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Environmenal Impact Assessment And Removal Of Endocrine Disrupting Compounds In Municipal Wastewater Treatment

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ENVIRONMENTAL IMPACT ASSESSMENT AND REMOVAL OF
ENDOCRINE DISRUPTING COMPOUNDS IN MUNICIPAL
WASTEWATER TREATMENT

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DEDICATION

To the most beautiful persons in my life: Sebastian Xavier Bezares and Gael Eduardo Bezares.

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ENDOCRINE DISRUPTING COMPOUNDS IN MUNICIPAL
WASTEWATER TREATMENT

by

JUAN CÉSAR BEZARES-CRUZ, M.S.

DISSERTATION

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ABSTRACT

The presence of compounds of emerging concern (CECs) such as endocrine disrupting compounds (EDCs) and herbicides in municipal wastewater present environmental challenges because conventional treatment systems were not designed to remove such compounds. The removal of Bisphenol-A (BPA), 17 β -Estradiol (E2), 17 α -Ethinylestradiol (EE2), nonylphenols (NP), and select herbicides and pesticides were investigated in two municipal wastewater treatment plants (WWTP) in El Paso, TX. In addition, the environmental impact of the two municipal wastewater treatment plants was investigated, including the theoretical addition of UV/H₂O₂. The use of UV/H₂O₂ was studied in a UV bench scale pilot unit, and its performance was compared to the use of peracetic acid (PAA) in the same system. The analysis of EDCs in the WWTPs revealed average removals of 93% and 94% for WWTP-A, and 87% and 99.6% for WWTP-B were observed for BPA and NP, respectively. Estrogen species were detected in less than 5% of the samples; herbicides and pesticides were below detection limits for all of the collected samples. EDC removal agreed with reductions in estrogenic activity observed by yeast bioassay. The environmental assessment of the WWTPs including the implementation of an advanced oxidation process (AOP) with the use of 10 mg/L H₂O₂ yield increments of 3% global warming potential, 2% acidification potential, 5% eutrophication potential, 3% freshwater aquatic ecotoxicity potential, and 42% in terrestrial ecotoxicity potential. A holistic Eco-Score Card was created for evaluating AOP implantation, and the addition of 10 mg/L of peroxide was observed to result in a 13% increase of the overall environmental impact, as compared with the current WWTP. In the bench scale AOP experiments, direct UV (1 J/cm³, 254 nm) irradiation was found to remove up to 19%, 11% and 61% of the initial concentrations of estradiol, BPA and NP respectively. The UV irradiation of solutions with 10 mg/L initial concentration of H₂O₂ yield removals of 99.4%, 94% and 84% for estradiol, BPA and NP respectively. The UV irradiation with 5 mg/L PAA showed removals of >99.9%, >99.9% and 24% for estradiol, BPA and NP, respectively.

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CHAPTER 1: INTRODUCTION

Municipal wastewater treatment is an important component in today's water management system. The performance of this treatment system plays a significant role in the impact and preservation of current water supplies. In the past decades, the presence of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) have been observed in wastewater treatment effluents [1]–[14]. The presence of PPCPs in municipal wastewater treatment presents a challenge to current municipal treatment processes, which were not designed for their removal [7], [15]. Recently, the presence of EDCs in drinking water treatment and wastewater treatment plants (WWTPs) has been reported around the world [16], [17]. Pesticides, as well as EDCs, have been reported to have estrogenic effects in biota and can potentially have a negative impact for human health [18], [19]. The presence of these EDCs in WWTPs effluents presents a potential threat to organism and human health, especially where discharge water is used for agricultural activities that impact the human food supply. The presence of EDCs at low concentrations have been known to cause reproduction reduction in FO (first generation) and F1 (second generation) generations, and sex ratio shift at low EDC concentration exposure (17 – 51 $\mu\text{g/L}$) in Medaka fish, respectively [20]. In addition, the exposure of these chemicals has been linked to child obesity, diabetes, and metabolism effects in humans [21]–[24]. The removal efficiency of these chemicals in different wastewater treatment processes will play an important role in the integrity and potential environmental impact of the effluent as well as the environmental performance of the municipal wastewater treatment systems.

In recent years, direct potable reuse has gained worldwide interest for the development of “new” water supplies, especially in semiarid regions. The presence of EDCs in wastewater effluents requires careful engineering design in direct potable reuse, and effective treatment could significantly increase operational cost and the carbon footprint, as compared with

conventional treatment systems. The enhancement and selection of sustainable means for wastewater treatment can yield many benefits such as the low cost acquisition of new water supplies, water stress mitigation, and preservation of existing water supplies.

The use of advance oxidation processes (AOPs) has been widely studied for wastewater treatment and reuse[15], [25]–[29]. Municipal wastewater treatment facilities commonly employ the use of UV systems for disinfection. Perhaps the engineering of such systems into UV/AOPs could increase effluent quality for the application of water reuse with a relatively small increase in carbon footprint. In addition, such modifications could lead to other environmental benefits such as reduced water stress, production of new water supplies and the mitigation of environmental impact by reduced chemical oxygen demand, biological oxygen demand, removal of recalcitrant pollutants such as pesticides and endocrine disrupting chemicals [25], [26], [30]–[32]. Commonly used UV/AOPs with the lowest operational cost and green house gas emissions include the use of ozone (O_3) and hydrogen peroxide (H_2O_2). The use of O_3 /UV and H_2O_2 /UV has been reported to have a cost and green house gas emissions of \$0.21/L and 5.54 Kg CO_2 -e/KL and \$0.14/L and 0.20 Kg CO_2 -e/KL, respectively [33]. The employment of these oxidants, especially H_2O_2 , could be even more affordable for wastewater treatment facilities equipped with UV disinfection units.

The overall aim of this research effort was to investigate the environmental performance of municipal wastewater treatment for the removal of EDCs and explore the environmental impacts and EDC removal enhancement by modifying a UV disinfection system into an AOP. In order to achieve this aim, the three main goals of this research were as follows:

1. The first goal of this study was to assess the performance of existing full-scale municipal wastewater treatment systems with respect to EDC removal. In order to accomplish this goal, the following three objectives were completed:
 - a. Analysis of municipal wastewater treatment flows and assessment of treatment performance as approximate cohorts based on the hydraulic detention time of the treatment processes.
 - b. Chemical analysis of EDC surrogates using GC-MS to identify recalcitrant compounds in municipal wastewater treatment.
 - c. Screening of samples for estrogenic potential using yeast biological assay to create an overall assessment of the treatment performance.
2. The second goal of this study was to assess the potential environmental impact for the modification of municipal wastewater UV disinfection systems into AOPs. To achieve this goal the following three objectives were completed:
 - a. Develop an annual inventory of municipal wastewater treatment plants and assess environmental performance based on current operational conditions.
 - b. Assess the environmental impact for the addition of peroxide dosing in the UV disinfection system as a potential AOP modification.
 - c. Compare this modification with the complete new addition of an H_2O_2 /UV AOP to municipal wastewater treatment plants based on the chemical dose and energy requirements.
3. The third goal of this study was to compare the use of ultraviolet light irradiation and peroxide (UV/ H_2O_2), and ultraviolet light and peracetic acid (UV/PAA) in advanced oxidation processes (AOPs) for the removal of bisphenol-A (BPA), estradiol (E2), and

nonyphenols (NP) in deionized (DI) water. In order to achieve this goal the following three objectives were completed:

- a. Characterize the residence time distribution (RTD) and actinometry of a lab-scale continuous-flow UV reactor.
- b. (b) Evaluate the use of UV/H₂O₂ and UV/PAA as chemical oxidants for the removal of EDCs.
- c. Estimate the required UV energy dose and initial chemical concentrations to achieve 90% removal of EDCs in aqueous solutions.

