

# Effectiveness of UV-based advanced oxidation processes for the remediation of hydrocarbon pollution in the groundwater: A laboratory investigation

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## Abstract

The effectiveness of advanced oxidation processes in a batch and a flow reactor was investigated for the remediation of hydrocarbon pollution in the groundwater underlying a petrochemical industrial site. The main organic contaminants present in the groundwater were MTBE, benzene, alkyl-benzenes and alkyl-naphthalenes. Experimental results with a batch reactor showed that for all the organic contaminants the removal efficiency order is  $UV/TiO_2 \approx UV/H_2O_2 > UV$  (medium-pressure) in a synthetic aqueous solution, compared to  $UV/H_2O_2 > UV$  (medium-pressure)  $> UV/TiO_2$  for the real polluted groundwater. The much lower performance of  $UV/TiO_2$  with respect to  $UV/H_2O_2$  was inferred to the matrix of the groundwater, i.e. the salt content, as well as the organic and particulate matter. In fact, it is likely that the salts and dissolved organic matter quench the superoxide anion  $O_2^{\bullet-}$  and hydroxyl radicals just formed at the surface of the  $TiO_2$  catalyst. MTBE was the hardest compound to remove with each of the investigated treatments. UV and  $UV/TiO_2$  treatments were not able to reach a residual concentration of  $10 \mu g/L$  (set by Italian legislation) even after 180 min. As for the  $UV/H_2O_2$  process, only the MTBE degradation rate resulted affected by the initial  $H_2O_2$  concentration, while for other compounds a complete removal was obtained within 20 min even with the lowest  $H_2O_2$  concentration used ( $0.13 g/L$ ). Only after 120 min of treatment, with an initial  $H_2O_2$  concentration of  $0.13 g/L$ , did the residual MTBE concentration fall below the above reported maximum admissible concentration. Instead, by using an initial concentration of  $2 g/L$  a residual concentration lower than  $5 \mu g/L$  was obtained after just 30 min of reaction. The  $UV/H_2O_2$  process was also investigated with a flow reactor. Results showed that it was more efficient than the batch reactor for removing MTBE, in terms of reaction time and initial  $H_2O_2$  concentration required. This is consistent with the higher power of the UV lamp and with the different geometry of the flow reactor, which has a much shorter optical path than the batch reactor. By-product characterisation was also performed showing that *t*-butyl-formate and low molecular weight organic acids are formed as intermediate and final by-products, respectively. Finally, a preliminary evaluation of the operational cost of the  $UV/H_2O_2$  process showed a value of  $1.7 \text{ €/m}^3$  under the optimised condition. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Advanced oxidation processes; Groundwater; Petrochemical industry; MTBE; BTEX; UV;  $TiO_2$

## 1. Introduction

The production and storage of oil-derived fuels, still increasing year after year, has led to the widespread release of these compounds into the environment. The contamination is particularly relevant for groundwater because of accidental gasoline release from underground storage tanks and pipelines in petrochemical industrial sites [1]. Moreover, the contamination of groundwater by methyl-*tert*-butyl-ether (MTBE), which has

been added to gasoline since the mid-eighties as an octane enhancer, is even more problematic due to its high water solubility. In fact, many cases are known of both surface waters and groundwaters contaminated by MTBE [2,3]. In order to restore the groundwater quality standards as required by the current legislation, activated carbon is often used [4,5] in combination with air stripping or with the groundwater circulation well-in well stripping technology [6–8]. However, the use of activated carbon is not expected to be a cost-effective treatment option, especially when MTBE and other organics that adsorb onto activated carbon better than MTBE are present in the water. This also applies when the MTBE concentration in the polluted water is quite high (several tens of parts per million) and its required

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concentration in the effluent is low, i.e. at the level of a few parts per billion. In fact, a cost analysis showed that activated carbon is more cost-effective for waters contaminated solely with MTBE since other organics will preferentially occupy adsorption sites and thereby increase carbon usage rates [8]. In addition, such processes, do not represent an environmentally sustainable solution because they merely transfer the organic pollutants from one phase to another.

As an alternative, biological and chemical methods can be employed. Biological oxidation for cleaning up hydrocarbon-contaminated sites has attracted increasing interest in recent years as a cost-effective remediation technology. The synthetic additive MTBE is particularly recalcitrant to biodegradation, because it contains an ether bond and a tertiary carbon, leading to a low biodegradation rate. Nevertheless, a variety of microbial species have been shown to be capable of metabolising MTBE, mostly in aerobic conditions [9,10] and field-scale bioremediation studies have already given promising results [11,12]. However, long degradation times, usually lasting several months, are required for a significant MTBE decrease [13].

Chemical remediation methods, instead, are known to be much faster in removing organic contaminants. Among them advanced oxidation processes (AOPs) such as UV/H<sub>2</sub>O<sub>2</sub>, ozone, ozone/H<sub>2</sub>O<sub>2</sub>, Fenton and UV/TiO<sub>2</sub> are known to be effective in removing several compounds contained in gasoline, such as MTBE and aromatic hydrocarbons [6,8,14–21]. However, data concerning the comparison of the effectiveness of UV-based AOPs on real polluted groundwater are scarce. In fact, the chemical composition of polluted groundwater, in terms of the concentration of metals, inorganic species, pH and organic substances, can dramatically affect the efficiency of the process with respect to the treatment carried out with synthetic solutions.

