Technical Note

Treatment of groundwater contaminated with gasoline components by an ozone/UV process

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ABSTRACT

In this paper, the treatment of real groundwater samples contaminated with gasoline components, such as benzene, toluene, ethylbenzene, and xylene (BTEX), methyl tert-butyl ether (MTBE), tert-butyl alcohol (TBA), and other gasoline constituents in terms of total petroleum hydrocarbons as gasoline (TPHg) by an ozone/UV process was investigated. The treatment was conducted in a semi-batch reactor under different experimental conditions by varying ozone gas dosage and incident UV light intensity. The groundwater samples contained BTEX compounds, MTBE, TBA, and TPHg in the ranges of 5–10 000, 3000–5500, 80–1400, and 2400–20 000 $\mu g\,l^{-1}$, respectively. The ozone/UV process was very effective compared to ozonation in the removal of the gasoline components from the groundwater samples. For the various gasoline constituents, more than 99% removal efficiency was achieved for the ozone/UV process and the removal efficiency for ozonation was as low as 27%. The net ozone consumed per mol of organic carbon (from BTEX, MTBE, and TBA) oxidized varied in the range of 5–60 for different types of groundwater samples treated by the ozone/UV process. In ozonation experiments, it was observed that the presence of sufficient amount of iron in groundwater samples improved the removal of BTEX, MTBE, TBA, and TPHg.

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1. Introduction

Groundwater is a significant source of water supply in many countries. The National Groundwater Association (NGWA, 2005) estimates that about 75%, 47%, 32%, 29%, and 15% of the population in Europe, the US, the Asian-pacific region, Latin America, and Australia, respectively, depend on groundwater for their drinking water supply.

In the US gasoline is the most common source of groundwater contamination (USEPA, 2007). The most toxic components of gasoline, such as benzene, toluene, ethylbenzene, and xylene (BTEX) are among the most frequently detected contaminants in US public drinking-water systems that rely on groundwater sources (USEPA, 2003). Polycyclic aromatic hydrocarbons (PAHs), including naphthalene, anthracene, and phenanthrene are gasoline constituents that are also commonly encountered in groundwater systems (Elder and Dresler, 1988; Paukstys et al., 1998). EPA has classified both BTEX and PAHs as pollutants of concern because of their toxicity and carcinogenicity to humans and animals (Dean, 1985).

These compounds find their way into the groundwater mostly from leaking underground storage tanks (USTs) and sometimes from spills at extraction wells, refineries, and distribution terminals; improper disposal; and catastrophic discharge during transport. Several US States reported that UST releases are the most common source of groundwater contamination in the US (USEPA, 2007). In the US, through 2006 there have been more than 460 000 gasoline releases from USTs since the 1984 federal UST program began (USEPA, 2007). Currently there are approximately 640 000 active USTs which are regulated by EPA or States designated by EPA.

Conventional treatment techniques commonly employed for the removal of gasoline components from contaminated waters include air stripping (Murray et al., 2000), granular activated carbon adsorption (Giffin and Davis, 1998; Yue et al., 2001), and biodegradation (CISB, 1993; Borole et al., 1997; Chapman et al., 1997; Meier-Loehr et al., 1998; Kao and Wang, 2000; Cunningham et al., 2001). Phytoremediation, the treatment of contaminated water or soil through the use of plants, has also been evaluated as alternative treatment method to deal with MTBE contaminated sites (Yu and Gu, 2006). Conventional treatment techniques have some inherent disadvantages; for example, in air stripping and granular activated carbon adsorption the gasoline components are transferred from one medium to another which needs further treatment before final disposal. In biodegradation, the effectiveness of the process depends among other things, on gasoline composition or formulation, presence of microorganisms with potential to biodegrade the target chemicals, accessibility of the target chemicals to microorganisms, availability of electron acceptors, and absence of toxic substances (Hutchins et al., 1991; Lovley et al., 1994; Corseuil and Alvarez, 1996; Anderson and Lovley, 2000).

