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Ozonation of Diesel Range Petroleum Hydrocarbon

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Abstract

The use of diesel fuel in waterways transportation often leads to contamination of petroleum hydrocarbon in the environment with adverse effects on water quality and aquatic lives. While bioremediation has limitations in petroleum removal, chemical oxidation is more promising. Ozonation is an effective process for treating organic matters. This study investigated the effect of ozone on diesel range hydrocarbon using synthetic water sample with 100 and 500 mgTPH/L. The experiment was conducted in a batch reactor with ozone supplied from a small scale generator (32.64 mgO_3/min). Total Petroleum Hydrocarbon (TPH) removal of 87 and 90% were achieved, in 100 and 500 mgTPH/L respectively, with the removal capability of 0.75 $mgTPH/mgO_3$. After ozonation, aliphatic fraction of diesel range hydrocarbon (C10 – C28) was reduced to some extent. Of all the 6 Polycyclic Aromatic Hydrocarbons (PAHs), present in smaller amount in raw sample, only Naphthalene remained after ozonation. With sufficient ozone dosage, biodegradable portions of TPH were removed. Biodegradability of TPH was very low with BOD removal rate constant (K_T) of 0.14 and 0.10 d^{-1}. The values were lowered to 0.07 and 0.04 d^{-1} after the ozonation treatment.

Keywords : ozonation; total petroleum hydrocarbon; diesel range organic; PAH

Introduction

Crude oil is a mixture of hundreds of different compounds, mainly hydrocarbons in aliphatic and aromatic structure. Petroleum-based compounds are divided in fractions and it is more practical to measure them as total amount of hydrocarbons – Total Petroleum Hydrocarbon (TPH) [1]. A wide variety of products derived from crude oil or petroleum-based products (for example fuel oil, mineral oil, asphalt, and plastic polymer) are widely used in everyday life, so petroleum hydrocarbon contamination in the environment is inevitable. When petroleum HC is released to water, certain fractions will float and form thin surface film. The heavier fractions will settle and accumulate in the sediment affecting bottom feeding fish and microorganisms. Some derivatives and refined products of crude oil are toxic to aquatic lives, the effect ranges from physiological and behavioral disorders to death. Some TPH fractions may be broken down by aquatic organisms (primarily bacteria and fungi) while some are recalcitrant. While bioremediation is cost effective, it may not work on all fractions. Chemical oxidation is a good alternative for treating TPH.

Ozone (O_3), known to have a strong oxidizing power, can change complex molecules to ones with simpler structures, making them more biodegradable. In water, O_3 rapidly decomposes through a series of reactions resulting in formation of various types of radicals. Hydroxyl radical (OH*) is an important radical formed, with higher oxidizing power than O_3 and the reaction that is not selective [2]. Ozone oxidation can occur by direct reaction (O_3 reacts directly with target substance) or by indirect reaction (by radicals formed during ozone decomposition) [3].

Ozone and hydroxyl radical (produced by ozone) can react with a variety of organic matter. The mechanisms of ozone attacking saturated HC proposed by Hellman and Hamilton [4] can be illustrated by the following pathway:

$$RH + O_3 \rightarrow R^{*} + H\,O_3^{*} \rightarrow ROOOH \rightarrow R^{*} + HO^{*} + O_2 \rightarrow R{=}O + ROOH$$

$$R^{\cdot} + H\,O_3 \rightarrow ROH + O_2^{*}$$

Aromatic structure of benzene ring, normally exhibiting higher resistant to oxidation, may also be attacked by O_3 and OH*. It was proposed that the attack could result in ring cleavage or generation of phenol (which can be further oxidized) [5, 6].

As a strong oxidant, O_3 has potential in many applications including water and wastewater treatment, mainly for removal of contaminants and disinfection [7]. The advantage of O_3 over other chemical oxidants is that it does not leave harmful residue after the reaction. It is produced on-site, reducing the problems due to chemical handling and storage. O_3 also gains interest in the treatment of petroleum contamination. Previous studies on ozonation of petroleum based contaminants showed that TPH was effectively reduced and organic compositions altered. Some TPH fractions were partially oxidized - high MW compounds changed to low MW [8]. Some changed from non-biodegradable to biodegradable compounds [9, 10].

