TREATABILITY OF ORGANIC CONSTITUENTS IN THE PAŞAKÖY WASTEWATER TREATMENT PLANT EFFLUENT BY O_3 AND O_3/H_2O_2

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Abstract – Effluent from Paşaköy Advanced Wastewater Treatment Plant (PAWTP) was subjected to oxidation using ozone (O_3) and O_3 combined with hydrogen peroxide (O_3/H_2O_2). While O_3 was applied at constant dosage all throughout the experiments, H_2O_2 injection dose was changed so that varying H_2O_2 to O_3 mole ratios could be tested. DOC, COD, UV_{254}, total coliform, dissolved ozone and some EDCs were monitored during oxidation. Results showed that O_3 provided superior disinfection while exhibiting lower reductions in DOC, COD and EDCs compared to O_3/H_2O_2 applied at 0.5 and 1 molar ratio. When DOC, COD and EDC removal efficiencies of O_3/H_2O_2 at three different mole ratios were compared, higher removals were achieved at 0.5 mol ratio. The benefit of H_2O_2 addition for advanced oxidation reduced significantly when the mole ratio was increased to 2. Therefore, the mole ratio of H_2O_2 to O_3 seems to be a critical parameter for the design of wastewater oxidation by O_3/H_2O_2.

Keywords: disinfection, endocrine disrupting compounds, ozonation, reuse, wastewater

Abbreviations & Symbols

EDC	Endocrine disrupting compound
AOP	Advanced oxidation process
TOC	Total organic carbon
COD	Chemical oxygen demand
PAWTP	Paşaköy Advanced Wastewater Treatment Plant
E1	Estrone
E2	17 β-estradiol
17a-E2	17 α-estradiol
EE2	17 α-ethinylestradiol
E3	Estriol
BPA	Synthetic chemical bisphenol A
UV_{254}	UV absorbance at 254 nm

Introduction

Due to the shortage in fresh water resources and increase in water demand, wastewater reuse is becoming an attractive option for extending available water resources. Especially effluents from municipal wastewater treatment plants are regarded as secondary water resources because they are produced in relatively larger volumes and contain small number of contaminants. Advanced treatment techniques must be applied to biotreated municipal waste water to avoid the presence of organic pollutants in the treated effluent. Various advanced wastewater treatment technologies are considered for the production of effluents that can be suitable for specific applications such as irrigation of agricultural and urban areas, industrial applications or enrichment of groundwater bodies [1]. Since the 1970s, ozonation is used for the inactivation of coliform and viruses [2]. Recently, several studies have shown the ability of ozonation to oxidize certain micropollutants such as endocrine disrupting compounds and pharmaceuticals in water and wastewater [3,4,5]. Disinfection and micropollutant oxidation properties of ozonation make it an attractive alternative

for advanced wastewater treatment. Similarly, ozone based advanced oxidation processes (AOP) such as addition of H_2O_2 are also considered for the removal of residual organic pollutants present in biotreated effluents. The efficiency of applying ozone in combination with H_2O_2 for emerging contaminant removal has been demonstrated earlier [6]. AOPs are more severe oxidation processes because they rely on production of highly reactive $OH^{\bullet}$ radicals. Therefore, in general AOPs are much more efficient in the removal of organic pollutants than ozonation alone [7,8,9].

In this context, the objective of this study is to evaluate the effect of ozone oxidation alone and O_3/H_2O_2 combination on the removal of organic pollutants indirectly measured as dissolved organic carbon (DOC) and chemical oxygen demand (COD) and some specific micropollutants which act as endocrine disruptors in the effluent of Paşaköy Advanced Biological Wastewater Treatment Plant (PAWTP). In the meanwhile, the disinfection efficiency of the oxidation processes is monitored by measuring coliform. The endocrine disrupting compounds (EDC) monitored in this study were selected based on their environmental relevance and frequent human exposure. They include estrogenic hormones; estrone (E1), 17 β-estradiol (E2), 17 α-estradiol (17a-E2), 17 α-ethinylestradiol (EE2), estriol (E3), and synthetic chemical bisphenol A (BPA). These are the most common estrogenic compounds detected in the wastewater treatment plant effluents in the United States, Europe, Japan and Australia [10,11,12,13]. E2 and 17a-E2 are natural female hormones. E1 and E3 are the metabolites of E2. EE2 is a synthetic hormone commonly found in oral contraceptives. BPA is mainly used by the plastics industry for the production of polycarbonate and epoxy resins, unsaturated polyester–styrene resins, and flame retardants. BPA is manufactured in large quantities with an estimated worldwide production of 2.5 million tons/year. Presence of BPA in wastewater treatment plant effluents is a major concern because it is proved that BPA has estrogenic activity even at concentrations below 1 ng/L [14].

