APPLICABILITY OF SULFATE RADICAL BASED ADVANCED OXIDATION PROCESSES FOR DRINKING WATER TREATMENT

Dilsizoğlu-Akyol N.[1], Ölmez-Hancı T.[1]

[1]İstanbul Technical University, Department of Enviromental Engineering, Maslak/İstanbul

Corresponding author: Nergis Dilsizoğlu Akyol
e-mail: dilsizoglu18@itu.edu.tr

Abstract Natural Organic Matter (NOM) is a complex mixture of organic compounds that are naturally present in water sources. NOM itself is not toxic, but its presence can have negative impacts on the quality of drinking water. It is important to remove NOM from drinking water sources through various treatment processes, such as coagulation, sedimentation and filtration, in order to ensure that the water is safe and aesthetically pleasing for consumption. "Advanced Oxidation Processes" is one of the promising treatment technology to remove NOM in drinking water sources. The aim of this study is to examine the effects of sulfate radical ($SO_4^{\bullet-}$) based photochemical oxidation process (persulfate/UV-C) on the efficiency of organic carbon removal from drinking water sources. In the present study the effect of the initial oxidant concentration on the total organic carbon (TOC) removal efficiency, residual oxidant concentration, alteration of pH and UV_{254} were examined. Moreover, particle size distribution (PSD) analysis was applied to determine treatment efficiency of each particle size during oxidation process. All experiments were conducted in raw water that originated from a drinking water treatment plant located in İstanbul. According to the experimental studies, it was observed that organic carbon was effectively removed (55%) during the reaction time of 60 minutes by using PS/UV-C at an initial oxidant concentration of 1.0 mM. According to PSD analysis, all particles are smaller than 450 nm and approximately 60% of them were removed by using PS/UV-C process. In experimental studies, decreasing of pH (from 8.3 to 6.5) and UV_{254} (from 0.097 to 0.013) shows that degradation of TOC. In conclusion, sulphate radical-based photochemical advanced oxidation processes can effectively provide degradation of organic carbon in natural waters.

Keywords: Advanced oxidation processes, drinking water treatment, organic carbon degradation, persulfate, UV-C light.
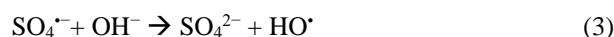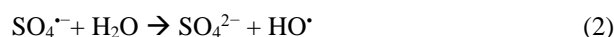
1. Introduction

The presence of organic matter in water is the most important factor affecting water quality. The effects of organic matter on conventional drinking water treatment plants have been investigated by researchers for many years. (Poyatos et al., 2009). Organic matter in water cause undesirable problems in many cases such as color, taste and odor problem in drinking water systems, changing of microbiological quality negatively, necessity of additional treatment units etc. (Chow et al., 2006). For this reason, organic matter removal is becoming more and more important day by day.

Today, several advanced water treatment methods have been used to remove organic matter from drinking water, including modified coagulation-flocculation, electrocoagulation, photocatalytic treatment and advanced oxidation processes (Goslan et al., 2006; Vilhunen et al., 2010). Therefore, advanced oxidation processes (AOPs) have become more prominent in the treatment of various organic and inorganic contaminants (Budaev et al., 2021). There are many advanced oxidation processes include fenton, photo-fenton, photolysis, ultraviolet etc. that are used to degrade refractory organic pollutants in wastewater by strong oxidants (ozone, hydrogen peroxide, free radicals etc.). (Olmez-Hanci et al., 2014; Tian et al., 2021).

Recently, many researches show that efficient methods to generate highly reactive sulfate radicals $SO_4^{\bullet-}$ are by activating PS through exposure to ultraviolet (UV) light in sulfate radical-based AOPs (SR-AOPs) (Budaev et al., 2021). Common organic pollutants are oxidized to polar and harmless compounds through these technologies and mineralized CO_2 and H_2O (Yang et al., 2019). The peroxide bond can break and form two sulfate radicals as indicated in Eq. 1 for PS (Saien and Jafari, 2022). In an aqueous solution, the part of $SO_4^{\bullet-}$ can spontaneously transform into $HO^{\bullet}$ depending on the pH (Eq. 2). At alkaline pH values, a stronger conversion can take place (Eq. 3).