These goals and objectives have resulted in the identification of resilient EDCs to current municipal wastewater treatment, assessment of the environmental impact of modifying an existing UV disinfection system into an AOP, and evaluation of a relatively new chemical oxidant for AOP systems.

CHAPTER 2: DETECTION AND REMOVAL OF ENDOCRINE DISRUPTING COMPOUNDS (EDCS) AND ESTROGENICITY IN MUNICIPAL WASTEWATER TREATMENT FACILITIES IN EL PASO, TX

ABSTRACT

The presence of compounds of emerging concern (CECs) such as endocrine disrupting compounds (EDCs) and herbicides in municipal wastewater present environmental challenges because conventional treatment systems were not designed to remove such compounds. The removal of Bisphenol-A (BPA), 17 β -Estradiol (E2), 17 α -Ethinylestradiol (EE2), nonylphenols (NP), and select herbicides and pesticides were investigated in two municipal wastewater treatment plants (WWTP) in El Paso, TX. Samples were collected and analyzed as *cohorts* based on the hydraulic detention times to determine the EDC removal and estrogenicity reduction by unit process for both WWTPs. EDC concentrations were analyzed by SPME-GC-MS, and average influent concentrations of BPA and NP were 0.316 $\mu\text{g/L}$ and 10.6 $\mu\text{g/L}$ for WWTP-A and 0.487 $\mu\text{g/L}$ and 72.1 $\mu\text{g/L}$ for WWTP-B, respectively. *Cohort*-average removals of 93% and 94% for WWTP-A, and 87% and 99.6% for WWTP-B were observed for BPA and NP, respectively. Estrogen species were detected in less than 5% of the samples; herbicides and pesticides were below detection limits for all of the collected samples. EDC removal agreed with reductions in estrogenic activity observed by yeast bioassay.

INTRODUCTION

The presence of endocrine disruptors such as Bisphenol-A (BPA), 17 β -Estradiol (E2), 17 α -Ethinylestradiol (EE2), nonylphenols (NPs), as well herbicides and pesticides in wastewater influents present a challenge because conventional treatment systems were not designed to remove these trace compounds [7]. In recent years the presence of endocrine disrupting compounds (EDCs) in drinking water treatment and wastewater treatment plants (WWTPs) has

been reported around the world [16], [17]. Pesticides, as well as EDCs, have been reported to have estrogenic effects in biota and can potentially have a negative impact for human health [18], [19]. Human exposure to EDCs has been linked to child and adolescent obesity, diabetes, and advanced puberty [34]–[37]. The presence of these contaminants of emerging concern in WWTPs effluents presents a potential threat to organism and human health, especially where discharge water is used for agricultural activities that impact the human food supply. The removal efficiency of these chemicals in different wastewater treatment processes will play an important role in the integrity and potential environmental impact of the effluent. Some of the detected EDCs have been reported to be recalcitrant, resulting in their detection in WWTPs effluents [38]. The occurrence of pesticides in water samples have been related to their land use in agricultural and residential areas [39], [40], and their annual use in the USA is about 1 billion pounds [41].

In semi-arid areas, such as the southwestern region of the US, the effluents of WWTP processes play an important role in the quality of the available surface water [42]. For instance, in El Paso, TX the effluent produced by the municipal WWTPs constitutes a small fraction of river flow during the irrigation season, but in recent years, the municipal WWTP effluents dominate the river flow during the non-irrigation season. Rivers and streams are key water sources for society, and understanding the performance of existing municipal wastewater treatment processes discharging water to the river can ultimately inform improvements to ecological conditions of the river.

While recent studies have found a seasonal variation in the detectable concentrations in the influent and effluent of WWTPs worldwide [13], [43], [44], this study focused on the removal of EDCs and reduction of estrogenicity by employing sample collection and analysis as

cohorts, accounting for hydraulic detention through individual unit processes in the treatment systems. The goal of this study was to analyze the performance of WWTP unit processes in removing EDCs. The first objective was to determine the concentration and removal of estrogenic EDCs such as BPA, NP, and pesticides in each unit process in the WWTPs. The second objective was to analyze the reduction in total estrogenic activity (estrogenicity) in each unit process in the WWTPs.

The goal of this study is to assess the EDC removal performance of municipal wastewater treatment. To achieve this goal three objectives were included: (a) analysis of municipal wastewater treatment operational conditions to create a sampling design to capture representation of treatment performance as *cohorts*, (b) chemical analysis EDC surrogates using GC-MS to identify resilient compound to municipal wastewater treatment, and (c) screening of samples for estrogenic potential using yeast biological assay to create an overall assessment of the treatment performance.

MATERIALS AND METHODS

WASTEWATER TREATMENT PLANTS (WWTPS)

Two municipal wastewater treatment facilities, WWTP-A and WWTP-B, were investigated for the removal of several EDCs. The selected treatment facilities receive wastewater from different regions of El Paso. WWTP-A receives municipal wastewater from the west side of El Paso and has a total design capacity of 17.5 million gallons per day (MGD). WWTP-B receives municipal wastewater from the central region of El Paso (and sludge from WWTP-A) and has a total design capacity of 27.7 MGD.

The average hourly flow shows a similar diurnal cycle for each season for both WWTPs, as shown in Figure 2.1. The months of April, August, and December 2012 were selected to represent the spring, summer and winter seasons, respectively. These diurnal variations are similar to typical municipal wastewater flow cycles [45]. WWTP-A has a minimum influent flow near 6AM (2.4 MGD), peak inflow near 12PM (10.9 MGD), and an average influent flow of 7.6 MGD (Figure 2.1). WWTP-B has an average minimum influent flow near 6AM (11.2 MGD), average peak inflow near 2PM (24.2 MGD), and an average influent flow of 19.2 MGD (Figure 2.1). El Paso Water Utilities (EPWU) provided the volume and redundancy of each unit process in each WWTP, and hydraulic detention times (listed in Figure 2.2) were calculated based the average daily influent flow. Total plant detention times were calculated to be 18.8 hours and 11.3 hours for WWTP-A and WWTP-B, respectively.