In the present work, the remediation of the groundwater of a petrochemical industrial site was investigated by UV-based AOPs. The main objectives of the study were (i) to evaluate the influence of the groundwater matrix on the treatment efficiency of some UV-based AOPs (medium-pressure UV, UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub>); (ii) to optimise the effectiveness of the most efficient AOP in removing the principal organic contaminants of the polluted groundwater, in compliance with the current Italian legislation for groundwater remediation, that sets a maximum admissible concentration for MTBE, benzene, toluene, *p*-xylene, styrene and ethylbenzene at 10, 1, 15, 10, 25 and 50 µg/L, respectively [22,23]; and (iii) to perform a preliminary operation cost evaluation of the most efficient of the treatment options under investigation.

## 2. Experimental methods

### 2.1. Chemicals and real groundwater

All solvents were pesticide grade and purchased from Baker. H<sub>2</sub>O<sub>2</sub> (30% solution) was used as received from Baker. MTBE, aliphatic as well as aromatic compounds were purchased from Aldrich and used as received. Standard stock solutions (in the range 10–250 g/L) were prepared in methanol. When neces-

sary, working standard solutions were prepared fresh daily, using organics-free groundwater from a local well (for real groundwater tests) or using tap water (synthetic solution tests). The used TiO<sub>2</sub> was “Degussa P25” (non-porous anatase; surface area, 50 m<sup>2</sup>/g; mean diameter, approximately 30 nm). Groundwater was sampled at a petrochemical site, located in southern Italy, where reservoirs used for oil-derived fuels have been located for many years. The following sampling procedure was used: an immersion pump equipped with a Teflon tube was initially inserted into the piezometer, then the water column already present was pumped out and discharged. Next the aqueous phase was allowed to refill the piezometer and finally, a 30 L sample was withdrawn at a proper flow rate (usually 0.5–2.0 L/min) into a stainless steel container equipped with Teflon sealing, leaving as small as possible a head space (i.e. less than 50 mL). The sample was then immediately transported to the laboratory where it was kept refrigerated overnight, to allow the suspended material to settle, and analysed for hydrocarbons. The aqueous phase was then transferred into 1 L amber-glass bottles equipped with Teflon septa, without leaving headspace. The average chemical composition of the investigated groundwater, in terms of bulk parameters, is reported in Table 1. As for its organic composition, the characterisation carried out (see below) revealed the presence of a great number (>70) of aliphatic and aromatic hydrocarbons, 29 of which were univocally identified by the use of authentic standards (Fig. 1). The other compounds were tentatively identified on the basis of matching background-subtracted mass spectra against those of the NIST mass spectra library. In particular, apart from MTBE and benzene, the identified hydrocarbons can be divided into two main categories, namely alkyl-benzenes and alkyl-naphthalenes.

### 2.2. AOP experiments

A 1 L cylindrical glass four-necked reactor was used for performing all degradation batch experiments. Two light sources were employed (Helios Italquartz, Italy): a 17 W low-pressure mercury arc lamp (emitting at 254 nm) for UV/H<sub>2</sub>O<sub>2</sub> and

Table 1  
Average chemical composition of the groundwater of the investigated petrochemical industrial site

Parameter	Concentration (mg/L)
Conductivity (20 °C)	1660 (µS/cm)
pH	8.3
Total alkalinity	880 (as CaCO <sub>3</sub> )
Total hardness	245 (as CaCO <sub>3</sub> )
Settleable solids	17 (mL/L)
MTBE	25.6
Benzene	2.6
Toluene	0.018
Ethyl-benzene	0.010
<i>p</i> -Xylene	0.014
Alkyl-benzenes	1.8
Alkyl-naphthalenes	0.2
Hydrocarbons C10-C40	2.3
Fe	0.58
Mn	1.9