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet-} \tag{1}$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + HO^{\bullet} \tag{2}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + HO^{\bullet} \tag{3}$$

2. Materials and Methods

2.1. Chemicals and reagents

In PS/UV-C experiments, potassium persulfate ($K_2S_2O_8$, >99.5%) purchased from Sigma Aldrich. All the other chemicals were used in analytical grade.

2.2. Sampling

A drinking water treatment plant (Istanbul, Turkey) with a capacity of 400,000 m^3/day, provided the raw water. In **Table 1**, the characterization of raw water was given.

Table 1. Raw water characterization

Parameter	Unit	Raw Water
pH	-	7.64
TOC	mg/L	4.64
UV254	cm^{-1}	0.07
Turbidity	NTU	9.55
Free Chlorine	mg/L	<0.20
Chloride	mg/L	103.7
Conductivity	25°C µS/cm	613
Color	mg/L Pt-Co	9.1
Total Alkalinity	mg CaCO$_3$/L	139
Total Hardness	mg CaCO$_3$/L	224
Ammonia	mg/L	0.05
Ammonium	mg/L	<0.05
TDS	mg/L	299
Bicarbonate	mg/L	169.6
Calcium	mg/L	61.7
Magnesium	mg/L	17
Sodium	mg/L	65.1
Potassium	mg/L	5.68
Sulfate	mg/L	91.5
Nitrate	mg/L	0.59
Nitrite	mg/L	<0.02

2.3. Batch experiments

Each experiment was carried out in a 500 mL three-neck quartz flask at room temperature (25±2 °C) by using a Luzchem UV device equipped with a digitally controlled thermometer, a digital timer, a power meter and a magnetic stirrer. All experiments were performed with the original pH of the raw water sample. The radiation fluxes in the UV-C reactor were monitored at the beginning and end of the experiment by using a power meter, and the optimum condition was set at 10 lamps.

The experiments were repeated with different initial PS concentrations (0.0 mM, 0.1 mM, 0.2 mM, 0.5 mM, and 1.0 mM) and time intervals (0, 15, 30 and 60 min) in

order to examine the effect of operating conditions on the total organic carbon (TOC) removal efficiency. In addition, samples were filtered directly through 0.45 µm millipore membranes to analyse UV$_{254}$, residual PS concentrations and pH.

2.4. Analytical methods and instrumental analysis

TOC was measured by a Shimadzu V$_{CPN}$ analyzer (Japan). The UV$_{254}$ measurements were performed with a Schimadzu UV-1800 spectrophotometer at a wavelength of 254 nm with a 1 cm quartz cell. Residual PS concentration was determined by a colorimetric procedure (Arslan-Alaton et al., 2018). pH measurements were carried out with the Thermo Orion 720A+ pH meter.

PSD analysis was performed by consecutive filtration and ultrafiltration experiments conducted under positive pressure (0.6-1.2 atm) using N$_2$ as inert gas in a continuously mixed cell with a capacity of 400 mL to physically separate all particles. Typical filters with pore diameters of 1200–1600 nm (Millipore AP40, glass fiber), 450nm (Durapore HV, PVDF), and 220 nm (Durapore GV, PVDF) were used to filter the samples consecutively (Millipore Corp., Bedford, MA 01730).

Ultrapure water for the chromatographic measurements was prepared with an Arium 611UV water purification system (Sartorius AG, Germany).

