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Reduction of Organic Compounds in Palm Oil Mill Effluent Using Ultrasonic Irradiation with and Without Activated Carbon Addition

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Application of ultrasonic irradiation or sonication to wastewater treatment is well known technique. It is a safe, clean and effective method. Ultrasonic irradiation can also be used as a standard single process or it can be integrated or combined with other treatment methods. When water is exposed to ultrasonic irradiation, $H^•$ and $OH^•$ radical are produced. The latter is a strong oxidizing agent and can react with organic pollutants. In this study, raw and biologically treated palm oil mill effluent (POME) were used as test media to investigate the effectiveness of ultrasonic irradiation in reducing organic compounds based on chemical oxygen demand concentration. The media were subjected to three types of experimental conditions. They were ultrasonic irradiation, activated carbon and combination of ultrasonic irradiation with activated carbon. Results showed that the percentage reduction of chemical oxygen demand was highest when the test media were exposed to ultrasonic irradiation for 45 min after addition of activated carbon. The combined process achieved 63.1 and 95.6 % reduction of chemical oxygen demand for raw and biologically treated palm oil mill effluent, respectively. This indicated that ultrasonic irradiation after activated carbon addition improved the quality of both palm oil mill effluent effluents thus has potential to be used as tertiary treatment since it is capable of reducing the chemical oxygen demand level in biologically treated palm oil mill effluent to acceptable discharge level.

Key Words: Palm oil mill effluent, Chemical oxygen demand, Ultrasonic irradiation, Combination, Activated carbon.

INTRODUCTION

Sonochemical decomposition of organic pollutants in aqueous solution occurs due to the formation and collapse of high-energy cavitation bubbles. Upon collapse, the solvent vapour is subjected to the enormous increases in both temperature and pressure[1]. Under such extreme conditions the solvents molecules undergo hemolytic bond breakage to generate radicals. When water is sonicated, $H^•$ and $OH^•$ radicals

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are produced. The latter is a strong oxidizing agent and can react with organic pollutants[2]. In addition, ultrasonic irradiation through its mechanical waves, is known to have an effect on the sorption process. Furthermore, ultrasonic irradiation waves strongly affect mass transfer between two phases[3].

Palm oil mill effluent is the matrix selected for this study. Oil palm production is a major agricultural industry in Malaysia. Every single year the production of palm oil increased rapidly. As the production of palm oil increased, more palm oil mill effluent is generated annually. The palm oil mill effluent must be treated to acceptable quality before it can be discharged into watercourse or land application[4]. Currently, biological treatments are employed by the palm oil mill industry to treat palm oil mill effluent.

However, there are several problems associated with biological treatments (ponding systems). Biological treatment needs long retention time (90-120 days) and requires a large land area to accommodate series of ponds in order to achieve the desired characteristics for discharge[5,6]. In addition, the treated palm oil mill effluent is still coloured and contains high concentration of non-biodegradable organics (high chemical oxygen demand) which requires further treatment even though the BOD concentration of the effluent is less than 100 mg/L[4,7]. Furthermore, land application of biologically treated palm oil mill effluent has a disadvantage since it can leach nitrate and phosphate into sub-surface environment which indirectly cause contamination of surface water and groundwater resources. In order to reduce these problems, alternative treatment process is required.

Ultrasonic has been used widely to degrade organic compounds from waste water for years. Many reports have been published about the sonochemical degradation of individual organic compounds[8]. Specifically, previous studies have focused on the effect of ultrasonic irradiation on specific organic compounds such as phenol and PAH. Limited study focuses on the application of ultrasonic irradiation for treating industrial wastewater containing high organic compounds like palm oil mill effluent. Therefore, this study is investigate the effectiveness of ultrasonic irradiation in degrading organic compounds or particularly reducing chemical oxygen demand concentration value in palm oil mill effluent. This study aimed to provides additional information on the applicability of ultrasonic irradiation as alternative treatment process for complex wastewater like palm oil mill effluent.

EXPERIMENTAL

The raw and biologically treated palm oil mill effluent used in this study were collected from palm oil mill located in Rantau, Negeri Sembilan, Malaysia. Samples were refrigerated at 4 ºC to retard biological decomposition during transportation to laboratory and storage before analysis.