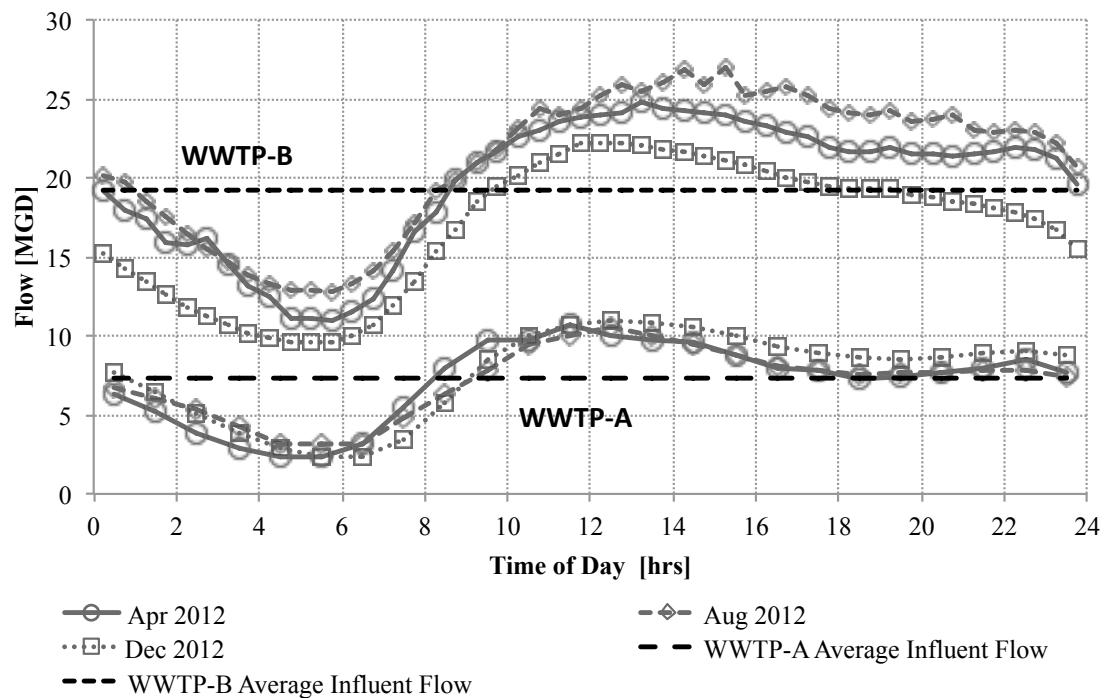
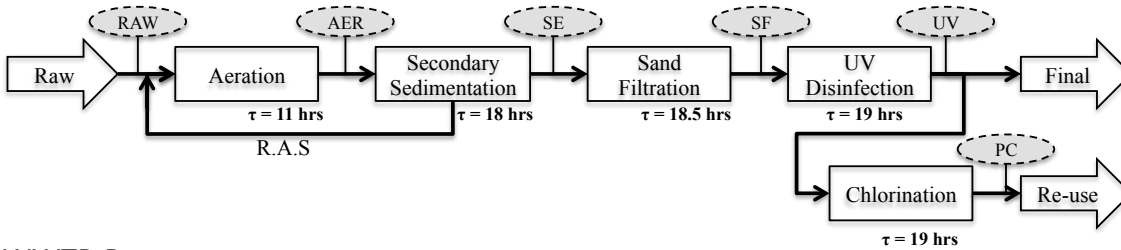


Figure 2.1 Average diurnal wastewater influent flow during the months of April 2012, August 2012 and December 2012, for the selected municipal WWTPs.

WWTP-A



WWTP-B

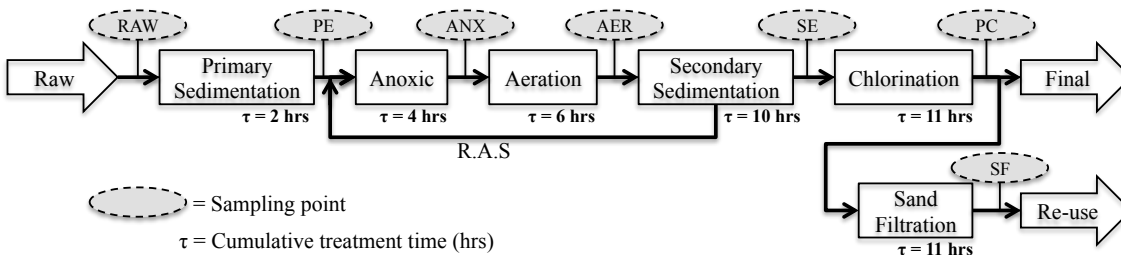


Figure 2.2 Schematic layout, sampling locations and cumulative treatment time (τ) of selected Municipal Wastewater Treatment Facilities in El Paso, TX. Sampling points included wastewater influent (RAW), primary clarifier effluent (PE), anoxic basin effluent (ANX), aeration basin effluent (AER), secondary clarifier effluent (SE), sand filtration effluent (SF), chlorination (PC) and ultraviolet (UV) disinfection effluents.

As illustrated in Figure 2.2, the WWTP-A process includes aeration, secondary sedimentation, sand filtration, and ultra violet (UV) disinfection before the water is discharged to the Rio Grande. A portion of the effluent is reclaimed and treated in a chlorination basin for municipal reclamation (purple pipe) for landscape irrigation. Sludge from WWTP-A is currently conveyed to the raw influent of WWTP-B.

As illustrated in Figure 2.2, the WWTP-B process includes primary sedimentation, anoxic denitrification, aeration, secondary sedimentation, and a chlorination basin before the final treated effluent is typically discharged to an agricultural irrigation canal. A portion of the

final effluent is reclaimed and filtered through a sand filtration basin for municipal reclamation (purple pipe) for landscape irrigation.

SAMPLE COLLECTION

The hourly influent flow rate was analyzed for the year 2012 to understand potential seasonal variations, under the assumption that similar flow behavior would be observed in the consecutive years. Based on the hydraulic detention time, samples were collected two consecutive days every 6 hours for a period of 42 hours. This sample frequency included characteristic diurnal low influent flow (6AM), peak influent flow (12PM) and decreasing influent flow (6PM). In addition the 6 hour sample frequency coincided with the average hydraulic detention times of several processes in the selected municipal WWTPs. In each sampling campaign, 48 samples (six sampling locations sampled eight times) were collected for WWTP-A, and 56 samples (seven sampling locations sampled eight times) were collected from WWTP-B. As shown in Figure 2.2, WWTP-A samples included the raw influent (RAW), aeration basin missed liquor effluent (AER), secondary sedimentation effluent (SE), sand filter effluent (SF), UV disinfection effluent (UV), and chlorination effluent (CL). WWTP-B samples included the raw influent (RAW), primary sedimentation effluent (PE), anoxic denitrification effluent (DN), aeration basin mixed liquor effluent (AER), secondary sedimentation effluent (SE), chlorination effluent (CL), and sand filter effluent (SF). Samples were collected and analyzed in August 2013, October 2013, July 2014, October 2014 and January 2015. Samples were collected in 100 mL amber glass bottles and stored in a sample storage fridge at 4 °C prior to extraction and derivatization.