3. Results and Discussion

3.1. PS/UV-C treatment

The effect of initial PS concentration on the removal efficiency of TOC (%) was given in **Fig. 1a**. Control experiment was conducted by using only PS (1.00 mM) without UV-C irradiation. As a result of this control experiment, decreasing of TOC concentration can not be determined. On the other hand, another control experiment was conducted by using only UV-C irradiation. The control experiment results show that TOC concentration is decreased to 3.9 mg/L from 4.7 mg/L (Removal efficiency = 17%). Additionally, TOC removal efficiency increased with increasing initial concentration PS during the PS/UV-C process, and reached 55% in the reaction time of 60 minutes in the
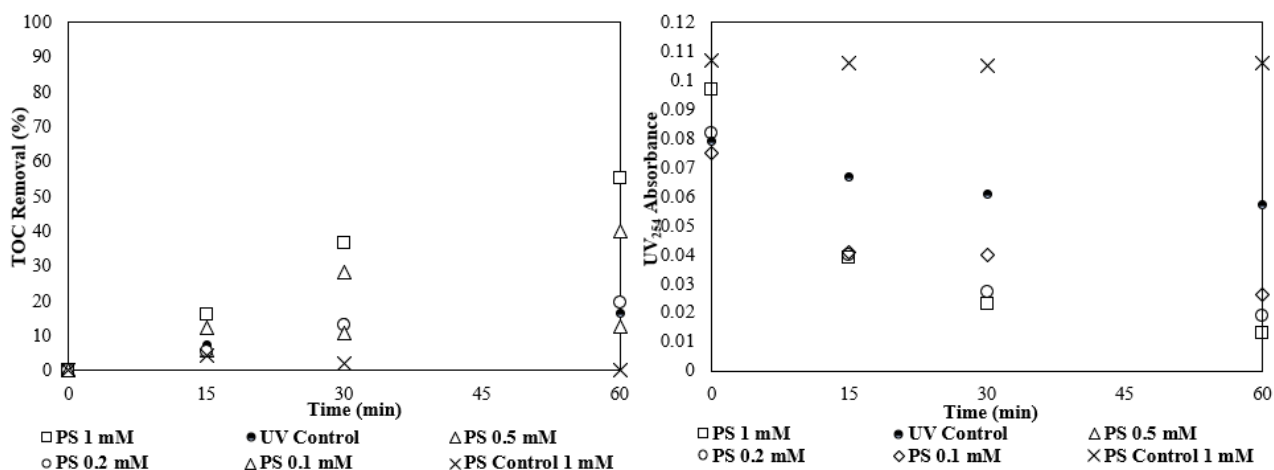

Figure 1. The effect of initial PS concentrations on **(a)** TOC removal and **(b)** UV$_{254}$

experiment that conducted with 1 mM PS/UV-C at the same experimental conditions. The final removal rates were 19%, 40% and 55% at PS doses of 0.2 mM, 0.5 mM and 1.0 mM, respectively. The results indicated that PS/UV-C can significantly reduce TOC in surface water, especially at higher PS doses.

Fig. 1b shows that UV_{254} profiles during 60 minutes of the PS/UV-C treatment. As can be seen from figure, while there was a clear downward trend of UV_{254} in the first 30 minutes of the 1.0 mM PS/UV-C process, it remained almost the same at the end of the 60th minute. Furthermore, the concentration of PS influenced the decrease of UV_{254}. In case of 1.0 mM PS/UV-C process,