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Therefore, there is a need for alternative treatment methods for the removal of gasoline components from contaminated groundwater. Advanced oxidation processes (AOPs), which involve the application of various combinations of O_3, H_2O_2, UV, and semiconductors (e.g., TiO_2), provide promising treatment options. The major advantage of AOPs is attributed to the hydroxyl radical ($\cdot$OH) which attacks indiscriminately almost any organic compound with a very high reaction rate constant. In addition, the $\cdot$OH oxidizes a wide variety of organic pollutants into innocuous intermediates and end products, as opposed to conventional treatment methods in which pollutants are transferred from one medium to another. The application of TiO_2 photolysis (Goswami et al., 1993; Madabushi et al., 1998) and solar light/H_2O_2 and solar light/TiO_2 (Cho et al., 2006) for the removal of gasoline components from aqueous solutions have been reported in the literature.

This study investigated the removal of gasoline components, such as BTEX, methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), and total petroleum hydrocarbons as gasoline (TPHg) from contaminated groundwater samples by an ozone/UV process under different experimental conditions by varying ozone gas dosage and incident UV light intensity.
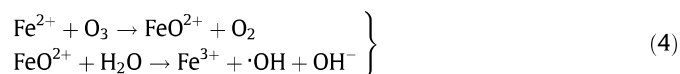
The decomposition of aqueous ozone in pure water is initiated by its reaction with OH^-, and this reaction leads to the production of radicals that propagate the decomposition process by chains of radical–radical or radical–solute reactions and produce $\cdot$OH (Staehelin and Hoigne, 1982; Buhler et al., 1984; Staehelin et al., 1984).

$$O_3 \xrightarrow{OH^-} \cdot OH \tag{1}$$

The above process is known to occur very slowly at low pH levels (Staehelin and Hoigne, 1982) and the decomposition process can be further accelerated with UV radiation. In aqueous phase, the photolysis of ozone produces H_2O_2 as primary product (Peyton and Glaze, 1988), which then can photolyze into $\cdot$OH directly and can react with aqueous ozone to produce $\cdot$OH as shown below. The principal reactions involved in an ozone/UV system in natural waters were summarized in an earlier publication; and interested readers are referred to Table 2 of the publication (Garoma and Gurol, 2004).

$$O_3 + H_2O \xrightarrow{h\nu} H_2O_2 \begin{cases} +O_3 \rightarrow \cdot OH \\ \xrightarrow{h\nu} \cdot OH \end{cases} \tag{2}$$
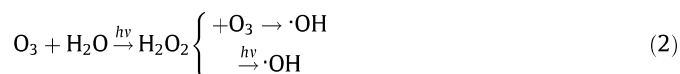
It is also known that UV radiation of iron salts produce $\cdot$OH through photo-Fenton reaction (Mazellier and Bolte, 2001) as shown in Eq. (3). In addition, through "dark" reaction, Fe(II) catalytically decomposes ozone and produces $\cdot$OH through series of reaction Eq. (4) (Loegager et al., 1992).

$$Fe(OH)^{2+} \xrightarrow{h\nu} \cdot OH + Fe^{2+} \tag{3}$$

$$\left. \begin{array}{l} Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \\ FeO^{2+} + H_2O \rightarrow Fe^{3+} + \cdot OH + OH^- \end{array} \right\} \tag{4}$$

2. Experimental approach

The same experimental setup described in an earlier publication (Garoma and Gurol, 2004) was used to conduct the laboratory studies. The setup consists of a quartz reactor placed inside a concentric photochemical chamber that contained 16 removable low-pressure mercury lamps. The reaction vessel has an internal diameter of 13 cm, and was filled with 3 l of solution during experiments. The lamps emit UV light primary at 254 nm at a power source of 2.2 W per lamp as specified by the manufacturer. A glass diffuser was used to sparge ozone gas into the solution at a constant flow rate of 1.5 l min^{-1}.

The reactor was operated in semi-batch mode and the contents were stirred continuously using a magnetic stirrer. For each experiment, the appropriate numbers of UV lamps were inserted into the photochemical chamber and the groundwater sample was placed inside the reactor. At time zero, ozone gas was introduced into the reactor at desired flow rate and UV lamps were switched on. The experiments were conducted at room temperature and the increase in temperature due to UV light exposure was less than 2 °C. Aliquot samples were withdrawn periodically and analyzed for residual concentration of gasoline components.