In Bangkok, transportation along the Chao Praya River is widely used by commuters on a daily basis. The use of diesel engines in boats (vehicles) contributes to deterioration of water quality around the piers. Ozonation is a potential candidate for the treatment of the petroleum hydrocarbon. This study investigated the effects of ozone on Diesel Range Hydrocarbon (compositions and biodegradability). It is envisaged that the results will be a part of a guideline for remediation of diesel fuel contamination.

Materials and Methods

The experiment was conducted in a laboratory scale batch reactor using synthetic water sample, prepared as TPH contaminated water by mixing diesel with distilled water at the concentration of 100 and 500 mg/L. The system setup for ozonation experiment, shown in Figure 1, consisted of a sample bottle (1.5 L) connected with 3 consecutive flasks of 2%KI solution serving as excess ozone traps. Ozone from the generator was supplied to the sample bottle.

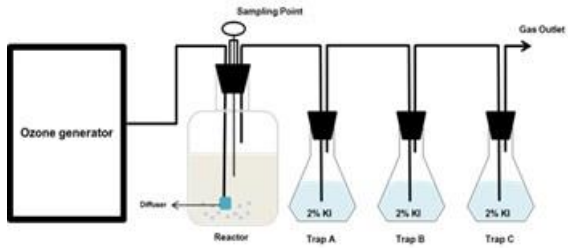


Figure 1 Ozonation system

Prior to the experiment, ozone production rate was determined using Wet Chemistry Iodide method [11]. Ozone from the generator was directed to the first of the three KI flasks. The generator was allowed to operate until the third flask started to turn yellowish, indicating that ozone started to enter the flask. KI solution from all the 3 traps was then mixed and 3 aliquots were titrated with standard $Na_2S_2O_3$ titrant. The ozone production rate was calculated using equation 1.

Ozone production rate (mgO_3/min) =
(A+B+C) * N * 24 / T (1)

Where A, B, C = mL of $Na_2S_2O_3$ used for titrating trap A, B, C
N = normality of $Na_2S_2O_3$ titrant
T = ozonation time (min)

In the ozonation experiment, ozone was continuously supplied, at the rate of 32.64 mgO_3/min, to a batch sample for 30 min. The treated samples were collected and determined for oil and grease (according to APHA, AWWA and WEF, 2012) [12] as total amount of diesel contamination or TPH. Ozone capability in TPH removal was also calculated from TPH removed per mg ozone consumed (the amount produced subtracted by the excess amount in KI traps.

Raw and treated samples were analyzed for Diesel Range Hydrocarbon (aliphatic, C10 – C28) and aromatic fractions (the 16 priorities PAHs listed by USEPA [13]). Gas Chromatograph-Mass Spectroscopy technique was employed (sample was extracted by C-18 Solid Phase Extraction, separation condition in HP5890 GCMS : HP5872A detector, column DB-5MS UI 30mx0.25mm, film thickness 0.25µm).

BOD of raw and treated samples was determined over the 15 days and BOD k-rate was determined by Thomas slope method [14, 15].

Results and Discussion

TPH removal by ozonation

The use of synthetic sample allowed for determination of oil&grease as TPH. The removal results of 100 and 500 mgDiesel/L were compared in Figure 2. It was found that a certain amount of ozone was necessary for diesel removal, as can be seen by the dormant activity in the first 5 minutes. After this the TPH removal rate initially (10 min ozonation time) increased dramatically with an increase in ozone dosage, after which it slowed down. At 15 min ozonation time (489.6 mgO_3/L) TPH was substantially removed. The effect of the initial concentration was small but noticeable. Removal Percentage was higher for the 500 mgTPH/L sample. However, at 30 min (979.2 mgO_3/L), removal percentages from the two samples were about the same, 87 and 90% removal in 100 and 500 mgTPH/L, respectively. The study on the effect of ozone on petroleum-based pollutants in water by Zhu et al. [10], achieved similar result of >80% removal.

