

[Research]

## Advanced oxidation processes against alkyl phenols in groundwater samples

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### ABSTRACT

Spectrophotometric examinations showed the presence of phenolic compounds in the organic residue collected from four groundwater resources located in vicinity of an oil refinery at the outskirts of Tehran. The average concentration of total phenolic compounds was about 0.38 mg.L<sup>-1</sup> in these samples using Folin-Ciocalteu method. GC-Mass analysis disclosed that alkylphenols were the major phenolic contaminants in the samples. Evaluation of the Advanced Oxidation Processes (AOPs) efficacy for removal of alkylphenols from real water samples is a hot topic of recent Environmental Research due to the decomposition of these compounds in soil and by microorganisms which may result in the formation of structures more resistant against various types of oxidation. To explore the efficacy of AOPs for removal of alkylphenols from the examined groundwater resources, the optimal conditions for three important AOP including Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV (Photo-Fenton), O<sub>3</sub>/UV and O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> were first sought using a recalcitrant lab sample containing different aromatic compounds with total concentration of 2 mg L<sup>-1</sup>. Consequently, two methods of O<sub>3</sub>/UV (2 mg L<sup>-1</sup> O<sub>3</sub>, 15 min UVC), and O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> (2 mg L<sup>-1</sup> O<sub>3</sub>, 5000 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>, 15 min UVC) were selected to be examined on the real samples. Although the selected methods were quantitatively effective on the lab sample, they resulted in average removal efficiencies of 79.71% and 84.16% on the real samples, respectively. With respect to the safety regulations, costs and easiness of implementation, the O<sub>3</sub>/UV method seems to be more promising for large-scale plans.

**Key words:** Alkylphenols, Underground water, Ozone, UV radiation, Hydrogen peroxide.

### INTRODUCTION

Phenol derivatives are among the most important synthetic chemicals, widely used in various industries. As a result, they are often observed in the effluents of manufacturing operations (Haghbeen *et al.* 2009). The physicochemical properties of phenolic compounds help them to enter water resources and contaminate human food chain (CCME, 1999). Because of their amphiphilic nature, alkylphenols are used in various synthetic products including household detergents, toiletries, pesticides, and plastic materials (Watanabe *et al.* 2007). After entrance into water

streams, alkylphenols are bioaccumulated in aquatic organisms and induce sex-related changes in fish (Pinheiro *et al.* 2017). Existing data suggests that alkylphenols such as bisphenol A are able to interfere with some endocrine functions targeting fertility, pubertal timing, and sexual behavior, especially during fetal development (Windsor *et al.* 2017).

Fast expansion of large cities in developing countries, such as Tehran, brings urban life in contact with industrial activities.

The lack of modern sewage collection system leaves the way open for organic contaminants to penetrate to groundwater resources.

Chlorination is still being used as the common water disinfection method in many countries. This can result in formation of chlorinated phenols and other by-products which have been reported as toxic and non-biodegradable (Doederer *et al.* 2014). Advanced oxidation processes (AOPs) are modern water treatment technologies which are anticipated to substitute for chlorination (Mosteo *et al.* 2010). These methods are based on oxidation of pollutants by in-situ formation of hydroxyl radicals (OH<sup>•</sup>) which is a strong oxidizing agent ( $E^0 = 2.8$  V) (Laine *et al.* 2007). Different oxidants such as ozone (O<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are able to produce hydroxyl radicals in water. These radicals are capable of destroying organic contaminants in water and wastewaters (Stasinakis 2008). Generation of OH<sup>•</sup> can be facilitated by applying UV radiation, addition of some metal ions, etc. Consequently, various combinations of oxidants and stimulators have been examined such as UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> (Fenton) and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV (Photo-Fenton) (Deng & Zhao 2015). The efficacy of each of these methods is dependent on the contaminant structure and the environmental conditions of the water sample (Andreozzi *et al.* 2006). Iran is a large oil producing and oil exporting country. Some of the refineries and the relevant industries are at the outskirts of populated cities such as Tehran. Examining some groundwater resources close to Tehran oil refinery revealed that alkylphenols were the major organic pollutants (data is presented in this paper) while chlorination is being used as the main water disinfection method.

Degradation of aromatic pollutants and phenolic compounds, in particular, is a common target of AOPs studies (Ikehata *et al.* 2004; Zangeneh *et al.* 2016). Literature review reveals that degradation of some important alkylphenol pollutants by AOPs has been studied (Rizzo 2011, Krishnan *et al.* 2016), but studying the removal of these pollutants from various real samples, especially from oil-producing countries, by different oxidation

methods is of great interest as the chemical structures of the organic pollutants gradually change in environment (Ning *et al.* 2007). These modifications may result in enhancing resistance of the modified structures and make them more hazardous to living organisms (Rizzo 2011, Lozano *et al.* 2012). Therefore, this research was devoted to a comparative study on the efficiency of three important AOPs including photo-Fenton, O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV for removal of alkylphenols from the real samples collected from underground resources located in vicinity of Tehran oil refinery.