The ultrasonic equipment used for this work was ultrasonic generator from Branson S-450D using a transducer probe of 6 mm diameter (Fig. 1). The operating frequency was 20 kHz. Ultrasonic power density can be adjusted by energy input control from 6-72 W. About 200 mL of sample volume was used in batch experiments. Ultrasonic irradiation was transmitted into sample through the tip of the probe for duration of 15, 30 and 45 min. The temperature of samples in the beaker was maintained by continuous circulation of cooling water at 28 ± 2 ºC. A transducer probe of the ultrasonic generator was inserted from the top into the samples about 2-3 cm. To avoid any airborne contamination, the reactor was placed inside of a waterproof sound abating enclosure at ambient pressure.

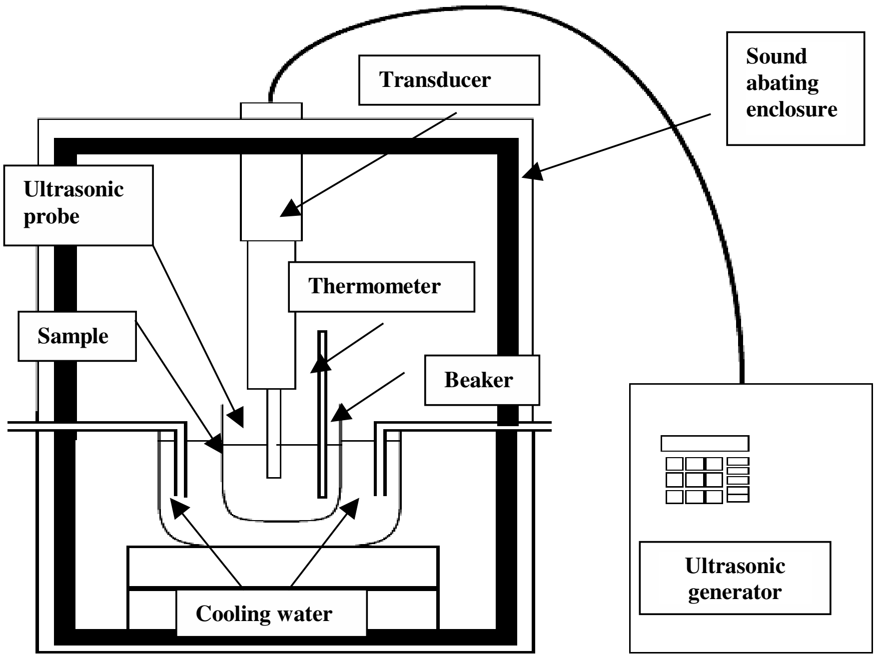

Fig. 1. Experimental setup of an ultrasonic probe

The concentrations of chemical oxygen demand (COD) in the samples before and after ultrasonic were analyzed according to the standard methods for examination of water and wastewater. Raw and biologically treated palm oil mill effluent was subjected to three types of experimental conditions namely ultrasonic irradiation, activated carbon addition and ultrasonic irradiation combined with activated carbon addition. Sample condition for raw and biologically treated palm oil mill effluent before analysis is different due to the physical characteristic of the samples.

Ultrasonic irradiation: To observed the effectiveness of ultrasonic irradiation, about 200 mL was exposed to ultrasonic irradiation at different power density and exposure duration of 15, 30 and 45 min[11]. Ultrasonic power density was adjusted by energy input control produced by the generator from 6-72 W. However, for this study, ultrasonic power of 6 and 11 W were chosen due to the lowest power that can be generated by the ultrasonic generator. This corresponds to an ultrasonic power density of 30 and 55W/L. After ultrasonic irradiation at each operating conditions, the raw palm oil mill effluent was allowed to flow by gravity into a glass container for 6 h sedimentation. After sedimentation process, the supernatant was filtered and analyzed for chemical oxygen demand concentration. The same procedure was also repeated for biologically treated palm oil mill effluent sample. However, only best power density was selected to observe the effect of ultrasonic irradiation alone.

Activated carbon addition: The granular activated carbon (Japan) was used as adsorbent for all experiments involved with activated carbon. Prior to use, the activated carbon was pre-treated by heating in a muffle furnace at temperature 1023 K for 2 h holding time and stored in a desicator until used[11]. The experiments were conducted by varying the amount of adsorbent. 200 mL of raw palm oil mill effluent samples were exposed to different doses of activated carbon of 2, 4 and 6 g, respectively. After activated carbon addition, the samples were stirred slowly for 60 s and allowed to settle for 6 h. Supernatant obtained was filtered and then analyzed for chemical oxygen demand concentration[12]. The same procedure was also repeated for biologically treated palm oil mill effluent sample using the amount of activated carbon that gave the highest chemical oxygen demand reduction of raw palm oil mill effluent.

