



Treatment of organophosphated flame retardants from waters by hydroxyl radical producing processes and toxicity investigation

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ABSTRACT

The toxic flame retardant (FR) substances present in water and wastewater have become an important problem like tris(2-chloroethyl) phosphate (TCEP), which is the most used organophosphated FR in various polymer and causes a directly neurotoxic or carcinogenic effect on the human. TCEP can be found in surface water, wastewater treatment plants, oceans and drinking water due to high solubility in water and it is defined as a persistent, bio-accumulative and toxic pollutant. The hydroxyl radical (OH^\bullet) producing processes can be used for this type of pollutant providing high removal efficiency. This presented study was investigated the performance of the hydroxyl radical producing processes on the degradation of TCEP. Hydrogen peroxide, photolysis, Fenton, homogeneous photolysis, and photo-Fenton treatment methods were used to remove 1,000 mg/L TCEP as a model compound of the organophosphated flame retardants. The removal efficiencies of these treatment methods were determined with total organic carbon (TOC) due to easy application, the suitability of the optimization and referring all organic degradation products of TCEP. The effectiveness of these treatment methods on TOC removal efficiency was observed that $\text{H}_2\text{O} < \text{UV} < \text{Fenton} < \text{UV-H}_2\text{O} < \text{UV-Fenton}$. The highest TOC removal efficiency was attained with 93.75% using 0.18 mM Fe^{2+} and 30 mM H_2O_2 in the photo-Fenton. The cytotoxicity was significantly reduced with the photo-Fenton process.

Keywords: Organophosphated flame retardants; Tris(2-chloroethyl) phosphate; Hydroxyl radical OH^\bullet producing processes; Total organic carbon; Cytotoxicity

1. Introduction

Fire risks have increased with the growth of industrialization, population and the effects of rapidly developing science and technology recently. Therefore, the use of flame retardant (FR) additives has become inevitable in many areas. FR chemicals might be added or applied to polymer materials to reduce fire risk or prevent fire growth [1]. Since the 1970s, FR chemicals have been used in the areas such as; electronics, textile, furniture, construction materials and transportation especially [2].

Halogenated flame retardant chemicals contain the F, Cl, Br and I elements in the periodic table. Bromine-containing

flame retardants are the most commonly used flame retardant additives [3]. Halogenated flame retardants like Br are effective in the gas phase removing OH^\bullet and H^\bullet free radicals from combustible gases [4]. All four halogens are effective in capturing radicals and the radicals capturing efficiency of these elements are listed as $\text{I} > \text{Br} > \text{Cl} > \text{F}$ [5]. The choice of each of these FR additives for a specific formulation or application is largely determined by the polymer system, and the desired flammability and physical properties [6,7]. The use of FR-containing additives has been discontinued due to the adverse effects on human health and the environment [8]. The brominated flame retardants affect the human with several

exposure pathways, and the lots of brominated FRs were restricted due to endocrine disruptive properties [9,10].

Phosphorus-based FR chemicals account for 20% of the flame retardant chemicals used in Europe in 2006, and they are suitable for processing with other chemicals and are easy to use as an alternative choice to bromine-containing flame retardants [10]. The FR mechanism for phosphorus-containing flame retardants is complex and is often believed to contain char formation (solid phase) and possible vapor phase activity (depending on the phosphorus product) [11]. Phosphorus-based FR technology has been used since the 1940–1950s and it has become even more widely used due to the lower toxic effects than the use of halogenated flame retardants. Although some particular phosphorus products are controversial about non-environmentally friendly products, phosphorous-containing FR products have not been prohibited or restricted to date [12]. As a fire retardant, the phosphorus-based flame retardants decompose to ammonia and phosphoric acid. Phosphoric acid serves as an acid catalyst in the dehydration of carbon-based polyalcohol. The phosphoric acid reacts with alcohol groups to phosphate esters. The esters decompose to release the carbon dioxide and regenerate the phosphoric acid catalyst. The release of non-flammable carbon dioxide helps to dilute the oxygen of the combustible material and the air of the flammable decomposition products [13–19]. There are toxicity problems with regard to the direct toxicity of fire retardant components, the toxicity of the combustion products of fire retardants, and the effects of fire retardants on the yield and toxicity of the other two combustion products [13]. Phosphate systems have the advantage of not producing environmentally permanent toxic combustion products and, depending on the system, can reduce both the yield of toxic products and the fire growth rate during fires. However, some organophosphated flame

retardants (OP-FRs) are directly neurotoxic or carcinogenic [14]. Mostly used OP-FRs can be listed as tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), triethyl phosphate (TEP), tripropyl phosphate (TPP), tri-*n*-butyl phosphate (TNBP), triisobutyl phosphate (TIBP), tricresyl phosphate (TMPP), triphenyl phosphate (TPHP). TCEP is the most used organophosphated flame retardant additive in lots of areas [15].

Tris(2-chloroethyl) phosphate (TCEP) is a pale yellow liquid that is used as organophosphate FR mainly used in the production of liquid unsaturated polyester resins, epoxy resin, and cellulose ester compounds [16]. TCEP can be defined as a persistent, bio-accumulative and toxic pollutants. It was estimated that 98.6% of the TCEP remains in the water and 1.4% is adsorbed to the sludge because of high water solubility [16]. It is also used in textile back coating formulations, it has a water solubility of 8 g/L, and it is not accepted readily biodegradable [17], and shows moderate acute oral toxicity (oral LD₅₀ = 1,150 mg/kg body weight in rat) [18]. TCEP has been detected with varying from ng/L to µg/L concentrations in the river water, seawater, drinking water, sediment, biota, various foods and groundwater and there is no reported data for TCEP levels in air samples given in Table 1 summarizing related literature [19–26].