3. Materials

All chemicals and reagents used in the research are analytical grade. MTBE and TBA were purchased from Fisher Scientific and Sigma–Aldrich, respectively. BTEX and gasoline standards were purchased from Restek Corporation (Bellefonte, PA). Other chemicals and reagents used in this study were purchased either from Sigma–Aldrich, Fisher Scientific, or J.T. Baker chemical companies. Ozone gas is generated from oxygen using Osmotic OREC V-10 ozone generator, and the amount of ozone produced in the oxygen gas was controlled by changing power input to the generator.

4. Analyses

The influent and effluent ozone gas concentration was measured at 258 nm by a Shimadzu UV-1601 spectrophotometer that was calibrated by the Potassium Iodide method (APHA, 1998). Ozone concentration in the liquid phase was determined by the Indigo method (Bader and Hoigne, 1981). The intensity of UV lamps as received in the photochemical reactor was measured by the method of Potassium Ferrioxalate Actinometry (Hatchard and Parker, 1956), and emitted and measured incident light intensities for lamp sets used in this study are presented in Table S1 of Supplementary material.

The COD and alkalinity of the groundwater samples were determined by the Dichromate and Titration Method, respectively according to the Standard Methods (APHA, 1998). Phenanthroline Method was used to determine the concentration of total iron in groundwater samples (APHA, 1998).

For the quantification of gasoline components, aqueous samples were analyzed by using a Perkin Elmer gas chromatograph (GC) equipped with flame ionization detector and capillary column (J&W Scientific, Model DB-624: 75 m × 0.53 mm with 5 μm film). The GC was connected to purge and trap concentrator (Tekmar–Dohrmann 3000 sample concentrator) and interfaced to Peak Simple workstation. The purge and trap unit was interfaced with Tekmar ALS-2016 purge auto-sampler and to an automatic sample heater. Aqueous samples, filtered using 0.45 μl disposable syringe filters, were injected to the purge and tarp, and then purged by the auto-sampler to the concentrator. From the concentrator samples were desorbed to the GC column. Helium was used as a carrier gas at 15 ml min^{-1}, while hydrogen and air were used to fuel the detector. The injector and detector were operated at temperatures of 170 and 300 °C, respectively. The initial oven temperature was 40 °C, which was kept isothermal for 13 min. Subsequently it was ramped at a rate of 25 °C min^{-1} to 200 °C and kept again isothermal for 2 min. The detection limit for MTBE and TBA was 0.1 μg l^{-1} and for BTEX the detection limit was 0.2 μg l^{-1}.

The concentration of TPHg was determined according to EPA Method 8015C. In this method, filtered groundwater samples were injected to the GC and the total area in the retention range of 2-methylpentane and 1,2,4-trimethylbenzene was used to calculate the corresponding concentration of TPHg using a calibration factor. Standard stock solutions, containing gasoline components, prepared at various concentrations were injected to the GC. From

the plot of total area within the retention time range versus total mass injected, a calibration factor was obtained. Similarly, the concentration of total xylene was obtained by adding the area of the three xylene components, i.e., *m*-xylene, *o*-xylene and *p*-xylene.

5. Results and discussion

5.1. Characteristics of groundwater samples

Groundwater samples were obtained from three wells located in San Diego, California and for convenience the samples were denoted as GW-1, GW-2, and GW-3. The groundwater samples were stored in glass jars, I-CHEM brand (Thermo Fisher Scientific, Inc.), in cold room. The jars are Teflon-lined and meet EPA's performance based specification for semi-volatiles/pesticides/PCBs. No airspace was left in the storage jars to prevent stripping of BTEX, MTBE, TBA, and other gasoline components. Yet, reduction in the concentrations of the organic compounds was observed with time (Tables S2, S3, and S4 of Supplementary material), probably due to hydrolysis and biodegradation.

