

Removal of TCEP from syntetic wastewater by coagulation, Electrocoagulation and Fenton

Fadime KARAER OZMEN ^{1*} (ORCID: <https://orcid.org/0000-0003-4423-205X>)

Abstract—Flame retardants were threatened human health by water, soil and air pollution and the halogenated and organophosphorus flame retardants are often seen in wastewater treatment facilities especily. Within the scope of this study, treatment of tris(2-chloroethyl) phosphate (TCEP), which are known as halogenated and organophosphorus flame retardants flame and it is often seen in wastewater treatment facilities with their concentrations varying from ng/l to mg/l, was investigated by using traditional and advanced treatment methods. Treatability of TCEP and removal efficiency was compared by chemical coagulation, electrocoagulation, adsorption, and Fenton oxidation and the serial and hybrid application of these methods. While the removal efficiency was found around % 30 by conventional treatment methods, the removal efficiency was increased to % 90 by using of advanced treatment methods.

Index Terms— tris(2-chloroethyl) phosphate (TCEP), coagulation, Electrocoagulation, Fenton, COD

I INTRODUCTION

Chemical pollutants in water and wastewater are causes negative effects on the environment and human health. Flame retardants are increasingly used in the plastics industry since 1970's [1]. Halogenated flame retardants chemicals such as, brominated, chlorinated and fluorinated compounds, was forbidden by EPA and WHO because of their harmful effects on environmental and public health, but they are still used in developing countries increasingly [2]. Flame retardants using in this industry; were threaten human health by water, soil and air pollution [3]. Specially halogenated and organophosphorus flame retardants are often seen in waste water treatment facilities [4].

Flame retardant or flame-retardant products aim to make the ignition difficult and prevent the spread of flame to save human from fire [5]. Textile materials easily ignite during the fire and cause the fire to grow. Therefore, the effort to ensure the safety of human life has made it compulsory to use flame retardant chemicals. Many of these chemicals used in textile have serious impacts on the environment and public health. The areas of use of flame-retardant textiles can be listed as houses (clothes, pajamas, bed linen, blankets, upholstery fabrics, carpets and curtains), offices, public buildings, areas for transportation purposes (clothes, tent cloths, parachutes, seat covers for vehicles such as airplanes, cars, trains, etc.), work places (related fire like industrial technician and fireman clothes) in many areas [6-8].

Halogenated flame-retardant chemicals includes VII. group elements in periodic table (F-, Cl-, Br- and I-) and they improve the flame resistance of textile enormously. They has been used since the 1930s for reasons such as cost-effectiveness and applicability to lots of polymer

[9]. They are most effective groups of flame-retardant chemicals and they affect in gas phase on fire. They raise the formation of smoke during combustion and lead to the formation of corrosive -toxic gases such as HCl and HBr [10]. They are extremely toxic on environmental and human health. It causes cancer in humans, hormonal disorders, neurotoxicity and effects on reproductive systems, also they are also observed in the aquatic environment [11-14].

Organophosphated (OP) compounds have replaced brominated flame retardants (BFRs) due to their technical properties and have been widely used worldwide in recent years [15]. OPs are widely used as flame retardants, plasticizers and antifoam agents in a variety of industries including plastics, furniture, textiles, electronics, construction, vehicles and petroleum industries [16]. Mostly used OPs are Tris (2-kloroetil) phosphate (TCEP), Tris (2-kloroizopropil) phosphate (TCIPP), Tris (1, 3-dikloro-2-propil) phosphate (TDCPP), Tritely phosphate (TEP), Tripropil phosphate (TPP), Tri-n-butyl phosphate (TNBP), Tri-iso-butyl phosphate (TIBP), Trikresil phosphate (TMPP, Triphenyl phosphate (TPHP) [17]. TCEP is most used organophosphated flame retardant additives in lots of areas. TCEP is considered as non-biodegradable. It is seen that the almost 100 % of TCEP remains in water rather than sludge. In the treatment of wastewater, TCEP degradation rate is very low under aerobic and anaerobic conditions. TCEP was also detected in groundwater affected by rainwater, runoff and rainwater infiltration [18]. They are transported with atmospheric conditions to water and soil environment. Organophosphated flame retardants were also detected in the aquifer parts in ground water. Previous studies indicated that TCEP was found

*Corresponding author mail: fadimek@eskisehir.edu.tr (<https://orcid.org/0000-0001-7565-3899>)

