)

in case of CPW, at 1% H_2O_2 dose. Mater *et al.* (2007) reported 28% TOC removal at 1% H_2O_2 and 1 mM Fe^{3+} . Results showed that a H_2O_2 dose of 1% was found to be optimal, as higher H_2O_2 doses were not so effective in pollutants removal.

Also, H_2O_2 dose higher than 1% has toxic effect on survival of microorganisms. As seen, TN removal was very low and did not exceed 29.46%. The significant increase in ammonia oxidation potential compared to non-oxygenated controls during treatment process is the reason of low TN removal, as reported by Jennifer *et al.* (2010). VSS removal was significantly dependent upon H_2O_2 dose. However, OHP pathway consists of an attack by hydroxyl radicals on the alkyl chain of fatty acids. The aromatic rings attached with hydroxyl groups exist in the fatty acids are ruptured by powerful OH radicals. This results in formation of water-soluble compounds by means of abstraction of hydrogen and insertion of oxygen atoms in presence of ferrous and/or ferric ions. The consequence of this reaction yields minor aliphatic compounds, derived from the eradicating of the longer hydrocarbon chains (C-C) of fatty acids and eventually leads to the mineralization of the antecedent organics. Organic substances exists in POME are utilized by microorganisms (methanogenesis) as nutrients and are transformed in to simple end products (Sumathi, 2004; Milton, 2008; Hong *et al.*, 2009; Nazlina *et al.*, 2009).

Effect of H_2O_2 on BDOC: The effect of H_2O_2 oxidation on BDOC was shown in Fig. 2a-b. BDOC is the indicator of bacterial re-growth potential in terms of biodegradable organic matter in the wastewater (Tripathi *et al.*, 2011). The BDOC fraction consists of organic molecules the heterotrophic bacteria can use as a source of energy and carbon.

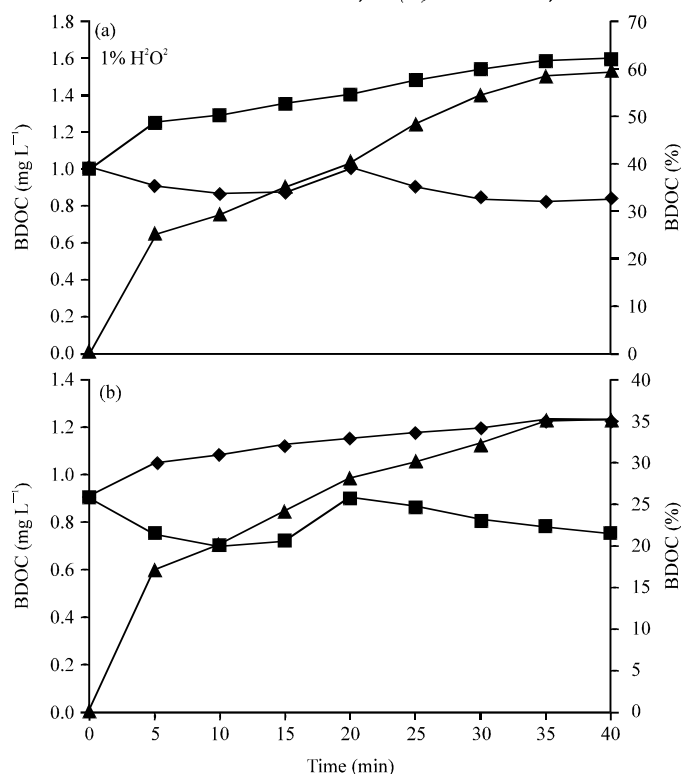


Fig. 2(a-b): (a) Increase in BDOC at 1% H_2O_2 dose with different exposure duration in POME and (b) Increase in BDOC at 1% H_2O_2 dose with different exposure duration in CPW (■: BDOC initial, ◆: BDOC final, ▲: BDOC increasing%)