Ultrasonic irradiation combines with activated carbon addition: Experiments to investigate the effect of ultrasonic irradiation after addition of activated carbon were conducted by adding the selected amount of granular activated carbon (based on previous mentioned experiments) to 200 mL of raw and biologically treated palm oil mill effluent.

Data analysis: The results of the experiments were statistical analyzed using t-test, One-way Anova and correlation analysis.

RESULTS AND DISCUSSION

Raw palm oil mill effluent: Raw palm oil mill effluent is a brown coloured suspension, which is slightly acidic and consists mainly 94-96 % of water. Freshly discharged palm oil mill effluent is viscous and oily with obnoxious odour[13]. For this study raw palm oil mill effluent was allowed to settle for 6 h and the supernatant obtained was analyzed for chemical oxygen demand concentration. The supernatant before experiments has the following characteristics: chemical oxygen demand = 14667 ± 680 mg/L, TSS = 4629 ± 41 mg/L and pH = 3.92.

Biologically treated palm oil mill effluent: Biologically treated palm oil mill effluent contains high concentration of non-biodegradable organic compounds and coloured. For this study biologically treated palm oil mill effluent was filtered before chemical oxygen demand analysis in order to remove suspended impurity. Parameter TSS and pH were analyzed without modification. The characteristic of sample were chemical oxygen demand = 4187 ± 114 mg/L, TSS = 339 ± 17 mg/L and pH = 7.7.

Effect of ultrasonic irradiation

Raw palm oil mill effluent: The effect of ultrasonic irradiation at power density 30 and 55 W/L on percentage reduction of chemical oxygen demand in supernatant raw palm oil mill effluent was shown in Fig. 2. Power density at 30 W/L increased the chemical oxygen demand reduction efficiencies from 4.2-18.7 % when the exposure duration increased from 15-45 min. According to sonochemistry theory, when the ultrasound intensity reaches or exceeds the cavity threshold, bubbles will be formed easily and the cavities collapsed violently. The destruction of volatile compounds more likely occurs inside the cavitation bubbles thus the sonochemical degradation rate should be related to the number of bubbles present if each bubble releases enough energy to 'burn' the organic pollutant[8,14]. Power density 55 W/L showed the negative result after 30 and 45 min after exposed to ultrasonic irradiation. According to Tiehm *et al.*[15], when sludge is exposed to ultrasonic energy the first effect is a de-agglomeration of the sludge flocs. The flocs are separated and dispersed without disrupting the cells. After longer treatment time or higher ultrasonic energies, the micro-organism's cell walls are broken and intracellular material is released into the liquid phase. Consequently, the amount of chemical oxygen demand is increased.

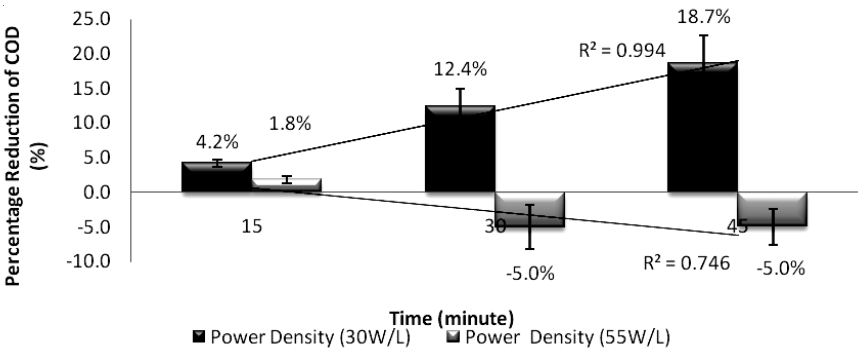

Fig. 2. Effect of ultrasonic power density on the percentage reduction of COD in the supernatant of raw palm oil mill effluent

From statistical analysis, there was positive and strong correlation ($R^2 = 0.99$) between power density 30 W/L and percentage reduction of chemical oxygen demand while power density 55 W/L and percentage reduction of chemical oxygen demand showed negative correlation ($R^2 = 0.75$). Percentage reduction of chemical oxygen demand at power density 30 W/L was significantly ($p < 0.000$) higher than power density 55 W/L. Power density 30 W/L was chosen for subsequent experiments.