## MATERIALS AND METHODS

### Samples

Lab sample was made as follows: First, stock solution (20 mg L<sup>-1</sup>) of 5 selected aromatic compounds including bisphenol A (BPA), 4-chlorophenol (4CP), 2,4-dichlorophenol (DCP), 4-aminobenzoic acid (4AB), and guaiacol (Fig. 1) were prepared by dissolving 2 mg of each substance in 100 mL of double distilled water and stored in an amber-glass bottle at 4°C. The lab sample was prepared by mixing 2mL of each stock solution of the above-mentioned substances (total 10 mL) and diluting the resulting mixture to 100 mL. This gave the lab sample solution a total concentration 2 mg L<sup>-1</sup> with respect to the selected aromatic compounds. This concentration was well above the concentration of phenolic pollutants found in the real samples. Real samples were taken from 4 groundwater resources at the Western outskirts of Tehran (Table 1). Random sampling was carried out in dry (September) and wet (March) seasons.

### Reagents, solutions and instruments

Guaiacol, BPA, 4CP, DCP, 4AB, Folin-Ciocalteu reagent, H<sub>2</sub>O<sub>2</sub> (30% wt) and FeSO<sub>4</sub>·7H<sub>2</sub>O were analytical grade (Merck, Darmstadt, Germany). Catalase was purchased from SERVA (Heidelberg, Germany) and N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) was purchased from Sigma-Aldrich (St. Louis, Missouri, US). H<sub>2</sub>O<sub>2</sub> stock solution (1 mM) was made by diluting H<sub>2</sub>O<sub>2</sub> 30% (10 μL) to 100mL in

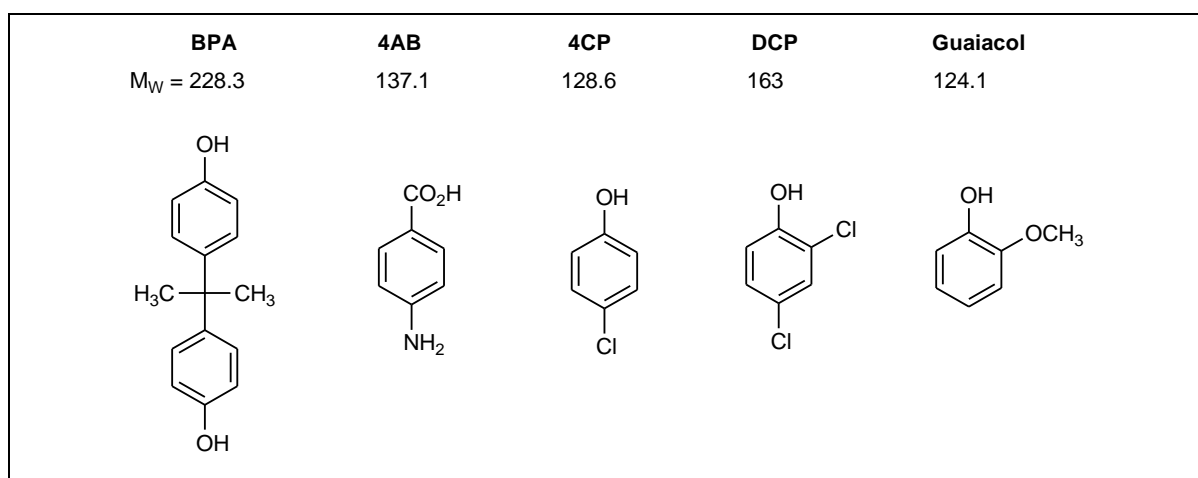
a standard analytical flask. Residual amount of H<sub>2</sub>O<sub>2</sub> was measured by the method introduced

by Zaribafan *et al.* (2014). Double distilled water was used exclusively.

**Table 1.** Geographical positions of the examined groundwater resources, the profiles, and the total phenolic compounds concentrations of the examined samples.

Water resource	X (m)*	Y (m)*	TDS** (mg L <sup>-1</sup> )	EC (μS cm <sup>-1</sup> )	pH	Phenols (mg L <sup>-1</sup> )†	Phenols (mg L <sup>-1</sup> )‡
1	525794	3954574	354.7	645	7.70	0.406	0.399
2	528578	3952712	266.2	484	7.52	0.490	0.373
3	500478	3963146	702.9	1278	7.92	0.574	0.275
4	499969	3960482	631.4	1148	7.20	0.287	0.270

\* X and Y are in UTM System; \*\* TDS (Total dissolved solids) was measured by a HM Digital TDS meter and EC (Electrical conductivity) calculated based on formula: [TDS (mg L<sup>-1</sup>) = K (= 0.55)\* EC (μS cm<sup>-1</sup>)]; dry† and wet‡ seasons.



**Fig. 1.** Chemical structures of the compounds used for making the lab sample.

UV<sub>C</sub> radiation was produced by low pressure mercury vapor lamp (radiant flux of 127 kW.m<sup>-2</sup> at λ > 254 nm) equipped with a power transformer Vossloh-Schwabe (NahJ-250 model, Ulf Hilsenberg, Germany). Ozone was produced by a continuous ozone reactor, Ozonica (Oz 20, Qom, Iran) with 20 g O<sub>3</sub> h<sup>-1</sup> productivity and 3.26 L min<sup>-1</sup> outlet. Input compressed air was provided by an HP air compressor (Guangdong, China) with a maximum output of 110 L min<sup>-1</sup>. Ozone concentration in the water samples was measured in mg O<sub>3</sub> L<sup>-1</sup> by an Ozone specific colorimeter (Palintest 1000 ozone meter model, Heworth, UK) using Palintest photometer grade test tablets (DPD No. 4). Upon addition of DPD (N,N-diethyl-p-phenylenediamine) to a tube containing water sample, the reagent was oxidized by the oxidant. The colorful product was measured with the colorimeter (Buchan *et al.* 2005). Spectrophotometric measurements were carried out in a conventional quartz cell

by analytic spectrophotometer (Specord 210 model, Jena, Germany) at 20°C.