energy (Eq. 1) (Dhaka et al., 2018). Past researches had also shown that PS degrades organic matter in raw water at neutral pH without disadvantages effectively (Starling et al., 2021). However, the degradation of organic matter with the PS/UV-C process could lead to a decrease in the pH of the system (Liang et al., 2021). There was a considerable reduction in pH at high PS concentrations, except for the control experiment, but pH remained stable during the first 15 minutes of the reaction (**Fig. 2b**). Overall, the pH decreased at a lower rate and remained constant in the last 30 minutes. The decreasing of pH could lead to reduction in the formation of active sulphate radicals hence declining in removal efficiency.
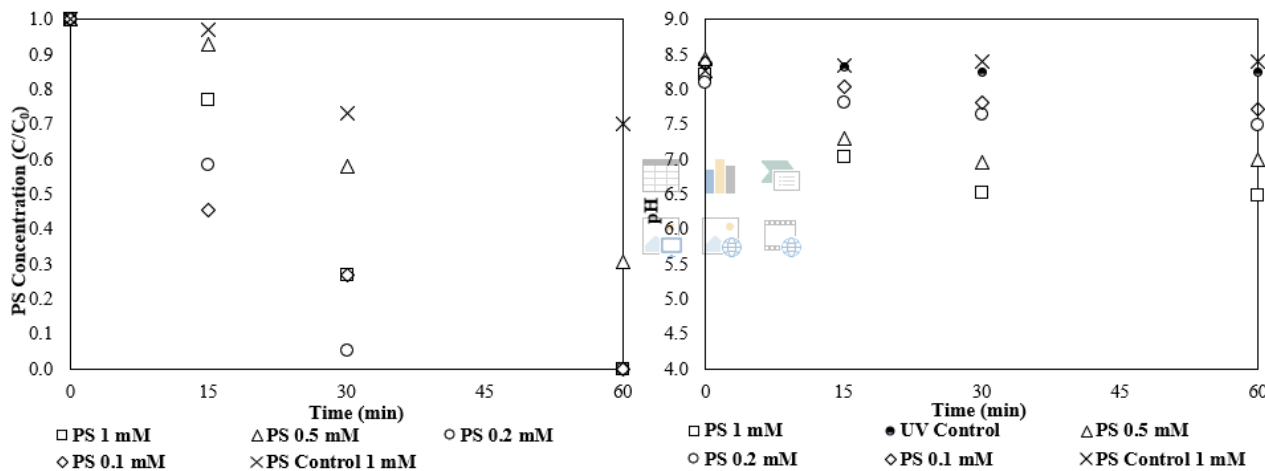

Figure 2. The time-dependent changes in **(a)** PS concentration and **(b)** pH during the PS/UV-C process

UV_{254} decreased from 0.097 to 0.013, while, it decreased from 0.075 to 0.026 in the 0.1 mM PS/UV-C process.

The specific ultraviolet absorbance (SUVA) values based on the measurements of UV_{254} and DOC were calculated as shown in **Table 2**. According to these values, the decreasing SUVA values in all experiments indicate that the organic carbon removal was successful, as well as the UV_{254} measurements.

$$SUVA \left(\frac{L}{mg.M} \right) = \frac{UVA \, (cm^{-1})}{DOC \, (mg/L)} \times 100 \, \frac{cm}{M} \tag{4}$$

$$UVA \, (cm^{-1}) = \frac{UV \, Absorbance \, at \, 254 \, nm}{The \, quartz \, cell \, path \, length \, (cm)} \tag{5}$$

Table 2. SUVA calculations of PS/UV-C process.

Time (min)	Control (1.0 mM)	0.1 mM	0.2 mM	0.5 mM	1.0 mM
0	2.48	1.71	1.93	1.96	1.89
60	1.87	0.66	0.64	0.52	0.65

The effect of the initial concentration of PS on the residual PS concentration was determined in **Fig. 2a**. PS was completely consumed at the end of the 60 min reaction time at initial concentrations of 0.1, 0.2 and 1.0 mM. However, the 0.5 mM PS may not be completely consumed because of the lower interaction possibilities. Even though PS is a reasonably powerful oxidant, it is occasionally feasible to identify lower consumption rates of oxidants for the degradation of a particular pollutant (Deng et al., 2014; Dogan et al., 2016).

$SO_4^{\cdot-}$ was expected to be present in a higher concentration at neutral pH due to its lower activation

3.3. PSD Analysis

PSD of 1.0 mM PS /UV-C treatment effluent was analyzed to determine the efficiency of organic carbon degradation at different particle sizes. The PSD values of the water sample taken at the end of the PS/UV-C treatment process are compared with the PSD values of the raw water.