Biologically treated palm oil mill effluent: The effect of ultrasonic irradiation at power density 30 W/L on percentage reduction of chemical oxygen demand in biologically treated palm oil mill effluent is shown in Fig. 3. Power density 30 W/L was chosen based on capability of ultrasonic irradiation reducing chemical oxygen demand in raw palm oil mill effluent.

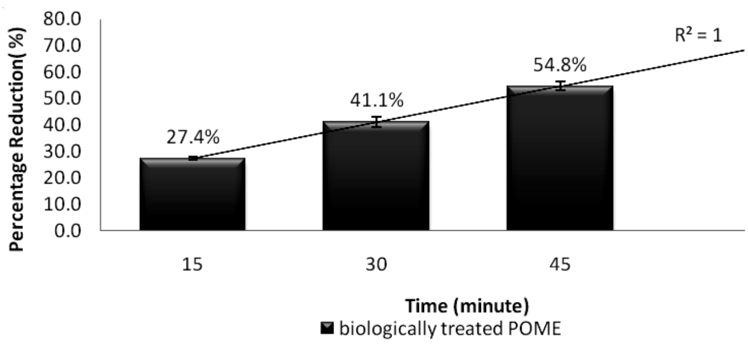

Fig. 3. Effect of ultrasonic power density 30W/L on the percentage reduction of COD in the biologically treated palm oil mill effluent

Results showed clearly, positive and strong correlation ($R^2 = 1$) between time and percentage reduction of chemical oxygen demand. Ultrasonic irradiation can reduce chemical oxygen demand in biologically treated palm oil mill effluent 27.4, 41.1 and 54.8 % after being exposed for 15, 30 and 45 min, respectively. In addition, results shows clearly as the duration of exposure to irradiation increased, the efficiency of chemical oxygen demand reduction also significantly increases ($p < 0.000$). It is believed that the destruction of organic compounds more likely occurs inside the cavitation bubbles thus the sonochemical degradation rate should be related to the number of bubbles present if each bubbles releases enough energy to 'burn' the organic pollutant[8,14].

However, ultrasonic irradiation alone did not have capability to reduce chemical oxygen demand in raw and biologically treated palm oil mill effluent to acceptable discharged level. Ultrasonic alone cannot provide high enough rate of decomposition to be used practically. One option to increased chemical oxygen demand removal efficiency is to add activated carbon prior to ultrasonication.

Effect of activated carbon: In order to determine the optimum weight of activated carbon required, experiments on raw palm oil mill effluent were conducted by varying the amount of adsorbent used. Results of the percentage reduction of chemical oxygen demand after activated carbon addition are presented in Table-1. It indicated that 6 g of activated carbon significantly gave the highest reduction of chemical oxygen demand of 28.6 % when compared to the chemical oxygen demand reduction with 2 and 4 g activated carbon addition.

Therefore, 6 g of activated carbon was chosen to be added to biologically treated palm oil mill effluent. The result showed that 6 g of activated carbon can reduce chemical oxygen demand about 38 % for biologically treated palm oil mill effluent as presented in Table-2. The reduction factor on samples might be due to adsorption of the organic into the fresh granular activated carbon pore[16].

TABLE-1
EFFECT OF ACTIVATED CARBON ADDITION ON THE PERCENTAGE REDUCTION OF COD IN THE SUPERNATANT OF RAW PALM OIL MILL EFFLUENT. DATA WERE ANALYZED USING ONE-WAY ANOVA

Amount of activated carbon (g)	Percentage reduction ± SE	p-Value
2	11.23 ± 0.44	
4	20.86 ± 2.25	0.005
6	28.60 ± 3.15	

TABLE-2
EFFECT OF ADDITION 6 g ACTIVATED CARBON ON THE BIOLOGICALLY TREATED PALM OIL MILL EFFLUENT BASED ON THE PERCENTAGE REDUCTION OF COD

Sample	Initial conc (mg/L) (value ± SE)	Activated carbon treatment	
	COD value (mg/L)	Reduction % ± SE	COD value (mg/L)
Biologically treated POME	4187 ± 114	38.0 ± 2.36	2595

Effect of combine process of ultrasonic irradiation after activated carbon addition: Based on the previous experiment, ultrasonic irradiation and activated carbon alone did not have capability to reduced chemical oxygen demand of raw and biologically treated palm oil mill effluent to acceptable discharge level.

Experiment of the ultrasonic irradiation after activated carbon addition was done to increase the capability in reducing organic compounds in palm oil mill effluent. According to Entezari *et al.*[3], ultrasonic irradiation can increase the surface area and also the mass transfer which both lead to higher sorption process.