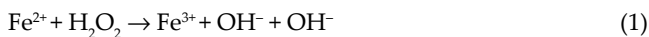
It is difficult to remove toxic organic compounds, which are resistant to biological treatment by conventional wastewater treatment methods. Therefore, hydroxyl radical (OH[•]) producing processes) have become an alternative method providing high efficiency to reduce these organic pollutants. In general, its effectiveness depends on the selected hydroxyl radical (OH[•]) producing methods, the physical and chemical properties of the target pollutant, and the operating conditions [27]. The hydroxyl radical (OH[•]) producing

Table 1
TCEP concentration found in environmental samples reported by the previous studies

Sample/Environment	TCEP concentration	Sources	Analysis method	References
Dust	±4.0 mg/kg	Foams, paints, varnishes, wallpapers	GC-MPD GC-MS	[19]
River	0.35 µg/L	Flame retardants	GC-MS	[20]
Underground and rain water	0.017–1.510 µg/L	Flame retardants	GC-MS	[20]
Water treatment plant	0.3–9.2 ng/L	Flame retardants		[21]
Wastewater treatment plants	0.5 µg/L	Flame retardants	GC-MS	[22]
Drinking water	0.3 ng/L	Polyurethane foams	GC-MS	[23]
River	13–130 ng/L	Flame retardants	GC-MS	[24]
Wastewater from washing textile	42.8 µg/L–65.5 µg/L	Clothes, furniture foams	UPLC-AP- PI-MS/MS	[25]
House dust	1.380 µg/L	Home, office, carpets, curtains, furniture	UPLC-AP- PI-MS/MS	[25]
Municipal wastewater treatment plants	Influent: 986 ng/L Effluent: 352 ng/L	Polyurethane foams	GC-MS	[26]
Industrial wastewater treatment plant	Influent: ~2 µg/L Effluent: <1 ng/L	Polyurethane foams	GC-MS	[26]

processes) can convert toxic and persistent organic matter into harmless end products [27]. The hydroxyl radical (OH^\bullet) producing processes is usually performed with hydrogen peroxide (H_2O_2) or ozone (O_3), catalysts (iron ions, electrodes, metal oxides) and UV irradiation [28]. The hydroxyl radical producing processes involve the combination of strong oxidizing agents, UV light, sunlight, ultrasound, and their sequence and hybrid application [29].

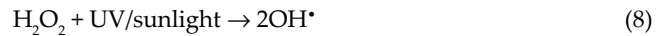
In recent years, advanced oxidation methods have been developed to eliminate organic pollutants in wastewater. The Fenton process is a homogeneous oxidation process that produces hydroxyl radicals (OH^\bullet) under acidic conditions [30]. Fenton and related reactions include the reaction of peroxides (usually H_2O_2) with iron ions (Fe^{2+}) to form active oxygen species which oxidize organic or inorganic compounds. Fenton reactions can be carried out at an ambient temperature, the reagents are readily available, are easy to store, are relatively safe to use and environmentally friendly [31]. Fenton reactions are widely used hydroxyl radical producing processes to remove most organic compounds. The iron ion initiates the decomposition of H_2O_2 ; and hydroxyl radicals are formed, after the formation of radicals in the form of a complex reaction chain [Eqs. (1)–(6)] in aqueous solutions [32]. The resulting ferric ions catalyze hydrogen peroxide and decomposition of organic pollutants into water and carbon dioxide finally [33].



When UV radiation is used for the formation of OH^\bullet in advanced oxidation processes, this hydroxyl radical producing process is called “UV oxidation technologies” or “photolysis”. UV radiation and sunlight can be used in these hydroxyl radical-producing processes. UV/oxidation technologies are a process that occurs in a homogeneous medium by the addition of a suitable oxidant (H_2O_2 or O_3) or in a heterogeneous medium containing semiconductor particles like titanium dioxide (TiO_2). According to the reaction environment, photolysis are classified as homogeneous processes (UV/ H_2O_2 , UV/ O_3) and heterogeneous processes (UV/ TiO_2) [34].



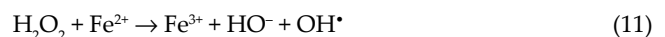
H_2O_2 is a strong chemical oxidant and it is photochemically unstable under UV irradiation. Irradiation of H_2O_2 by UV light in Eq. (8) produces more OH^\bullet radical than obtaining from Eq. (7). The OH^\bullet radical is known to react with a large number of chemicals for reduction [35].



The $\text{H}_2\text{O}_2/\text{UV}$ advanced oxidation process is an alternative to conventional water treatment methods such as air stripping, adsorption and membrane technique. The design of the lowest cost $\text{H}_2\text{O}_2/\text{UV}$ process for applications requires the identification of important design and operational variables such as optimum oxidant and irradiation dosages within the reactor [36]. In the $\text{H}_2\text{O}_2/\text{UV}$ oxidation process, the main oxidation agent OH^\bullet formed by UV radiation in the presence of hydrogen peroxide converts the pollutant molecule into CO_2 and H_2O . UV light activates hydrogen peroxide, allowing it to decompose into two hydroxyl radicals. The resulting radicals react with organic pollutants and perform chemical oxidation of organic matter. In this way, a H_2O_2 decomposition cycle occurs [36].



The combination of Fe^{2+} , H_2O_2 and UV radiation is called a photo-Fenton process. In the photo-Fenton process produces more hydroxyl radicals than the Fenton process and significantly increases the rate of degradation and mineralization of the organic pollutant. The lower $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions are needed due to the conversion of iron ions which are reduced to Fe^{2+} by photochemically and oxidized again to Fe^{3+} in Fenton reactions [34]. With UV irradiation, the oxidizing power of the Fenton reaction can be greatly increased at wavelength values greater than 300 nm [37]. One of the most important reasons for this is the formation of more OH^\bullet radicals due to the effect of UV light and the return of Fe^{3+} to Fe^{2+} to Fenton cycle as a result of Fenton reactions [37].



In this study, the treatment of tris(2-chloroethyl) phosphate (TCEP) was investigated by advanced treatment methods from water and wastewater. Photolysis (UV), homogenous photolysis (UV- H_2O_2), Fenton (Fe^{2+} - H_2O_2) and photo-Fenton (Fe^{2+} - H_2O_2 -UV) advanced oxidation process were examined and the toxicity of these hydroxyl radical producing processes were evaluated for TCEP removal from wastewater.