While TPH removal percentage in the 100 and 500 mg/L samples looked comparable, the capability of ozone in the 2 samples were significantly different. Capability of ozone can be determined from the ratio of TPH removed to ozone dosage (mgTPH removed/mgO_3). As can be seen in Figure 3, ozone capability was higher in the 500mg/L sample, with the highest value of 0.75 mgTPH/mgO_3. The same ozone dosage in the 100 mg/L sample was an oversupply, leading to low capability. Oversupply also occurred in the 500 mg/L sample when the dosage was increased over 300 mgO_3/L.

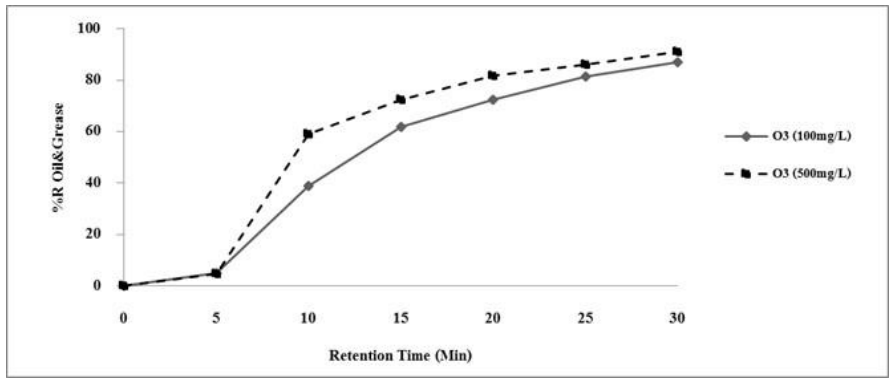


Figure 2 Oil&grease (as TPH) removal in diesel contaminated (100 and 500 mg/L) samples by ozone

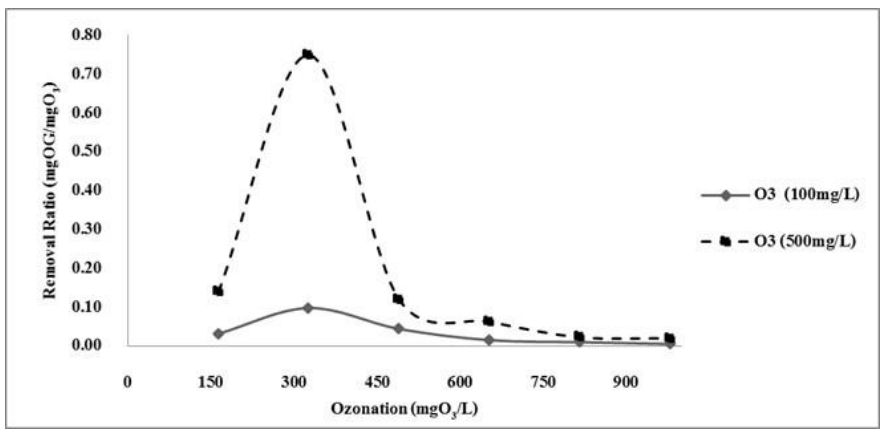


Figure 3 Ozone capability in TPH removal in diesel contaminated (100 and 500 mg/L) samples

Effect of ozone on composition of Diesel Range Hydrocarbon in the sample

Diesel fuel is a mixture of hydrocarbon compounds, with main compositions of aliphatic hydrocarbon in the range of C10 – C28 (Diesel Range Organic). Polycyclic aromatic hydrocarbons (PAHs) may also be present. Since ozone reacts to different compounds differently, the effect of ozone on compositions of diesel fuel was of interest in this study. Samples of 100 mgTPH/L, raw and treated for 30 min with 979.2 mgO_3/L, were analyzed for TPH composition (C10-C28 aliphatic HC) and the 16 priorities PAHs (listed by USEPA) by GC-MS. The results presented in Figure 4 exhibits typical composition of diesel range hydrocarbon compounds with major peaks in the range of C16 – C23. The treated sample showed lower peak in all compositions.

