



Effect of temperature, flow rate and pH on diesel fuel degradation using ozone technique

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ABSTRACT

The influence of the operating parameters such as contact time, ozone flow rate, water temperature and pH was studied. To destruct diesel fuel by ozonation, the maximum degradation was achieved at 25°C, pH 7 and 830 mg/min ozone flow rate. The highest TPH removal was up to 75 % after 60 min. Increasing ozone flow rate positively affected TPH removal. A direct correlation existed between reaction time and removal percentage. Higher contact time exhibited higher removal efficiency in experiments. The pseudo first-order rate constant depended on the ozone flow rate (mL/min). The highest $t^{1/2}$ of 30 min was observed for 60 min ozonation. Half-life times were 28, 53 and 99 min for TPH with ozone flow rate of 430, 600 and 830 (mL/min), respectively.

Keywords: Ozone; Diesel fuel; Degradation; Water pollution; TPH

1. Introduction

Petroleum compounds are among the major contaminants of water. Many petroleum hydrocarbons are toxic and hazardous. Thus, these pollutants must be removed from the environment [1]. Total Petroleum Hydrocarbons (TPH) are an important parameter commonly used to evaluate how seriously polluted a petroleum contaminated body [2]. Several remediation technologies have been developed for petroleum hydrocarbon treatment, including physical, chemical and biological processes as well as combined approaches [3,4].

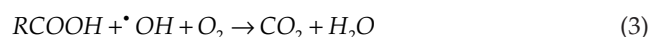
Chemical oxidations are among the appropriate technologies known as an efficient process for degradation of these compounds in water [5]. In recent years, advanced oxidation processes (AOPs) in which highly reactive radicals (particularly $\cdot\text{OH}$) are generated have been increasingly applied for degradation of various classes of organic compounds [6]. It has been determined that ozonation is an important and AOPs on the removal of organic and per-

sistent water pollutants without formation of harmful products in the system [7,8].

Degradation of diesel fuel by ozone can be explained by these reactions according to Yu and co-authors, 2007 [9]:



where R-H is an alkane, and RCOOH is a carboxylic acid. However, the carboxylic acid can be break down to carbon dioxide in the final stage of treatment as presented in Eq. (3)



Xiao et al. [10] suggested the same mechanism for removal of organics during photo-catalytic ozonation.

Many advantages of the ozonation process such as high oxidation potential of ozone, its high efficiency in decomposition of organic matter, addition of oxygen to water, production of more biodegradable compounds [11] and its low sensitivity to changes in temperature use of this method in recent years have considerably been the effective factors in

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ozonation, ozone dose, contact time, ozone mass transfer and pH [12,13]. Longer oxidation time leads to a higher degree of oxidation and higher removal when chemical oxidation is the sole treatment. However, a higher overall removal does not necessarily occur at long chemical oxidation times in a combined system [14].

The present study aimed to evaluate and analyze degradation kinetics for the water contaminated by diesel using ozone and to investigate the effect of parameters such as ozone flow rate, pH and contact time to develop a process for maximal diesel degradation capacity.

2. Material & methods

2.1. Reagents

Diesel fuel was obtained from Tehran Refinery, Iran. Specific gravity of diesel was 0.87 g/cm^3 and saturated hydrocarbons content (mostly alkanes) was approximately 30 wt%. All the reagents were HPLC grade (supplied by Merck, Darmstadt, Germany) and were used without further purification. Solution of diesel with a concentration of 1 g/L at different solution temperature and pH in distilled water was prepared. Tween 80 as a surfactant was added to a concentration of 1 g/L to reduce surface tension and increase diesel solubility.

2.2. Experimental

The ozone experiments were carried out in the batch set-up shown in Fig. 1. It consists of a compressed air system, an ozone generator, a contactor (reactor) and an off-gas collection system. Experiments were conducted at three temperatures of 10, 25 and 40°C for regular time intervals. The samples were prepared and analyzed after 5, 10, 23, 35, 47 and 60 min. The reactor was a Pyrex-glass gas washing with a working volume of 1 L (4 cm diameter 45 cm height). A compact ozone generator (Arda, France) is employed as described by hag high at and co-authors (2016) [15]. The inflow and outflow of the ozone gas line in the reactor were fitted with a laboratory stopper at the top of the reactor, and sample was taken from the bottom of the reactor. Compressed air with a flow rate of 2 L/min was passed into the ozone generator.