Fluorescence measurements were carried out in 1 cm path quartz cells by a Varian Fluorescence Spectrophotometer (Cary Eclipse model, Santa Clara, US).

#### Determination of total phenolic content

The real samples were evaporated at room temperature in the dark. The residue was ground to fine powder and washed by diethyl ether. The isolated organic substances were dissolved in methanol (1 mL) and subjected to spectrophotometric examinations and Folin test.

#### Folin-Ciocalteu test

Folin-Ciocalteu tests (Singleton *et al.* 1999) were performed by mixing Folin reagent (100 μL), water (1.58 mL) and different amounts (50, 200 and 400 μL) of each sample. The resulting mixture was kept at 20°C for 5 min, and then

reacted with 300  $\mu\text{L}$  of  $\text{Na}_2\text{CO}_3$  solution (20% w/w). To complete the reaction, the mixture was maintained at 20 °C in the dark for 2 hours before spectrophotometric reading at 750 nm against the blank (water). The standard curve was prepared using different concentrations of the mentioned phenols of the lab sample. The standard curve was linear between 0.1 to 2.5 mg  $\text{L}^{-1}$  with the regression index above 0.992 (Fig. S1, Supplementary document). The amount of the phenolic additive in diethyl ether was precisely measured and considered in the calculations.

#### Gas chromatography - Tandem Mass spectrometry analysis

Samples were subjected to derivatization by BSTFA at 65 °C for 30 min (Proestos *et al.* 2013). They were then injected into Varian GC-MS system (2200 Series, Palo Alto, California, USA) equipped with a capillary low-bleed column CP-Sil 8 CB-MS (30 m  $\times$  0.25 mm id, 0.25  $\mu\text{m}$  film thickness) The GC-MS conditions were optimized to minimize the time of analysis while allowing all target compounds to elute in acquisition groups containing a suitable number of ions for monitoring. GC injection was performed in splitless mode. The injector was set at 205 °C and flow rate of the carrier gas (helium) was maintained at 1 mL  $\text{min}^{-1}$ . The oven temperature was set at 50 °C for 2 min and then increased to 300 °C at a constant rate of 2 °C  $\text{min}^{-1}$ . The mass spectrometer was set on Electron Impact mode (70 eV). The temperatures of the ion trap, manifold and transfer line were set at 180°C, 140 °C and 170 °C respectively. Compounds identification was carried out by comparing the retention times and mass spectra of the peaks with those of the authentic compounds. Each determination was carried out in duplicate. For the identification purpose, we used full scan mass spectrum, the ratios of four characteristic ions and the  $\pm 0.5\%$  relative retention time (RRT) tolerance criteria in comparison with the standards (Watanabe *et al.* 2007).

#### Advanced oxidation experiments

Two designs of batch and continuous flow of the water samples were used in AOPs experiments. Batch method, described below, was used for the photo-Fenton reactions. Continuous method was used in ozone-based processes. Ozone was continuously bubbled into the current of water sample which was exposed to  $\text{UV}_\text{C}$  radiation, (Fig. 2). All experiments were carried out under the hood shielded by an aluminum cover. Each experiment was performed separately and each test was repeated at least 5 times. In this study, degradation of phenols was followed via reduction in the absorption spectra of the samples between 220 to 330 nm. Phenols concentration was measured by methods explained above. Complete mineralization of the aromatic pollutants was confirmed from disappearance of both the corresponding absorption spectra in the region of 220 to 330 nm and fluorescence emission spectra from 270 to 350 nm region using 280 nm for the excitation beam.

#### $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ (Photo-Fenton reaction)

In this study,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (0.3 to 50 mg  $\text{L}^{-1}$ ) was added to the lab samples containing various concentrations (2000 to 10000 mg  $\text{L}^{-1}$ ) of  $\text{H}_2\text{O}_2$  at pH 3. The resulting solution (20 mL) produced a depth of 1 cm in a glass petri dish (5 cm diameter). This solution was subjected to  $\text{UV}_\text{C}$  radiation (10 and 15 min). Similar experiments were also carried out at pH 7.

#### $\text{O}_3/\text{UV}$

In these experiments, concentration of  $\text{O}_3$  was adjusted to 2 mg  $\text{L}^{-1}$  in the samples (100 mL, pH  $7 \pm 0.5$ ).

The selected dose of ozone was close to the dosage usually used in water treatment plants (Mosteo *et al.* 2010).

The resulting mixture was subjected to  $\text{UV}_\text{C}$  radiation for the intended time (0 to 15 min) at 25 °C.