2. Methods

1,000 mg/L tris(2-chloroethyl) phosphate (Sigma-Aldrich, Darmstadt, Germany-TCEP- $\text{C}_6\text{H}_{12}\text{Cl}_3\text{O}_4\text{P}$ -MW: 285.4898 g/mol, 97% purity) solution as synthetic wastewater was used for treatment studies to compare the performance of different hydroxyl radical producing processes. Time-dependent samples were taken under recycled flow

Table 2
Characteristic of synthetic wastewater

Parameter/unit	Value
TCEP concentration (mg/L)	1,000.00 ± 50.00
TOC concentration (mg/L)	288.00 ± 15.00
pH	8.00 ± 0.40
Conductivity (µS/cm)	34.10 ± 1.71

conditions from all treatment processes during 90 min retention time and the removal efficiency of TCEP was evaluated with total organic carbon (TOC) equivalent due to easy application, the suitability of the optimization and referring all organic degradation product of TCEP. TOC value of all collected samples from treatment processes desired time interval were determined with TOC Analyzer (SHIMADZU, TOC-LCP and ASI-L, Tokyo, Japan). The synthetic wastewater characteristic was given in Table 2.

The reaction kinetic of photolysis (UV), homogenous photolysis (UV-H₂O₂), Fenton (Fe²⁺-H₂O₂) and photo-Fenton (Fe²⁺-H₂O₂-UV) advanced oxidation process given in Table 3 were determined with first-order reaction kinetic model.

$$\text{Reaction rate} = \frac{dC}{dt} = kC \quad (15)$$

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (16)$$

For the optimum treatment condition obtained in these hydroxyl radical producing processes, the cytotoxicity experiments were conducted for the untreated synthetic wastewater and effluent samples after the utilization of H₂O₂. The toxicity tests of effluent samples after treatment and influent samples were analyzed with Microtox[®] Model 500 Analyzer (Azur Environmental, Carlsbad, California, USA) as a cytotoxicity study. The lyophilized *Vibrio fischeri* bacterium (NRRL number B-11177, Microtox Acute reagent, Modern Water, California, USA) with luminescence characteristics was used as a test microorganism. The *Vibrio fischeri* bacterium was incubated with reconstitution solution (Non-toxic Ultrapure Water, Modern Water) and osmotic adjuster solution (22% sodium chloride, Modern Water, California, USA) at 15°C for 15 min in glass cells. Four serial dilutions of the sample were prepared with dilution solution (2% sodium chloride, Modern Water, California, USA). Toxic effects of the test result Microtox calculation software (95% confidence) incubated at 15°C *Vibrio fischeri* light emission reduction percent value of 15 min exposure values were recorded for each sample.

2.1. Photolysis

Photolysis (UV) studies were performed in a UV reactor using a UV-C lamp with 254 nm wavelength applying 8 W power at room temperature. In a metal flow-controlled reactor with a length of 25 cm, an inner diameter of 2.5 cm and an outer diameter of 4 cm were used in UV treatment

Table 3
Treatment conditions of performed hydroxyl radical producing processes

Type of performed hydroxyl radical producing processes	Treatment conditions	
Photolysis (UV)	254 nm UV-C 8 W, pH = 8.00	
Hydrogen peroxide (H ₂ O ₂)	30 mM H ₂ O ₂ ; pH = 7.98	
	60 mM H ₂ O ₂ ; pH = 7.96	
	90 mM H ₂ O ₂ ; pH = 7.96	
Homogenous photolysis (UV + H ₂ O ₂)	UV + 30 mM H ₂ O ₂ ; pH = 7.97	
	UV + 60 mM H ₂ O ₂ ; pH = 7.97	
	UV + 90 mM H ₂ O ₂ ; pH = 7.97	
Fenton (Fe ²⁺ -H ₂ O ₂)	0.04 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.08 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.12 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.14 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.18 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.36 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.95	
	0.36 Fe ²⁺ + 60 mM H ₂ O ₂ ; pH = 3.93	
	0.36 Fe ²⁺ + 90 mM H ₂ O ₂ ; pH = 3.93	
	Photo-Fenton (Fe ²⁺ -H ₂ O ₂ -UV)	0.04 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96
		0.08 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96
0.12 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96		
0.14 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96		
	0.18 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96	
	0.36 Fe ²⁺ + 30 mM H ₂ O ₂ ; pH = 3.96	

given in Fig. 1a. 400 mL model wastewater containing 1,000 mg/L TCEP was treated in a recycled flow operated at a flow rate of 25 mL/min during 90 min retention time, and time depended samples were taken from the system with 10 min intervals. TOC value of these samples was determined to calculate the removal efficiency of photolysis.

2.2. Homogeneous photolysis

Homogeneous photolysis (UV-H₂O₂) treatment was studied in the UV reactor given in Fig. 1a using three different H₂O₂ (Merck, Darmstadt, Germany 35% w/w) concentrations. The H₂O₂ concentrations were adjusted as 30, 60 and 90 mM H₂O₂ in model wastewater solution containing

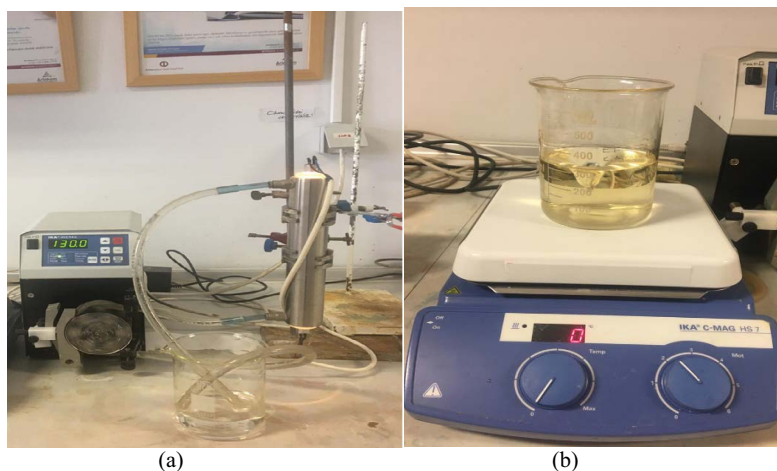


Fig. 1. Hydroxyl radical producing processes setup (a) photolysis, homogenous photolysis, photo-Fenton and (b) Fenton.

1,000 mg/L TCEP using suitable primary H_2O_2 stock solutions. During 90 min treatment period, the samples were collected from treated wastewater, and their TOC values were determined immediately.