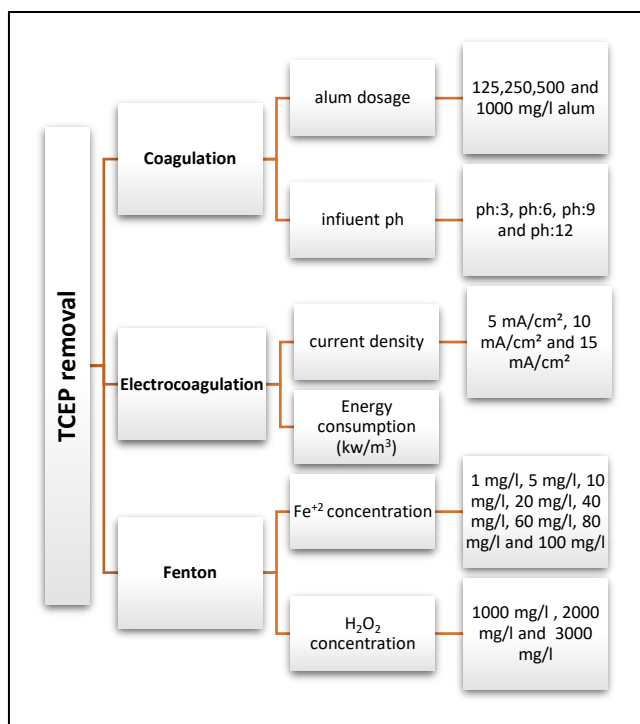
Department of Environmental Engineering, Eskişehir Technical University, Eskişehir Technical University İki Eylül Campus, 26555, Eskişehir, TURKEY

in domestic waste water, industrial waste water, drinking water, surface water (such as streams, rivers, lakes), groundwater, rain waters and dust samples taken from houses varying its concentration from ng/l to mg/l [19].

Within the scope of this study, treatment of tris(2-chloroethyl) phosphate (TCEP), which are known as halogenated and organophosphorus flame retardants flame and it is often seen in wastewater treatment facilities with their concentrations varying from ng/l to mg/l, was investigated by using traditional and advanced treatment methods. Treatability of TCEP and removal efficiency was compared by chemical coagulation, electrocoagulation, adsorption, and Fenton oxidation and the serial and hybrid application of these methods.

II MATERIALS AND METHODS

The schematic diagrams of the studied for TCEP removal was illustrated in the Figure 1.



A Chemicals and reagents

Properties of TCEP flame retardants were given in Table 1. 1000 mg/l Tris(2-chloroethyl) phosphate ($C_6H_{12}Cl_3O_4P$, 97%, Sigma Aldrich, Germany) solution was used for treatment studies. All solutions were prepared in distilled water. Sodium sulphate (Na_2SO_4 , 100%), iron (II) chloride ($FeCl_2$, 98%) sodium hydroxide ($NaOH$, 97%), hydrogen peroxide (H_2O_2 , 35%) and hydrochloric acid (HCl , 37%) were purchased from Merck (Darmstadt, Germany).

TABLE 1
Properties of Tris(2-chloroethyl) phosphate (TCEP)

Chemical structure		
Molecular Formula		$C_6H_{12}Cl_3O_4P$
Molecular weight		285.4898 g/mol
Density		1.385 g/cm ³
Purity		97%
Melting point		-51°C
Water solubility		7 g/L (20°C)
Vapour pressure		0.0045 mmHg (25°C)

TABLE 2
Characteristic of syntetic wastewater including TCEP

TCEP concentration (mg/l)	1000
COD (mg/l)	875
Influent pH	8
Conductivity ($\mu S/cm$)	34.10

B Chemical coagulation experiment

Alum ($Al_2(SO_4)_3 \cdot 18H_2O$) is used in chemical coagulation studies. Jar test apparatus used in chemical coagulation studies is given in Figure 1. 125,250,500 and 1000 mg/l alum were used in coagulant dosage optimization. pH optimization studies were performed at pH:3, pH:6(acidic pH); pH:9 –pH:12 (basic pH). Flocculation: 100 rpm at 1 min, Coagulation: 30 rpm at 15 min, Sedimentation: no mixing at 30 min.