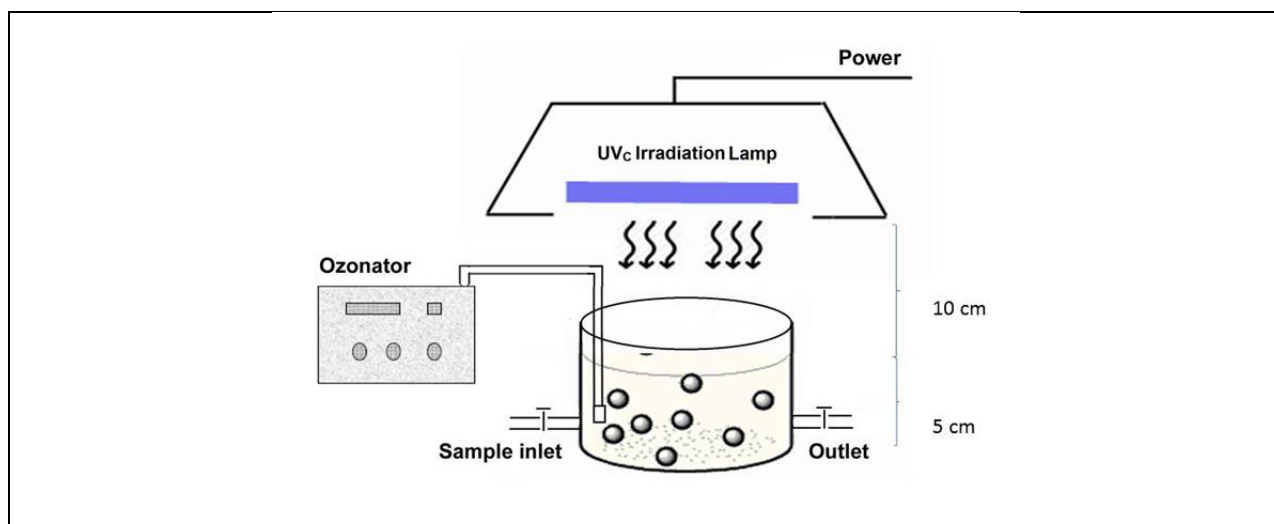


Fig. 2. Experimental setup for continuous ozone-based oxidations.

### O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV

Ozone concentration was adjusted to 2 mg L<sup>-1</sup> in the samples (100 mL, pH 7 ± 0.5) containing various concentrations (100 to 5000 mg L<sup>-1</sup>) of H<sub>2</sub>O<sub>2</sub>.

The reaction took place in 20 min. The resulting solution was subjected to the spectrophotometric measurements. In parallel experiments, the resulting solution was subjected to UVC radiation for 0 to 15 min prior to the spectrophotometric measurements.

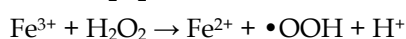
## RESULTS AND DISCUSSION

### Examination of AOPs on the lab sample

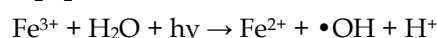
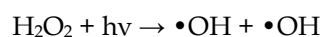
The efficacy of different AOPs was first studied on a lab sample, which was a mixture of five aromatic compounds from both synthetic and natural origin (illustrated in Fig. 1). These compounds were selected because they had different substituents and different half-wave oxidation potentials ranging from 420 mV (for DCP) to 714 mV (for 4 A,B) (Suarez-Ojeda *et al.* 2005). Results of these studies are presented in the following sections.

### Photo-Fenton process

Fenton process is based on the reaction of Fe<sup>2+</sup> with H<sub>2</sub>O<sub>2</sub> which generates hydroxyl radicals through the following mechanism:



Results showed that the degradation rate of organic pollutants by Fenton process is accelerated significantly if UV radiation is concurrently applied (Babuponnusami *et al.* 2012).