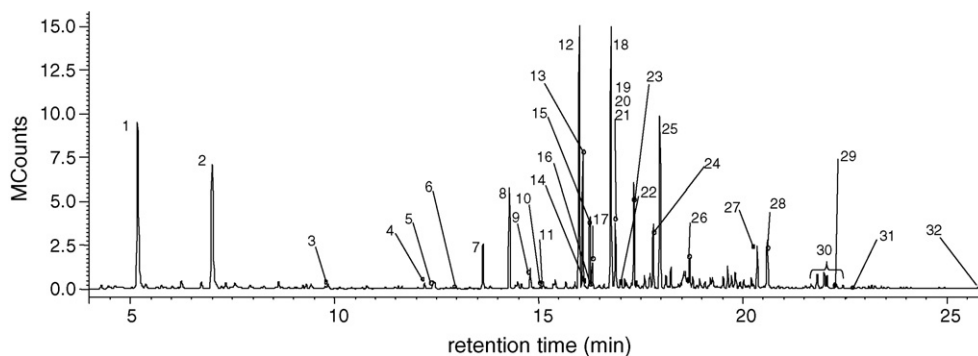


Fig. 1. SPME/GC/MS chromatogram of the investigated real groundwater. Peak identification: (1) MTBE; (2) benzene; (3) toluene; (4) ethyl-benzene; (5) *p*-xylene; (6) nonane; (7) cumene; (8) propyl-benzene; (9) ethyl-toluene; (10) decane; (11) trimethyl-benzene; (12) indane; (13) 1,3-diethyl-benzene; (14) indene; (15) 1,2-diethyl-benzene; (16) butyl-benzene; (17) 1,4-diethyl-benzene; (18) 1,2-dimethyl-4-ethyl-benzene; (19) undecane; (20) 1,2,3,5-tetramethyl-benzene; (21) methyl-indane isomer; (22) dimethyl-styrene; (23) 1,2,4,5 tetramethyl-benzene; (24) methyl-indane isomer; (25) methyl-indane isomer; (26) naphthalene; (27) 2-methyl-naphthalene; (28) 1-methyl-naphthalene; (29) 1,4-dimethyl-naphthalene; (30) dimethyl-naphthalenes; (31) acenaphthene; (32) phenanthrene.

UV/TiO<sub>2</sub> experiments, and a 125 W medium-pressure one, the latter for UV only experiments. The lamp was kept fixed at the central axis of the reactor or, in the case of the high-pressure lamp, of the inner cooling jacket. The reactor light path was 1.8 cm. All experiments were carried out on 500 mL of aqueous solution at room temperature. During irradiation the solution was magnetically stirred. The low-pressure UV lamp was characterised by actinometry (uridine) obtaining a fluence rate of 0.098 W/cm<sup>2</sup>. As for the UV/H<sub>2</sub>O<sub>2</sub> and UV/TiO<sub>2</sub> experiments, different concentrations of H<sub>2</sub>O<sub>2</sub> (0.13, 0.33, 0.66, 1.33 and 2 g/L) and TiO<sub>2</sub> (0.02 and 0.2 g/L) were tested. Continuous UV/H<sub>2</sub>O<sub>2</sub> degradation tests were performed with a 0.5 L flow reactor (Helios Italquartz, Italy) equipped with a 40 W low-pressure mercury arc lamp emitting at 254 nm. The reactor light path was 0.75 cm and the fluence rate, measured by means of uridine actinometry, was 0.229 W/cm<sup>2</sup>. Groundwater was fed through the reactor by a peristaltic pump and H<sub>2</sub>O<sub>2</sub> was delivered by a second peristaltic pump placed just before the reactor entrance through a tee connection. All the connecting tubes were made of Teflon or Viton<sup>TM</sup>. The progress of the reactions was monitored by withdrawing at scheduled times small aliquots (0.8 mL) of the reaction mixture that were analysed, after filtration in the case of UV/TiO<sub>2</sub> reactions, as described below.

### 2.3. Analytical determination

The characterisation of groundwater organic pollutants, as well as their degradation during UV treatments, was performed by solid phase micro extraction/gas chromatography/mass spectrometry (SPME/GC/MS) using a Varian Saturn 2200 GC/MS system (electron impact ion source) equipped with a 8200 autosampler and a SPME syringe (Supelco) with a 100 μm (non-bonded) polydimethylsiloxane fibre. Aqueous samples (0.8 mL) were placed into 2 mL vials equipped with silicone/Teflon septa and the SPME fibre was exposed to the vapour phase for 30 min in order to adsorb the volatile organics. Then the SPME syringe was automatically introduced into the injector of the GC/MS system in order to desorb and analyse the compounds. The column used was a Factor Four VF-5 ms (60 m length, 0.25 mm i.d.

and 0.25 μm film thickness) from Chrompack. Its end part was inserted directly into the ion source, heated to 180 °C, through a transfer line heated to 220 °C. The operative conditions were: carrier gas, helium at a constant flow of 1.0 mL min<sup>-1</sup>; injector temperature, 250 °C; desorption time, 5 min; starting column temperature, 40 °C (5 min); temperature rate, 10 °C/min up to 200 °C then 20 °C/min up to 280 °C. Electron impact mass spectra (electron energy 70 eV), were recorded by scanning the MS from 40 to 350 Da at 0.6 s/scan. The quantification of organic contaminants was performed by external calibration, analysing at least four standard solutions prepared using uncontaminated groundwater (real groundwater tests) or tap water (synthetic solution tests) as a solvent, in order to have a similar matrix effect as that of the treated samples. Dissolved metal concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis using an Optima 3000 instrumentation (Perkin-Elmer).

Organic acid determination was carried out by a GS50 system (Dionex) equipped with an AS50 autosampler, an ED50 conductivity detector and an ASRS-ultra suppressor, operated at 100 mA in external water mode. Samples, injected via a 25 μL loop, were eluted at a flow rate of 0.5 mL/min through an analytical IonPac AS-11 column (250 mm × 2 mm) equipped with a IonPac AG-11 guard-column (50 mm × 2 mm) with the following gradient: from 10/0/90 (NaOH 5 mM/NaOH 100 mM/water), held for 2.5 min, to 100/0/0 in 3.5 min, then to 50/50/0 in 12 min, held for 5 min.