2.3. Chemical analysis:

The concentration of diesel fuel in water was determined by Agilent 7890 gas chromatograph Gas Chromatograph (GC) with a flame ionization detector (FID) using a fused capillary column ($30 \text{ m} \times 320 \mu\text{m}$ id, film thickness $0.25 \mu\text{m}$). The sample injection volume was $1 \mu\text{L}$. The initial oven temperature was 40°C and held for 5 min and ramped to 280°C at 5°C/min for 7 min. The total retention time was 60 min. The injector temperature and detector temperature were 280°C and 300°C , respectively. High-purity helium gas was used as the carrier gas. A set of four standards of known concentration (50, 100, 200 and 1000 ppm) of diesel in water was run before each set of unknown samples. Gas chromatograph calibration was achieved using these external standards. The ozone concentrations in the inlet and outlet gas streams were determined by the iodometric method [16]. Indigo method [17] was used to measure the residual O_3 concentration in the liquid phase using a spectrophotometer.

A flow of N_2 was added to the feed gas to help to reduce build-up of deposits in the generator (Gong et al., 2015). Analysis and QA/QC were performed according to the US-EPA procedures [18].

2.4. Kinetic and half-life time study

Kinetic is an essential concept for ozonation process comprehension, degradation speed evaluation and efficiency increase of pollutants removal methods [19]. Reaction half-life is the time taken for concentration of a reactant to drop to half of its original value. Chemical half-lives are required for utilization reactions such as chemical and environmental evaluations and to show the pollutants environmental fate [3].

3. Results and discussion

3.1. Effect of temperature

The solubility of ozone in water decreases with the rise of reaction temperature, leading to decline of utilization ratio [14]. Temperature affects dispersion and decomposi-

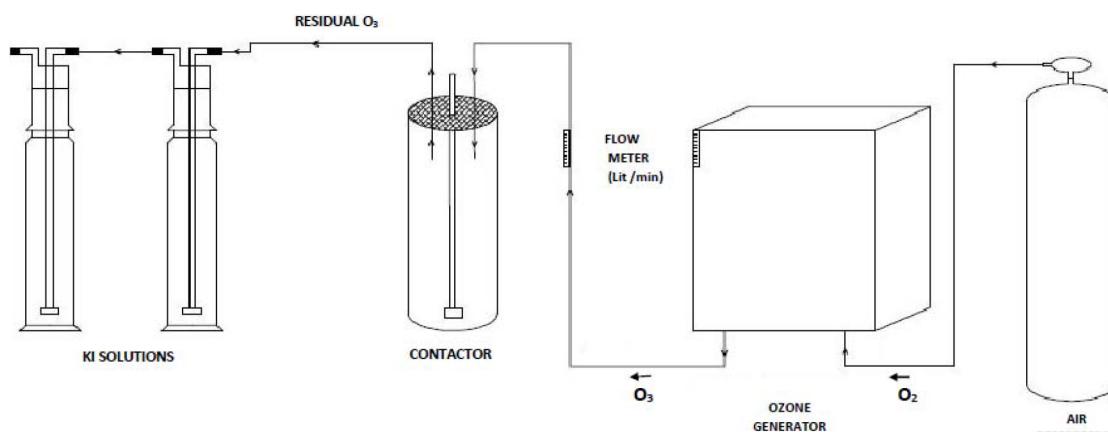


Fig. 1. The schematic of the experimental set-up.

tion of ozone in water, and formation of OH radicals [20]. In addition, reaction rate constant of ozone with organics in water increases with the rise of temperature [13]. The solution temperatures were regulated at 10, 25 and 40°C. As Fig. 2 shows, the solution temperature obviously influences the diesel removal rate by ozonation. The highest removal was at 25°C. The ozonation rate of diesel is fastest at 25°C as the optimal value. The rates decrease with increasing solution temperature when the temperature is over 25°C, due to the increased water evaporation pressure inside the bubble. Increasing water vapor pressure attenuates the efficacy of cavitation collapse and results in worse-dispersion of ozone [21]. However, at higher temperatures, the faster reaction rates were observed below 25°C as higher temperatures to enhance the reaction of TPH with ozone. The solution temperature can also influence the type of intermediates formed: maleic acid and other lower dicarboxylic acids are favored at the optimal temperature (25°C), showing that the rate of mineralization of diesel and its intermediates depends on the hydrodynamic cavitation condition [22].

Kusvuran et al. [13] reported that increasing ozonation temperature positively affected the removal percentages of some pesticides. Mehrjouei et al. [23] examined the effect of temperatures in the range of 10–70°C on the degradation of oxalic acid. The increasing temperature from 10 to 55°C enhanced the degradation rate of oxalic acid, while even higher temperatures up to 70°C negatively affected and reduced the degradation rate.

