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Treatment of water contaminated with methyl tertiary butyl ether using UV/chlorine advanced oxidation process

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ABSTRACT

Methyl tertiary butyl ether (MTBE) is a widely used gasoline additive to improve the air quality by increasing the oxygen content of the fuel. After extensive use for some years in the USA, it was recognized as a groundwater contaminant. Several remediation techniques are available for the removal of MTBE from contaminated water systems. However, the inherent limitations of each removal technique makes further research promising. The aim of this study was to investigate the MTBE degradation in water with chlorine-based advanced oxidation process (AOP). A bench scale study was carried out by varying the experimental conditions such as UV radiation intensity, pH, chlorine doses, and treatment time. Free chlorine was used as a chemical oxidant in combination with low-pressure (LP) and medium-pressure (MP) mercury lamps to degrade MTBE in water. LP and MP UV/chlorine were able to degrade more than 99% of MTBE in deionized water within 15–30 min at pH 5 and 7, respectively. The MTBE removal in groundwater sample with LP UV/chlorine and MP UV/chlorine is greater than 99 and 90% after 30 min respectively. The electrical energy per order estimated for LP UV/chlorine and MP UV/chlorine to treat ground water sample was 4.01 and 54.67 kW h/m^3 respectively. Chlorine-based AOP could be a promising technique for treating water contaminated with MTBE.

Keywords: MTBE; AOP; Ultraviolet; Chlorine; Ground water

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1. Introduction

Methyl tertiary butyl ether (MTBE) is a well-known groundwater contaminant which is produced by petrochemical industries. High production level and widespread use of MTBE make it likely to be present in groundwater source. Leakage from underground storage tanks and pipelines is the major source of environmental contamination. The detection of MTBE in drinking water has raised considerable concern among health officials and water suppliers. The US Environmental Protection Agency considers MTBE to be a potential human carcinogen, and sets an advisory level of 20–40 μg/L [1]. Removal of MTBE from water is challenging and expensive due to its high solubility in water, low biodegradability, low Henry's constant, very low affinity for common

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adsorbents, and high mobility in the environment [2–5]. Advanced oxidation processes (AOPs) have been acknowledged as promising treatment technology for groundwater, municipal and industrial wastewater contaminated with organics like MTBE [6,7]. Ultraviolet (UV)-driven AOPs are primarily based on the generation of powerful oxidizing species such as the hydroxyl radical ($OH^{\cdot}$) and chlorine radical ($Cl^{\cdot}$). Ideally, AOPs make use of hydroxyl radical ($OH^{\cdot}$) to completely degrade organic pollutants present in water into carbon dioxide and water [8].

Chlorine-based photochemical oxidation process (UV/Cl_2) is an emerging AOP to degrade organic contaminants in water [9,10]. The photo-chemistry of the UV/chlorine process predominantly generates $OH^{\cdot}$ in addition to chlorine radical ($Cl^{\cdot}$). The availability of free chlorine depends on the pH of the solution. The percent availability of free chlorine species at pH 5, 7.5, and 10 at room temperature is 99.7% HOCl; 52.3% HOCl plus 47.7% OCl^- and 99.6% OCl^- respectively. The photochemistry of UV/Cl_2 AOP was discussed in literature [7–14].

Recently, some studies investigated the use of aqueous chlorine as the chemical oxidant in UV-driven AOP as an alternative to other chemical oxidants like hydrogen peroxide (H_2O_2) and ozone. UV-induced chlorine AOP produces hydroxyl and other radicals when water is dosed with aqueous chlorine in the form of hypochlorous acid (HOCl) or hypochlorite ions (ClO^-) and exposed to UV light. Hypochlorous acid (HOCl) has higher UV absorbance and less scavenging rate than H_2O_2 at lower pH level. UV/Cl_2 was more efficient than UV/H_2O_2 in degrading trichloroethylene, methylisoborneol in synthetic water [9,15]. Another study reported that UV/Cl_2 AOP was also able to degrade emerging water contaminants with considerable energy saving, and overall cost reduction [10]. The use of UV/Cl_2 AOP for the degradation of organic contaminants in water and wastewater is at infant stage [10,12,16]. In this study, MTBE removal in aqueous solution by UV/Cl_2 process was the primary focus. Effect of chlorine dosage, pH, UV intensity, and contact time on the MTBE removal efficiency was studied.