About 6 g of activated carbon was chosen to be added to the raw palm oil mill effluent. Results presented in Table-3 showed that combine process of ultrasonic irradiation with activated carbon addition could reduce chemical oxygen demand of about 63.0 and 95.6 % in raw and biologically treated palm oil mill effluent, respectively, after 45 min exposure. This combine process could reduce chemical oxygen demand in biologically treated palm oil mill effluent to concentration of less than 200 mg/L which can be considered as an acceptable discharge level for wastewater. According to Sayan[17], ultrasonic irradiation only was insufficient for removal dye colour and chemical oxygen demand reduction.

Conclusion

Either ultrasonic irradiation or activated carbon could not reduce the concentration of organic compounds or chemical oxygen demand in palm oil mill effluent. The combine process of ultrasonic irradiation and activated carbon addition seems to have potential to be used as alternative treatment for wastewater treatment. However, more study needed to optimized the application of ultrasonic irradiation due to the complexity effect. For future research, the overall capacity and performance of the system combined with cost analysis should be done to study if the option is viable on a commercial scale.

TABLE-3
RESULT OF COMBINE PROCESS OF ULTRASONIC IRRADIATION WITH ACTIVATED CARBON ADDITION

Sample	Control (value ± SE)	Ultrasonic/activated charcoal 15 min		Ultrasonic/activated charcoal 30 min		Ultrasonic/activated charcoal 45 min	
		Reduction % ± SE	Value (mg/L)	Reduction % ± SE	Value (mg/L)	Reduction ± SE	Value (mg/L)
Raw POME	14667 ± 680	52.5 ± 1.89	6966	44.0 ± 2.85	8213	63.1 ± 2.98	5412
Biologically treated POME	4187 ± 114	79.8 ± 2.92	845	84.8 ± 3.25	636	95.6 ± 1.21	184

POME = Palm oil mill effluent.

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REFERENCES

1. V. Naddeo, V. Belgiorno and R.M.A. Napoli, *Desalination*, **210**, 175 (2007).
2. C.P. Chu, D.J. Lee, B.V. Chang and C.S. Liao, *Water Res.*, **35**, 1038 (2001).
3. M.H. Entezari, N. Ghows and M. Chamsaz, *J. Hazard. Mater.*, **131B**, 84 (2006).
4. N Bahiyah, Degradation of Palm Oil Mill Secondary Effluent (POMSE) using Biostructure, Master of Engineering Thesis, Universiti Teknologi Malaysia (2007).
5. M.A. Hassan, Universiti Putra Malaysia Inaugural Lecture Series: Waste to Wealth through Biotechnology for Profit, People and Planet (2008).
6. N. Saifuddin and S.A. Fazlili, *Am. J. Eng. Appl. Sci.*, **2**, 139 (2009).
7. K.S. Kee, Degradation of Palm Oil Mill Secondary Effluent (POMSE) with Solar Fenton, Master of Engineering Thesis, Universiti Teknologi, Malaysia (2007).
8. S. Wang, X. Wu, Y. Wang, Q. Li and M. Tao, *Ultrasonics Sonochem.*, **15**, 933 (2008).
9. G. Zhang, P. Zhang and Y. Chen, *Tsinghua Sci. Tech.*, **11**, 374 (2006).
10. E. Gonze, N. Commenges, Y. Gonthier and A. Bernis, *Chem. Eng. J.*, **92**, 215 (2003).
11. J.A. Menendez-Diaz and I.M. Gullon, in ed: T.J. Bandosz, Types of Carbon Adsorbents and Their Production, In Activated Carbon Surfaces in Environmental Remediation, pp. 49-105 (2006).
12. E.O. Aluyor and O.A. M. Badmus, *Afr. J. Biotech.*, **7**, 3887 (2008).
13. S. Bhatia, Z. Othmana and A.L. Ahmad, *J. Hazard. Mater.*, **145**, 120 (2007).
14. M. Goel, H. Hongqiang, A. Mujumdar and M. Ray, *Water Res.*, **38**, 4247 (2004).
15. A. Tiehm, K. Nickel, M. Zellhorn and U. Neis, *Water Res.*, **35**, 2003 (2001).
16. A.Y. Zahrim, F.M. Rachel, S. Menaka, S.Y. Su, F. Melvin and E.S. Chan, *World Appl. Sci. J.*, **5**, 26 (2009).
17. E. Sayan, *Chem. Eng. J.*, **119**, 175 (2006).

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