Prior to analysis, samples were grouped to determine the removal by unit process as *cohorts*. *Cohort* assignment was based on hydraulic detention times through the treatment process; samples not assigned to a specific *cohort* were discarded. A total of five *cohorts* were collected for WWTP-A, and six *cohorts* were collected for WWTP-B. Each *cohort* started with an influent sample at a given sample time and the samples of each unit process at appropriate subsequent sampling times, according to cumulative detention time. The cumulative removal ratio ($R_{x,i}$) of BPA and NP was calculated for each unit process:

$$R_{x,i} = 1 - \frac{C_{x,t_{0,i}+\tau_x}}{C_{0,i}} \quad \text{Equation 2-1}$$

where x is the sampling location; i is the *cohort* number; $C_{0,i}$ is the influent (RAW) concentration of *cohort* i (sampled at time $t_{0,i}$); and $C_{x,i}$ is the effluent concentration of process x of *cohort* i , sampled at time $t_{0,i}+\tau_x$ (where τ_x is the cumulative detention time from the influent to the effluent of unit process x). The *cohort*-average removal ratio of each process ($\overline{R_x}$) was calculated as:

$$\overline{R_x} = \frac{1}{n} \sum_{i=1}^n R_{x,i} \quad \text{Equation 2-2}$$

where $n = 5$ for WWTP-A and $n = 6$ for WWTP-B.

SAMPLE EXTRACTION AND DERIVATIZATION

Samples were analyzed by means of gas chromatography mass spectrometry (GC-MS) after solid-phase extraction by stir bar sorptive extraction [11]. Stir bar sorptive extraction (SBSE) is a technique that employs the use of a magnetic stir bar coated with a thin film of

polydimethylsiloxane (PDMS). The PDMS film provides a surface with low polarity, which extracts low polarity chemicals. Other chemicals with higher polarity could be extracted by chemical modification techniques such as derivatization, allowing the effective extraction of chemicals such as BPA, NPs and estrogens from water samples. The derivatization of BPA, NP, and estrogens was accomplished by adding 200 mg of Na₂CO₃ and 200 μ L of acetic acid anhydride into 20 mL of water samples. The stir bars are submerged in the aqueous samples for a period of 2 hours before being loaded into a thermal desorption unit (TDU) to inject extracted organic compounds into the Agilent GC-MS unit.

ANALYSIS OF ENDOCRINE DISRUPTING COMPOUNDS (EDCS)

Estrone (E1), 17 β -estradiol (E2), 17 α -ethynylestradiol (EE2), Bisphenol A (BPA), and nonylphenol technical mixtures (NP) were purchased from Sigma-Aldrich. The isotope internal standard for BPA (ring ¹³C₁₂) was purchased from Cambridge Isotope Laboratories, Inc (MA, USA). Lindane, alachlor, chlorpyrifos and endosulfan were purchased from Fisher Scientific (PA, USA). HPLC grade methanol, acetic acid anhydride, and sodium carbonate were purchased from VWR (USA). Stir bars (Twister[®], 10 mm \times 1 mm; coated with polydimethylsiloxane (PDMS)) were purchased from Gerstel Inc. (MD, USA). EDCs were prepared in 1000 ppm stock solutions in methanol for gas chromatography-mass spectrometry (GC/MS). For yeast assays, hormones were prepared in 10 mM stock solutions in ethanol. All solutions were stored at 4 °C until used.

GAS CHROMATOGRAPHY MASS-SPECTROMETRY (GC-MS)

After stir bar sorptive extraction, stir bars were loaded into the thermal desorption unit (TDU) (Gerstel, US) under splitless mode. The desorbed chemicals were then cryo-focused in a baffle liner in a cryo-injection system (CIS 4) at -40 °C under liquid nitrogen prior to injection. The gas chromatography separations were performed on a Zebron ZB-5MS capillary column

(0.25 mm×30 m×0.25 μ m, Phenomenex, CA). The carrier gas (ultra-pure helium) was set to a constant flow of 1.2 mL/min. The mass spectrometer was operated in the scan mode with electron-impact ionization (ionization voltage, 70 eV). Target compounds were measured based on the following mass to charge ratios (M/Z): 135 and 149 NP, 181 lindane, 160 alachlor, 197 chlorpyrifos, 241 endosulfan, 225 ^{13}C -BPA, 213 BPA, 270 estrone, 272 estradiol and 213 17α -ethynylestradiol. A seven-point calibration curve was prepared with concentrations ranging from 0.005 to 22 $\mu\text{g/L}$. Method detection limits (MDLs) were calculated as $\sigma \cdot t$ -value, where σ is the standard deviation of seven standard samples times the t-value of 2.477 [46]. The method detection limits (MDLs) for BPA, NP, lindane, alachlor, chlorpyrifos, estrone, estradiol and 17α -ethynylestradiol were 0.010, 0.371, 0.673, 0.107, 0.020, 0.982, 0.135 and 0.538 $\mu\text{g/L}$, respectively.

FOUR-HOUR YEAST BIOASSAY

Estrogenic activity of wastewater samples was determined using a yeast bioassay modified to measure wastewater samples directly without extraction, concentration, or sterilization, as describe in previous studies [11]. The yeast parent strain was co-transformed with a *TRP1*-marked constitutive human ER α expression plasmid (pG/ER) [47] and URA3-marked estrogen inducible β -galactosidase reporter plasmid (pUCASS-ERE) [48] and maintained in synthetic complete media lacking uracil and tryptophan (SC-UW) to select for plasmid retention. Briefly, the yeast reporter strain was cultured overnight in SC-UW at 30°C in a shaking water bath. After overnight culture, the cells were diluted back to an optical density of 0.08 at 600 nm (O.D.600) and incubated in a shaking water bath at 30°C until the culture reached an O.D.600 of 0.1. The yeast culture in log-phase growth was aliquoted into 15 mL centrifuge tubes at 1 mL per tube. The cells were then harvested by centrifugation and suspended in 1 mL of SC-UW prepared by mixing 750 μL of wastewater with 250 μL of $\times 4$ (four-times) concentrated SC-UW for each assay to be performed. The cultures were then incubated at 30°C

with shaking for two hours. An aliquot of 100 μL from each culture was then transferred to an opaque 96-well plate, and 100 μL of Tropix Gal- Screen in Buffer B (Applied Biosystems, Foster City, CA) was added to each well. The plate was incubated for an additional two hours at room temperature. For all assays, a 17β -estradiol standard calibration curve was performed by diluting (concentrations ranging from $1\text{E-}15\text{ M}$ to $5\text{E-}7\text{M}$) into distilled, deionized water and treating identically as the wastewater samples. The hormone-induced chemiluminescent signal was then measured on a Luminoskan Ascent microplate luminometer (Thermo Fisher Scientific Inc., Waltham, MA).