Experimental Study

Wastewater Treatment Plant

The Paşaköy Wastewater Treatment Plant is an advanced biological plant treating an average flow of 100,000 m^3/day. It has a capacity of 1,000,000 equivalent inhabitants and has been designated to treat wastewaters collected from the catchment area of Ömerli Reservoir. The treatment plant consists of inlet pumping station, fine screens, aerated grit chamber, selector-distribution chamber, 3 anaerobic tanks, 4 aeration tanks, 4 final clarifiers, DAF, aerated sludge storage tanks, sludge dewatering and return of dewatering supernatant to the distribution chamber. The A^2/O process (anaerobic zone followed by anoxic zone then oxic zones aeration units) is applied to provide carbon, nitrogen and phosphorous removal. It discharges its effluents to the Paşaköy River that finally flows into the Black Sea. Typical water quality characteristics of PAWTP effluent are given in Table 1.

Table 1. Characteristics of the PAWTP effluent

Parameters	Values
COD (mg/L)	22-35
BOD_5 (mg/L)	4-10
DOC (mg/L)	8-12
UV_{254} (cm^{-1})	0.140-0.225
pH	7.2-7.6

Analytical Methods

Analysis of EDCs included solid phase extraction, derivatization and detection by GC/MS. The details of the method are provided in a report submitted to the United States Geological Survey by Yue-wern Huang and Paul Nam [15]. Gas chromatography-mass spectrometry analysis was performed using a Shimadzu GC/MS QP-2010 Plus with Mass Range up to m/z 1090. The column utilized was DB-5M capillary column (30 m X 0.32 mm i.d. with 0.25 μm film) and the GC carrier gas was helium. All the EDC standards were purchased from Dr. Ehrenstorfer GmbH in their solid form. The detection limit was 0.1ng/100μL hexane. This concentration corresponded to 0.4 ng/L of EDC in water when 70% recovery was considered for the solid phase extraction of 1 L of sample.

DOC was measured by Teledyne Tekmar TOC analyzer after filtering the samples through a 0.45-μm filter to remove the suspended solids. COD was measured by Hach COD measurement unit and Hach DR 2500 spectrophotometer. UV absorbance at 254 nm (UV_{254}) was measured using Shimadzu UV/Vis spectrophotometer and total coliform measurement was performed by using Sartorious coliform filtration set. Dissolved and residual ozone were determined by standard methods [16].

Ozonation and H_2O_2 Application

The experiments were carried out in a 20 L semi-batch reactor. Each time 15 L of the effluent sample were placed in the reactor. Ozone was obtained from oxygen by a Wedeco ozone generator and was continuously diffused through the water sample at the selected ozone dosage of 15 mg/L and flow rate of 1.9 L/min. Fine pore, ozone compatible, ceramic diffuser was used. All the tubings and connections were Teflon. Watson-Marlow 323 S/D model peristaltic pump was used to pump the H_2O_2 solution into the ozonation reactor when necessary. Stock solutions of H_2O_2 were pumped into the reactor at appropriate flow rates so that H_2O_2 was introduced into the reactor at specific H_2O_2 to ozone mole ratios. Three different H_2O_2 to ozone mole ratios; 0.5, 1 and 2 were studied. Samples were taken from the reactor at specific time intervals to analyze for EDCs, DOC, COD, UV_{254} and coliform. Sodium thiosulfate was used to quench the remaining oxidants in the samples.