2.3. Fenton

Fenton (Fe^{2+} - H_2O_2) studies were conducted in a UV reactor given in Fig. 1b using three different H_2O_2 (Merck, Darmstadt, Germany 35% w/w) concentrations and six different Fe^{2+} concentrations. The $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck Darmstadt, Germany, 99% w/w) was used as a Fe^{2+} source in the Fenton treatment process. Firstly, The H_2O_2 concentrations were adjusted as 30 mM in model wastewater solution containing 0.04, 0.08, 0.12, 0.14, 0.18 and 0.36 mM Fe^{2+} using suitable primary $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ stock solutions to determine the effect of Fe^{2+} concentration. Secondly, Fe^{2+} concentration was set to 0.36 mM in model wastewater differing to 90 mM from 30 mM H_2O_2 concentration to enhance removal efficiency of TCEP from wastewater.

2.4. Photo-Fenton

In the photo-Fenton studies, (UV-Fe^{2+} - H_2O_2), Fenton treatments detailed in Section 2.3 were performed in the

UV reactor given in Fig. 1a applying the same Fe^{2+} and H_2O_2 concentrations. During 60 min treatment period, the samples were collected from treated wastewater, and their TOC values were determined immediately.

3. Results and discussion

The treatment results of photolysis (UV), hydrogen peroxide (H_2O_2), homogenous photolysis ($\text{UV-H}_2\text{O}_2$), Fenton (Fe^{2+} - H_2O_2) and photo-Fenton (Fe^{2+} - H_2O_2 -UV) advanced oxidation process were given in this section debating TOC removal and cytotoxicity reduction. The effects of photolysis (UV), H_2O_2 and homogenous photolysis ($\text{UV-H}_2\text{O}_2$) on TOC removal are given in Fig. 2.

When examining the effect of hydroxyl-producing processes on OP-FRs removal modeled with TCEP, it was observed that the degradation ability of H_2O_2 was limited even if its concentration was increased up to 90 mM from 30 mM. While TOC removal efficiency was determined as 22.9% in photolysis (UV) treatment, in the homogenous photolysis ($\text{UV-H}_2\text{O}_2$) process, 33.4%, 75.0% and 85.4% removal efficiencies were determined differing with 30 mM H_2O_2 , 60 mM H_2O_2 , and 90 mM H_2O_2 concentration respectively.

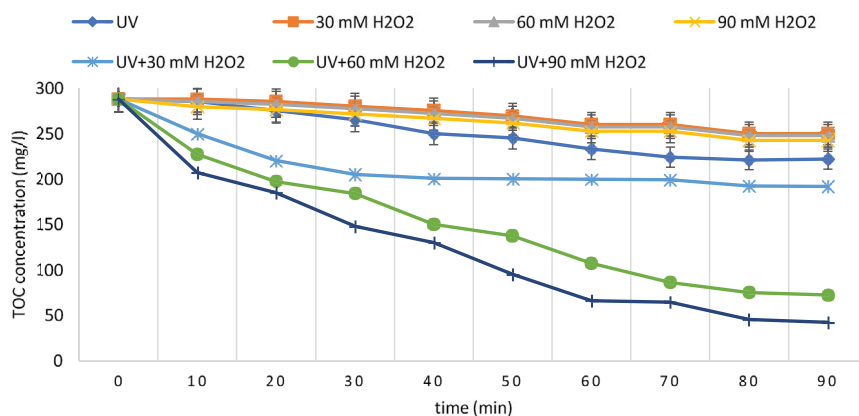


Fig. 2. Effects of UV, H_2O_2 and $\text{UV-H}_2\text{O}_2$ treatments (initial wastewater pH \approx 7.97).

Watts and Linden [35] studied photooxidation and subsequent biodegradability of TCEP and tri-*n*-butyl phosphate (TNBP) in water, which is commonly listed among a class of emerging contaminants associated with wastewater pollution of our freshwater resources as the halogenated, non-biodegradable organic compound. They used UV irradiation (254 nm), and 50 mg/L H_2O_2 to the removal of 5 mg/L TCEP and TNBP before the biodegradable organic carbon assays (BDOC) aiming the conversion of TOC to BDOC with photolysis. BDOC was determined with TOC analyses using the differences between the 0 d TOC value and 5 d TOC values. For 96% oxidation of 5 mg/L initial TCEP concentration, they reported the 100% Cl^- release, 20% removal TOC in treated waters. Also, they stated that UV- H_2O_2 oxidation of TCEP/TNBP would not be expected to impact pH or chloride concentrations. After UV- H_2O_2 oxidation of the TCEP/ converted to likely in non-halogenated aldehyde form, and these oxidation products is an available carbon source for bacterial growth. As it was seen in this study, while TCEP could be removed over 95% with the UV- H_2O_2 process, the removal efficiency of TOC might remain around 20% because TCEP was transformed into different intermediate organic by-products while being removed. Therefore, the organic matter could not be effectively removed although TCEP removal was provided, and moreover these by-products are generally more toxic than the initial pollutant to be removed. Therefore, while optimizing advanced oxidation processes such as hydroxyl production processes, it is necessary to monitor the organic matter that may be formed by treatment and TOC is an appropriate parameter for monitoring the organic matter. This presented study has investigated the performance of the different hydroxy radical producing processes on the degradation of TCEP, and the system performance was identified with TOC analyses to determine all organic degradation products of TCEP in addition to the easy application and optimization suitability of TOC.

Abdullah and O'Shea [36] investigated heterogeneous photocatalytic degradation (UV- TiO_2) of TCEP. Using UV (350 nm) and 10 mg TiO_2 particles for 30 μM , 100 mL TCEP solution. They demonstrated excellent Cl^- (98%) and

phosphate (PO_4^{3-}) (94%) using ion chromatography. They reported that the removal efficiency of TOC was higher than 95% after 120 min treatment period. The most important finding of their results is that the halogenated organophosphate esters are composed of carbon, hydrogen, oxygen, phosphorus, and halogen atoms. They explained that the formation of the main diester type compound of TCEP with three different mechanisms using an NMR spectrometer. These mechanisms were listed as hydrogen atom abstraction, electrophilic addition to the double bond, and electron transfer from a degradation product as a result of the reaction between hydroxyl radical (OH) and organic molecules [36]. Semiconductor particle used in heterogeneous photocatalysis is known to cause the decreasing effect of UV radiation due to light scattering. For this reason, even if high removal efficiencies obtain in TCEP degradation, the fact that the molecule cannot be oxidized completely, and is the most important problem in the heterogeneous photocatalytic degradation (UV- TiO_2). Because toxic or more toxic intermediate products and by-products can occur as much as TCEP. For this reason, homogeneous photocatalysis is more advantageous than heterogeneous systems.