The groundwater samples were filtered using a 0.45 μm pore membrane filters. For GW-1, the pH, total alkalinity, and COD were 7.8, 276 mg l^{-1}, and 13 mg l^{-1}, respectively. The pH, total alkalinity, and COD were measured as 7.5, 623 mg l^{-1}, and 23 mg l^{-1}, respectively for GW-2. For GW-3, 7.9, 460 mg l^{-1}, and 189 mg l^{-1} were the pH, total alkalinity, and COD, respectively.

6. Ozone/UV treatment of groundwater samples

The groundwater samples were treated by ozone/UV process under different experimental conditions, which are summarized in Table 1. Groundwater sample GW-2 and GW-3 contained iron at concentrations of 0.46 and 3.81 mg l^{-1}, respectively. Since iron is known to decompose ozone catalytically (Loegager et al., 1992), the treatment of groundwater samples GW-2 and GW-3 was also investigated in the absence of incident UV light intensity.

During a typical oxidation experiment, the groundwater sample was taken out of cold room and allowed to attain room temperature. Three liters of the groundwater sample was transferred into the experimental reactor. At time zero, ozone gas was introduced into the reactor at desired flow rate and UV lamps were switched on. Samples were withdrawn periodically and analyzed for residual concentration of BTEX, MTBE, TBA, and TPHg. For groundwater samples containing iron, treated samples were filtered using 0.45 μl disposable syringe filters before analysis.

Table 1
Experimental conditions for the oxidation of groundwater samples

| Groundwater sample	Exp. run	Incident UV light intensity (I_o) (W l^{-1})	$(O_3)_{inf}$ (mg l^{-1})	$(O_3)_{eff}$ (mg l^{-1})
GW-1	1	2.73	39	15
	2	4.28	29	9
GW-2	3	2.73	28	13
	4	2.73	50	27
	5	0	52	34
GW-3	6	2.73	51	30
	7	0	53	38

6.1. Ozone/UV treatment of GW-1

The residual concentrations of BTEX, MTBE, TBA, and TPHg, as a fraction of the initial concentration, are presented in Fig. 1 for experimental run 1. The initial concentration for each target chemical is presented in the legend of Fig. 1 and Table S2 (Supplementary material). Since TBA is also produced as a result of MTBE degradation (Stefan et al., 2000; Acero et al., 2001; Garoma and Gurol, 2006), the fraction in Fig. 1 was obtained by diving the residual concentration with the highest concentration of TBA accumulated during the course of the treatment process, which was 371 μg l^{-1} of TBA for experiment 1. In both experimental runs, more than 99% removal of BTEX and MTBE was achieved in 15 min. More than 99% of TBA and TPHg were removed in 30 min for both experiments. For both experimental runs, the residual concentration of MTBE and TBA fallen below the detection limit of 0.1 μg l^{-1} within 15 and 30 min of oxidation time, respectively. The concentration of BTEX present in the groundwater sample dropped below the detection limit of 0.2 μg l^{-1} in 5 min.

6.2. Ozone/UV treatment of GW-2

GW-2 was treated under three different experimental conditions, see Table 1. In experiment 3, the influent ozone gas concentration and the incident UV light intensity were 28 mg l^{-1} and 2.73 W l^{-1}, respectively. The incident UV light intensity was kept constant at 2.73 W l^{-1} while the influent ozone gas concentration was increased to 50 mg l^{-1} for experiment 4. The groundwater sample was treated by ozone alone at an influent ozone gas concentration of 52 mg l^{-1} for experiment 5.