Results and Discussion

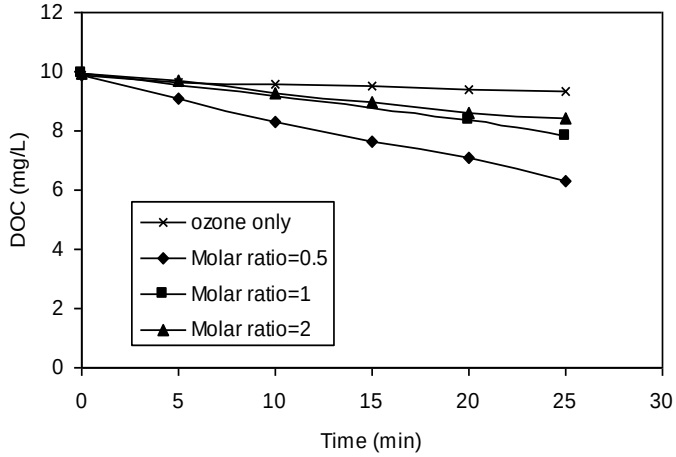

Figure 1. Effect of ozone and O_3/H_2O_2 treatment on DOC removal

DOC removal in the Paşaköy effluent sample subjected to oxidation was monitored to compare the mineralization effects of different oxidation conditions. As can be seen in Figure 1, ozone alone did not cause any significant change in DOC at all. Mineralization efficiencies of H_2O_2 addition at H_2O_2/O_3 mole ratios of 1 and 2 were quite similar, resulting in 22% and 15% DOC reductions after 25 minutes, respectively. The highest degree of mineralization, 36%, was achieved by H_2O_2 addition at 0.5 mole ratio. Furthermore, the linear trend of the DOC profile at this mole ratio suggests that higher mineralization efficiencies might be possible upon longer contact times. As it is very well established, the removal efficiency of H_2O_2/O_3 system depends on the degree of $OH^{\bullet}$ radical generation. $OH^{\bullet}$ radical generation in this system is performed by the following reaction;

$$2\ O_3 + H_2O_2 \longrightarrow 2\ OH^{\bullet} + 3\ O_2 \qquad (1)$$

The stoichiometry of Reaction 1 suggests that the theoretical mole ratio of H_2O_2 and O_3 is 0.5 for an effective $OH^{\bullet}$ radical generation. A molar ratio less than 0.5 will result in limited $OH^{\bullet}$ radical generation. When the ratio is higher than 0.5, the excess H_2O_2 is probably competing with the organic constituents in water for $OH^{\bullet}$ radical and thus acting as $OH^{\bullet}$ radical scavenger. [17]

COD reductions under different oxidation conditions further support the $OH^{\bullet}$ radical scavenging effect of excessive H_2O_2 species (Figure 2). Overall COD reduction was the lowest, 23%, for H_2O_2/O_3 application at mole ratio of 2. However, the reduction efficiency significantly improved to 82% when the mole ratio was decreased down to 0.5. Yet again, the COD removal at 0.5 mole ratio followed a linear trend suggesting higher removal efficiencies at longer reaction times. Overall COD reduction by ozonation was 28%.

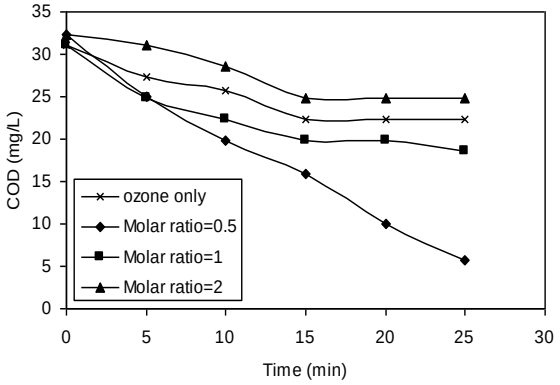

Figure 2. Effect of ozone and O_3/H_2O_2 treatment on COD removal

Figure 3 shows that UV_{254} absorbance declined quickly during the first 5 minutes of reaction following the ozone or O_3/H_2O_2 application. Within this time period, reduction in UV_{254} absorbance was 54% upon ozonation, and 60%, 49% and 55% upon O_3/H_2O_2 treatments at 0.5, 1 and 2 molar ratios, respectively. High UV_{254} reductions, and yet relatively low DOC reductions observed during this time suggest that UV-absorbing organic structures in the PAWTP effluent can be readily oxidized to non UV-absorbing organic constituents. In other words, the structures of the organics are changed but their complete mineralization is not achieved. Finally, Figure 3 shows that UV_{254} reduction rates after 5 minutes slowed down considerably achieving an overall reduction of 73% for only ozone application, and 81%, 67% and 67% for H_2O_2 additions at 0.5, 1 and 2 molar ratios, respectively.