C Electrocoagulation experiments

Electrocoagulation studies were performed in a sample volume of 400 ml, at a stirring speed of 200 rpm, using Al-Al electrodes. EC experimental setup consists of DC power supply (Statron, Type 3262), pH meter (Thermo Scientific, Orion STAR A215) and magnetic stirrer (Heidolph, MR3001). The initial pH of the solution was adjusted by using 0.1 M NaOH or 0.1M HCl. Electrocoagulation studies was performed in monopolar batch reactor consist of 6 parallel aluminum electrodes with total surface area of 100 cm². In electrochemical treatment studies, COD removal and energy consumption were determined at current density values of 5 mA/cm², 10 mA/cm² and 15 mA/cm² using 10 mM Na_2SO_4 during 60 min.

D Fenton experiments

FeCl₂ (Merck) as sources of Fe⁺² and H₂O₂(Merck) chemicals were used for Fenton process. Firstly, 1 mg/l, 5 mg/l, 10 mg/l, 20 mg/l, 40 mg/l, 60 mg/l, 80 mg/l and 100 mg/l Fe⁺² concentration applied to the syntetic waste water with 1000 mg/l H₂O₂ to optimize iron concentration. Secondly, 1000 mg/l, 2000 mg/l and 3000 mg/l H₂O₂ concentration applied to the syntetic waste water to optimize H₂O₂ concentration with 20mg/l Fe⁺² concentration during 60 min.

At the beginning of the study (t=0) and at certain intervals throughout the studies, samples were taken from the reactor and Chemical Oxygen Demand (COD) analysis was performed for TCEP utilization in the three treatment studies. The COD analyzes were carried out according to the Turkish Standard-TS 2789 Water Quality-Determination of Chemical Oxygen Demand.The COD removal was used to evaluate treatment efficiency. It was calculated according to the following Equation (1);

$$\text{Removal efficiency (\%)} = \frac{(\text{COD}_0 - \text{COD}_t)}{\text{COD}_0} \times 100 \quad (1)$$

where, COD₀ is initial COD of herbicide solution (mg/l), COD_t is COD concentration at time t (mg/l).

III RESULTS AND DISCUSSION

A Results of chemical coagulation

The optimization results of alum dosage were given in Figure 2 and the optimization results of influent pH was given Figure 3.

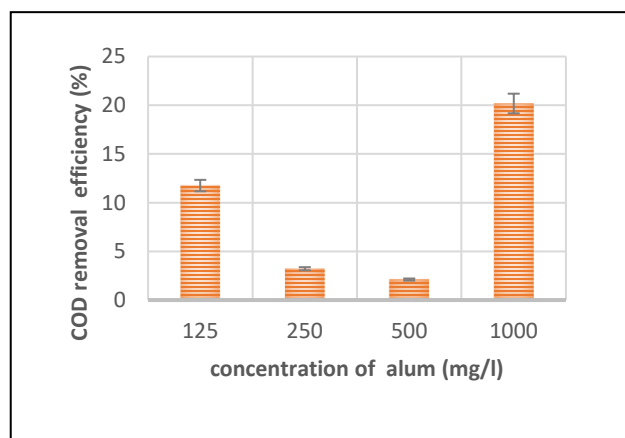


Figure 2. The optimization results of coagulant dosage at pH 8 (no pH adjusting)

In chemical coagulation studies performed with alum, the optimum dosage was found to be 1000 mg /L with 22% TCEP removal efficiency.

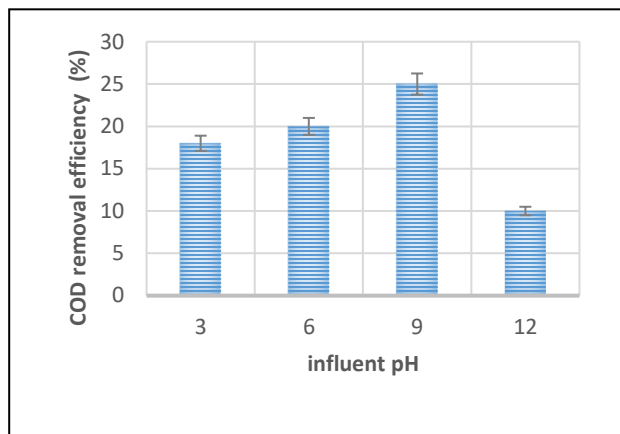


Figure 3. The optimization results of pH for coagulation with 1000 mg/l alum concentration

In chemical coagulation studies performed with alum, optimum pH was found as 9 with 26 % TCEP removal efficiency. In chemical coagulation studies, the optimum dosage was found as 1000 mg / L alum and the optimum pH was found as 9. In the literature, it was determined that alum gave the best removal efficiency in the range of 6-9 pH depending on the wastewater characteristics. However, It is difficult to remove toxic organic compounds, which are resistant to biological treatment by conventional wastewater treatment methods like chemical coagulation like TCEP. Therefore, the electrocoagulation could be an alternative method to chemical coagulation providing high efficiency to reduce these organic pollutants [20].