RESULTS AND DISCUSSION

DETECTION OF EDCS AND REMOVAL IN WWTPS

Estradiol, EE2, lindane, alachlor, chlorpyrifos and endosulfan were less than method detection limits for all of the collected samples. Estrone was detected in both WWTPs in less than 5% of the samples with concentrations of approximately 7 ng/L and 500 ng/L in WWTP-A and WWTP-B, respectively. BPA and NP were detected in all influent samples for both WWTPs; detection frequencies and average concentrations are listed by unit process in Table 2-1. The detected average *cohort* concentrations for BPA and NP grouped by unit process are also presented in Figure 2.3.

The *cohort* EDC concentrations in the WWTP influent and individual unit treatment effluents were compared, as described in $R_{x,i} = 1 - \frac{C_{x,t_{0,i}+\tau_x}}{C_{0,i}}$

Equation 2-1, to determine the EDC treatment process removal ratios as shown in Table 2-1. The average *cohort* influent concentrations and *cohort* average final effluent removal ratios for BPA were 316 ng/L and 93% for WWTP-A and 487 ng/L and 87% for WWTP-B, which

agrees with other reported BPA influent average concentration and removal ratios for similar municipal WWTP [14]. BPA influent concentrations ranged from 221 ng/L to 391 ng/L and 350 ng/L to 609 ng/L in WWTP-A and WWTP-B, respectively. The highest influent concentrations of BPA were observed in samples collected at 6PM and 12PM for WWTP-A and WWTP-B, respectively. This trend is similar to the diurnal trend of most municipal WWTP cycles [45]. The lowest influent concentrations of BPA were detected at 1PM and 7AM for WWTP-A and WWTP-B, respectively. *Cohort* average BPA removals for reclaimed water were 99% and 99.6% for WWTP-A and WWTP-B, respectively. Biological treatment (aerobic) provided significant BPA removal, with removal of 94% and 88% for WWTP-A and WWTP-B, respectively (raw versus aeration). This performance is similar to other reported biological treatments [49]–[51].

Table 2-1 Detected average cohort concentrations, sample detection frequency and average cohort removal ratios (\bar{R}_x) of BPA and Nonylphenols in municipal wastewater treatment plants in El Paso, TX.

WWTP-A	BPA (n = 5)*				NP (n = 5)**			
	Average Concentration (ng/L)	Standard deviation	Detection Frequency	\bar{R} (%)	Average Concentration (ng/L)	Standard deviation	Detection Frequency	\bar{R} (%)
RAW	315.5	75.6	1.00	-	10645.1	2003.8	1.00	-
AER	18.9	13.1	1.00	94	693.8	177.3	1.00	95
SE	8.5*	3.8	0.83	98	489.9	37.8	1.00	96
SF	49.4	79.5	1.00	85	565.2	61.5	1.00	96
UV(Final)	19.1	13.5	1.00	93	674.3	143.2	1.00	94
PC(RW)	13.5	9.3	0.33	99	304.8**	117.9	1.00	97
WWTP-B	BPA (n = 6)*				NP (n = 6)**			
	Average Concentration (ng/L)	Standard deviation	Detection Frequency	\bar{R} (%)	Average Concentration (ng/L)	Standard deviation	Detection Frequency	\bar{R} (%)
RAW	487.0	86.6	1.00	-	72129.2	31267.7	1.00	-
PE	381.2	104.3	0.92	32	54055.5	31598.5	1.00	17
ANX	114.8	155.5	0.96	90	1006.8	705.8	1.00	99.0
AER	70.0	93.6	0.83	88	701.3	425.0	1.00	99.0
SE	72.6	146.4	0.71	84	320.1**	69.7	1.00	99.5
PC(Final)	75.3	117.3	0.92	87	270.4**	62.0	1.00	99.6
SF(RW)	2.7*	3.4	0.58	99.6	313.9**	49.8	1.00	99.5

* MDL for BPA = 10 ng/L, **MDL for NP = 371 ng/L; n = number of cohorts

NPs were detected in all collected samples for both treatment facilities. The influent average concentration ranged from 10.6 $\mu\text{g/L}$ to 72.1 $\mu\text{g/L}$ in WWTP-A and WWTP-B, respectively. The NP final effluent average concentration was approximately 0.3 $\mu\text{g/L}$ for both treatment facilities; these concentrations are similar to those reported for NPs in WWTPs effluents and reclaimed waters [9], [52]. This final effluent concentrations are biological relevant for small organisms where it could potentially have developmental, reproduction, and growth effects [20]. The overall *cohort* NP removal was observed to be 94% and 99.6% for WWTP-A and WWTP-B, respectively. The biological treatment process provided significant NP removal, with 95% and 99.0% removal for WWTP-A and WWTP-B, respectively (raw versus aeration effluent). It is interesting to note that the biological treatment in WWTP-A provided a better removal of BPA than WWTP-B, but the biological treatment in WWTP-B

(including an anoxic denitrification basin) provided better removal of NPs than WWTP-A (raw versus aeration effluent). As previously described, the biological treatment in WWTP-A includes an aeration basin with a hydraulic treatment time of about 11 hours versus 2 hours (aeration basin) in WWTP-B (Figure 2.2). Perhaps the aerobic treatment more effectively removes BPA [53], which could cause higher BPA removal in WWTP-A. NP removal (final effluent) was found to be about 4% higher in WWTP-B than WWTP-A.

ESTROGENIC ACTIVITY

An assessment of the reduction in the estrogenic activity in wastewater treatment processes was performed employing a four hour yeast bioassay [11]. This assay allows for assessing the total estrogenic activity from the mixture of EDCs in wastewater, including contaminants not analyzed by GC-MS in this present study. WWTP-A was observed to have higher estrogenic activity for both influent and effluent samples. The WWTP influent and effluent estrogenic activity expressed as estradiol equivalent concentration was determined to be 19.9 nM (5,418.2 ng/L) EEQ and 0.8 nM (227.8 ng/L) EEQ respectively (96% decrease in estrogenic activity, RAW versus final) for WWTP-A and 1.4 nM (368.6 ng/L) EEQ and 0.3 nM (84.0 ng/L) EEQ (79% decrease in estrogenic activity, RAW versus final) for WWTP-B. The greatest reduction in estrogenic activity was observed in biological treatment (aeration basin, as shown in Figure 2.3), as was also observed for BPA and NP removal (Figure 2.3). For the WWTP-A treatment system, unit process effluents downstream of the aeration basin were observed to have higher estrogenic activity than a blank sample (265 pM EEQ), including the WWTP-A final effluent (Figure 2.3). However, for WWTP-B, the unit processes downstream of aeration exhibited estrogenic activity similar to the blank.