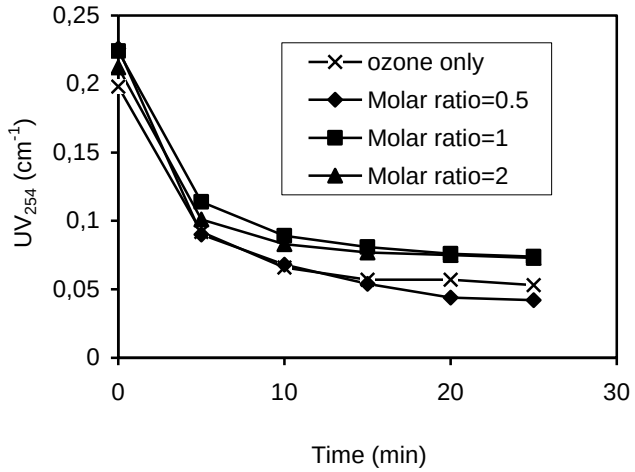

Figure 3. Effect of ozone and O_3/H_2O_2 treatment on UV_{254} absorbance

Disinfection is the primary mechanism for the inactivation or destruction of pathogenic organisms. Wastewater disinfection before reuse is absolutely required to prevent spread of waterborne diseases [18]. On that account, disinfection capacity of each treatment was monitored by total coliform tests. The results are presented in Table 2. The highest degree of disinfection is achieved by ozone oxidation as indicated by the maximum log reduction value of 4.83. Furthermore, disinfection is complete in 15 minutes. Disinfection efficiency is significantly reduced when O_3 is combined with H_2O_2. These results coincide with the results reported by Wert et al. (2007) [19]. Ozone has been proved to be one of the most effective disinfectants. H_2O_2, on the other hand, is known to be a rather poor disinfectant compared to ozone [20,21]. Furthermore, as can be seen in Figure 4, addition of H_2O_2 decreases the dissolved ozone concentration significantly. In the absence of H_2O_2, ozone concentration in water reaches to 2.3 mg/L after 20 minutes. When H_2O_2 is fed into the reactor, however, ozone concentration is always less than 0.4 mg/L. Therefore, the reduction in disinfection efficiency is attributed to the lowered concentration of dissolved ozone in water.

Table 2. Coliform test results.

oxidation time (min)	Coliform (CFU/100mL)			
	Ozone only	O_3/H_2O_2 Molar ratio=0.5	O_3/H_2O_2 Molar ratio=1	O_3/H_2O_2 Molar ratio=2
0	67700	67700	67700	67700
5	1427	1192	2167	2574
10	220	264	1342	2440
15	0	119	195	883
20	0	13	85	115
25	0	10	54	105
log reduction	*4.83*	*3.84*	*3.10*	*2.81*

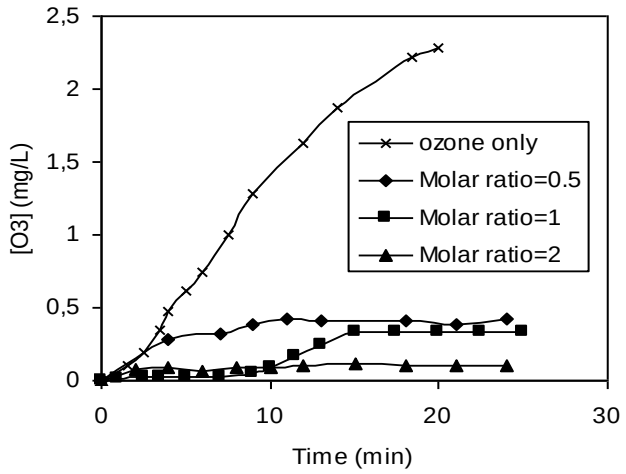

Figure 4. Dissolved ozone concentrations

Table 3 shows the measured concentration ranges of the selected EDCs in the influent of PAWTP, and their percent removals at the treatment plant. Concentrations of the selected EDCs in the PAWTP influent and effluent have been monitored in summer of 2009. Samples were taken from the treatment plant influent and effluent every other week and analyzed for EDCs. These preliminary results indicate that removal efficiencies vary significantly. Generally, higher removal rate for a specific EDC was obtained when its concentration was at the lower range. Among the 6 EDCs monitored, removal of BPA was almost always the lowest.