Ruan et al. [37] were studied TCEP degradation with homogeneous photocatalytic degradation. They reported that light intensity, initial pH and concentration of TCEP and H_2O_2 , and reaction time affected the degradation efficiency of TCEP. The TOC removal rates, and the yield rates of Cl^- and PO_4^{3-} reached up to 86%, 94% and 97%, respectively, under the optimized conditions in their present study. TCEP molecules were converted to chlorinated alcohol/aldehyde, and/or non-chlorinated aldehyde with a small molecular weight with homogeneous photocatalytic degradation (UV- H_2O_2). Finally, these produced small organic molecules were oxidized to acids, most of them were finally mineralized to CO_2 and H_2O according to their GC-MS finding.

As it could be realized in the summarized studies on OP-FR removal in the literature above, they have been studied from μM to a few mg/L TCEP concentration. The main reason for using a high TCEP concentration of 1,000 mg/L in this presented study was that the

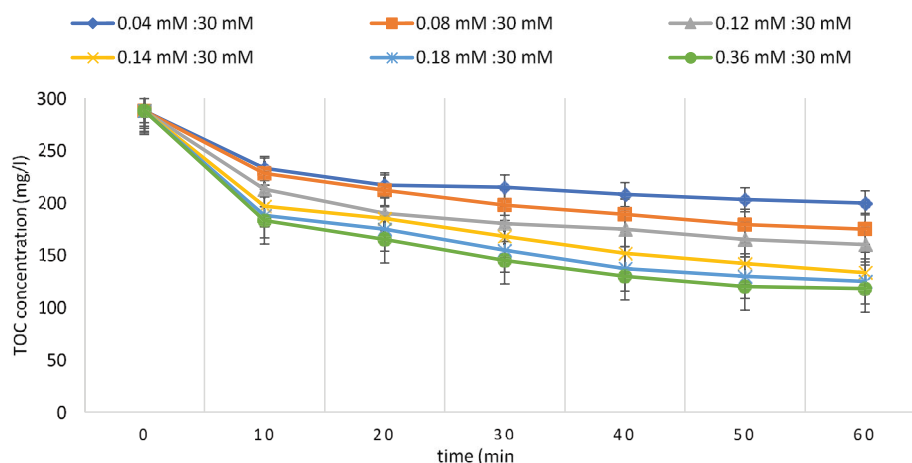


Fig. 3. Effect of Fe^{+2} concentration in Fenton treatments when H_2O_2 concentration set as 1,000 mg/L (scale was indicated Fe^{+2} concentration: H_2O_2 concentration; pH \approx 3.95).

performances of the used treatment processes could be compared more easily in contrary to the literature. Also, these experiments were conducted with 1,000 mg/L TCEP even if the amount of TCEP found in water and wastewater bodies changed from ng/L to several mg/L because the removal performance capacities of the used hydroxy radical producing processes were shown in a more distinctive way. The high-water solubility of TCEP also enabled to a demonstration of the difference in the removal capacity of these processes. Unlike the two studies summarized above, this study presented that the purification performance of the homogeneous photocatalysis process at higher pollutant concentration. These results summarized above correlated our TOC removal efficiencies determined in photolysis (UV) and homogenous photolysis (UV-H₂O₂) treatment. It is expected that obtaining high removal efficiency for higher initial TCEP concentration is required high H₂O₂ concentration obviously. The 30 mM, 60 mM and 90 mM H₂O₂ concentrations were used in our study for 1000 mg/L TCEP. This showed that increasing the H₂O₂ concentration had a favorable effect on the TOC removal efficiency in the homogenous photolysis (UV-H₂O₂) treatment.

Fenton was the most used hydroxy producing process with high removal performance when toxic micropollutants like TCEP. The Fenton process can be carried out requiring any operating costs in the chemical treatment unit, which already present in the treatment plan. The Fenton process generally takes place in four stages: pH adjustment, oxidation reaction, neutralization, and coagulation-precipitation [32]. These stages can be performed in the chemical coagulation–flocculation unit in the treatment plant. The removal efficiency of the Fenton process was investigated for this TCEP wastewater with TOC analyses. Also, the effects of different Fe²⁺ concentrations on TOC removal are given in Fig. 3 in Fenton (Fe²⁺-H₂O₂) studies to show the single effect of Fenton on TCEP removal.

When the H₂O₂ concentration was set as 30 mM, the TOC removal efficiency raised to 59.0% from 30.6% as the concentration of Fe²⁺ was raised from 0.04 to 0.36 mM. It was determined that the applied Fe²⁺ concentrations showed the same TOC removal trend.

In order to determine the H₂O₂ concentration effect on the Fenton process, 30, 60 and 90 mM H₂O₂ was used to enhance TOC removal when the Fe²⁺ concentration was 0.36 mM, which provided the highest TOC removal in Fig. 4. It was determined that the applied H₂O₂ concentrations accelerated TOC removal due to increasing OH[•] radicals released by the reaction given in Eqs. (11)–(14). In Fig. 4, it was obviously seen that the H₂O₂ was totally depleted at 40 min when 30 mM H₂O₂ concentration was applied according to these equations. Increasing the H₂O₂ concentration was affected the equilibrium time and reaction rate of the decay. The efficiency of the Fenton process in TOC removal efficiency was determined by optimizing Fe²⁺ and H₂O₂ in the Fenton process. It was observed that increasing the concentration of H₂O₂ in the Fenton process indicated a greater effect on the TOC removal efficiency than Fe²⁺.