At applied dose of 1% H_2O_2 for 5 min contact time BDOC value is increased from initial value 1.0-1.25 to 1.34-1.59 $mg\ L^{-1}$ that was 59% improvement was realized in case of POME. On the other hand, 35% improvement was realized in case of CPW, whereas BDOC value is increased from initial value 0.90-1.08 to 1.17-1.22 $mg\ L^{-1}$ for CPW. The reaction between H_2O_2 , aromatics and unsaturated organic compounds in the waste yields formation of saturated polycarbonaceous compounds; moreover, it also reacts on aliphatic acids generating hydroxyl radicals. Due to these conditions, BDOC increases (Volk *et al.*, 1996; Khan *et al.*, 2009). From this comparison, it can be stated that the biodegradability of CPW is less than POME. The reason may be due to highly branched and cyclic saturated hydrocarbons as well as aromatic compounds are more resistant to biodegradation. The result also indicated that oxidation by H_2O_2 can significantly improve the biodegradability of the effluent, in the other words; the biochemical treatment efficiency can be improved by oxidation.

Activated sludge and catalase activity: Figure 3 illustrates catalase activity in activated sludge ($mg\ g^{-1}$) both for POME and CPW. Initially, when activated sludge was 10 $mg\ g^{-1}$, Catalase activity was 3 and 7 units mg^{-1} for POME and CPW, respectively. As noted, the results indicated that catalase activity gradually increases simultaneously with the increase of activated sludge both in POME and CPW. Finally, when activated sludge was 90 $mg\ g^{-1}$, Catalase activity was found 57 and 29 units mg^{-1} in case of POME and CPW, respectively. From the comparison of the two curves it can be concluded that the magnitude of catalase activity in CPW is less compared to that of POME. Activation of catalase requires wide range of pH (4-10) and its activity continues until pH is below 3.5 (Guwy *et al.*, 1999).