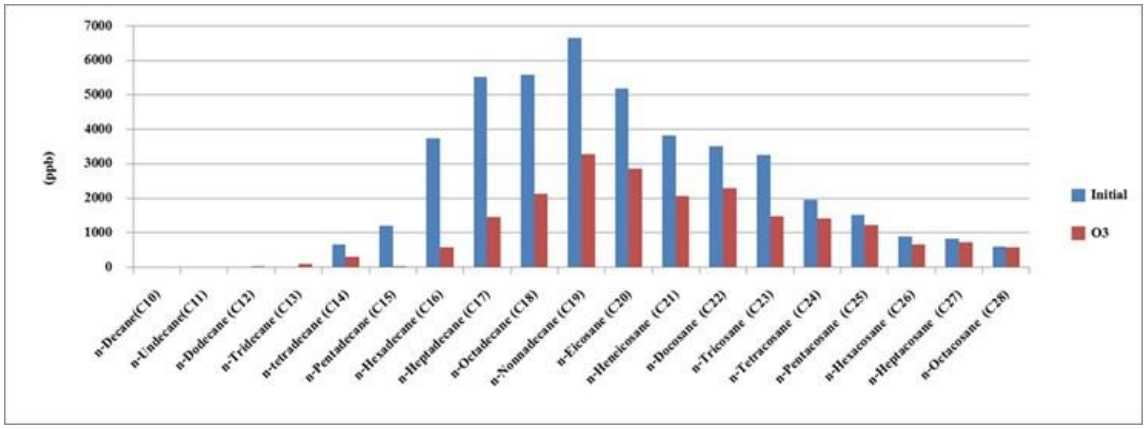


Figure 4 Composition of Aliphatic fraction of Diesel Range Hydrocarbon in raw sample (100 mgTPH/L) compared to sample treated with 979.2 mgO_3/L

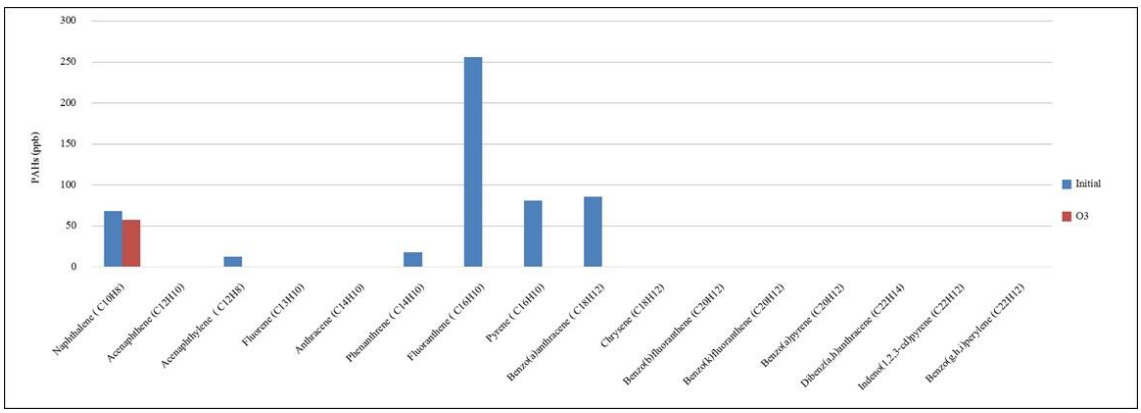


Figure 5 Composition of PAHs in raw sample (100 mgTPH/L) and sample treated with 979.2 mgO_3/L