B Results of Electrocoagulation

The effect of current density on Electrocoagulation removal efficiency was given in Figure 4 and its effect on energy consumption was illustrated in the Figure 5.

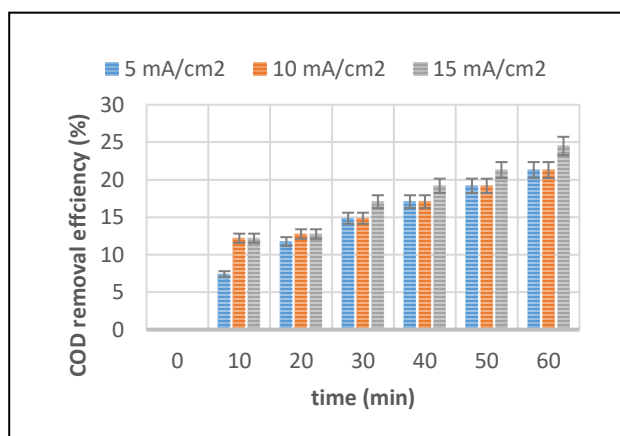


Figure 4. Effect of current density on electrocoagulation (C₀=1000 mg/l TCEP, natural pH)

The optimum current density was selected with 10 mA/cm² as a result of the effect of current density on COD removal and energy consumption. A treatment yield of 21% was obtained under these conditions.

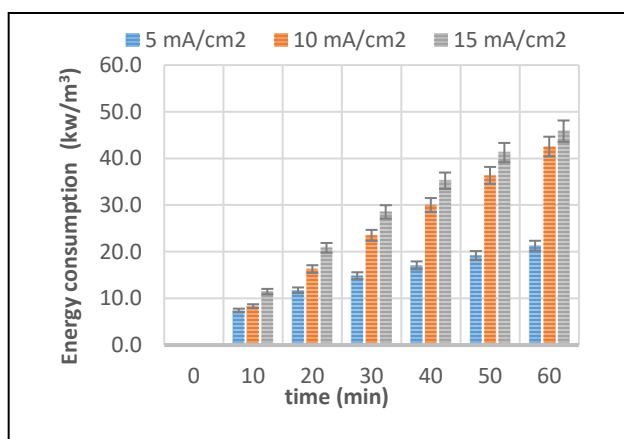


Figure 5. Effect of current density on energy consumption ($C_0=1000$ mg/l TCEP, natural pH)

In literature, 65% of suspended solids can be removed by chemical coagulation, but only 35% of dissolved organic compounds can be removed. TCEP is an organic compound soluble in water up to 7000 mg/l. Therefore, the removal efficiency remained around 30% by electrochemical coagulation. The reason is that TCEP dissolves on a molecular basis and it is observed that effective removal efficiency cannot be achieved by electrochemical coagulation. Abdullah and O'Shea investigated heterogenous photocatalytic degradation (UV-TiO₂) of TCEP. Using UV (350 nm) and 10 mg TiO₂ particles for 30 μM, 100 ml TCEP solution [21]. They demonstrated by excellent Cl⁻ (98%) and phosphate (PO₄³⁻) (94%) using ion chromatography. They reported that light intensity, initial pH and concentration of TCEP and H₂O₂, and reaction time affected the degradation efficiency of TCEP. The total organic carbon (TOC) removal rates, and the yield rates of Cl⁻ and PO₄³⁻ reached up to 86%, 94% and 97%, respectively [22]. Therefore, it is possible to achieve higher removal efficiencies by using advanced oxidation methods such as UV, ozone and Fenton oxidation rather than electrocoagulation.