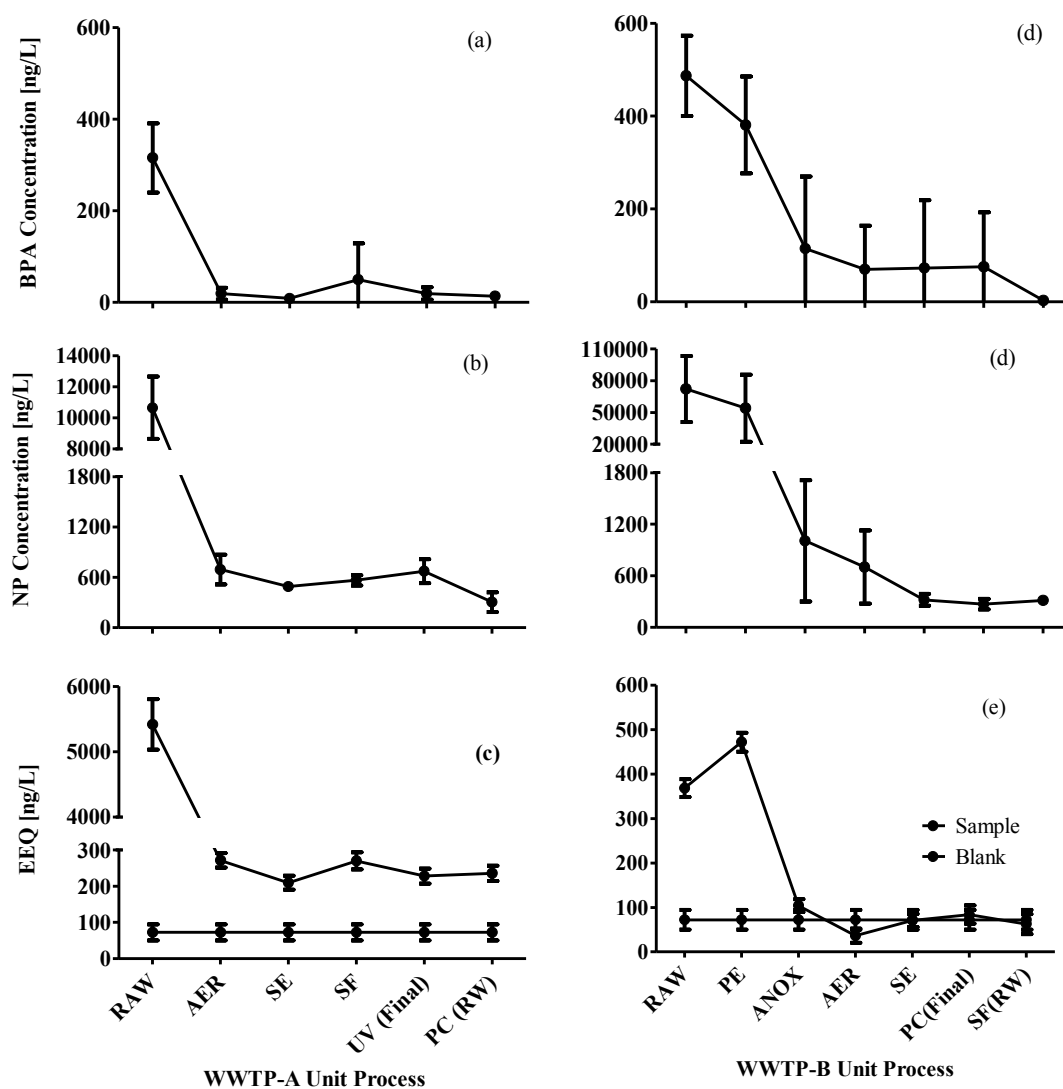


Figure 2.3 Average *cohort* concentrations of BPA, NP, and measured estradiol equivalent concentrations by bioassay (EEQs) throughout each unit process for WWTP-A (a, b, and c) and WWTP-B (d, e, and f), respectively. Error bars show ± 1 standard deviation.

CONCLUSIONS

The goal of this research was to assess EDC removal in municipal wastewater treatment processes. The municipal WWTPs selected for this study have different unit treatment processes; WWTP-B includes both primary sedimentation and an anoxic basin before aeration,

but WWTP-A does not include either. Analysis of WWTPs revealed that the biological treatment in WWTP-A provided better removal efficiency of BPA than WWTP-B, but the biological treatment in WWTP-B (including anoxic treatment) provided better removal efficiency of NP.

Overall removal was observed to be 96% and 99% for BPA and 97% and 99.5% for NP for WWTP-A and WWTP-B, respectively (Table 2-1 and Figure 2.3). Bioassays revealed much greater estrogenic activity in the influent of WWTP-A than WWTP-B, but both WWTP-A and WWTP-B produced a final effluent with relatively low estrogenic activity and near-blank estrogenic activity (Figure 2.3) in WWTP-A and WWTP-B, respectively. The concentration of NP in the final effluent was 674 ng/L and 270 ng/L for WWTP-A and WWTP-B. These concentrations could potentially have biological effects to small organisms such as growth reduction and shifted sex ratios, which have been reported at 1 to 6.7 µg/L [20], [54]. The long term exposure of NP concentrations similar to the effluents of WWTP-A could have adverse effects in the ecosystem. This could potentially result in a long term impact to human population as NP could bio-accumulate in the food chain, and potentially impact drinking water resources resulting in accumulation in human adipose tissue and human breast milk [55]–[57]. The effect could potentially be more detrimental to children during the developmental stage [58], [59]. The presence of these chemicals in wastewater effluents creates the need to explore sustainable means to mitigate long term human and environmental impact.

CHAPTER 3: LIFE CYCLE IMPACT ASSESSMENT (LCIA) OF AOPS IN MUNICIPAL WASTEWATER TREATMENT FACILITIES

ABSTRACT

The environmental impact of two municipal wastewater treatment plants in El Paso, TX was investigated. The study considered the addition of UV/H₂O₂ and the corresponding impacts in global warming potential, acidification potential, eutrophication potential, and freshwater aquatic ecotoxicity potential impact categories. The use of 10 mg/L H₂O₂ in a municipal wastewater treatment facility employing UV for effluent disinfection, yield increments of 3% global warming potential, 2% acidification potential, 5% eutrophication potential, 3% freshwater aquatic ecotoxicity potential, and 42% in terrestrial ecotoxicity potential. The results were evaluated in a developed Eco-Score Card in which it was observed 13% increase of the overall environmental impact with the addition of 10 mg/L peroxide. Similar analysis was performed for a second municipal wastewater facility, which resulted in lower Eco-Score values, but double the environmental impact increase. The results indicate the potential use of UV disinfection systems as potential UV/H₂O₂ advanced oxidation processes in wastewater treatment with relatively low environmental impact for municipal wastewater treatment with current use of UV disinfection.

INTRODUCTION

With a continuously increasing global population and imminent water scarcity in semiarid regions we face a global need to develop more sustainable water supply alternatives. In recent years, direct potable reuse has gained worldwide interest for the development of “new” water supplies, especially in semiarid regions. The enhancement and selection of sustainable means for wastewater treatment can yield many benefits such as the low cost acquisition of new water supplies, water stress mitigation and preservation of existing water supplies. The use of

advance oxidation processes (AOPs) has been widely studied for wastewater treatment and reuse [15], [25]–[29]. On the other hand, close to 4% of the current energy demand in the United States is attributed to water and wastewater treatment, and the selection of AOP methods could potentially increase the current energy demand, operational cost, and carbon footprint of WWTP facilities [33], [60], [61], possibly outweighing the environmental benefits.