In Fig. 2a–c, the residual fraction of BTEX, MTBE, TBA, and TPHg are presented for experiments 3, 4, and 5, respectively. The highest
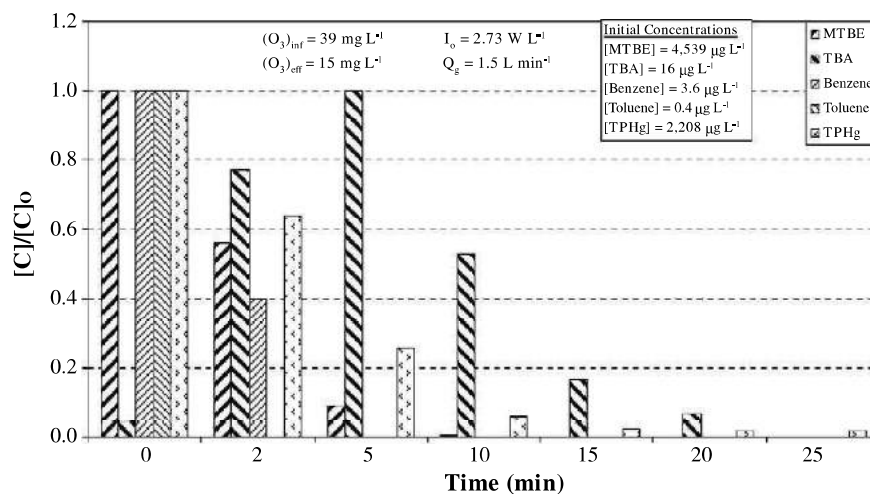
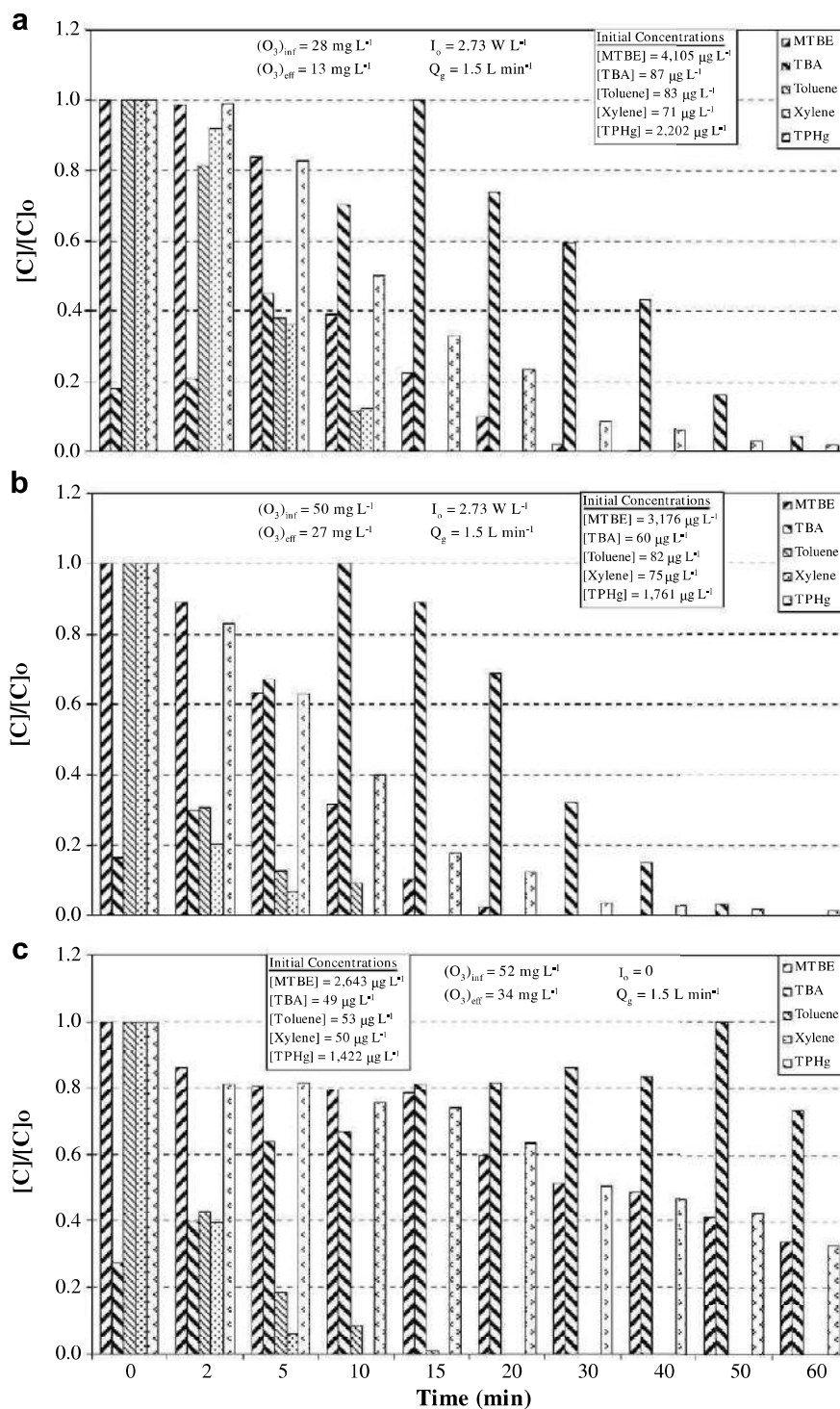Fig. 1. Gasoline components removal during treatment of GW-1.