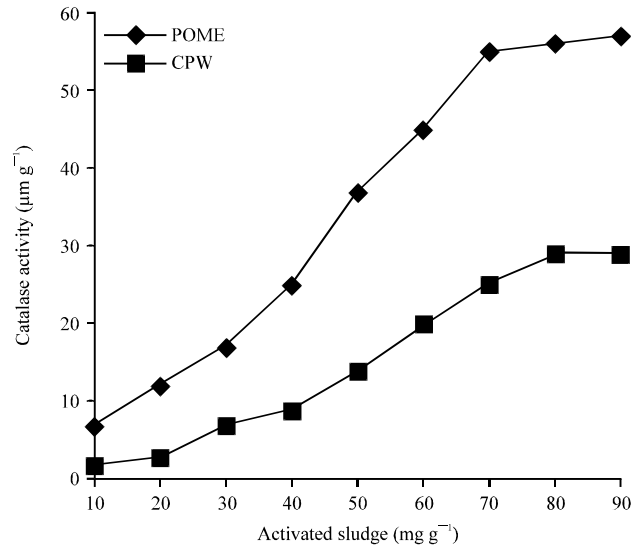


Fig. 3: Increase in catalase activity with respect to ASB

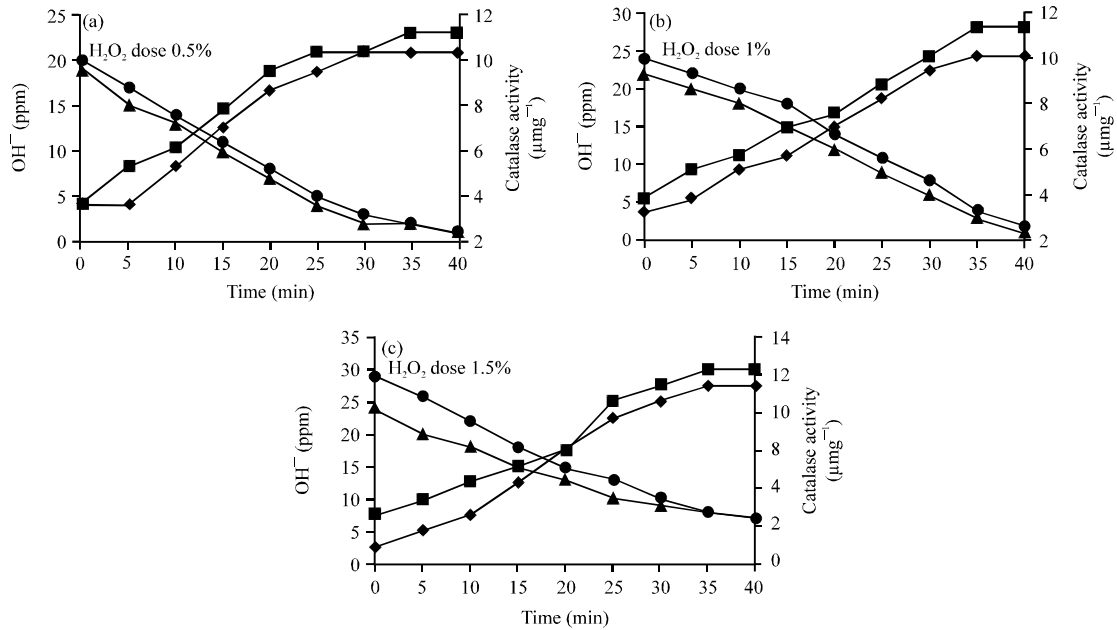


Fig. 4(a-c): (a) Response of catalase activity (CA) at 0.5% H₂O₂ dose, (b) Response of catalase activity (CA) at 1% H₂O₂ dose and (c) Response of catalase activity (CA) at 1.5% H₂O₂ dose (●: OH⁻ in POME, ▲: OH⁻ in CPW, ■: Catalase activity in POME, ◆: Catalase activity in CPW)

OH⁻ to catalase activity and chemical toxicity removal: Figure 4 (a-c) describes the response of catalase activity on application of different H₂O₂ dose. The catalase activity was greatly influenced by H₂O₂ dose (Mitozo *et al.*, 2011). Maximum catalase activity was found at 1% H₂O₂ dose.

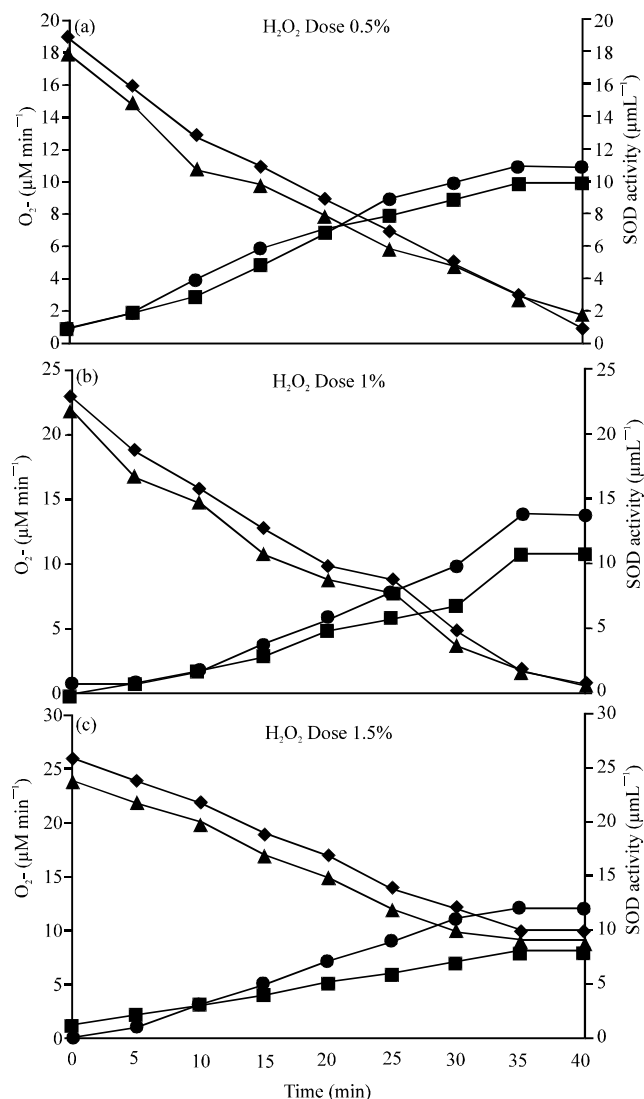


Fig. 5(a-c): (a) Response of SOD activity on removal of superoxide radical at 0.5% H_2O_2 dose, (b) Response of SOD activity on removal of superoxide radical at 1% H_2O_2 dose and (c) Response of SOD activity on removal of superoxide radical at 1.5% H_2O_2 dose (◆: O_2^- in POME, ▲: O_2^- in CPW, ●: SOD activity in POME, ■: SOD activity in CPW)