2. Materials and methods

2.1. Chemicals used

Sigma-Aldrich HPLC grade 99.99% purity MTBE and Tert-Butyl Formate (TBF), and 5.25% sodium hypochlorite were used. Deionized water obtained from Milli-Q direct purification system was used for the preparation of stock solutions. The stock solutions were stoppered tightly, wrapped with aluminum foil, and kept in the refrigerator at 4°C. 1 N Sodium hydroxide (NaOH) and 1 N sulfuric acid (H_2SO_4) were used for pH adjustment. N,N diethyl-p-phenylenediamine (DPD) was used to measure the free chlorine.

2.2. Photoreactor setup

Continuous-flow batch experiments were carried out in a NORMAG® tabular photoreactor with forced liquid circulation. The photoreactor vessel has a total volume of 500 ml and two types of ultraviolet mercury lamps, namely low-pressure (LP) and medium-pressure (MP) lamps manufactured by Heraeus Holding GmbH, Germany. As per the manufacturer, LP lamp emits radiation at a wavelength of 254 nm with intensity of $6.5 \times 10^{-3}\ W/cm^2$ from 15-W power source (TNN 15/32, 55 V, Cat No. SAA 09370) and MP lamp delivers a broad spectrum over the range of 200–400 nm with intensity $5.3 \times 10^{-2}\ W/cm^2$ from 150-W power source (TQ 150, 85 V, Cat No. SAA 09360). LP lamp produces a spectrum mainly at 254 nm and it can be described practically as monochromatic, while MP lamp gives much weaker intensity at 254 nm wavelength, but it has significant UV peaks at higher wavelengths including 365 nm. It also emits very strong peaks within the visible region [17].

2.3. Experiment design

Bench-scale experiments were conducted based on the following experimental design: (a) blank run: circulation of MTBE-spiked water to study the loss of MTBE due to circulation; (b) chlorine oxidation: treatment of MTBE-spiked water by free chlorine alone at pH 5, 7, and 9; (c) UV/Cl_2 oxidation: treatment of MTBE-spiked water by a combination of UV lamp types and chlorine dosages at different pH levels and contact time. For each experimental run, the water spiked with MTBE was circulated for 10 min in order to homogenize MTBE in the reactor. Initial MTBE concentration was determined before starting the treatment. The desired amount of chlorine was then injected and the selected lamp type was turned on. During all experiments, samples were collected at 0, 5, 10, 15, 30 min and tested for the MTBE residual and degradation by-product.

2.4. Analytical methods

Thermo Scientific ISQ single quadrupole GC/MS system equipped with TriPlus for headspace injection was used to analyze MTBE residual and degradation by-product in water sample. A 60-m long, 0.32-mm internal diameter Rtx-502.2 (Restek Corp., USA) capillary column was used for separation. The carrier gas was helium flowing at the rate of 1.7 mL/min. The column temperature was programmed to rise from 50 to 220˚C at the rate of 20˚C/min. The mass spectrometer was operated in the selected ion mode. The instrument was calibrated with the MTBE and by-product standard solution [18]. One milliliter of the collected water sample was immediately transferred to the head space of Thermo Scientific standard vials and placed in the Autosampler sequence for the analysis of MTBE and degradation by-product. The GC/MS output was acquired, stored, and processed by Thermo Scientific™ Xcalibur software. The residual chlorine level was measured using Analytik Jena's SPECORD® 50 UV–vis spectrophotometerusing DPD reagent. Analysis was carried out in duplicate for all collected samples.

3. Results and discussion

3.1. Blank runs

Blank runs were conducted to estimate the loss of MTBE due to stirring alone at pH 5,7, and 9 at room temperature. In this experiment, 1,000 ppb of MTBE was spiked into deionized water, and continuously circulated for 30 min at a constant flow rate in the closed system of photoreactor. Fig. 1 shows about 1–2% MTBE loss at pH 5, 7, and 9 was observed while circulating for 30 min. Another study reported 6% MTBE loss due to volatilization during circulation [19]. In this study, the loss is very minimal than that of the other reported values. This could be due to the low MTBE concentration (i.e. 1 ppm) in this study, while the other study used 100 ppm initial MTBE concentrations [19]. There was no degradation of MTBE observed during circulation alone, which was confirmed by the absence of the degradation by-product.