C Results of Fenton

Fenton oxidation methods have been developed to eliminate organic pollutants in wastewater. The Fenton process is a homogeneous oxidation process that produces hydroxyl radicals (OH⁻) under acidic conditions [23]. Fenton and related reactions include the reaction of peroxides (usually H₂O₂) with iron ions (Fe⁺²) to form active oxygen species which oxidize organic or inorganic compounds. The effect of Fe⁺² concentration on Fenton treatment was given in Figure 5 while the effect of H₂O₂ concentration on the system was shown in the Figure 6.

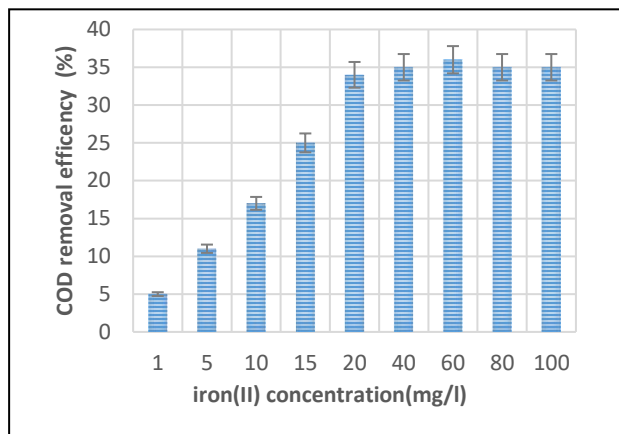
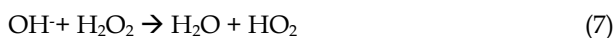
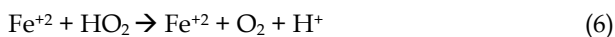
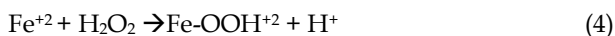
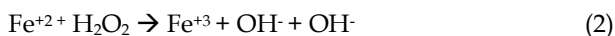


Figure 5. Effect of Fe⁺² concentration on COD removal

In Fenton studies, the optimum Fe⁺² concentration was found to be 20 mg/l with 34% TCEP removal efficiency. According to their results of the experiment conducted by Çetinkaya et al., pH = 3, 100 mg/ Fe⁺², 2200 mg/l H₂O₂ were found to be the best experimental values for Fenton process to attain 95% color removal similarly [24]. In the further study, optimum conditions for Fenton process were found as pH = 3, [Fe⁺²] = 30 mg/l, [H₂O₂] = 50 mg/l as a result of the experiments conducted by Basturk and Karatas [25]. Fenton reactions can be carried out at ambient temperature, the reagents are readily available, are easy to store, are relatively safe to use and environmentally friendly. Fenton reactions are widely used hydroxyl radical producing processes to remove most organic compounds. The iron ion initiates the decomposition of H₂O₂; and hydroxyl radicals are formed, after the formation of radicals in the form of a complex reaction chain (Equations 1-7) in aqueous solutions [26]. The resulting ferric ions catalyze hydrogen peroxide and decomposition of organic pollutant into water and carbon dioxide finally [27].



In Fenton studies, the optimum H₂O₂ concentration was found to be 3000 mg/l with 82% TCEP removal efficiency. 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.

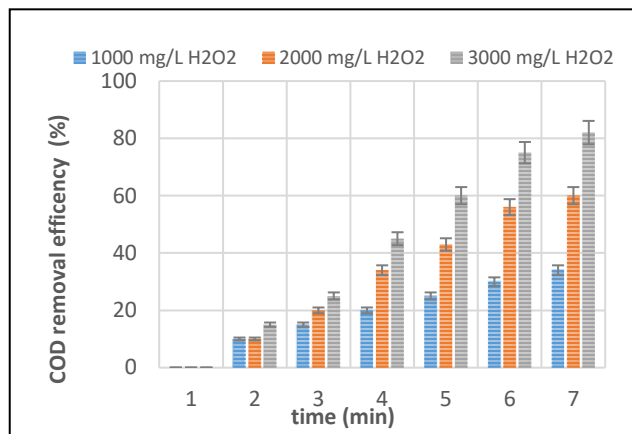
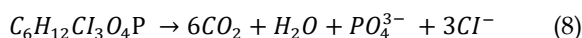


Figure 6. Effect of H₂O₂ concentration on COD removal

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. Xu et. all were determined the acute and chronic toxicity of TCEP and its degradation product after the oxidation in 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 harmful effect on fish, daphnia magna and green algae respectively. They stated that TCEP oxidation process were generally not harmful to three typical aquatic species [28]. It was stated that the degradation of TCEP occurred with two or three step chemical reactions, which they included converting TCEP to firstly TCEP-diester, then TCEP-monoester, finally CO₂ with releasing of H₂O, PO₄³⁻ and Cl⁻, in literature [29]. The total degradation reaction of TCEP (C₆H₁₂Cl₃O₄) was given in Equation 8. 15. After the Photo-Fenton treatment, PO₄³⁻ and Cl⁻ were probably mineralized to wastewater [30].