## 3. Results and discussion

### 3.1. Degradation tests with synthetic aqueous solution

As a preliminary investigation, the degradation of selected organic pollutants representative of the real groundwater of the investigated industrial site was performed in a synthetic aqueous solution (tap water). The selected organics and the initial concentrations are reported in Table 2. The removal efficiencies after 30 min of reaction of the investigated treatments, namely UV/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub> and UV (both low and medium-pressure), are reported in Fig. 2. It is possible to note that the

Table 2  
Chemical composition of the synthetic aqueous solution

Compound	Concentration (mg/L)
MTBE	4
Benzene	1
Toluene	1
Styrene	1
Hexadecane	0.2
Nonane	0.2
1,4-Dimethyl naphthalene	0.2
Phenanthrene	0.2

efficiency order is  $UV/TiO_2 \approx UV/H_2O_2 > UV$  (high P)  $\gg UV$  (low P). In particular, the results shown in Fig. 2 show that the  $UV/H_2O_2$  performed less well than  $UV/TiO_2$  in removing hexadecane (75% removal efficiency); medium-pressure UV partially failed to remove MTBE (45%) and hexadecane (35%); while low-pressure UV generally failed to remove all investigated compounds. Moreover, further experiments showed that the initial  $TiO_2$  concentration, in the range of 0.02–0.1 g/L, has no influence, since the removal efficiency for all organics was always higher than 99.9%, and using an initial  $H_2O_2$  concentration of 2 g/L did not improve the  $UV/H_2O_2$  process. The above reported efficiency order is consistent with the different hydroxyl radical production levels of the investigated processes, and with fact that the  $TiO_2$  catalyst degradation mechanism is different. In fact,  $UV/H_2O_2$ , compared to UV processes (both low- and medium-pressure) is known to generate hydroxyl radicals more efficiently. Instead, the better performance of  $UV/TiO_2$  with respect to  $UV/H_2O_2$  in removing hexadecane may also be due to the formation of superoxide anion  $O_2^{\bullet-}$  as a result of  $O_2$  reduction by free photoelectrons in the conduction band of the  $TiO_2$  catalyst.

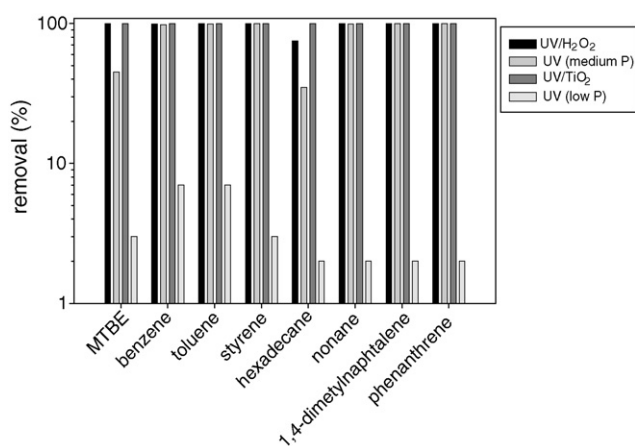


Fig. 2. Removal efficiencies of  $UV/H_2O_2$ ,  $UV/TiO_2$  and UV (both low and medium-pressure) treatments for selected organic contaminants in a synthetic aqueous solution. Reaction time 30 min, initial  $TiO_2$  concentration 0.02 g/L, initial  $H_2O_2$  concentration 0.13 g/L. Initial organic concentrations: MTBE 4 mg/L, benzene 1 mg/L, toluene 1 mg/L, styrene 1 mg/L, hexadecane 0.2 mg/L, nonane 0.2 mg/L, 1,4-dimethyl naphthalene 0.2 mg/L, phenanthrene 0.2 mg/L. For other experimental conditions see text.

### 3.2. Degradation tests with real groundwater

The removal percentages of MTBE, benzene, alkyl-benzenes and alkyl-naphthalenes (the two main compounds plus the two most abundant categories of compounds identified in the real polluted groundwater) by the investigated UV-based treatments after 30 min of reaction are reported in Fig. 3. The main result evident from these figures is that a different efficiency order, namely  $UV/H_2O_2 > UV$  (medium-pressure)  $> UV/TiO_2$ , was obtained with the real groundwater. In particular, especially for MTBE, benzene and alkyl-benzenes the  $UV/TiO_2$  process generally performed poorly. This finding suggests that particular care should be taken when extrapolating organic degradation results obtained with synthetic aqueous solutions and applying them to real polluted groundwater, because the efficiency order obtained for different AOPs may be completely different. The far lower efficiency of the  $UV/TiO_2$  process compared to the  $UV/H_2O_2$  one in removing most of the investigated pollutants was quite unexpected, since it is well known that the effectiveness of the  $UV/TiO_2$  process with model solutions is equal to, or even better than, that of  $UV/H_2O_2$  [24] and that effective applications of  $UV/TiO_2$  with real wastewater have also been reported [25]. It follows that the matrix of the groundwater, i.e. the salt and organic content as well as the particulate matter, has to be responsible for the observed lack of efficiency of the  $UV/TiO_2$  process. In fact, it is probable that the salts and the organic matter dissolved may quench the  $O_2^{\bullet-}$  and hydroxyl radicals just formed at the surface of the  $TiO_2$  catalyst as well as scavenge the valence band holes. In addition, the particulate matter may be adsorbed onto the catalyst surface. Therefore, the macroscopic effect of these processes is a noticeable reduction of the treatment performance. Furthermore, as far as the  $UV/TiO_2$  process is concerned, the results reported in Fig. 3 show that the  $TiO_2$  concentration has little influence on the degradation rate and, for some compounds (MTBE, *p*-xylene, cumene, alkyl-naphthalenes), at higher dosages a lower efficiency was even obtained. This is consistent with a catalyst poisoning effect. In fact, at higher  $TiO_2$  concentration the removal of MTBE and other compounds was lower because of the lower light penetration in the solution that does affect the degradation process since the inner portion of the solution, closer to the light source, induces a scattering which is much more severe at higher titania content causing, in turn, a lack of absorption of the outer fraction of the solution.