As seen, OH^- toxicity was successfully scavenged by catalase activity up to 1% H_2O_2 dose, whereas OH^- could not completely scavenged by catalase activity at 1.5% H_2O_2 dose. As noted, 8 ppm OH^- was yet to be scavenged by catalase activity at 1.5% H_2O_2 dose which may cause cell damage of microbes. Hence, survival of microorganisms was higher at 1% H_2O_2 dose compared to 1.5% H_2O_2 dose. Mater *et al.* (2007) reported that low reagent concentrations (1% H_2O_2 and 1 mM Fe^{2+}) were sufficient to start the degradation process, which could be continued using microorganisms.

Similarly, Fig. 5 (a-c) illustrates the effect of Super Oxide Dismutase (SOD) activity at different H_2O_2 dose on superoxide (SO) radical (Chen and Pan, 1996). Result showed that at 1% H_2O_2 dose the SOD activity was maximum in case of POME and CPW both.

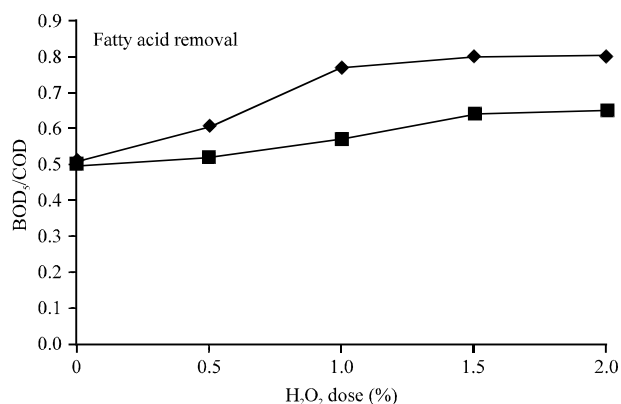


Fig. 6: Increase in biodegradability index at different H₂O₂ dose (◆: POME, ■: CPW)

As seen, O₂⁻ toxicity was successfully scavenged by SOD activity up to 1% H₂O₂ dose, whereas O₂⁻ could not completely scavenged by SOD activity at 1.5% H₂O₂ dose. Hence, survival of microorganisms was higher at 1% H₂O₂ dose compared to 1.5% H₂O₂ dose. A number of physiological reactions such as the electron flow in the chloroplasts and mitochondria and from some redox reactions in cells generates superoxide radical (•O₂⁻) as a by-product in aerobic organisms. •O₂⁻ can react with H₂O₂ to produce •OH⁻, one of the most reactive molecules in the living cells (Chen and Pan, 1996). •OH⁻ can cause per oxidation of membrane lipids, breakage of DNA strands and inactivation of enzymes in cells. To ameliorate the damage caused by •OH⁻ formed from •O₂⁻ and H₂O₂, organisms have evolved mechanisms to control the concentration of the two reactants. (SOD, EC 1.15.1.1) is a group of isozymes functioning as superoxide radical scavenger in the living organisms.

H₂O₂ on biodegradability index indicating fatty acid removal: The biodegradability index (BOD₅/COD), indicating fatty acid removal in waste water should be in the range of 0.40 to 0.80 to be treated by biological process as reported by many authors (Chen and Pan, 1996). Fig. 6 describes the initial value of BOD₅/COD ratio was 0.50 and 0.51 in POME and CPW and hence pretreatment was planned to be done by chemical oxidation by H₂O₂.

At the end of 30 min of chemical oxidation in different dosing biodegradability index (BOD₅/COD) was enhanced up to 0.80 and 0.65 both for POME and CPW. Oxidation with Fenton reagent based on ferrous ions may possess the capability to attack on the alkyl chain of fatty acids generating most effective hydroxyl radicals (Babu *et al.*, 2010; Elmolla and Chaudhuri, 2010). Fenton treatment of Palm oil shell wastes converts high molecular weight fatty acids in to small weight fatty acids such as acetic acid, formic acid. It can be concluded from the result that eliminating oxidizing organics present in both POME and CPW the chemical oxidation by H₂O₂ removes fatty acid as reported by Mae *et al.* (2000).