The Fenton process occurs under acidic conditions and there are many studies examining the effect of influent pH ranging from 2 to 4 [33]. Although the initial pH of the model working solution was around 7 in this study, the pH of working solutions fell dramatically below pH 4 due to its acidity after the addition of Fe²⁺ and H₂O₂. In this study, influent pH trials were not carried out and Fenton studies were carried out around the pH = 4 in order to avoid the use of the additional chemicals. The pH values measured in each treatment study were given in the relevant table and the footer note of all figures.

According to their results of the experiment conducted by Cetinkaya et al. [38], pH = 3, 100 mg/Fe²⁺, 2,200 mg/L H₂O₂ were found to be the best experimental values for Fenton process to attain 95% color removal similarly. In the further study, optimum conditions for Fenton process were found as pH = 3, [Fe²⁺] = 30 mg/L, [H₂O₂] = 50 mg/L as a result of the experiments conducted by Basturk and Karatas [39]. They reported that the optimum conditions for the Sono-Fenton process were to be pH = 3, [Fe²⁺] = 10 mg/L, [H₂O₂] = 40 mg/L rising color removal efficiency from 93.5% to 88% attained in the Fenton process [39].

In addition to these advantages of Fenton listed above, the release of additional Fe²⁺, Fe³⁺ and H₂O₂ chemicals to the water is a limiting factor in the use of Fenton treatment.

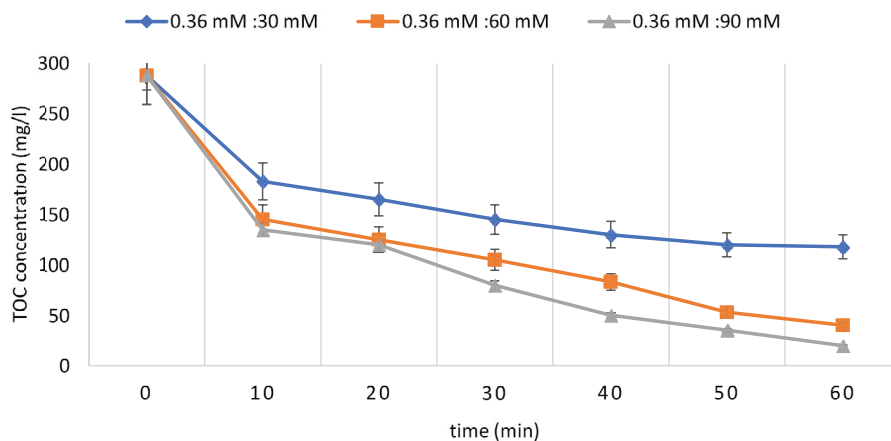


Fig. 4. Effect of H₂O₂ concentration in Fenton treatments when Fe²⁺ concentration set as 20 mg/L (scale was indicated Fe²⁺ concentration: H₂O₂ concentration; pH ≈ 3.93).

The $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ optimization studies used in Fenton treatment were performed for photo-Fenton studies ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) to decrease the chemical requirement in the hydroxyl radical producing processes. Even if the highest TOC removal efficiency obtained using $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio with 1:150 (0.36 mM Fe^{2+} and 90 mM H_2O_2) as a result of Fenton, photo-Fenton studies ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) were examined with 30 mM H_2O_2 . In this study, homogeneous photocatalysis was performed before the hybrid photo-Fenton study in order to determine the singular effect of homogeneous photocatalysis at high concentrations due to the high water solubility of TCEP. The effects of different Fe^{2+} concentrations on TOC removal were given in Fig. 5 in photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) studies to show the single effect of Fenton on TCEP removal. The organic loading rate of biological treatment can be reduced in chemical treatment units with totally oxidizing TCEP to CO_2 and H_2O converting homogenous photolysis ($\text{UV-H}_2\text{O}_2$) to hybrid photo-Fenton in the same unit.

The TOC removal efficiency was 99% in photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) treatment. The increasing Fe^{2+} concentration raised the removal efficiency in photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) treatment thanks to the increasing effect of UV on reaction rate and a mass transfer rate of Eqs. (11)–(14). While like Fenton treatment ($\text{Fe}^{2+}\text{-H}_2\text{O}_2$) provided the 93.1% TOC removal efficiency with 0.36 mM Fe^{2+} and 90 mM H_2O_2 concentration, photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) succeeded higher TOC removal with 0.18 mM Fe^{2+} and 30 mM H_2O_2 concentration.

As a result, the most important hesitation, which was the release high amount of Fe^{2+} , Fe^{3+} and H_2O_2 chemicals into the water body, about Fenton treatment in literature is eliminated with the hybrid photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) treatment. Even if the H_2O_2 can be depleted in water with sunlight, the usage of higher H_2O_2 dosage in water can cause more aggressive or reactive chemical species especially for high Cl^- containing wastewater. If the Fe is found in the water even with low concentration, it gives taste to water. Thus, the photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) treatment can be used as a more effective, environmentally friendly and health-protecting method if the advanced oxidation process is required for special pollutants

like TCEP can be found in water and wastewater at the point of reducing chemical.

The results of treatment studies were expressed as the average of three independent experiments with an error bar using standard deviation (SD). Each experiment was performed with three parallels. Statistical significance of the difference of each treatment study was determined by analysis of variance (ANOVA) using the two-way test. In order to show the reliability of measurement, the p -value obtained from the two-way ANOVA test was given in Table 4 for each treatment study. The results of the analysis of variance (ANOVA) using the two-way test, the p -value was calculated 0.3×10^{-11} within groups and the p -value was calculated 0.005 between groups. These values showed that there is no significant difference within groups of each three independent experiment because the p -value was lower than 0.05. To conclude, the two-way ANOVA test indicated that the hydroxyl radical producing processes on the degradation of TCEP gave reliable and repeatable results.

The effectiveness of single and hybrid hydroxyl radical producing processes used in the paper were compared in Fig. 6 with TOC removal efficiency. It was clearly stated the increasing effect of UV on reaction rate and mass transfer rate for the photo-Fenton ($\text{UV-Fe}^{2+}\text{-H}_2\text{O}_2$) treatment in Fig. 6, the reaction kinetics of these treatment methods were studied based on TOC removal according to pseudo-first-order kinetic giving in Fig. 7. According to Fig. 7, four type hydroxyl radical producing processes used in this work showed pseudo-first-order kinetic fitting high linear regression ($R^2 > 0.99$). The first-order reaction rates of photolysis, homogeneous photolysis, Fenton and photo-Fenton were determined as 0.004, 0.0076, 0.0125, and 0.0554 min^{-1} , respectively.