Fig. 2. Gasoline components removal during treatment of GW-2: (a) Exp. run 3, (b) exp. run 4 and (c) exp. run 5.

concentrations of TBA accumulated during the course of the treatments were 477, 368, and 179 µg l^{-1} for experiments 3, 4, and 5, respectively. In experimental runs 3 and 4, more than 99% of BTEX and MTBE were removed in 30 min. The same removal rate was achieved for TBA and TPHg in 60 min. In experiment 5 more than 99% of the BTEX present in the groundwater sample were removed in 20 min. On the other hand only 66%, 27%, and 67% of MTBE, TBA, and TPHg, respectively, were removed at the end of the 60 min for experiment 5.

The result shows that for same influent ozone gas concentration, the ozone/UV system (Fig. 2b) was very effective for the removal of gasoline components compared to ozonation (Fig. 2c). This is expected because the ozone/UV process generates ·OH which reacts with most organic compounds at a very high rate constant compared with aqueous ozone. In addition, an increase in the influent ozone gas concentration for the same incident UV light intensity resulted in increased removal rate of the gasoline components (Fig. 2a and b). This is because an increase in influent ozone gas concentration results in an increase in dissolved ozone concentration, which then decomposes by OH$^-$ or UV light and generates ·OH through a series of reaction intermediates as indicted by Eqs. (1) and (2).

6.3. Ozone/UV Treatment of GW-3

Groundwater sample GW-3 was treated by ozone/UV (experiment 6) and ozone alone (experiment 7). In Fig. 3a and b, the residual concentration, as a fraction of the initial concentration, are shown for experiments 6 and 7, respectively. The maximum concentrations of TBA accumulated during the course of the experiments were 298 and 466 $\mu g\,l^{-1}$ for experiments 6 and 7, respectively. For both experiments, more than 99% of the BTEX were removed in 30 min. By the end of 60 min, more than 99% MTBE and TPHg for experiment were removed for experiment 6. However, only about 83% and 97% of MTBE and TPHg, respectively, were removed at the end of 60 min for experiment 7. At the end of 60 min about 57% for experiment 6 and about 51% for experiment 7 of TBA were removed.

The results for GW-3 indicate that in the ozone/UV process the presence of iron reduced the removal rate of the gasoline components. It was observed the groundwater sample became turbid as experiment progressed, likely due to the reaction of iron with ozone that might have resulted in reduction of UV light absorbed by the solution, Eq. (3). However, comparison ozonation experiments conducted for GW-2 (Fig. 2c) and GW-3 (Fig. 3b) reveals that the presence of 3.81 $mg\,l^{-1}$ of iron in GW-3 sample (compared with 0.81 $mg\,l^{-1}$ in GW-2) improved the removal of gasoline components. This could be due to catalytic decomposition of ozone by iron, which in turn will enhance the generation of ·OH as shown in Eq. (4).

6.4. Reduction in organic carbon

Fig. 4 presents the residual concentration of organic carbon during the course of experiment for each experimental run. The molar concentration of organic carbon (MOC) was obtained by multiplying the molar concentration of BTEX, MTBE, and TBA by the number of carbons contained in them and summing up the results. For GW-1, more than 90% of the organic carbon from BTEX, MTBE, and TBA was removed in 20 min. To achieve the same removal efficiency about 50 min is needed for GW-2 in experimental runs 3 and 4. Ozonation alone achieved about 64% and 96% removal efficiency for GW-2 and GW-3, respectively. The higher removal efficiency in GW-3 compared to GW-2 for ozonation experiment could be attributed to the higher concentration of total iron present in GW-3. This is because in "dark" reaction iron is known to decompose ozone catalytically and produces ·OH through series of reaction as shown in Eq. (4).