As for the  $UV/H_2O_2$  process, from Fig. 3 it is possible to note that it generally has a very high efficiency rate at both  $H_2O_2$  concentrations tested. It is also worth noting that previous experiments (results not shown) showed that  $H_2O_2$  alone is not effective at all in removing the organic compounds, while low-pressure UV treatment allows just a partial removal of them. In addition, as iron is present in the groundwater (Table 1), experiments were performed with  $H_2O_2$  alone at pH 3 in order to check the possibility for a Fenton treatment with the iron already present in the groundwater. However, the results showed no organic removal, excluding the possibility of using such an option. In fact, the Fenton reaction probably did not take place because the Fe concentration was too low and the molar ratio  $H_2O_2/Fe$  was too high for iron to catalyze  $H_2O_2$  decom-



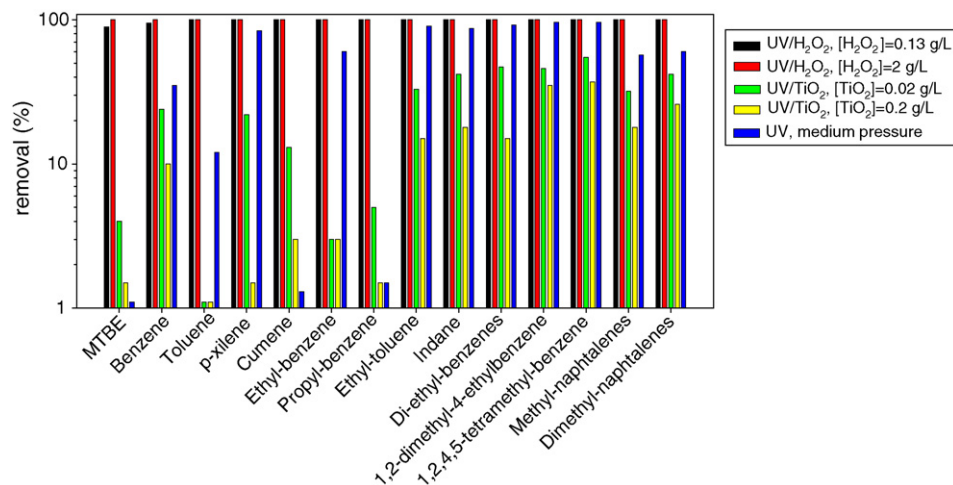


Fig. 3. Efficiencies of UV/H<sub>2</sub>O<sub>2</sub>, UV/TiO<sub>2</sub> and UV (medium-pressure) treatments for removing the main organic pollutants detected in the real investigated groundwater. Reaction time 30 min, for other experimental conditions see text.

position. Instead, the good degradation efficiency obtained by medium-pressure UV for the majority of compounds and classes of compounds can also be ascribed to the iron already present in the groundwater enhancing the production of hydroxyl radicals through the photo-Fenton pathway.

Next, in order to compare better the investigated AOPs and to transfer the results obtained to a real remediation application, a degradation profile of the organics during the reaction time was produced and tests with a flow reactor were performed. The resulting concentration profiles of MTBE, benzene, alkyl-benzenes and alkyl-naphthalenes during the reaction time with most of the treatments of Fig. 3, namely UV, UV/TiO<sub>2</sub> (0.02 g/L) and UV/H<sub>2</sub>O<sub>2</sub> (0.13 and 2 g/L) are depicted in Fig. 4. They show that benzene cannot be completely removed by medium-pressure UV and UV/TiO<sub>2</sub> even given a long reaction time. In particular, a removal of 74% at 120 min and of 66% at 180 min was obtained with UV and UV/TiO<sub>2</sub>, respectively. In addition, the residual benzene concentration at the end of both the UV and UV/TiO<sub>2</sub> treatments was much higher than the maximum admissible concentration set by the current Italian legislation for groundwater remediation (1 μg/L). Finally, MTBE was the hardest compound to remove; with both UV and UV/TiO<sub>2</sub> treatments its degradation level was negligible in all cases. As for the UV/H<sub>2</sub>O<sub>2</sub> process, only the MTBE degradation rate resulted clearly affected by the initial H<sub>2</sub>O<sub>2</sub> concentration while for other compounds a complete removal was obtained within 20 min, even with the lowest H<sub>2</sub>O<sub>2</sub> concentration used. However, it is important to point out that, although the MTBE removal percentages at prolonged reaction time and with all investigated

H<sub>2</sub>O<sub>2</sub> concentrations were found to be in the same range (greater than 99.99%), the residual concentrations were significantly different. In particular, when the initial H<sub>2</sub>O<sub>2</sub> concentration was 0.13 g/L, only after 120 min of treatment did the residual MTBE concentration fall below the maximum admissible concentration (10 μg/L) set by the Italian regulation [23]. Instead, by using an initial concentration of 2 g/L a residual concentration lower than 5 μg/L was obtained after just 30 min of reaction.