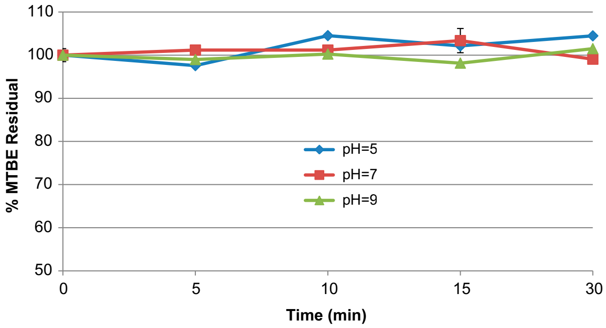

Fig. 1. Percent MTBE residual after continuous circulation for 30 min, 1,000 ppb initial [MTBE], pH 5, 7, and 9 at room temperature.

3.2. Removal of MTBE by UV/chlorine process

To understand the conditions under which MTBE is removed from the aqueous solution, treatment parameters such as oxidant dosage, pH, UV type, and contact time were varied and their effects on the removal efficiency of MTBE was determined.

3.2.1. pH effect on MTBE removal efficiency by LP UV/chlorine

As shown in Fig. 2 better MTBE removal was observed at pH 5 than pH 7 and 9. In general, regardless of pH effect, MTBE was completely degraded to TBF and other by-products by LP UV and 25 ppm of free chlorine after 30 min of exposure time. The removal mechanism of the UV/chlorine could be due to the synergistic effect of UV photolysis, radical oxidation, and chemical oxidation by free chlorine. However, the radical oxidation is the main reason of the removal. The dominant reacting radical mainly generated from the UV/chlorine AOP is hydroxyl ($OH^{\cdot}$) in addition to chlorine radical. The quantum yield of OH radical production from HOCl at a wavelength of 254 nm was found to be 1.4 molE/s which is greater than that of hydrogen peroxide (1.0 molE/s). The higher $OH^{\cdot}$ formation in irradiated HOCl solutions relative to hydrogen peroxide may be a function of higher molar absorption coefficients of HOCl. The reaction of HOCl with OH radical was determined as $8.5 \times 10^4\ M^{-1}\ s^{-1}$ which indicates lesser scavenging effect than H_2O_2 with OH radical having reaction rate

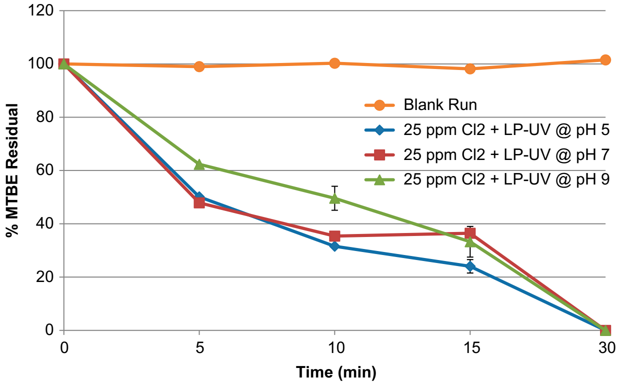

Fig. 2. Percent of MTBE residual after treatment of MTBE in deionized water with LP UV and with 25 ppm of chlorine, 1,000 ppb [MTBE], pH 5, 7, 9, and 30 min contact time.

of $2.7 \times 10^7\ M^{-1}\ s^{-1}$ during the photolysis of free chlorine at pH < 5.5 [16]. Fig. 3 presents the degradation by-product (i.e. TBF) generated from the MTBE degradation. It was observed that some of the TBF was also degraded to tertiary butyl alcohol (TBA), and acetone after 15 min (data not provided).

3.2.2. *pH effect on MTBE removal efficiency by MP UV/chlorine*

MP UV lamp and 25 ppm of free chlorine were used to degrade MTBE from synthetic water. Fig. 4 shows a greater MTBE degradation performance at pH 5 than pH 7, and 9. This might be due to higher availability of HOCl at pH < 5.5, and lower scavenging rate for OH radicals. The degradation mechanism could be dominantly due to OH radical [20]. The removal trends at pH 7 and 9 were overlapping. The MP UV/chlorine at pH 5 also shows minimal TBF concentration (Fig. 5). This could be due to the indiscriminate reaction of OH radicals with the organics present in the synthetic water which includes MTBE and its by-products. Regardless of pH effect, the TBF level generated peaked and then declined after 10 min of treatment time and this could be due to further degradation to other by-products like TBA and acetone.