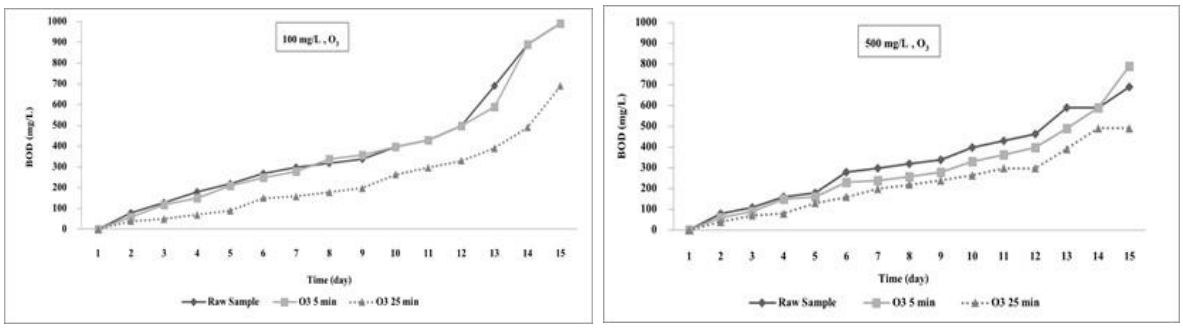
PAHs composition was shown in Figure 5, out of the 16 priorities PAHs, only 6 were found in the raw sample: Naphthalene, Acenaphthylene, Phenanthrene, Fluoranthene, Pyrene, Benzo(a)anthracene. The concentrations were 12.6-256.2 ppb. Among these, Fluoranthene's peak was dominant. The result was compatible with those from previous studies, reporting that priorities PAHs with low molecular weight were major component in diesel fuel from many sources [16-18]. After the treatment, only naphthalene remained while the other 5 PAHs were not detected. Comparing to what happened with aliphatic fraction, aromatic fraction was more susceptible to ozone reaction. Ozone reaction to organic compounds was explained to be partial oxidation or destruction of complex to simpler molecules [9, 10].

Biodegradability

An adverse effect of TPHs on the environment is that they are not readily bio-degradable. BOD-5 (biochemical oxygen demand at 5 day) of organic matter that is not readily bio-degradable is much lower than the ultimate BOD. The data of BOD over longer period

(10-20 days) and the reaction rate give clearer information on biodegradability. To investigate the effect of ozone on biodegradability of Diesel Range Organics, raw samples (100, 500 mgTPH/L) and treated samples (5, 25 min ozonation time) were tested for BOD over 10 days period. As can be seen in Figure 6a and Figure 6b, BOD of all samples showed an increasing trend all through the test period. For readily biodegradable organics, BOD normally reaches plateau at 5 day and the value accounted for 80-90% of ultimate BOD. The continuously increasing trend indicated that TPH in the samples were low in biodegradability. However, BOD of the treated samples were lower than those of raw sample, showing removal of degradable fraction. In both TPH concentrations, the lower dosage from 5 min ozonation resulted in insignificant removal while the higher dosage from 25 min showed substantial removal. This showed that biodegradable portion of TPH were removed by ozone.

BOD reaction rate constant (K_T) was determined from the above BOD data by Thomas slope method. Generally, K_T of raw sewage (rich in biodegradable organic) is in the range of 0.30-0.40 d^{-1}. The lower K_T of 0.14 and 0.1 d^{-1} of the raw samples (shown in Table 1) indicated TPH in raw sample was not highly degradable. Those of the treated sample was even lower, indicating that the products remaining after ozonation were hard to degrade.



a) b)

Figure 6 BOD (at 0-15 days) of Diesel contaminated sample treated with ozone
a) 100 mgDiesel/L b) 500 mgDiesel/L

Table 1 BOD K rate of the raw and treated samples

TPH concentration	K_T (d^{-1})		
(mg/L)	Raw sample	5 min ozonation	25 min ozonation
100	0.14219	0.07530	0.00362
500	0.10442	0.10252	0.03728

Conclusion

The effect of ozone on diesel range hydrocarbons was investigated. The experiment was conducted in a batch reactor using synthetic water sample with 100 and 500 mgTPH/L, with ozone supplied from a small scale generator (32.64 mgO_3/min). Total Petroleum Hydrocarbon (TPH) removal of 87 and 90% were achieved, respectively, with the removal capability of 0.75 $mgTPH/mgO_3$. Aliphatic fraction of diesel range hydrocarbon (C10 – C28), major compositions, was reduced to some extent by ozonation. Determination of the 16 priorities Polycyclic Aromatic Hydrocarbon (PAHs) revealed the contamination of Naphthalene, Acenaphthylene, Phenanthrene, Fluoranthene, Pyrene, Benzo(a)anthracene in smaller amount. Only Naphthalene was detected after ozonation. With sufficient ozone dosage, biodegradable portions of TPH were removed. Biodegradability of TPH was very low with BOD removal rate constant (K_T) of 0.14 and 0.10 d^{-1}. The values were lowered to 0.07 and 0.04 d^{-1} after the treatment.