As the UV/H<sub>2</sub>O<sub>2</sub> process resulted the most efficient among those tested, it was further investigated with a continuous reactor, as described in the Section 2, in order to get information about a possible scale-up on the industrial site. The results obtained for three different reaction times (coincident with the residence time as the reactor is a plug flow reactor) and initial H<sub>2</sub>O<sub>2</sub> concentrations (Table 3) confirm that the latter is the key parameter. In fact, with an initial H<sub>2</sub>O<sub>2</sub> concentration of 0.13 g/L, a residual concentration of MTBE lower than 10 μg/L in the treated effluent was never obtained, even in the maximum residence time tested. Instead, at higher H<sub>2</sub>O<sub>2</sub> concentrations, the effluent MTBE concentration was always in compliance with the above-cited guideline. With just a 10 min residence time and 0.34 g/L of H<sub>2</sub>O<sub>2</sub> the average MTBE concentration was quite close to the guideline limit, since several measured MTBE concentration values during reactor operation (normal operation time: 8 h) exceeded it. The fact that with the flow reactor it was possible to remove the MTBE (the hardest compound to remove) at milder operative conditions, in terms of reaction time and initial H<sub>2</sub>O<sub>2</sub> concentration, than with the batch reactor is consistent with the higher power of the UV lamp that leads to a much

Table 3  
Average residual MTBE concentration of the flow reactor effluent during the real groundwater UV/H<sub>2</sub>O<sub>2</sub> treatment

Reaction time (min)	Initial H <sub>2</sub> O <sub>2</sub> concentration (g/L)		
	0.13 (0.4 mL/L)	0.34 (1 mL/L)	0.68 (2 mL/L)
10	59	9.3	1.9
15	61	4	<1
20	45	1.2	<1

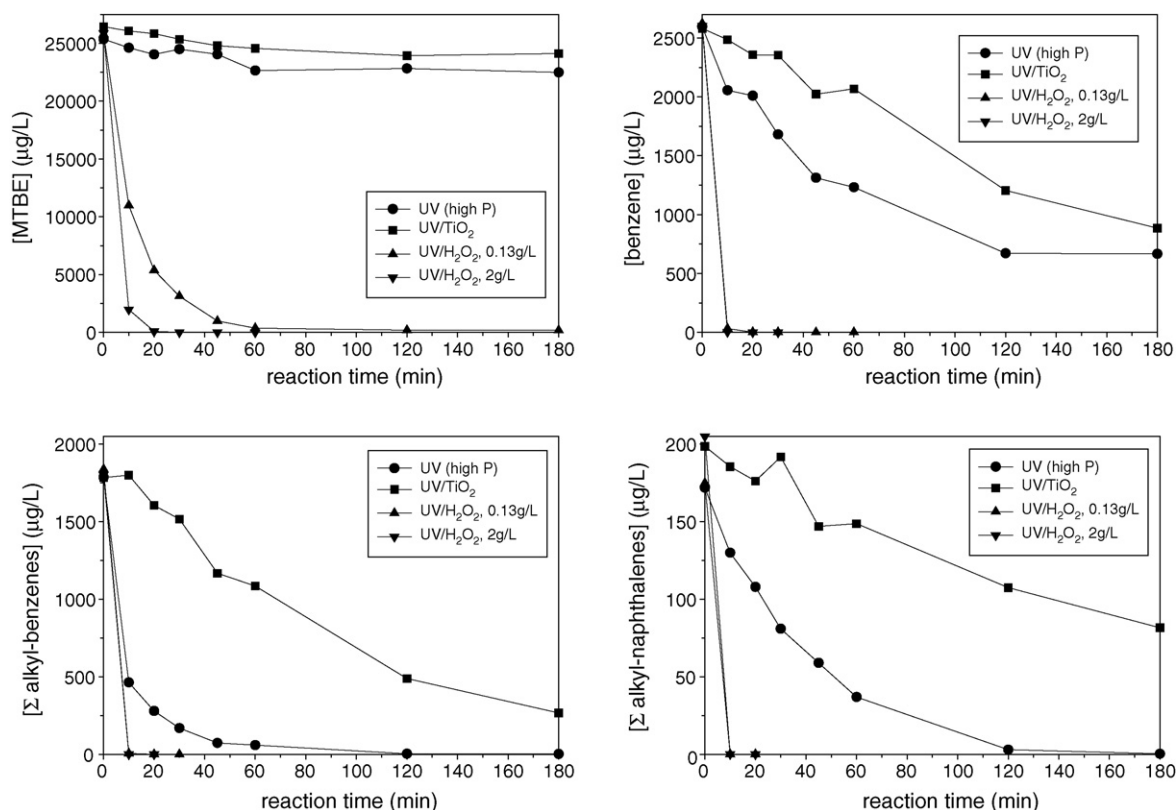


Fig. 4. Concentration profiles of MTBE, benzene, alkyl-benzenes and alkyl-naphthalenes during treatments of real groundwater by UV (medium-pressure lamp), UV/TiO<sub>2</sub> (0.02 g/L) and UV/H<sub>2</sub>O<sub>2</sub>. For experimental conditions see text.

higher fluence rate (0.229 W/cm<sup>2</sup> with respect to 0.098 W/cm<sup>2</sup> of the batch reactor) and with the different geometry of the flow reactor, which has a shorter optical path than the batch reactor.