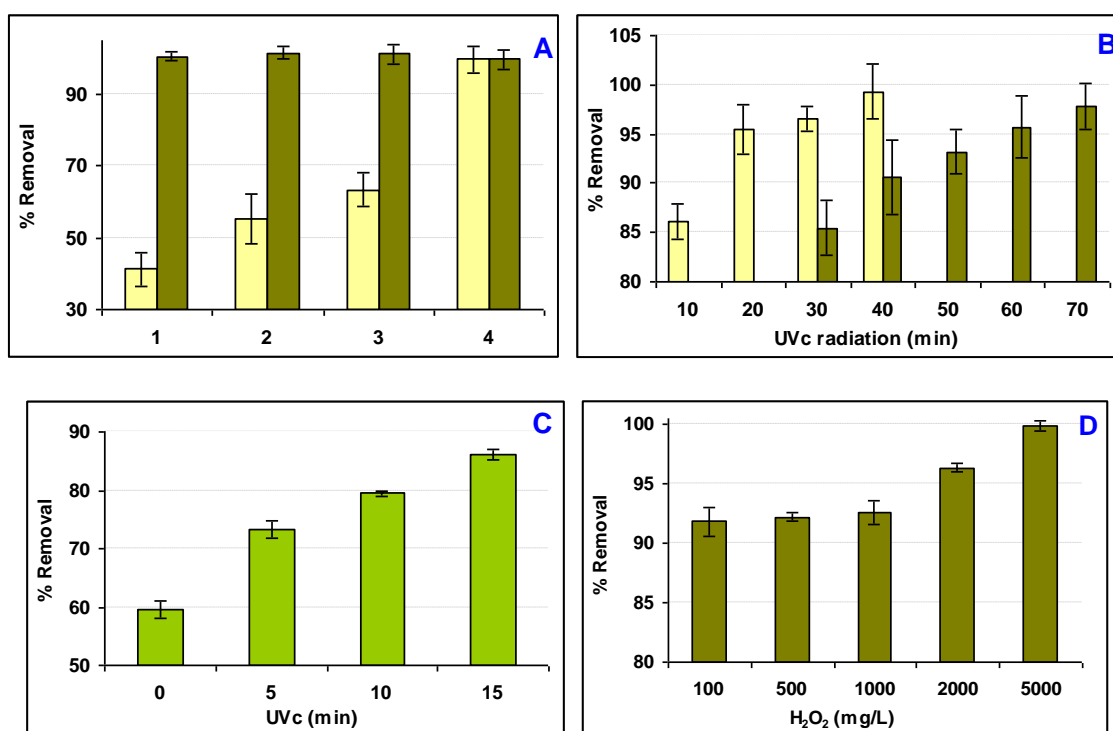


This method was first examined at pH 3 (Fig. 3A). Results showed that the combination of H<sub>2</sub>O<sub>2</sub> (1000 mg L<sup>-1</sup>), Fe<sup>2+</sup> (100 mg L<sup>-1</sup>) and UVC radiation for 10 min (7.5 kJ cm<sup>-2</sup>) removed all the organic compounds (2 mg L<sup>-1</sup>) from the lab sample solution. These results also indicated that the complete degradation of the aromatic compounds occurs at lower concentrations of Fe<sup>2+</sup> (0.3 mg L<sup>-1</sup>, the accepted Secondary Maximum Contaminant Level in drinking water) (US EPA, 2013) and H<sub>2</sub>O<sub>2</sub> (100 mg L<sup>-1</sup>) when radiation time was increased from 10 to 15 min (bars in dark color, Fig. 3A). Martins *et al.* (2015) reported 100% removal of Diuron and Hexazinone from the samples using same concentration of H<sub>2</sub>O<sub>2</sub> (988 mg L<sup>-1</sup>), but more prolonged UVC irradiation (30 min) and higher concentration of FeSO<sub>4</sub> 7H<sub>2</sub>O (140 mg L<sup>-1</sup>) at pH 2.8 (Martins *et al.* 2015). In a study on the organic pollutants removal from an industrial wastewater sample by photo-Fenton, Ebrahiem *et al.* (2013) reported over 95% COD removal under the optimized conditions of H<sub>2</sub>O<sub>2</sub> (333

mg L<sup>-1</sup>), FeSO<sub>4</sub> 7H<sub>2</sub>O (750 mg L<sup>-1</sup>) and UVC radiation time (40 min) (Ebrahiem *et al.* 2013). To simulate the common conditions of drinking water, the photo-Fenton reactions were also studied at pH 7. Since iron starts to precipitate as oxy hydroxide at this pH in the absence of a chelating agent (Chen *et al.* 2015), the freshly-prepared solutions were immediately used in the experiments. Fe<sup>2+</sup> concentration was adjusted to 0.3 mg L<sup>-1</sup>.

The illustrated results (Fig. 3B) indicate that the highest removal efficacy (99.31%) was obtained when H<sub>2</sub>O<sub>2</sub> (2000 mg L<sup>-1</sup>) and 40 min UVC radiation (30.57 kJ cm<sup>-2</sup>) were applied to the samples.

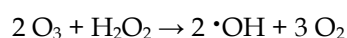
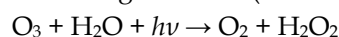
It is assumed that the gradual precipitation of iron reduces the efficiency of photo-Fenton process at this pH.



**Fig. 3.** Removal of the aromatic compounds from the lab samples with the initial concentration of 2 mg L<sup>-1</sup> by A) Photo-Fenton method in pH 3 with the respective concentration of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> 7H<sub>2</sub>O, 1) 10,000, 0.3 mg L<sup>-1</sup>, 2) 10,000, 20 mg L<sup>-1</sup>, 3) 2000, 50 mg L<sup>-1</sup>, 4) 1000, 100 mg L<sup>-1</sup> (bars in light and dark color show duration of UV<sub>C</sub> radiation for 10 and 15 minutes respectively); B) Photo-Fenton method at pH 7. Bars with the dark and light colors show concentrations of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub> 7H<sub>2</sub>O: 1000, 0.3 mg L<sup>-1</sup> and 2000, 0.3 mg L<sup>-1</sup> respectively; C) O<sub>3</sub>/UV method; D) O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV method with 15 minutes, UV<sub>C</sub> radiation. O<sub>3</sub> concentrations in C and D were 2 mg L<sup>-1</sup>.

### Ozone-based AOPs

Simultaneous applications of UV<sub>C</sub> radiation and ozone increase the rate of the hydroxyl radicals' generation (Stasinakis 2008):



In this study, two combinations of O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV were optimized for the removal of the pollutants from the lab sample in pH

close to neutral (Figs. 3C and 3D). The results showed that O<sub>3</sub> (2 mg L<sup>-1</sup>) with a concentration time value (CT = concentration of ozone in medium multiplied by the ozone contact time with the substrates) of 30 mg min L<sup>-1</sup> removed about 86% of the aromatic compounds from the lab sample under UV<sub>C</sub> radiation for 15 min (0.56 kJ cm<sup>-2</sup>). Studying different combinations of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> showed that a combination of O<sub>3</sub> (2 mg L<sup>-1</sup>, CT = 30 mg min L<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub>

(5000 mg L<sup>-1</sup>) increased removal of the aromatic compounds to 97.33%.

These results indicated that H<sub>2</sub>O<sub>2</sub> can work as a substitute for UV<sub>C</sub> radiation. However, this concentration of H<sub>2</sub>O<sub>2</sub> raises concerns about the safety standards of the method. Guzzella *et al.* (2002) showed that applying H<sub>2</sub>O<sub>2</sub> (35% v/v) with a flow rate of 2 mL min<sup>-1</sup> and UV<sub>C</sub> radiation (30-120 min) in the presence of ozone (0.4 mg L<sup>-1</sup>) increased the removal of organic chemicals (with maximum initial concentration of 10 mg L<sup>-1</sup>) from water by over 50% (Guzzella *et al.* 2002).