3.2.3. *Chlorine dosage effect on MTBE removal efficiency by LP UV/chlorine*

Chlorine doses of 10, 25, and 50 ppm in combination with LP UV at pH 5 were tested to remove MTBE in water. The higher chlorine dosage (i.e. 50 ppm) shows better degradation at 5–10 min of treatment time. However, after 15 min the lower dose (i.e. 10 ppm) and the moderate dose (25 ppm) able to degrade MTBE completely as presented in Fig. 6. The lower degradation efficiency observed at 50 ppm of free chlorine might be due to the radical scavenging effect of excess HOCl as discussed by Watts and Linden [16]. In this study, >99% of MTBE removal was obtained at lower and moderated chlorine doses. The finding of this study is supported by the comparative pilot-scale study conducted by Rosenfeldt et al. that reported 80–90% removal of 2-methylisobreneol in water by UV/chlorine process. These authors concluded that UV/chlorine AOP requires low oxidant, short treatment time, and lower operation costs than UV/H_2O_2 AOP [15]. The differences might be described by the study scale, the low initial concentration of the target pollutant, and water quality differences. Sichel et al. compared the degradation efficiency of UV/chlorine and UV/H_2O_2 to treat emerging contaminants: desethylatrazine, sulfame

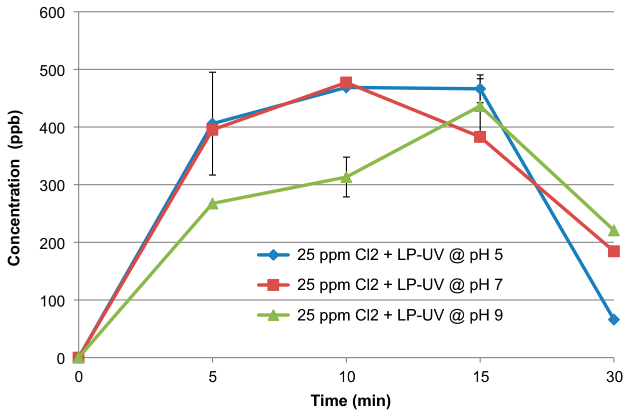

Fig. 3. TBF formation after treatment of 1,000 ppb MTBE from deionized water with LP UV and 25 ppm free chlorine, pH 5, 7, 9, and 30 min treatment time.

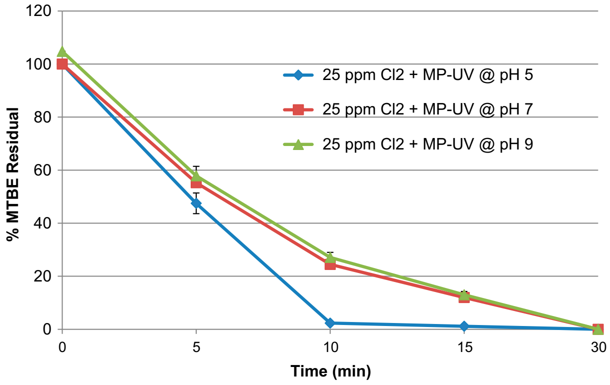

Fig. 4. Percent of MTBE residual after treatment MTBE in deionized water with MP UV and 25 ppm of chlorine, 1,000 ppb [MTBE], pH 5, 7, 9, and 30 min contact time.

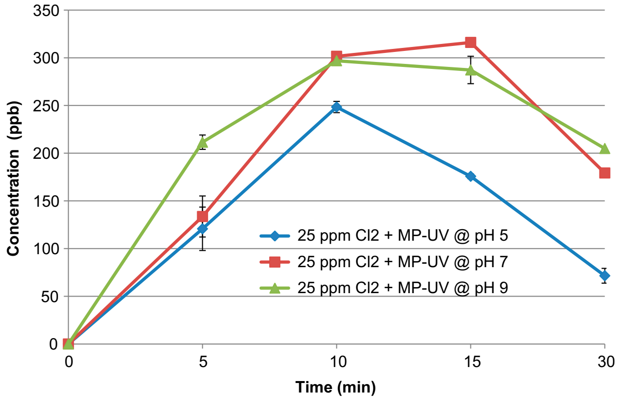

Fig. 5. TBF formation after treatment of 1,000 ppb MTBE from deionized water with MP UV and 25 ppm free chlorine, pH 5, 7, 9, and 30 min treatment time.