In Fenton treatment studies, TCEP removal was obtained as 82% explaining possible degradation way given in the E. TCEP, TCEP-diester or TCEP-monoester should be remained in wastewater nearly 180 mg/l according to mass balance. Fenton process is a treatment method that provides higher organic matter removal by oxidation of toxic biodegradable water-soluble organic compounds than the chemical coagulation and Electrocoagulation. In this study showed that TCEP can be successfully removed by Fenton.

IV CONCLUSION

It has been determined that the utilization efficiencies of chemical coagulation, Electrocoagulation and Fenton processes for TCEP, which is most used organophosphated flame retardant additives, removal from water. It has been determined that advanced treatment methods, like Fenton,

should be used where this chemical cannot be removed by conventional treatment. Chemical coagulation and Electrocoagulation cannot be used for organic materials dissolved in water on a molecular basis like TCEP. If the organic materials dissolved in water molecular basis, advanced oxidation processes should be selected like Fenton. Efficient, environmental, health and cost perspectives should be utilized when selecting the appropriate treatment method.

For future work suggestion, Electrochemical oxidation process can be used for TCEP such as, electro-oxidation, electro-Fenton and sono-electro-Fenton. Toxicological investigation of advanced treatment methods must be performed to ensure the minimization of treatment method risk. Other flame retardants can be found in aquatic environment must be investigated for treatability with conventional and advanced treatment methods.

REFERENCES

- [1] L.S. Birnbaum and D.F. Staskal, Brominated flame retardants: cause for concern, Environmental health perspectives, 112(1), 9-17, 2004.
- [2] S. Posner, Guidance on alternative flame retardants to the use of commercial pentabromodiphenylether (c-PentaBDE). Norwegian Pollution Control Authority (SFT), United Nations Environment Programme, United Nations, 2009.
- [3] T. Grover, A. Khandual, K.N. Chatterjee and R. Jamdagni, Flame Retardants: An Overview. Colourage, 61, 29-36, 2014.
- [4] A.R. Horrocks and D. Price, Fire retardant materials. Woodhead Publishing, England, 2001.
- [5] I. Van der Veen and J. De Boer, Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis, Chemosphere, 88(10), 1119-1153, 2012.
- [6] S. Shaw, Halogenated flame retardants: do the fire safety benefits justify the risks, Reviews on environmental health, 25(4), 261-306, 2010.
- [7] A. Innes and J. Innes, Flame retardants, In: Applied Plastics Engineering Handbook, William Andrew Publishing, pp. 469-485, 2011.
- [8] E.D. Weil and S.V. Levchik, Flame retardants in commercial use or development for polyolefins, Journal of Fire Sciences, 26(1), 5-43, 2008.
- [9] G.A. Knudsen, M.F. Hughes, K.L. McIntosh, J.M. Sanders and L.S. Birnbaum, Estimation of tetrabromobisphenol A (TBBPA) percutaneous uptake in humans using the parallelogram method, Toxicology and applied pharmacology, 289(2), 323-329, 2015.
- [10] T. Hamers, J.H. Kamstra, E. Sonneveld, A.J. Murk, M.H. Kester, P.L. Andersson, and A. Brouwer, In vitro profiling of the endocrine-disrupting potency of brominated flame retardants, Toxicological Sciences, 92(1), 157-173, 2006.
- [11] M. Döring and J. Diederichs, Halogen-free flame