6.5. Ozone consumption

The number of mol of ozone gas consumed per mol of organic carbon removed during the treatment of groundwater samples by ozone/UV process is shown, as a function of percent organic carbon removed, in Fig. 5. The ratios were computed by using the following molar stoichiometric expression:
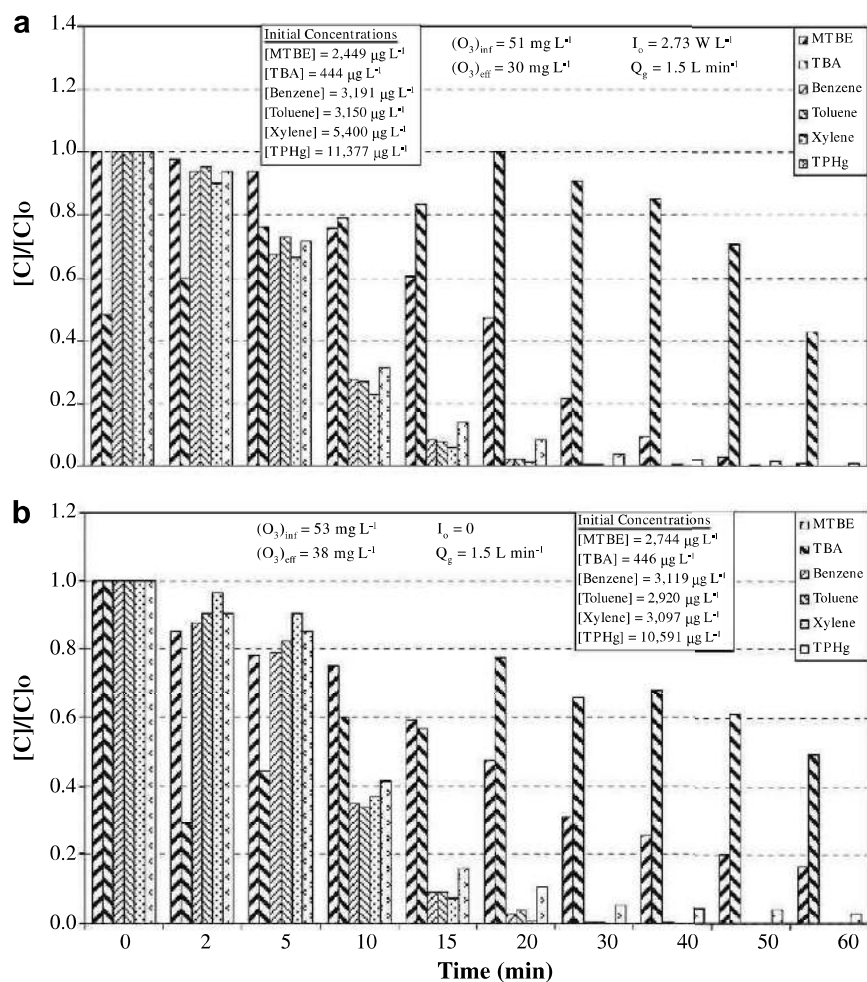