Municipal wastewater treatment facilities commonly employ the use of UV systems for disinfection. Perhaps the engineering of such systems into UV/AOPs could increase effluent quality for the application of water reuse with a relatively small increase in carbon footprint. In addition, such modifications could lead to other environmental benefits such as reduced water stress, production of new water supplies and the mitigation of environmental impact by reduced chemical oxygen demand, biological oxygen demand, removal of recalcitrant pollutants such as pesticides and endocrine disrupting chemicals [25], [26], [30]–[32]. Commonly used UV/AOPs with the lowest operational cost and green house gas emissions include the use of O_3 and H_2O_2 . The use of O_3 /UV and H_2O_2 /UV has been reported to have a cost and green house gas emissions of \$0.21/L and 5.54 Kg CO_2 -e/KL and \$0.14/L and 0.20 Kg CO_2 -e/KL, respectively [33]. The employment of these oxidants, especially H_2O_2 , could be even more affordable for wastewater treatment facilities equipped with UV disinfection units. This study focuses on assessing the environmental impact of the implementation of UV/ H_2O_2 in two municipal wastewater treatment facilities (WWTP-A and WWTP-B) in El Paso, TX.

The goal of this study is to assess the potential environmental impact for the modification of municipal wastewater UV disinfection systems into AOPs. To achieve this goal three objectives are included: (a) develop an annual inventory of municipal wastewater treatment plants and assess environmental performance based on current operational conditions, (b) assess

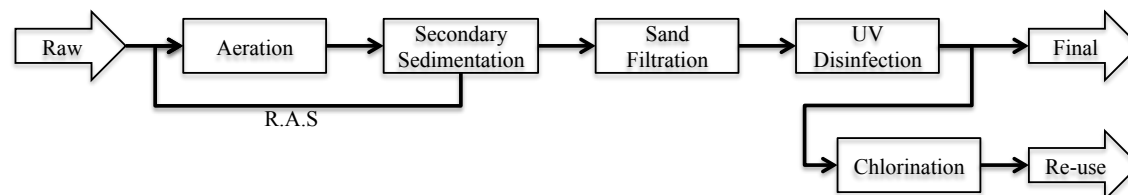
the environmental impact for the addition of peroxide dosing in the UV disinfection system as a potential AOP modification, and (c) compare this modification with the complete new addition of an $\text{H}_2\text{O}_2/\text{UV}$ AOP to municipal wastewater treatment plants based on the chemical dose and energy requirements.

METHODS

WASTEWATER TREATMENT PLANTS (WWTPS)

Two municipal wastewater treatment facilities, WWTP-A and WWTP-B, were selected for the life cycle impact assessment. Both WWTPs include secondary municipal treatment, but only one treatment facility currently employs UV for disinfection. As illustrated in Figure 3.1, the WWTP-A process includes aeration, secondary sedimentation, sand filtration, and ultra violet (UV) disinfection before the water is discharged to the Rio Grande. A portion of the effluent is reclaimed and treated in a chlorination basin for municipal reclamation (purple pipe) for landscape irrigation. Sludge from WWTP-A is currently conveyed to the raw influent of WWTP-B and approximately accounts for 20% of the total produced sludge. The WWTP-B process includes primary sedimentation, anoxic denitrification, aeration, secondary sedimentation, and a chlorination basin before the final treated effluent is typically discharged to an agricultural irrigation canal. A portion of the final effluent is reclaimed and filtered through a sand filtration basin for municipal reclamation (purple pipe) for landscape irrigation.

WWTP-A



WWTP-B

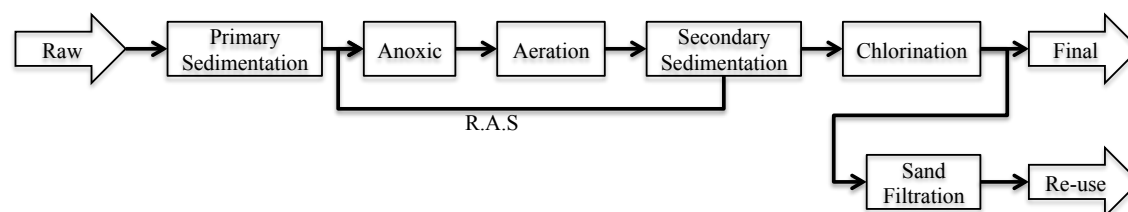


Figure 3.1 Schematic layout of selected Municipal Wastewater Treatment Facilities in El Paso, TX.

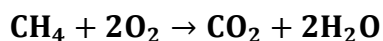
LCIA FUNCTIONAL UNIT AND SYSTEM BOUNDARIES

The environmental impact assessment was determined creating a life cycle inventory assessment (LCIA) based on a 3-year average inventory for each wastewater treatment plant. The inventory was normalized to a functional unit of 1 billion gallons (BGal) of effluent. The LCIA was based on four impact categories: Global Warming Potential (GWP), Eutrophication Potential (EUP), Acidification Potential (AP) and Freshwater Aquatic Ecotoxicity Potential (FAEP). The 2012-2014 average annual effluent productions for WWTP-A and WWTP-B were 2.51 and 5.24 billion gallons (BGal), respectively. Based on the annual average effluent production, a functional unit of 1.0 BGal was selected for the environmental assessment. All items included in the inventory were normalized to the functional unit. A gate to gate analysis was chosen to perform the environmental assessment. The inventory includes chemicals, tap water, energy, and natural gas consumption. Nutrients and other constituents in the effluent and sludge cake were excluded from the analysis, because they would not be affected by the AOP.

WWTPS LCIA INVENTORY

Three years of monthly data (calendar years 2012-2014) were collected for both municipal wastewater treatment facilities. The data included the energy consumption, chemical use, tap water consumption, methane production, as well as wastewater influent and effluent flow rates for both treatment facilities, as listed in Table 3-1. Carbon dioxide production was calculated assuming complete combustion ($\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Equation 3-1) of the mass of natural gas and biotic methane consumed. The abiotic methane is produced in the treatment and digestion of the wastewater sludge. An average of 20% of the sludge treated in WWTP-B originates from WWTP-A, therefore 20% of the CO₂ emissions produced during the energy cogeneration with abiotic methane was assigned to WWTP-A as listed in Table 3-1. The data were used to calculate yearly average inventory, which was normalized to a functional unit of 1.0 BGal of effluent produced (Table 3-1).



Equation 3-1

Table 3-1 Normalized annual average Life cycle inventory (LCI) for WWTP-A and WWTP-B.