Potable water treatment plants based on O<sub>3</sub>/UV method such as that in Terrebonne are expanding. According to the developer company, treatment results exceed regulation requirements (Warda 2011).

Adding H<sub>2</sub>O<sub>2</sub> to the O<sub>3</sub>/UV combination enhances the efficiency of the oxidation (Lucas *et al.* 2010). Fig. 3D shows that adding 2000 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> to the O<sub>3</sub>/UV resulted in 96.41% removal of the aromatic compounds with initial concentration of 2 mg L<sup>-1</sup>, while increasing H<sub>2</sub>O<sub>2</sub> concentration to 5000 mg L<sup>-1</sup> caused total removal of the organic compounds from the samples. To some researchers, the combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV is the most effective AOP for removing organic compounds (Priac *et al.* 2017). One of the first studies on this method for the water treatment purpose was carried out for the US Department of Energy, Kansas City plant, Missouri. The main source of contamination was volatile organic compounds such as perchloroethylene, trichloroethylene, 1, 2-dichloroethylene and vinyl chloride.

They reported a removal efficiency of 94.6% (Clarín *et al.* 1998). In a different study on phenol removal, Kusic *et al.* (2006) examined various ozone-based AOPs. They reported total mineralization of phenol by a combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV at pH 7.

They applied ozone at a rate of 7.86 mg min<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> (340 mg L<sup>-1</sup>, 10 mM) and UV radiation for 30 min. They concluded that from both the eco- and cost-effectiveness points of view, this method was the most suitable process (Kusic *et al.* 2006). Im *et al.* (2012) used O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV

process for removing carbamazepine from water. They reported the optimal ratio of [0.91 (mg L<sup>-1</sup>)/5.52 (mg L<sup>-1</sup>)/2.98 (mW cm<sup>-2</sup>)] for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV which resulted in complete removal of the contaminant in 5 min (Im *et al.* 2012).

#### Determination of phenolic contaminants in the real samples

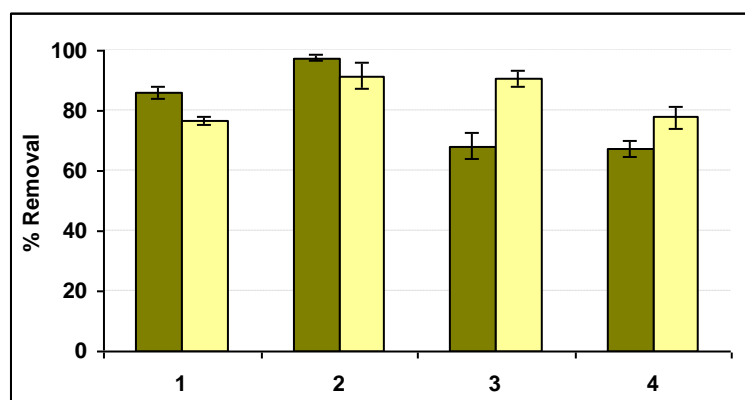
Real samples were taken from four groundwater resources (Table 1). These resources were selected because of their close proximity to the urban area and the ongoing industrial activities such as oil refineries in the region. The organic residue of each sample was examined by the wavelength scan spectrophotometric method. Fig. 4 shows the overlaid spectra of one of these samples and the lab sample. The high similarity between these spectra (typical absorbance peak about 270 nm) indicated the presence of aromatic organic contaminants in the real samples (Haghbeen *et al.* 2009). Total phenolic content of the collected organic residue was measured by Folin-Ciocalteu method. Analysis results confirmed the presence of phenolic contaminants in the real samples with an average concentration of 0.38 mg L<sup>-1</sup> (Table 1). GC-Mass analysis identified 16 compounds which were closely related to phenols. Structures of 7 compounds which were observed in all 4 resources are illustrated in Fig. S2 (Supplementary document). Resulting match points score for library (Wiley and NIST) search of the identified compounds were always higher than 90%. All the 16 assigned phenolic pollutants were belonged to alkylphenols family.

#### AOPs on the real samples

Considering the results obtained from the experiments on the lab sample, O<sub>3</sub>/UV and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV methods were chosen to be examined on the real samples. Results of these experiments (Fig. 5) indicated that the combination of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV (2 mg L<sup>-1</sup>, 5000 mg L<sup>-1</sup>, and 15 min, respectively) was the most efficient method for the removal of phenolic pollutants from the samples collected from the resources 1 and 2, while the combination of

O<sub>3</sub>/UV (2 mg.L<sup>-1</sup> and 15 min, respectively) was the most efficient method for the samples collected from the water resources 3 and 4. On average, the removal efficiencies of 79.71%, and 84.16% were observed for the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV methods, respectively, using the optimal values obtained from the experiments carried out on the lab samples. Close average results were anticipated as both methods were similarly effective on the lab samples. The observed discrepancies between the removal efficiencies of these methods on the lab and the

real samples can be ascribed to the different nature of these samples. The effect of the chemical identity of the real sample on the removal efficiency of the applied AOP has been reported by other researchers (Stasinakis 2008). This phenomenon was best studied by Tony *et al.* (2012). They studied the efficacy of various Fenton-based methods on three types of oil-contaminated waters collected from oil-refinery environment. They reached efficacies between 50 to 75% depend on the sample type (Tony *et al.* 2012).



**Fig. 5.** Removal of phenolic pollutants from the real samples (1 to 4) by the selected AOPs: O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV (dark colored bars) and O<sub>3</sub>/UV (light colored bars). See Materials and Methods for the experimental details.