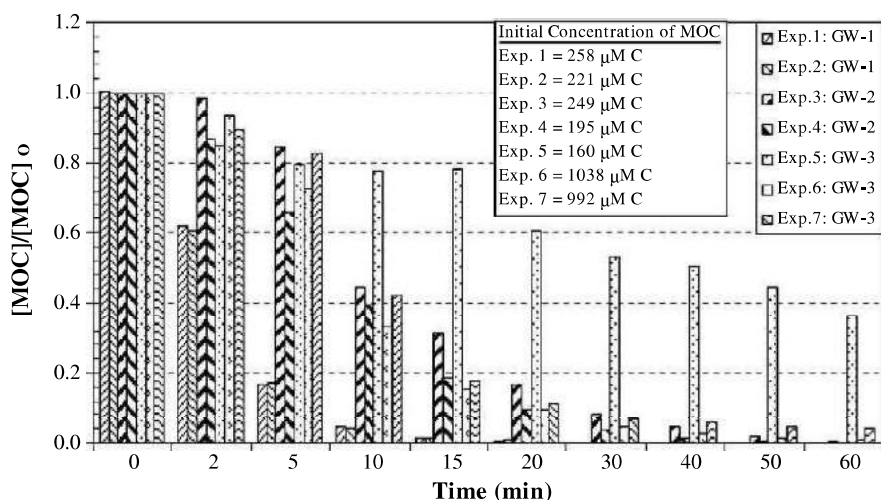**Fig. 3.** Gasoline components removal during treatment of GW-3: (a) Exp. run 6 and (b) exp. run 7.

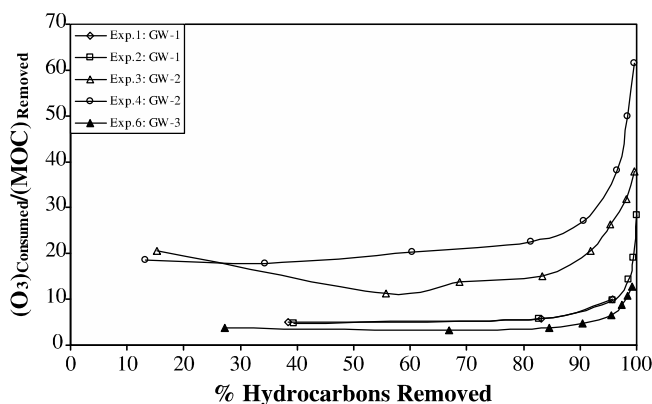**Fig. 4.** Reduction in molar concentration of organic carbon.

Fig. 5. Ozone molar stoichiometric ratios for organic carbon removal.

$$\frac{(O_3)_{consumed}}{MOC_{removed}} = \frac{\left\{\frac{\left[(O_3)_{inf} - (O_3)_{eff}\right]*t_x*Q_g}{48\,000}\right\}}{[MOC]_o * \frac{X}{100} * V} \tag{5}$$

where $(O_3)_{consumed}$ is the number mol of ozone gas consumed, $(MOC)_{removed}$ represents the number of mol of organic carbon removed, $(O_3)_{inf}$ and $(O_3)_{eff}$ are influent and effluent ozone gas in mg l^{-1}, respectively, t_x is time needed for $X\%$ of MOC removal in min, Q_g is ozone gas flow rate in l min^{-1}, $[MOC]_o$ is initial molar concentration of organic carbon (from BTEX, MTBE, and TBA) in M l^{-1}, and V is volume of reactor in l.

The net ozone consumption per mol of organic carbon oxidized varied in the range of 5–30 for GW-1 (experiments 1 and 2), 20–60 for GW-2 (experiments 3 and 4), and 5–15 for GW-3 (experiment run 6). The results reveal that there is a trend towards higher ratios as percent hydrocarbons removed increases, as indicated Fig. 5. This is because at higher percent removal there is less organic matter to utilize ·OH and more inorganic matter to consume ·OH.

7. Summary

In this study, the degradation of gasoline components, such as BTEX, MTBE, TBA, and TPHg in groundwater samples by an ozone/UV process was investigated. The ozone/UV process was very effective compared to ozonation in the removal of gasoline components from the groundwater samples. In the ozone/UV process the presence of iron reduced the removal rate of the gasoline components. It was observed that the sample became turbid as experiment progressed, likely due to the reaction of iron with ozone that might have resulted in reduction of UV light absorbed by the solution. On the other hand, it was observed that the presence of sufficient amount of iron in the groundwater sample could improve the removal of BTEX, MTBE, TBA, and TPHg in ozonation experiments. Moreover, it was also observed that complete mineralization of the gasoline components could be achieved in the ozone/UV process, if desired.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.06.061.

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