3.2 Effect of pH

Investigation of initial pH values effect on ozonation is necessary. Fig. 3 presents the decrease of TPH concentration at varying initial pH values as a function of ozonation time in an aqueous diesel solution without buffer. At pH 3, the decomposition of TPH is slower than being under neutral and basic conditions most probably since only the molecular ozone directly reacts to the organic molecule owing to suppression of the formation of hydroxyl radicals.

The degradation rate of TPH at pH 7 is the fastest one most probably as a result of a higher HO radical attached to ozone molecules. In general, it is expected and also con-

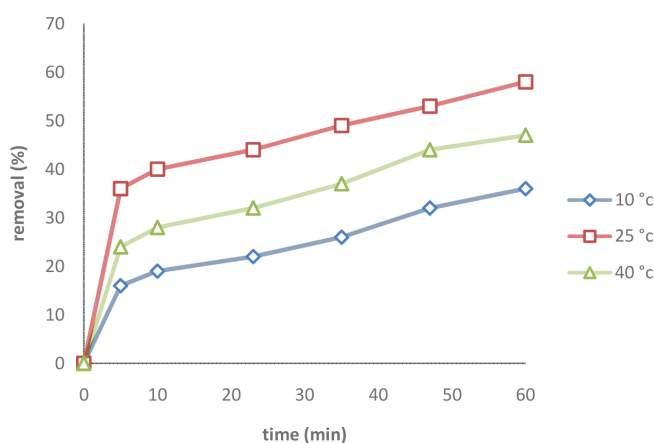


Fig. 2. TPH removal by ozonation at different temperatures.

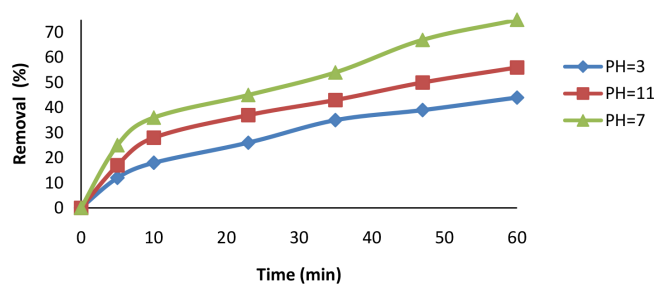


Fig. 3. Effect of pH (3, 7, 11) on the TPH removal during ozonation.

firmed by numerous authors [20] that removal of concerned chemicals in aquatic environment is fastest at pH value higher than 7, since both the ozone molecule and hydroxyl radicals are oxidizing agents.

At pH 11, the TPH degradation is slower than being at pH 7. This result could be explained by the fact that the generated degradation products are attacked at the same time, both becoming important scavengers of hydroxyl radicals. Li et al. [24] report the similar trend for oxytetracycline. They investigated the effect of different pH values (3, 7 and 11) on this antibiotic removal. Results showed that the degradation rate was highest at pH 7.

Soares et al. [25] have observed that ozone decomposition is directly affected by the solution pH. Hydroxyl radicals are formed from ozone decomposition at high pH values, while molecular ozone remains as the main oxidant at low pH. Hydroxyl radicals have a greater oxidative power and are less selective than molecular ozone, leading to a decrease in TPH degradation and an increase in mineralization at higher pH. Most of researchers reported that the optimum pH for removal of organics was around 7 [10,14].

3.3 Effect of ozone flow rate

Effect of ozone (gas mixture) flow rates on the diesel degradation was studied under fixed initial diesel concentration, pH and temperature. Fig. 4 shows the percentage removal of TPH. It can be seen that the increase in TPH removal percentage was boosted with increasing the ozone flow rates. The percentage of TPH removal efficiency was achieved from up to 75% at 60 min by the ozone flow rate of 830 mL/min. At higher ozone flow rates, the curves tend to be exponential,

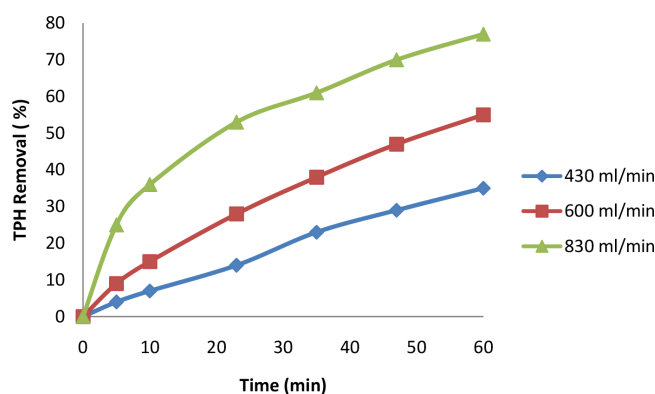


Fig. 4. Effect of ozone flow rate on the degradation of diesel.

indicating the first-order kinetic behaviors, whereas linear dependency was observed at lower ozone flow rates.