Figure 3a shows the TOC values in the raw and treated water of the PS/UV-C process in mg/L. As can be seen from the figure, TOC concentration of peak points were 1.75 mg/L and 2.24 mg/L in the range of 13-220 nm and 5-8 nm, respectively and removed by the PS/UV-C process. In addition, the particles that were shifted to an earlier size range due to polymerisation of small colloidal particles were clearly seen in this figure.

Similarly, the range of particle size was investigated with the comparison of raw water and PS/UV-C treated sample in **Figure 3b**. The removal of organic carbon was observed for each particle size. The size of all particles was smaller than 220 nm. It was found that 52% of particles smaller than 450 nm and 59% of particles smaller than 220 nm were successfully removed. Moreover, the removal efficiency was 35%, 47%, and 8% for particles that are smaller than 13 nm, 8 nm, and 5 nm, respectively.
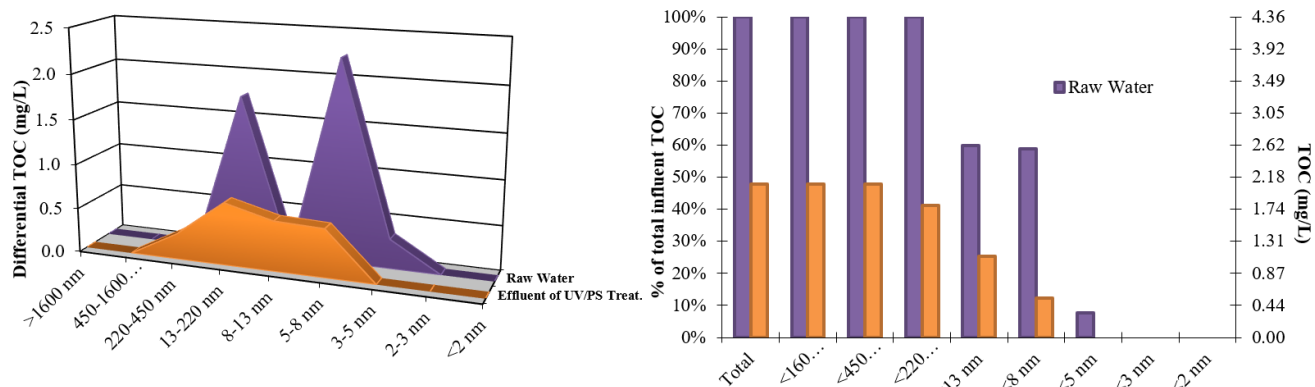
Figure 3. (a) Comparison of particle size distribution and **(b)** comparison of percentage of total influent TOC in certain particle size range in raw water and effluent of PS/UV-C treatment.

4. Conclusion

In this study, it was aimed to investigate the applicability of sulfate radical ($SO_4^{\bullet-}$) based persulfate (PS)/UV-C photochemical advanced oxidation process in organic carbon removal. The process at issue, were studied at different oxidant concentrations in order to determine the optimum operating conditions and process mechanisms, and the process performances were determined by considering the total organic carbon (TOC) removals. In addition, within the scope of this study, PSD analyzes were carried out in both raw water sample and after PS/UV-C treated samples, and removal efficiencies were investigated according to particle size.

As a result of this study, it was determined that the organic matter in the water can be removed effectively by using sulfate radical-based photochemical advanced oxidation processes. It is thought that the investigated advanced oxidation processes can also be used in drinking water treatment successfully.

References

Arslan-Alaton, I., Kolba, O. and Olmez-Hanci, T. (2018), Removal of an X-ray contrast chemical from tertiary treated wastewater: Investigation of persulfate-mediated photochemical treatment systems, *Catalysis Today*, **313**, 134–141.