Effect of ASB on degradation of POME and CPW: The ASB is a mixed microbe (dead and living) biomass. To investigate the biodegradation rate of ASB in degrading pretreated waste water was tested for 5 days. However, ASB successfully reduced TOC and COD about 92.61, 98.6 and 71, 75% from POME and CPW respectively under specific operating conditions (Fig. 7a-b). The ASB utilizing the organic substances as nutrients breakdown the organic matter in to simple end-product through anaerobic digestion (Jafarzadeh *et al.*, 2006; Milton, 2008). Mentionable

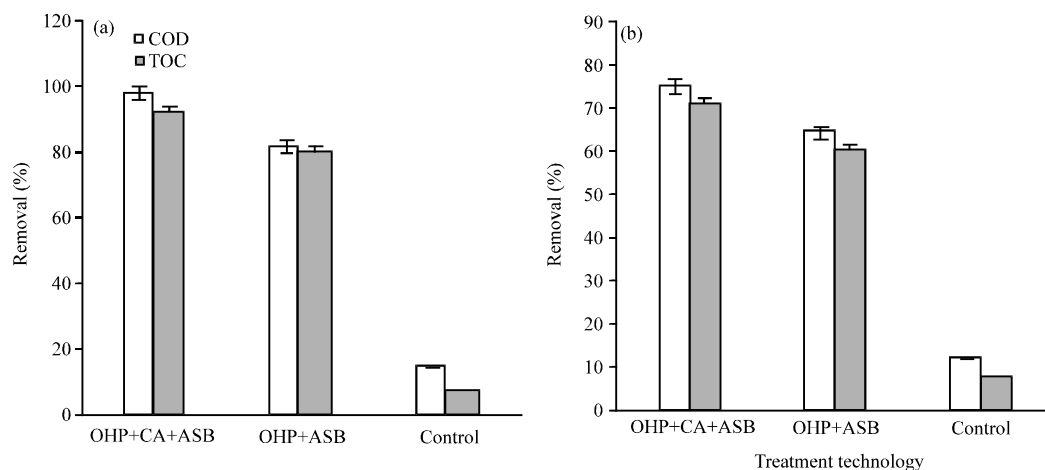


Fig. 7(a-b): Comparison of COD and TOC removal efficiency by coupled treatment with catalase activity (CA), coupled treatment without catalase activity (CA) and control in POME and CPW

that, VSS removal was 85 and 71% from POME and CPW respectively. VSS proves biological activity in waste water. Bacteria utilizing organic substances mature and die. Eventually, they become the part of granules. pH was adjusted to 6.5 in order to achieve maximum biological degradation. Adeyinka (1996) Studied 55.22% COD removal by 1% H_2O_2 dose with activated clay and sodium-ion exchange resin filtration. Babu *et al.* (2010) observed 86.12% COD removal by combined Electro-Fenton and biological oxidation process from POME but initial COD value was only 6712 mg L^{-1} . Scientist investigated 49% TOC removal from petrochemical industry waste water by a solar oxidation process, where initial COD was only 2000 mg L^{-1} (Parilti, 2010).

Effectiveness of catalase activity (CA) towards enhanced degradation: Figure 7 (a-b) represents the average COD and TOC removal efficiency by coupled treatment with catalase activity (OHP+ASB+CA), coupled treatment without catalase activity (OHP+ASB+CA) and control. The values were calculated based on 7 days mean removal efficiency. In increasing order control < coupled treatment without catalase activity < coupled treatment with catalase activity. Control has the lowest removal efficiency whereas, coupled treatment with catalase activity was the highest compared to coupled treatment without catalase activity. Hence, catalase activity has a significant influence on removal of pollutants. Scavenging H_2O_2 and protecting cells from damage caused by reactive oxygen species are the precious functions of Catalases (Mitozo *et al.*, 2011). As a result, survival of degradation capable bacteria is more in ASB, which leads to higher removal of pollutants in POME and CPW.