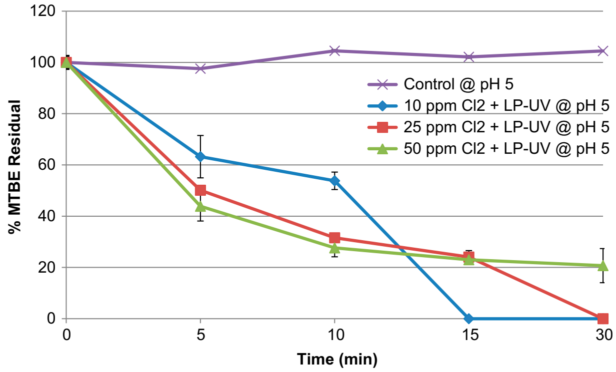

Fig. 6. MTBE residual after treating MTBE from deionized water with LP UV and 10, 25, and 50 ppm of chlorine, 1,000 ppb [MTBE], pH 5 and 30 min contact time.

thoxazole, carbamazepine, diclofenac, benzotriazole, tolyl-triazole, iopamidole, and 17a-ethinylestradiol (EE2) and reported 30–70% energy reduction and better removal efficiency of some contaminants [10]. Fig. 7 shows the monitored degradation by-product (i.e. TBF) increasing until 10 min and then declined to some extent.

3.2.4. Chlorine dosage effect on the MTBE removal efficiency by MP UV/chlorine

Chlorine doses of 2, 5, 10 ppm in combination with MP UV were used to remove MTBE in water at pH 5. Fig. 8 shows no significant difference in MTBE degradation at the three chlorine doses used. However, after 5 min of exposure time, 10 ppm of chlorine showed a better MTBE removal efficiency than other doses. This could be due to the yield of the radicals generated during the process. For the three chlorine dosages, MP UV/chlorine was able to degrade over 98% of MTBE after 30 min (Fig. 9).

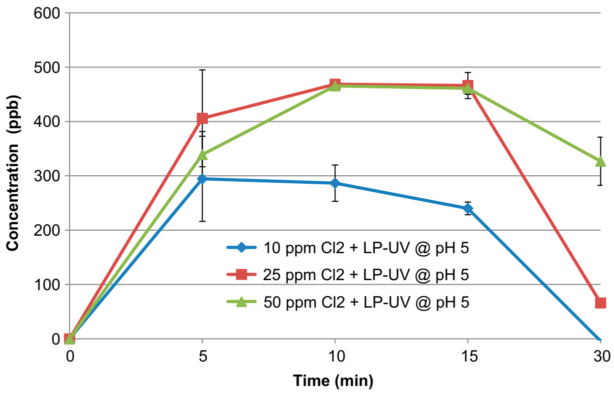

Fig. 7. TBF formation after treatment of 1,000 ppb MTBE from deionized water with LP UV and 10, 25, and 50 ppm free chlorine at pH 5 and 30 min treatment time.

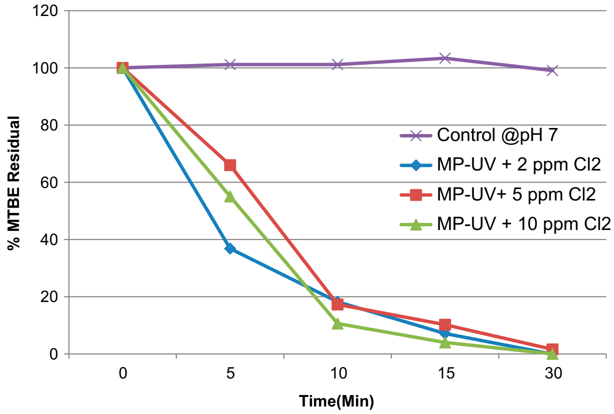

Fig. 8. Percent MTBE residual of 1,000 ppb MTBE after treatment with MP UV, and 2, 5, and 10 ppm of Chlorine at pH 7 and 30 min exposure time.

4. MTBE removal from spiked groundwater by UV alone and UV/chlorine

The optimum conditions obtained from the synthetic water experiment was tested on real ground water sample collected from King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia. The physical and chemical characterstics of the ground water used has been presented in the work done by Tawabini [18]. The optimum conditions determined for LP UV were: 10 ppm free chlorine and pH 5. And that of MP UV were: 5 ppm free chlorine

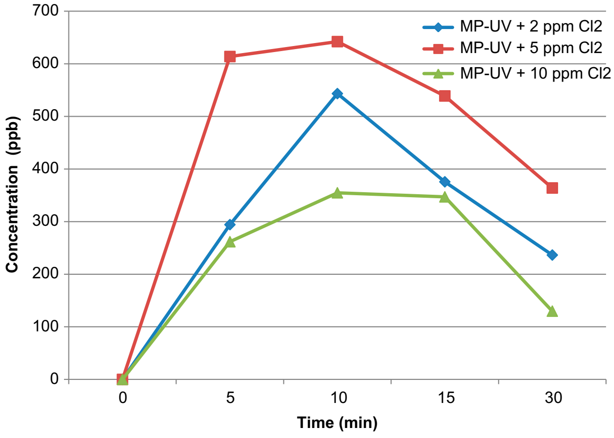

Fig. 9. TBF formation after treatment of 1,000 ppb MTBE from deionized water with MP UV and 2, 5, 10 ppm free chlorine, pH 7 and 30 min treatment time.