Similarly, Abdullah and O'Shea [36] reported that pseudo-first-order reaction kinetics was observed in TCEP degradation with heterogeneous photocatalytic degradation (UV-TiO_2). They found that the rate constants varied from 0.28 to 0.03 min^{-1} depending on the initial concentrations of TCEP, demonstrating the heterogeneous degradation process controlled by mass transfer (adsorption \leftrightarrow desorption) at the surface of TiO_2 . Also, Ruan et al. [37] informed that TCEP degradation with homogeneous

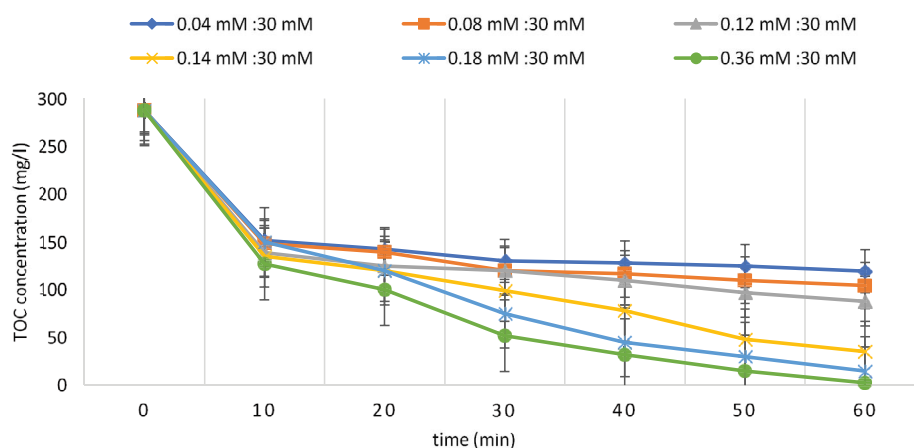


Fig. 5. Effect of Fe^{2+} concentration in photo-Fenton treatments (scale was indicated Fe^{2+} concentration: H_2O_2 concentration; $\text{pH} \approx 3.96$).

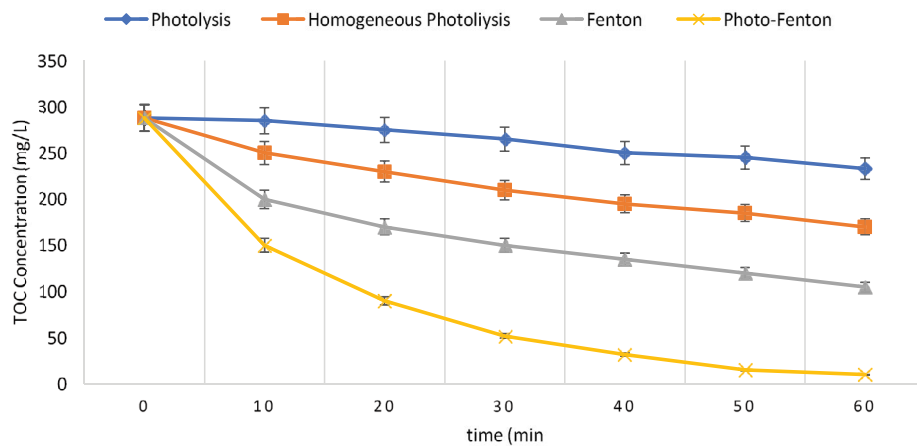


Fig. 6. Evaluation of the hydroxyl radical producing processes efficiencies on TOC removal.

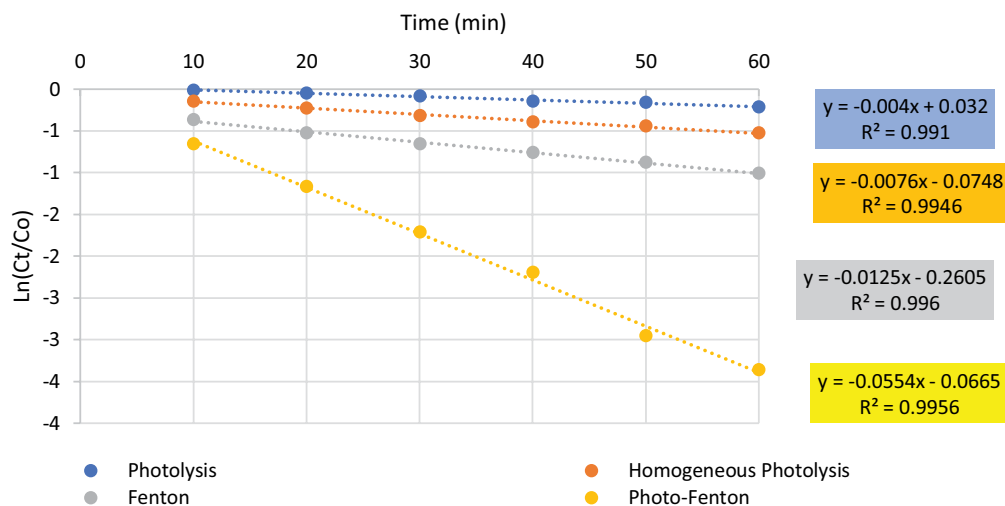


Fig. 7. Determination of reaction kinetics of advanced oxidation process based on TOC removal according to pseudo-first-order kinetic.

photocatalytic degradation (UV-H₂O₂) obeyed the pseudo-first-order kinetic reaction expressed as $\ln(C_t/C_0) = -0.0275t$ (R^2 of 0.9962) [37]. These results point out that synergistic effect UV and Fenton hybrid application was reduced Fe²⁺ and H₂O₂ concentration to attain the same yield in shorter treatment period for the reason that UV increases the production speed of hydroxyl radical via the increasing effect of mass transfer and reaction rate.

The toxicity reduction in parallel with TOC removal for TCEP containing wastewater are illustrated in Fig. 8.