CONCLUSION

In the present study, the effect of H_2O_2 dose with different contact times and ASB was studied on the physicochemical characteristics of POME and CPW. This study reveals that H_2O_2 dose of 1% (1 mM Fe^{3+}) with contact time of 5 min show a remarkable reduction in physicochemical parameters of POME and CPW. By this coupled technology BDOC increased in conjunction with remarkable survival of microbial activity, which accelerates treatment efficiency with cost effectiveness. In increasing order control < coupled treatment without catalase activity < coupled treatment with

catalase activity, which is directly corresponded with pollutants removal in industrial waste. pH adjustment, optimal H₂O₂ dosing, BDOC formation, Catalase activation, ASB stabilization are the key factors for enhanced degradation of waste water.

According to this result it is transparent that the chemo-biological process enhances biodegradation of POME and CPW in comparison with many other treatment technologies. So, it can be concluded that coupled treatment is an effective, sustainable and environment friendly technique for enhanced degradation of POME and CPW.

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REFERENCES

- Aboulhassan, M.A., S. Souabi and A. Yaacoubi, 2008. Pollution reduction and biodegradability index improvement of tannery effluents. *Int. J. Environ. Sci. Technol.*, 5: 11-16.
- Adeyinka, J.S., 1996. Waste water treatment through reverse osmosis: A kinetic study. *Proceedings of the International Conference Africa-USA on Manufacturing Technology*, August 12-15, 1996, Accra, Ghana.
- Ahad, J.M.E. and G.F. Slater, 2008. Carbon isotope effects associated with Fenton-like degradation of toluene: Potential for differentiation of abiotic and biotic degradation. *Sci. Total Environ.*, 401: 194-198.
- Ahmad, A., R. Ghufuran and W.M. Faizal, 2010. Cd(II), Pb(II) and Zn(II) removal from contaminated water by biosorption using activated sludge biomass. *CLEAN-Soil Air Water*, 38: 153-158.
- Babu, B.R., K.S. Meera, P. Venkatesan and D. Sunandha, 2010. Removal of fatty acids from palm oil effluent by combined Electro-Fenton and biological oxidation process. *Water Air Soil Pollut.*, 211: 203-210.
- Baharuddin, A.S., M. Wakisaka, Y. Shirai, S. Abd-Aziz, N.A. Abdul-Rahman and M.A. Hassan, 2009. Co-composting of empty fruit bunches and partially treated palm oil mill effluents in pilot scale. *Int. J. Agric. Res.*, 4: 69-78.
- Chance, B., H. Sies and A. Boveris, 1979. Hydroperoxide metabolism in mammalian organs. *Physiol. Rev.*, 59: 527-605.
- Chen, C.N. and S.M. Pan, 1996. Assay of superoxide dismutase activity by combining electrophoresis and densitometry. *Bot. Bull. Acad. Sin.*, 37: 107-111.
- Choorit, W. and P. Wisarnwan, 2007. Effect of temperature on the anaerobic digestion of palm oil mill effluent. *Electron. J. Biotechnol.*, 10: 376-385.
- Durai, G. and M. Rajasimman, 2011. Biological treatment of tannery wastewater-A review. *J. Environ. Sci. Technol.*, 4: 1-17.
- Dutta, M. and J.K. Basu, 2012. Statistical optimization for the adsorption of acid fuchsin onto the surface of carbon alumina composite pellet: An application of response surface methodology. *J. Environ. Sci. Technol.*, 5: 42-53.
- Elmolla, E.S. and M. Chaudhuri, 2010. Effect of photo-Fenton operating conditions on the performance of photo-Fenton-SBR process for recalcitrant wastewater treatment. *J. Applied Sci.*, 10: 3236-3242.