- retardants in E&E applications, Forschungszentrum Karlsruhe, Germany, 2007.
- [12] A.B. Morgan, and J.W. Gilman, An overview of flame retardancy of polymeric materials: application, technology, and future directions, *Fire and Materials*, 37(4), 259-279, 2013.
- [13] W. Wanzke, B. Nass, O. Schacker and E. Schlosser, Phosphorus containing flame retardants-Compounding and material properties. In *Flame retardants*, 10, 63-74, 2002.
- [14] G. Camino, L. Costa, and L. Trossarelli, Study of the mechanism of intumescence in fire retardant polymers: Part I—Thermal degradation of ammonium polyphosphate-pentaerythritol mixtures, *Polymer Degradation and Stability*, 6(4), 243-252, 1984.
- [15] C.D. Papaspyrides, and P. Kiliaris, *Polymer green flame retardants*, Elsevier, UK, 2014.
- [16] S. Hörold, S., Phosphorus-based and intumescent flame retardants, in *Polymer Green Flame Retardants*. Elsevier, pp. 221-254, 2014.
- [17] M. Lewin and E.D. Weil, Mechanisms and modes of action in flame retardancy of polymers, *Fire retardant materials*, 1, 31-68, 2014.
- [18] N. Honda, and T. Sugiyama, Halogen-free flame-retardant epoxy resin composition, U.S. Patent No. 5,994,429, DC: U.S. Patent and Trademark Office, Washington, 1999.
- [19] M. Sorais, M.J. Mazerolle, J.F. Giroux, and J. Verreault, Landfills represent significant atmospheric sources of exposure to halogenated flame retardants for urban-adapted gulls, *Environment International*, 135, 1-10, 2020.
- [20] S. Ameta and R. Ameta, *Advanced oxidation processes for wastewater treatment: Emerging green chemical technology*. Academic Press, Elsevier, 2018.
- [21] A.M. Abdullah and K.E. O’Shea, TiO₂ photocatalytic degradation of the flame-retardant tris (2-chloroethyl) phosphate (TCEP) in aqueous solution: A detailed kinetic and mechanistic study, *Journal of Photochemistry and Photobiology A: Chemistry*, 377, 130-137, 2019.
- [22] X.C. Ruan, R. Ai, X. Jin, Q.F. Zeng and Z.Y. Yang, Photodegradation of tri (2-chloroethyl) phosphate in aqueous solution by UV/H₂O₂. *Water, Air, & Soil Pollution*, 224(1), 1406, 2013.
- [23] J.J. Pignatello, E. Oliveros, and A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Critical reviews in environmental science and technology*, 36(1), 1-84, 2006.
- [24] Cetinkaya S.G., Morcali M.H., Akarsu S., Ziba C.A., Dolaz M., “Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater”, *Sustainable Environment Research*, 28(4), 165-170, 2018.
- [25] Basturk E., Karatas M., “Advanced oxidation of Reactive Blue 181 solution: A comparison between Fenton and Sono-Fenton Process”, *Ultrasonics Sonochemistry*, 21(5), 1881–1885, 2014.
- [26] H. Hansson, F. Kaczala, M. Marques and W. Hoggland, Photo-Fenton and Fenton Oxidation of Recalcitrant Wastewater from the Wooden Floor Industry, *Water Environment Research*, 87(6), 491-497, 2015.
- [27] A.S. Kopal, Sulardan Ultrases, Fenton ve Sono-Fenton Prosesleri ile Renk Giderimi, *Anadolu University of Sciences & Technology-B: Theoretical Sciences*, 6(2), 164-176, 2018.
- [28] X. Xu, J. Chen, R. Qu and Z. Wang, Oxidation of Tris (2-chloroethyl) phosphate in aqueous solution by UV-activated peroxymonosulfate: kinetics, water matrix effects, degradation products and reaction pathways, *Chemosphere*, 185, 833-843 (2017), .
- [29] J. Liu, J. Ye, Y. Chen, C. Li and H. Ou, UV-driven hydroxyl radical oxidation of tris (2-chloroethyl) phosphate: Intermediate products and residual toxicity, *Chemosphere*, 190 (2018) 225-233.
- [30] J. Ye, J. Liu, C. Li, P. Zhou, S. Wu, and H. Ou, Heterogeneous photocatalysis of tris (2-chloroethyl) phosphate by UV/TiO₂: Degradation products and impacts on bacterial proteome. *Water research*, 124 (2017) 29-38.

Dr. Fadime KARAER ÖZMEN is lecturer at the Department of Environmental Engineering, Faculty of Engineering, Eskişehir Technical University, Eskişehir, Turkey. Her research interests include environmental toxicology, environmental microbiology, water and wastewater treatment technologies.