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References

[1] American Petroleum Institute. 1994. Interlaboratory Study of Three Methods for Analyzing Petroleum Hydrocarbons in Soils. API Publication No. 4599. American Petroleum Institute, Washington, DC

[2] Hoigne, J. and Bader, H. 1975. Ozonation of water : role of hydroxyl radical as oxidizing intermediates. Science. 190: 782-783.

[3] Hoigné, J. The chemistry of ozone in water. In: Stucki, S. Process Technologies for Water Treatment, 1988. Plenum Publishing Corp., New York.

[4] Hellman, T.M., Hamilton, G.A. 1974. Mechanism of alkane oxidation by ozone in the presence and absence of iron(III) chloride. Journal of the American Chemical Society. 96(5): 1530-1535.

[5] Bailey, P.S. 1982. Ozonation in Organic Chemistry V2: Nonolefinic Compounds. Elsevier.

[6] Zeng, Y., Hong, P.K.A. and Wavrek, D.A. 2000. Integrated Chemical-Biological Treatment of Benzo[a]pyrene. Environmental Science & Technology. 34(5): 854-862.

[7] Zouboulis, A., Samaras, P., Ntampou, X. and Petala M. 2007. Potential ozone applications for water/wastewater treatment. Separation Science and Technology. 42(7): 1433-1446.

[8] Wang, J, Zhang, X., and Li, G. 2013. Compositional changes of hydrocarbons of residual oil in contaminated soil during ozonation. Ozone: Science & Engineering. 35(5): 366-374.

[9] Chen, T., Delgado, A.G., Yavuz, B.M. et al. 2016. Ozone enhances biodegradability of heavy hydrocarbons in soil. Journal of Environmental Engineering and Science. 11(1): 7-17.

[10] Zhu, M., Wang, H., Su, H., You, X. and Jin, W. 2010. Study on oxidation effect of ozone on petroleum-based pollutants in water. Modern Applied Science. 4(1): 6-11.

[11] Rakness , K., Gordon, G., Langlais, B. et al. 1996. Guideline for measurement of ozone concentration in the process gas

from an ozone generator. Ozone Science and Engineering. 18: 209-229.

[12] APHA, AWWA and WEF. 2012. Standard Methods for Examination of Water and Wastewater. American Public Health Association. Washington, D.C.

[13] U.S. Environmental Protection Agency. 1993. Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. EPA 600-R-93-089.

[14] Thomas, H.A. 1937. The 'slope' method of evaluating the constants of the first-stage biochemical oxygen demand curve. Sewage Works Journal. 9(3): 425-430.

[15] Snoeyink, V.L. and Jenkins, D. Biochemical Oxygen Demand. In: Snoeyink, V.L. and Jenkins, D. Water Chemistry. 1980. Wiley

[16] De Souza, C.V. and Correa, SM. 2016. Polycyclic aromatic hydrocarbons in diesel emission, diesel fuel and lubricant oil. Fuel. 185: 925-931.

[17] Lim, M.C.H., Ayoko, G.A., Morawska, L., Ristovski, Z.D. and Jayaratne, E.R. 2005. Effect of fuel composition and engine operating conditions on polycyclic aromatic hydrocarbon emissions from a fleet of heavy-duty diesel buses. Atmospheric Environment. 39: 7836-7848.

[18] Marr, C.L., Kirchstetter, T.W., Harley, R.A., Miguel, A.H., Hering, S.V. and Hammond, S.K. 1999. Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. Environmental Science and Technology. 33: 3091-3099.