- Ferguson, S.H., A.Z. Woinarski, I. Snape, C.E. Morris and A.T. Revill, 2004. A field trial of *in situ* chemical oxidation to remediate long-term diesel contaminated Antarctic soil. *Cold Reg. Sci. Technol.*, 40: 47-60.
- Gaetani, G.F., S. Galiano, L. Canepa, A.M. Ferraris and H.N. Kirkman, 1989. Catalase and glutathione peroxidase are equally effective in detoxification of hydrogen peroxide in human erythrocytes. *Blood*, 73: 334-339.
- Ghosh, P., A.N. Samanta and S. Ray, 2011. Kinetics based on mechanism of COD reduction for industrial effluent in Fenton process. *Int. J. Chem. Technol.*, 3: 26-36.
- Guwy, A.J., M.H. Martin, F.R. Hawkes and D.L. Hawkes, 1999. Catalase activity measurements in suspended aerobic biomass and soil samples. *Enzyme Microb. Technol.*, 25: 669-676.
- Hong, S.K., Y. Shirai, A.R. Nor Aini and M.A. Hassan, 2009. Semi-continuous and continuous anaerobic treatment of palm oil mill effluent for the production of organic acids and polyhydroxyalkanoates. *Res. J. Environ. Sci.*, 3: 522-529.
- ITRC, 2001. Technical and Regulatory Guidance for *In situ* Chemical Oxidation Of Contaminated Soil and Groundwater. Interstate Technology and Regulatory Council, Washington, DC., USA.
- ITRC, 2005. Technical and Regulatory Guidance for *In situ* Chemical Oxidation of Contaminated Soil and Groundwater. Interstate Technology and Regulatory Council, Washington, DC., USA.
- Jafarzadeh, M.T., N. Mehrdadi, A.A. Azimi and S.J. Hashemian, 2006. Petrochemical wastewater treatment using an anaerobic hybrid reactor. *Pak. J. Biol. Sci.*, 9: 1037-1042.
- Jennifer, G.A., W.B. Marc, R.C. Doglas and M.F. Allison, 2010. Effects of oxygenation on ammonia oxidation potential and microbial diversity in sediment from surface-flow wetland mesocosms. *Bioresour. Technol.*, 101: 1389-1392.
- Jeworski, M. and E. Heinzle, 2000. Combined chemical-biological treatment of wastewater containing refractory pollutants. *Biotechnol. Ann. Rev.*, 6: 163-166.
- Khan, E., W. Wirojanagud and N. Sermsai, 2009. Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds. *J. Hazard. Mater.*, 161: 1024-1034.
- Kim, I. and H. Tanaka, 2010. Use of ozone-based processes for the removal of pharmaceuticals detected in a wastewater treatment plant. *Water Environ. Res.*, 82: 294-301.
- Kong, S.H., R.J. Watts and J.H. Choi, 1998. Treatment of petroleum-contaminated soils using iron mineral catalyzed hydrogen peroxide. *Chemosphere*, 37: 1473-1482.
- Mae, K., I. Hasegawa, N. Sakai and V. Miura, 2000. A new conversion method for recovering valuable chemicals from oil palm shell wastes utilizing liquid-phase oxidation with H_2O_2 under milled conditions. *Energy Fuels*, 14: 1212-1218.
- Magram, S.F. and M.M. Abdel-Azeem, 2008. Efficiency of anaerobic digestion of low-strength sludge under different thermophilic conditions. *Asian J. Scientific Res.*, 1: 510-517.
- Mater, L., E.V.C. Rosa, J. Berto, A.X.R. Correa, P.R. Schwingel, C.M. Radetski, 2007. A simple methodology to evaluate influence of H_2O_2 and Fe^{2+} concentrations on the mineralization and biodegradability of organic compounds in water and soil contaminated with crude petroleum. *J. Hazard. Mater.*, 149: 379-386.
- Milton, N.G.N., 2008. Homocysteine inhibits hydrogen peroxide breakdown by catalase. *Open Enzyme Inhib. J.*, 1: 34-41.
- Mitozo, P.A., L.F. De Souza, G.L. Neckel, S. Flesch and A.F. Maris *et al.*, 2011. A study of the relative importance of the peroxiredoxin-, catalase- and glutathione-dependent systems in neural peroxide metabolism. *Free Radical Biol. Med.*, 51: 69-77.