Literature review discloses that most of the reports about the application of various (direct and indirect) AOPs for degradation of alkylphenols are focused on the fate of the known contaminants such as BPA, nonylphenol, nonylphenol ethoxylate and compounds with similar structures (Priac *et al.* 2016; Zangeneh *et al.* 2016). However, results of this work indicate that the structures of the contaminants can be more diverse as a result of the specific activities in the region of interest. In the absence of advanced sewage collection systems, in addition to urban life, oil refineries can be the source of organic pollutants which gradually affect bioactivity of the soil (Bagheri *et al.* 2009, Mao *et al.* 2012). These parameters increase complexity of the organic pollutants in the groundwater resources. This, in turn, affects the efficacy of the AOPs which were optimized for treatment of a recalcitrant lab sample. Although heterogeneous

photocatalysis (Gultekin *et al.* 2007) and the combination of AOP with photocatalysis (Hegedús *et al.* 2015) have come to attention especially for treatment of alkylphenols, costs and the intricacy of the methods question the feasibility of these methods for large scale plants. Results of this study are in favor of ozone-based AOPs and the combination of O<sub>3</sub>/UV in particular. In agreement with to our conclusion, Hyunook *et al.* (2007), through exploring for the effective degradation conditions of nonylphenol and nonylphenol ethoxylate, concluded that ozonation could be the preferred technology for oxidizing these substances. Similarly, Zhang *et al.* (2008) studied the ozonation of nonylphenol and octylphenol in aqueous solutions containing CH<sub>3</sub>CN as co-solvent. They also concluded that ozonation could be the feasible process for removal of alkylphenols from contaminated waters (Zhang *et al.* 2008). In a research on the



contaminated drinking water resources in China, Lv *et al.* (2016) observed that ozonation produced the best removal results for alkylphenols. However, this is important to

note that, because of the intrinsic discrepancies between the real samples, optimization has to be done in pilot studies prior to large-scale implementation (Krishnan *et al.* 2016).

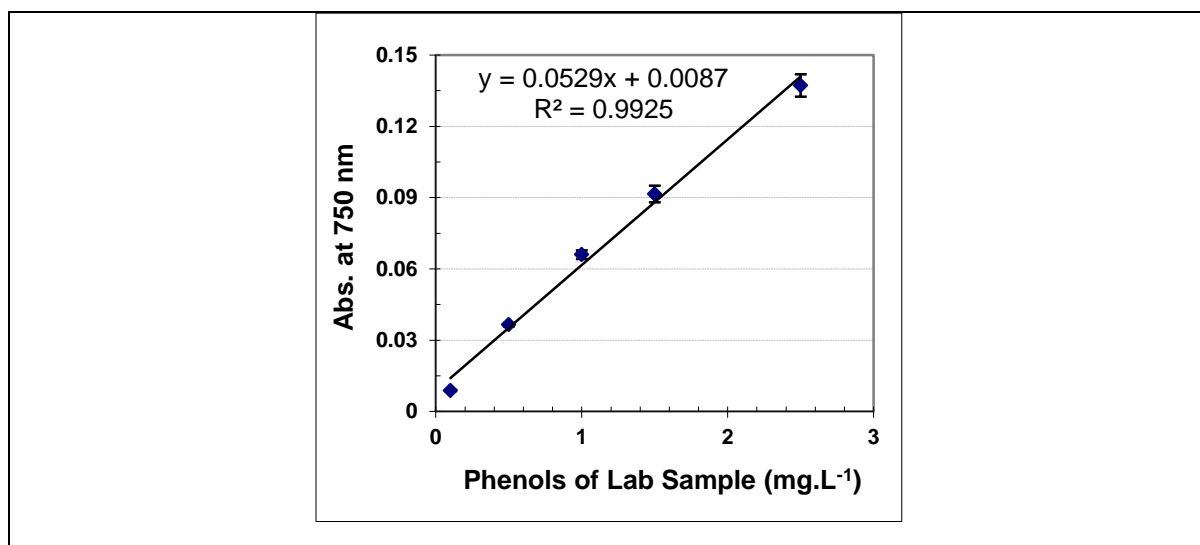


Fig. 7. (suppl. 1). Folin standard curve.