### 3.3. By-product formation and preliminary treatment cost evaluation

The UV/H<sub>2</sub>O<sub>2</sub> process was also characterised in terms of by-product formation. This is an important task in groundwater remediation because it has to be assessed whether or not the treatment employed leads to the formation of toxic compounds. The concentration profiles of the principal by-products detected are reported in Fig. 5. As expected for MTBE degradation, *t*-butyl-formate was the only intermediate by-product detected which was also removed, given a longer reaction time [17]. Other intermediate by-products among those already known to derive from MTBE oxidation (*t*-butyl-alcohol, acetone) [16,17] were also detected in smaller amounts but not quantified. In addition, Fig. 5 shows that low molecular weight organic acids (formic, acetic and oxalic acid) were detected both in the early stage and after a long reaction time of the polluted groundwater treatment by UV/H<sub>2</sub>O<sub>2</sub>. These compounds reach a maximum level of formation and then slowly disappear. This indicates that a certain grade of organic mineralisation can be also obtained by UV/H<sub>2</sub>O<sub>2</sub> despite the matrix of the groundwater. However, it is worth noting that the low molecular weight organic acids detected are not considered to be toxic compounds therefore their

presence in the treated groundwater is not expected to constitute an environmental concern.

As a final task, a preliminary evaluation of the UV/H<sub>2</sub>O<sub>2</sub> treatment cost was also performed. As the major organic contaminant in the investigated groundwater is MTBE and the experimental results obtained show that it is the hardest compound to remove, cost evaluation was focused on this pollutant. The procedure for the evaluation of the treatment cost has already been described [6,26] and, therefore, a brief description is given

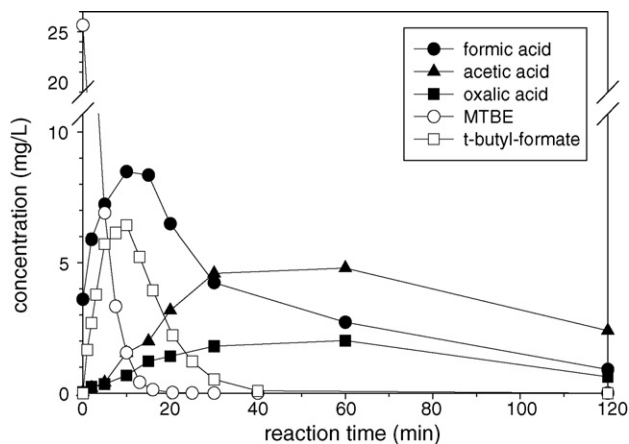


Fig. 5. Concentration profiles of MTBE and organic by-products (*t*-butyl-formate, formic acid, acetic acid, oxalic acid) detected during treatment of real polluted groundwater by UV/H<sub>2</sub>O<sub>2</sub>. Operative conditions: batch reactor, initial H<sub>2</sub>O<sub>2</sub> concentration: 0.66 g/L, for other experimental conditions see text.

Table 4  
Estimated operating cost for the UV/H<sub>2</sub>O<sub>2</sub> treatment of the real groundwater of a petrochemical industrial site with a flow reactor

Initial H <sub>2</sub> O <sub>2</sub> concentration (g/L)	H <sub>2</sub> O <sub>2</sub> dosage (mL/L)	Operating cost (€/m <sup>3</sup> )	EE/O of MTBE (kWh/m <sup>3</sup> )
0.13	0.4	3.5	7.6
0.34	1	1.7	2.8
0.68	2	2.1	2.6

Key parameters for the computation: initial MTBE concentration, 25.6 mg/L; required final MTBE concentration, 0.010 mg/L; cost of H<sub>2</sub>O<sub>2</sub> (30%, v/v), 0.49 €/L; unit cost of the electrical energy, 0.1 €/kWh.

here. The key variables that affect the treatment cost are the H<sub>2</sub>O<sub>2</sub> concentration and the UV power radiated per unit volume of treated water more commonly referred to as the UV dose. The latter parameter combines flow rate, residence time and light intensity into a single term and, of course, it is also greatly dependent on the H<sub>2</sub>O<sub>2</sub> concentration. The optimal UV dose can be calculated in an iterative manner, for each H<sub>2</sub>O<sub>2</sub> concentration, using the following general equation:

$$\text{UV dose (kWh/m}^3\text{)} = \frac{1000 \times \text{UV power (kW)}}{60 \times \text{flow (L/min)}}$$

Design tests have to be necessarily performed to measure the UV dosage required to achieve the desired effluent concentration, namely that set by the current legislation.