3.4. Kinetic evaluation

Pollutant removal studies followed the pseudo first-order kinetics in the ozonation process [26,27]. The initial diesel concentration is a constant. Fig. 5 presents pseudo-first-order degradation kinetics of diesel. Therefore, Eq. (4) was employed in this analysis:

$$C = C_0 e^{-kt} \quad (4)$$

where C is the concentration of hydrocarbons (g/L) at time t , refers to the contact time (day), C_0 is the initial concentration of hydrocarbons (g/L) and k is rate constant of the change in the hydrocarbon content (min^{-1}).

From TPH analysis data, $-\ln(C/C_0)$ versus reaction time for different ozone flow rates was plotted. From the linear portion, the slope (K) was computed. Table 1 shows the calculated apparent first-order rate constants. At lower ozone flow rates, the first-order linearity of the first order was good with correlation coefficient values greater than 0.97, implying the applicability of the first order for this system. Whereas only at lower ozone flow rates, zero order was found from the plot.

3.5. Estimation of degradation half life times

The formula for calculating half life ($t^{1/2}$) is presented in Eq. (5) [4,28].

$$t_{1/2} = \frac{\ln(2)}{k} \quad (5)$$

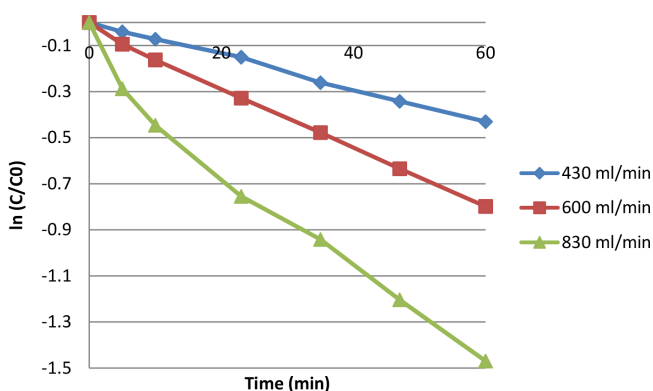


Fig. 5. Pseudo-first-order degradation kinetics of diesel.

Table 1
Kinetic expression and half life times in different ozone flow rates

No	Diesel (mg/L)	Ozone flow rate (mL/min)	Kinetic expression	k	R^2	$t^{1/2}$ (min)
1	1000	430	$y = -0.0072x + 0.0001$	0.007	0.9978	99
2	1000	600	$y = -0.0131x - 0.0211$	0.014	0.9986	53
3	1000	830	$y = 0.0228x - 0.143$	0.026	0.9775	28

where K defines the rate constant presented in the kinetic expression list in Table 1. The highest $t^{1/2}$ of 99 days was observed for 430 mL/min ozone flow rate. In diesel concentration of 1000 mg/L, this was reduced to 53 days and 28 days for 600 and 830 mL/min ozone flow rate, respectively. Thus, a significant correlation between ozone flow rate and amount of TPH reduction was observed.

Low concentration of ozone cannot be recognized as a sufficient technique due to very long half time of 99 min. Zhu et al. [29] reported that the removal efficiency of petroleum-based pollutants increased with the rise of temperature, pH, amount of ozone and reaction time.

4. Conclusions

The results of this study indicate that the oxidation effect of ozone on the TPHs is associated with several parameters such as water temperature, pH, reaction time and ozone flow rate. The highest ozone flow rate in this study was 830 mg/min. The pseudo first-order rate constant increased by raising ozone flow rate. Half-life times were 28, 53 and 99 min for TPH with the ozone flow rate of 430, 600 and 830 (mL/min), respectively. The results on laboratory scale demonstrated that ozone had good compatibility to diesel oil degrading, and ozonation was an effective process to TPH removal from contaminated water. In conclusion, our work demonstrated that ozonation treatment could be implemented for future application to increase TPH removal efficiency in water environments through using an easy, speedy, and low-cost process.

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