Table 3. Concentrations and removal rates of the selected EDCs at PAWTP

Compound	Conc. in the PAWTP influent (ng/L)	Degree of removal at PAWTP, %
Bisphenol A (BPA)	6.7-165	15-55
Estrone (E1)	bdl-4.8	25-60
17 α-estradiol (17a-E2)	1.3-54.2	54-85
17 β-estradiol (E2)	1.2-57.7	45-75
17 α-ethinylestradiol (EE2)	14.5-58.3	52-74
Estriol (E3)	4.2-133.8	36-82

Table 4 shows the concentrations of the EDCs found in the PAWTP effluent used for oxidation treatments. Removal efficiencies of the applied oxidation techniques are also presented in Table 4. Under the given experimental conditions, the highest degree of EDC removal was achieved by O_3/H_2O_2 treatment at 0.5 molar ratio. The removal efficiencies of ozonation and O_3/H_2O_2 application at molar ratio of 1 are comparable. Oxidation of various EDCs in water using O_3 has been demonstrated earlier [22,23,24]. Consistent with these earlier findings, relatively high E1, 17a-E2, E2, EE2 and E3 removals were achieved by ozone application only even though the DOC reduction was insignificant.

Table 4. Concentrations of the selected EDCs in the PAWTP effluent before treatment and their removal rates following O_3 or O_3/H_2O_2 treatment

Compound	Conc. in the PAWTP effluent before oxidation (ng/L)	Oxidation Technique Applied		
		Percent removal by O_3	Percent removal by O_3/H_2O_2 Molar ratio=0.5	Percent removal by O_3/H_2O_2 Molar ratio=1
Bisphenol A (BPA)	18.5	44	66	47
Estrone (E1)	3.4	75	80	72
17 α-estradiol (17a-E2)	28.0	69	90	60
17 β-estradiol (E2)	16.6	82	95	60
17 α-ethinylestradiol (EE2)	22.0	76	92	78
Estriol (E3)	62.0	82	95	86

Conclusion and Recommendations

For the reclamation of municipal wastewater treatment plant effluent, the oxidation and disinfection efficiencies of O_3 and O_3 combined with H_2O_2 were investigated. In the absence of H_2O_2, no significant DOC decay was obtained after 25 minutes of ozonation. On the other hand, when H_2O_2 was injected together with ozone, DOC removal was improved. Among different H_2O_2 to O_3 mole ratios tested, O_3/H_2O_2 applied at 0.5 mol ratio showed the highest efficiency for removing the organics in the wastewater effluent. A DOC decay of about 36% was obtained after 25 minutes. When the H_2O_2 injection dose was increased to yield higher mole ratios such as 2, mineralization efficiency decreased down to 15%. This behavior was attributed to hydroxyl radical scavenging effect of excess H_2O_2. For disinfection of the effluent, total coliform could be effectively inactivated within 15 minutes of ozonation. Addition of H_2O_2, however, lowered the disinfection efficiency, probably due to the lower dissolved ozone concentrations in water in the presence of H_2O_2. Ozonation alone and ozonation with H_2O_2 addition were both effective in removing UV-absorbing organic substances. On average, 72% UV_{254} reduction was obtained after 25 minutes, from which most part (55%) took place during the first 5 minutes of reaction. O_3/H_2O_2 process applied at 0.5 mol ratio was highly effective for removal of most EDCs. Among all the oxidation conditions tested, with and without H_2O_2 addition, O_3/H_2O_2 process at molar ratio of 1 resulted in the lowest EDC degradation. This suggests that the ratio of H_2O_2 injected with respect to ozone dosage is critical in the design of wastewater reclamation by O_3/H_2O_2. BPA removal was significantly lower than the removals obtained for other EDCs under all conditions.

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Acknowledgement

This research was supported by Marmara University Scientific Research Fund (BAPKO) (project no: FEN-A-030408-0079).