Since the Fenton reaction occurs in the pH range between 2 and 4, the non-toxic organic load cannot be treated in this process should be neutralized if the wastewater sent to biological treatment. The toxicity test at this stage should be evaluated whether the intermediate products and by-products may occur in wastewater after Fenton treatment other processes to send biological treatment.

Toxicity assessment showed that 1,000 mg/L TCEP containing wastewater had a highly toxic effect on *Vibrio fischeri* bacteria. The phenol solution was used as control

according to Microtox Test Procedure with 50 mg/L concentration. The LC₅₀ concentration of untreated wastewater was calculated as 20 mg/L (2%). Xu et al. [40] determined the acute and chronic toxicity of TCEP and its degradation product after the oxidation in an aqueous solution by UV-activated peroxymonosulfate. They predicted by the ECOSAR that LC₅₀ concentrations of TCEP were listed as 5.1 mg/L indicating toxic effect, 102.6 mg/L indicating not harmful effect, and 13.9 mg/L indicating a harmful effect on fish, *Daphnia magna* and green algae respectively. They stated that the TCEP oxidation process was generally not harmful to three typical aquatic species. It was stated that the degradation of TCEP occurred with two or three-step chemical reactions, which included converting TCEP to firstly TCEP-diester, then TCEP-monoester, finally CO₂ with releasing of H₂O, PO₄³⁻ and Cl⁻, in literature [41,42]. The total degradation reaction of TCEP (C₆H₁₂Cl₃O₄) is given in Eq. (15). After the photo-Fenton treatment, PO₄³⁻ and Cl⁻ were probably mineralized to wastewater. After photo-Fenton treatment achieving 99% TOC removal, TCEP, TCEP-diester

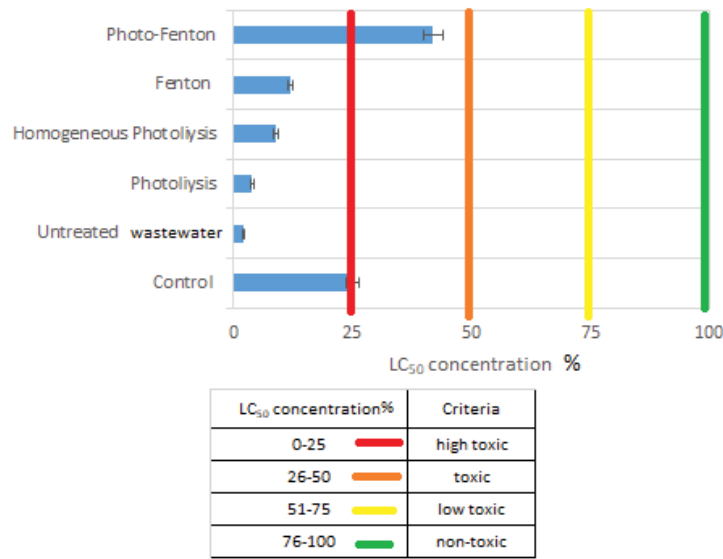
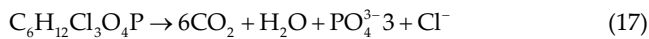


Fig. 8. Cytotoxicity evaluation of advanced oxidation process (phenol solution was used as control with 25 mg/L concentration).

or TCEP-monoester should remain in wastewater nearly 10 mg/L according to mass balance.



In this paper, even if the photolysis, homogenous photolysis and Fenton treatment slightly reduced the toxicity of untreated wastewater in parallel with TOC removal, the toxicity of wastewater was significantly decreased with photo-Fenton (UV-Fe²⁺-H₂O₂) treatment. However, the wastewater treated with photo-Fenton (UV-Fe²⁺-H₂O₂) still showed toxic characteristics after 99% TOC removal. The reason why the wastewater had a toxic character

can be that mineralization products (PO₄³⁻ and Cl⁻) can be converted to more aggressive or reactive chemical species.

4. Conclusion

In this study, the efficiency of different hydroxyl-producing treatment processes on OP-FR removal modeled with TCEP was investigated. Hydrogen peroxide, photolysis, Fenton, homogeneous photolysis, and photo-Fenton treatment methods were used for TCEP removal. Treatment performances of these treatment methods at high TCEP concentrations were compared. It was observed that the removal performance of H₂O₂ and UV methods was limited at high pollutant concentration. In Fenton process, the effects of

Table 4
ANOVA table and descriptive statistical values the treatment studies

ANOVA: two-way						
Summary	Number	Total	Average	Standard deviation		
Influent TOC concentration (mg/L)	3.00	864.00	288.00	207.36		
Effluent TOC concentration after photolysis (mg/L)	3.00	699.00	233.00	135.72		
Effluent TOC concentration after homogeneous photolysis (mg/L)	3.00	510.00	170.00	72.25		
Effluent TOC concentration after Fenton (mg/L)	3.00	315.00	105.00	27.56		
Effluent TOC concentration after photo-Fenton (mg/L)	3.00	30.00	10.00	0.25		
Trial 1	5.00	806.00	161.20	11,832.70		
Trial 2	5.00	765.70	153.14	10,679.01		
Trial 3	5.00	846.30	169.26	13,045.55		
ANOVA-descriptive statistical values						
Standard deviation resources	SS	df	MS	F	P-value	F-critic
In groups	141,992.40	4.00	35,498.10	1,200.00	3.83E-11	3.84
Between groups	649.64	2.00	324.82	10.98	0.005	4.46
Error	236.65	8.00	29.58			
Total	142,878.69	14.00				

Fe²⁺ and H₂O₂ concentration on system performance were examined obtaining more than 80% TOC removal efficiency by using 0.36 mM Fe²⁺ and 90 mM H₂O₂. It was detected that increasing the concentration of H₂O₂ is more effective than Fe²⁺ on the TOC removal efficiency in the Fenton process. With the hybrid-photo-Fenton process, the required Fe²⁺ amount decreased by 1/2 and the H₂O₂ concentration reduced by 1/3 for Fenton, when the TOC removal efficiency increased to 93.75%. As a result of toxicity studies, it was seen that the initial toxicity of wastewater decreased with treatment and the photo-Fenton method was the most effective method on toxicity removal. The effectiveness of these treatment methods on TOC removal efficiency was observed that hydrogen peroxide < photolysis < Fenton < homogeneous photolysis < photo-Fenton.

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