- Muganlinskii, F.F. and J.S. Adeyinka, 1987. Low temperature oxidation of hydrochloric acid in industrial waste water using hydrogen peroxide. Science Report, AZINEFT KHIEMIE (BAKU 1987).
- Najafpour, G.D., A.A.L. Zinatizadeh, A.R. Mohamed, M. Hasnain Isa and H. Nasrollahzadeh, 2006. High-rate anaerobic digestion of palm oil mill effluent in an up-flow anaerobic sludge-film bioreactor. *Process Biochem.*, 41: 370-379.
- Nazlina, H.M.Y., A.R.N. Aini, F. Ismail, M.Z.M. Yusof and M.A. Hassan, 2009. Effect of different temperature, initial pH and substrate composition on biohydrogen production from food waste in batch fermentation. *Asian J. Biotechnol.*, 1: 42-50.
- Oberley, L.W. and D.R. Spitz, 1985. Assay of Superoxide Dismutase Using Nitroblue Tetrazolium. In: *Handbook of Methods For Oxygen Radical Research*, Greenwald, R.A. (Ed.). CRC Press, Boca Raton, FL., pp: 217-221.
- Parilti, N.B., 2010. Treatment of petrochemical industry wastewater by a solar oxidation process using the Box-Wilson experimental design method. *Ekoloji*, 19: 9-15.
- Park, C.W., C.Y. Lee, S.Y. Kim, Y. Chen and H.A. Chase, 2005. Upgrading of anaerobic digestion by incorporating two different hydrolysis processes. *J. Biosci. Bioeng.*, 100: 164-167.
- Rajendran, R., S.K. Sundaram and K.U. Maheswari, 2011. Aerobic biodecolorization of mixture of azo dye containing textile effluent using adapted microbial strains. *J. Environ. Sci. Technol.*, 4: 568-578.
- Saif-Ur-Rehman, M., A. Muhammad, A. Shafeeq, M.A. Chughtai, A.M. Ali and F. Ahmad, 2008. Decolorization of turquoise blue dye by ozonation, O_3/H_2O_2 and fenton processes. *Res. J. Environ. Sci.*, 2: 310-315.
- Siedlecka, E.M. and P. Stepnowski, 2005. Phenols degradation by Fenton reaction in the presence of chlorides and sulfates. *Polish J. Environ. Stud.*, 14: 823-828.
- Sumathi, S., 2004. Removal of residue oil from palm oil mill effluent (pome) using chitosan. Master's Thesis, Universiti Sains Malaysia, Malaysia.
- Tengrui, L., A. Al-Harbawi, Z. Jun and L.M. Bo, 2007. The effect and its influence factors of the fenton process on the old landfill leachate. *J. Applied Sci.*, 7: 724-727.
- Tripathi, S., V. Pathak, D.M. Tripathi and B.D. Tripathi, 2011. Application of ozone based treatments of secondary effluents. *Bioresour. Technol.*, 102: 2481-2486.
- Volk, C., P. Roche, J. C. Joret and H. Paillard, 1996. Comparison of the effect of ozone, ozone-hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution. *Wat. Res.*, 31: 650-656.
- Yeh, C.K.J., C.Y. Hsu, C.H. Chiu and K.L. Huang, 2008. Reaction efficiencies and rate constants for the goethite-catalyzed Fenton-like reaction of NAPL-form aromatic hydrocarbons and chloroethylenes. *J. Hazard. Mater.*, 151: 562-569.
- Yeh, C.K.J., H.M. Wu and T.C. Chen, 2003. Chemical oxidation of chlorinated non-aqueous phase liquid by hydrogen peroxide in natural sand systems. *J. Hazard. Mater.*, 96: 29-51.
- Zhou, T., Y. Li, F.S. Wong and X. Lu, 2008a. Enhanced degradation of 2,4-dichlorophenol by ultrasound in a new Fenton like system (Fe/EDTA) at ambient circumstance. *Ultrason. Sonochem.*, 15: 782-790.
- Zhou, T., Y. Li, J. Ji, F.S. Wong and X. Lu, 2008b. Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/ H_2O_2 Fenton-like system: Kinetic, pathway and effect factors. *Sep. Purif. Technol.*, 62: 551-558.