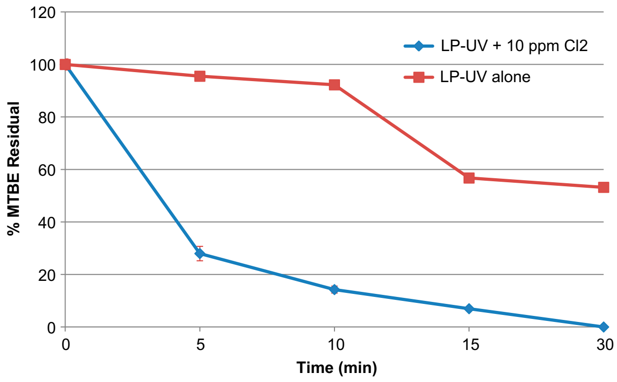

Fig. 10. Percent MTBE residual after treatment of 1,000 ppb MTBE from groundwater with LP UV and 10 ppm chlorine, at pH 5 and treatment time of 30 min.

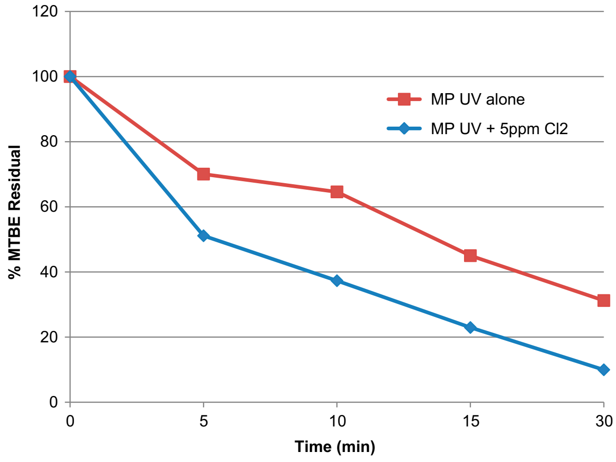

Fig. 11. Percent MTBE residual after treatment of 1,000 ppb MTBE from groundwater with MP UV and 5 ppm chlorine, at pH 7 and treatment time of 30 min.

and pH 5. As shown in Fig. 10, more than 99% MTBE was removed by LP UV/chlorine while only 47% was removed by LP UV alone. In the case of MP UV, about 90% MTBE was removed by MP UV/chlorine, while less than 70% of MTBE was removed by MP UV alone (Fig. 11). From the energy consumption point, LP UV/Chlorine is more economical than MP UV/Chlorine process. The electrical energy order (EEO) of 4.01 kW h/m^3 for LP UV/chlorine and 54.67 kW h/m^3 for MP UV/chlorine was estimated for the removal of 1,000 ppb MTBE from ground water. LP UV shows superior MTBE removal efficiency over the MP UV in terms of low level of by-products generated, and less energy consumption. This study shows a better MTBE removal efficiency than UV/H_2O_2 AOP conducted by Tawabinni which might be due to higher OH radical yield and less scavenging effect of HOCl. Our conclusion contradicts that of Tawabini which reported that MP is superior to LP in removal of MTBE in groundwater [18]. This might be due to the difference of oxidant used, and low radical (OH) scavenging effect of hypochlorous [21].

5. Conclusion

MTBE removal efficiency by UV/chlorine advanced oxidation was studied under different treatment conditions and optimized. More than 99% MTBE removal was observed from both spiked deionized and ground water. The favorable pH of 5, lower dose of free chlorine, 30 min of treatment time, and less energy consumption were determined for the maximum MTBE removal by LP UV/chlorine. LP UV AOP is economical than MP UV because of the low EEO obtained even though MP UV/chlorine AOP can also degrade MTBE from synthetic and real groundwater. TBF was seen as abundant MTBE degradation by-products and also degraded to other by-products to some extent.

Generally, free chlorine species (HOCl) show promising results as an alternative chemical oxidant in the AOP. However, the issue of new by-products related to this process should be well addressed.

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