Budaev, S. L., Batoeva, A. A., Tsybikova, B. A., Khandarkhaeva, M. S., and Aseev, D. G. (2021), Photochemical degradation of thiocyanate by sulfate radical-based advanced oxidation process using UVC KRCL-EXCILAMP, *Journal of Environmental Chemical Engineering*, **9**(4), 105584.

CCOT (Calgon Carbon Oxidation Technologies), (1995), *The AOP Handbook*, Markham, Ontario.

Chow C., Fabris R., Wilkinson K., Fitzgerald F. and Drikas M. (2006). Characterising NOM to assess treatability, *AWA Water*, **33**, 74-85.

Deng, D., Peng, L., Guan, M. and Kang, Y. (2014), Impact of activation methods on persulfate oxidation of methyl tert-butyl ether, *Journal of Hazardous Materials*, **264**, 521–528.

Dhaka, S., Kumar, R., Lee, S.-hun, Kurade, M. B. and Jeon, B.-H. (2018), Degradation of ethyl paraben in aqueous medium using advanced oxidation processes: Efficiency evaluation of UV-C supported oxidants, *Journal of Cleaner Production*, **180**, 505–513.

Dogan, M., Ozturk, T., Olmez-Hanci, T. and Arslan-Alaton, I. (2016), Persulfate and hydrogen peroxide-activated degradation of bisphenol A with nano-scale zero-valent iron and aluminum, *Journal of Advanced Oxidation Technologies*, **19**(2).

Goslan, E. H., Gurses, F., Banks, J. and Parsons, S. A. (2006), An investigation into reservoir nom reduction by UV photolysis and advanced oxidation processes, *Chemosphere*, **65**(7), 1113–1119.

Liang, L., Yue, X., Dong, S., Feng, J., Sun, J., Pan, Y. and Zhou, M. (2021), New insights into the effect of adsorption on catalysis in the metal-free persulfate activation process for removing organic pollutants, *Separation and Purification Technology*, **272**, 118923.

Olmez-Hanci, T., Arslan-Alaton, I., and Genc, B. (2014). Degradation of the nonionic surfactant Triton™ X-45 with Ho and – based advanced oxidation processes, *Chemical Engineering Journal*, **239**, 332–340.

Poyatos, J. M., Muñio, M. M., Almecija, M. C., Torres, J. C., Hontoria, E., and Osorio, F. (2009), Advanced oxidation processes for wastewater treatment: State of the art, *Water, Air, and Soil Pollution*, **205**(1-4), 187–204.

Saien, J., and Jafari, F. (2022), Methods of persulfate activation for the degradation of pollutants: Fundamentals and influencing parameters, *Persulfate-Based Oxidation Processes in Environmental Remediation*, 1–59.

Tian, K., Hu, L., Li, L., Zheng, Q., Xin, Y. and Zhang, G. (2021), Recent advances in persulfate-based advanced oxidation processes for organic wastewater treatment, *Chinese Chemical Letters*.

V. M. Starling, M. C., Mendonça Neto, R. P., Pires, G. F. F., Vilela, P. B. and Amorim, C. C. (2021), Combat of antimicrobial resistance in municipal wastewater treatment plant effluent via solar advanced oxidation processes: Achievements and perspectives, *Science of The Total Environment*, **786**, 147448.

Vilhunen, S., Vilve, M., Vepsäläinen, M. and Sillanpää, M. (2010), Removal of organic matter from a variety of water matrices by UV photolysis and UV/H_2O_2 method, *Journal of Hazardous Materials*, **179**(1-3), 776–782.

Yang, Q., Ma, Y., Chen, F., Yao, F., Sun, J., Wang, S., Yi, K., Hou, L., Li, X., & Wang, D. (2019), Recent advances in photo-activated sulfate radical-advanced oxidation process (SR-AOP) for Refractory Organic Pollutants Removal in water, *Chemical Engineering Journal*, **378**, 122149.