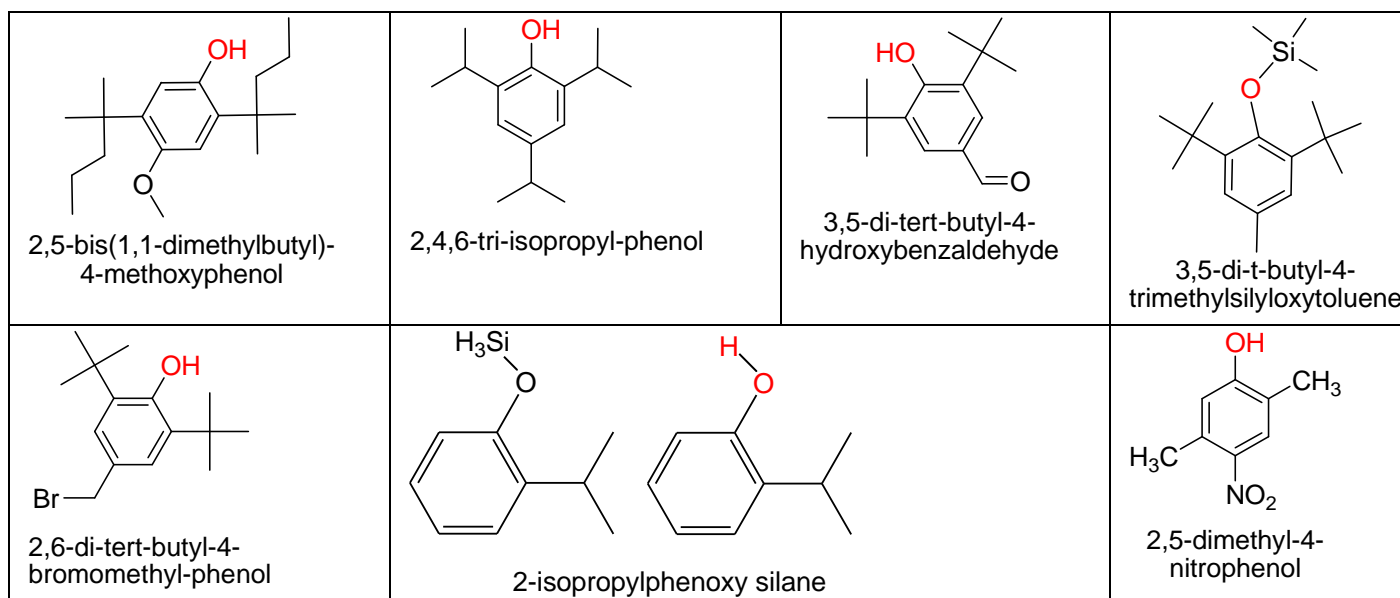


Fig. 8. (suppl. 2). Chemical structures of some of the aromatic pollutants found in the examined groundwater resources.

## CONCLUSIONS

This research showed that groundwater resources close to oil refinery in areas with an irregular pattern of industrial and urban activities are exposed to alkylphenols contamination. The results of this comparative study on 3 important AOPs showed that ozone-based processes were more effective for

removal of the aromatic compounds from a recalcitrant lab sample. By applying the optimal conditions ensued from the experiments on the lab sample for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UV and O<sub>3</sub>/UV methods, it was possible to remove up to 84% of the phenolic pollutants, which were mainly alkylphenols, from the examined real samples. Considering

these results and the concerns regarding the high concentrations of hydrogen peroxide, the O<sub>3</sub>/UV process seems to be more cost-effective and safe for treatment of such contaminated water resources.

According to this research, different nature of the polluted water resources originated from different environmental conditions such as various urban and industrial activities and different physicochemical properties of soil necessitates extra optimization of the method for the quantitative removal of organic pollutants such as alkylphenols in large-scale plans.

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## استفاده از روش اکسیداسیون پیشرفته در حذف آلکیل فنول‌ها در نمونه‌های آب زیرزمینی

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### چکیده

مطالعات اسپکتروفتومتری بر روی نمونه‌های آب جمع‌آوری شده از ۴ منبع زیرزمینی (چاه) آب در اطراف پالایشگاه نفت تهران، وجود ترکیبات فنلی را در این نمونه‌ها تایید کرد. با به‌کارگیری روش فولین، میانگین غلظت فنل تام در این نمونه‌ها ۰/۳۸ میلی‌گرم در لیتر تخمین زده شد. آنالیز مواد آلی استخراج شده از این نمونه‌ها توسط GC-Mass نشان داد که غالب آلاینده‌های فنلی، آلکیل فنل‌ها بودند. مطالعه کارایی روش‌های مختلف اکسیداسیون پیشرفته در حذف ترکیبات آلی از آب‌های آلوده واقعی با توجه به مجاورت آب با خاک و تأثیر خاک و ریزسازواره‌ها بر ساختمان اولیه آلاینده‌های آلی و افزایش تجزیه‌ناپذیری ترکیبات جدید، از اهمیت خاصی برخوردار است. برای بررسی کارایی فرآیندهای اکسیداسیون پیشرفته برای حذف آلاینده‌های فنلی، خصوصاً آلکیل فنل‌ها، از نمونه‌های ۴ منبع زیرزمینی مذکور، سه روش مهم  $Fe^{2+}/H_2O_2/UV$  (Photo-Fenton)،  $[O_3/UV, O_3/UV/H_2O_2]$  ابتدا برای حذف آلاینده‌های آلی از یک نمونه آزمایشگاهی حاوی ترکیبات پایدار آروماتیکی با غلظت کل ۲ میلی‌گرم در لیتر بهینه‌سازی شدند. سپس، با توجه به نتایج، ۲ روش با مقادیر بهینه:

$L^{-1} H_2O_2, 15 L^{-1} O_3, 15 \text{ min UVC}$ ), and  $O_3/UV/H_2O_2$  ( $2 \text{ mg.L}^{-1} O_3, 5000 \text{ mg } O_3/UV$  ( $2 \text{ mg}$ ))

(min UVC) بر روی نمونه‌های واقعی مورد آزمایش قرار گرفتند. گرچه این دو روش تحت شرایط بهینه شده به شکل کمی

سبب حذف ترکیبات فنلی از نمونه آزمایشگاهی شدند اما بازده آنها بر روی نمونه‌های واقعی به ترتیب ۷۹/۷۱٪ و ۸۴/۱۶٪ بود.

با وجود این، با توجه به مقررات ایمنی، سادگی روش و هزینه‌ها چنین به نظر می‌رسد که به‌کارگیری روش اکسیداسیون پیشرفته

( $O_3/UV$ ) در مقیاس بزرگ برای تصفیه خانه‌ها مناسب‌تر باشد.

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