As a more practical alternative, the following equation can be used for the calculation of the UV dose

$$\text{UV dose} = \text{EE/O} \times \log \left( \frac{C_i}{C_f} \right)$$

where EE/O is the electrical energy necessary for a one order removal of the investigated pollutant and  $C_i$  and  $C_f$  are the initial and final pollutant concentrations, respectively [26]. The EE/O term can be easily obtained from the pollutant degradation profile (at a fixed H<sub>2</sub>O<sub>2</sub> concentration) making the use of the latter equation much easier than that of the former for obtaining the optimal UV dose. In fact, as it is well known that organic degradation by UV/H<sub>2</sub>O<sub>2</sub> follows pseudo-first order kinetics, the logarithmic of the pollutant concentration is linear versus reaction time (and therefore versus the consumed electrical energy). It follows that, for a single H<sub>2</sub>O<sub>2</sub> concentration, from a single pollutant decay experiment (in this case MTBE) the EE/O can be obtained using the procedure as follows: (i) plot the contaminant concentration (on a log scale) as a function of time and measure the inverse slope of the decay linear regression; (ii) calculate the time required for a one order removal of the investigated pollutant; (iii) calculate the electrical energy consumed by the UV lamp for that irradiation time; (iv) finally calculate EE/O, by rescaling the latter obtained value, for one cubic meter of treated water. It should be noted that the above cited single pollutant decay experiment can be performed at whatever initial concentration because, on the basis of pseudo-first order kinetics, the slope of the decay is not dependent on the initial concentration. In addition, for streams with several contaminants, the required energy is not accumulative, but determined by the contaminant requiring the greatest UV dose (in the present case MTBE). Once the UV dose has been calculated, the operating cost of the UV/H<sub>2</sub>O<sub>2</sub> treatment can be obtained using the

following equation

operating cost

$$= \left[ \text{EE/O} \times \log \left( \frac{C_i}{C_f} \right) \times \text{electrical cost} \times 1.35 \right] + \text{H}_2\text{O}_2 \text{ cost}$$

that takes into account the cost of H<sub>2</sub>O<sub>2</sub>, the unit cost of electrical energy and the cost of lamp replacement (normally estimated to be about 35% of operational cost). The operating costs and the EE/O of MTBE obtained for the three H<sub>2</sub>O<sub>2</sub> concentrations investigated are reported in Table 4. The results show that a minimum operating cost of 1.7 €/m<sup>3</sup> is obtained at a 1 mL/L dosage of H<sub>2</sub>O<sub>2</sub>. This reflects a balance between the terms “EE/O” and “H<sub>2</sub>O<sub>2</sub> cost” in the above reported equation. In fact, by increasing the initial H<sub>2</sub>O<sub>2</sub> concentration, the EE/O decreases (because of the higher production rate of hydroxyl radicals) while the H<sub>2</sub>O<sub>2</sub> cost increases. In addition, when the initial H<sub>2</sub>O<sub>2</sub> concentration is very high (2 mL/L), little improvement, in terms of reducing EE/O and hence reaction time, is obtained with the concomitant disadvantage of using double the dosage of H<sub>2</sub>O<sub>2</sub> and, therefore, raising the cost to 2.1 €/m<sup>3</sup>. Instead, when the initial H<sub>2</sub>O<sub>2</sub> concentration is lowered to 0.13 g/L the saving in H<sub>2</sub>O<sub>2</sub> cost obtained is largely overcome by the UV energy cost due to the long reaction time required for reaching the target effluent concentration of organic pollutants, leading to a final operational cost of 3.5 €/m<sup>3</sup>.

#### 4. Conclusions

The removal of MTBE, aromatic and aliphatic hydrocarbons by UV-based AOPs was investigated in both synthetic solution and in a real polluted groundwater of a petrochemical industrial site. The results demonstrate that the efficiency order of the processes tested is completely different for the two aqueous solutions studied: the UV/TiO<sub>2</sub> treatment is the best option for the synthetic solution, while the UV/H<sub>2</sub>O<sub>2</sub> process is the best for the real polluted groundwater. This finding suggests that particular care should be taken when extrapolating organic degradation results obtained with synthetic aqueous solutions and applying them to real polluted groundwater. A preliminary evaluation of the cost of the real polluted groundwater treatment by UV/H<sub>2</sub>O<sub>2</sub> was performed using a flow reactor and having, as an effluent quality target, the current Italian limits for groundwater remediation which sets for MTBE a maximum admissible concentration of 0.010 mg/L. A total operation cost of 1.7 €/m<sup>3</sup> was obtained which demonstrates that the remediation by UV/H<sub>2</sub>O<sub>2</sub> of groundwater highly polluted with MTBE and aromatic hydrocarbons can be achieved at a rea-

sonable cost compared to activated carbon adsorption. In fact, in another study, where a MTBE removal efficiency similar to that employed in the present study (>99.95%), a cost between 1.8 and 4.6 \$/m<sup>3</sup> was obtained depending on water flow rate, type of carbon and carbon usage rate [6]. However, activated carbon adsorption does not resolve the environmental contamination problem, since it is only able to transfer the organic pollutants from one phase to another. Nevertheless, it should be taken into account that the selection of the best process for treatment of MTBE is site specific and must consider a variety of factors such as the type of matrix and the concentration of inorganic species.

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