Inventory Item	FU Normalized Annual Average	
	WWTP-A	WWTP-B
Life Cycle Inventory		
Influent (MG)	1,080	1,170
Chlorine (Kg)	18,630	47,447
Caustic Soda (Kg)	19,546	7,401
Bleach (Sodium Hypochlorite) (Kg)	9,968	4,804
Nitric Acid (Kg)	-	18
Ferrous Chloride (Kg)	-	45,598
Tap Water (Kg)	301,406	113,283
Electricity (MJ)	13,207,916	7,809,479
Electricity produced (MJ)	-	421,217
Natural Gas (Kg)	119,288	961
Outputs		
Effluent (MG)	1,000	1,000
Biotic Methane Production (Kg)	-	344,069
Methane Combusted (Kg)	-	161,355
Methane Flared (Kg)	-	182,714
CO ₂ (Kg) Emissions Total	2,230,252	1,571,095
CO ₂ (Kg) Emissions (NG + F)	428,534	404,854
CO ₂ (Kg) Emissions Co-Gen	88,745	354,981

LCIA MODEL IMPACT ASSESSMENT AND AOP MODIFICATIONS

The inventory was utilized to create a life cycle impact assessment (LCIA) in the life cycle assessment software GaBi version 6.106. The impact assessment was based on the selection of the most commonly used impact categories in the literature; including global warming potential (GWP), acidification potential (AP), eutrophication potential and fresh water ecotoxicity potential. Two basic models were created in GaBi to represent the overall treatment process for WWTP-A and WWTP-B based on their respective inventories (Figure 3.2). The model was based on the functional unit normalized inventory items for each WWTP and the GaBi built-in processes for electrical supply from Texas electrical grid, tap water supply and

natural gas supply for both WWTPs as well as the methane thermal energy cogeneration for WWTP-B. The LCIA model analysis results are listed in Table 3-2.

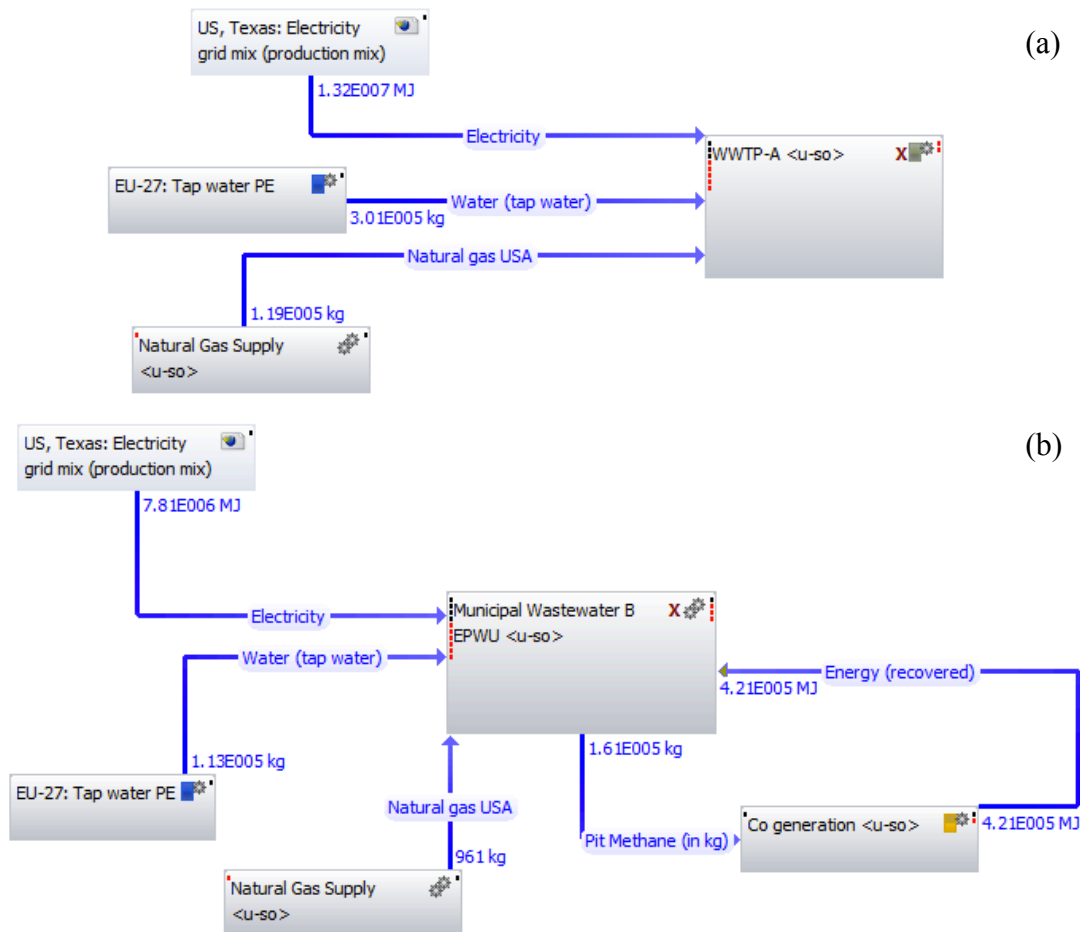


Figure 3.2 LCI models created in GaBi for WWTP-A (a) and WWTP (b).

ADVANCED OXIDATION PROCESSES SCENARIOS

Three UV/H₂O₂ scenarios resulting in the same product of oxidant dosage and energy requirement were selected for this study. The selection of the scenarios was based on typical H₂O₂ dosage and typical energy requirements for irradiation dosage assuming the use of 15% efficiency UV light bulbs. The three levels of required energy for UV dosing include 0.5, 1.0

and 1.5 KWH/m³, and the three levels of H₂O₂ dosage were 3, 5 and 10 mg/L. The levels were combined to create a constant UV-H₂O₂ product as follows; 1.5 KWH/m³ and 3 mg/L H₂O₂, 1.0 KWH/m³ and 5 mg/L H₂O₂, and 0.5 KWH/m³ and 10 mg/L H₂O₂. The levels were designed to create stress levels on either energy consumption and/or chemical dosage. This resource stress assignment could aide the selection of more sustainable alternatives. An Eco-Score (**EcoSocre** = $\sum \frac{IC_{Total}}{IC_{average}}$ Equation 3-2) was created to assess the overall impact of the selected scenarios (Table 3-4). The Eco-Score was determined as described bellow, where IC_{Total} is the total impact potential of the scored category and IC_{average} is the average of the total impact potential of all scenarios included in this study.

$$\mathbf{EcoSocre} = \sum \frac{IC_{Total}}{IC_{average}} \quad \text{Equation 3-2}$$

RESULTS AND DISCUSSION

LCIA COMPARISON OF WASTEWATER TREATMENT PLANTS

Two basic models based on a functional unit of 1.0 BGal of effluent produced were created in GaBi to represent the overall treatment process for WWTP-A and WWTP-B based on their respective inventories (Figure 3.2). The LCIA results for both WWTPs are listed in Table 3-2. From the results we can compare the environmental potential impact of both WWTPs into the four impact categories. As expected, based on the higher electrical energy consumption (E. Grid), the electric energy consumption accounted for a significant portion of the carbon footprint: 83% and 67% for WWTP-A and WWTP-B, respectively. This observation agrees with other reported values [33]. In addition WWTP-B had an average biotic methane production of 344,069 Kg per functional unit, 47% of the methane is used for thermal energy cogeneration that decreases the electrical demand by the plant and the remaining 53% is flared. The methane consumed in this process produces a carbon footprint of 443,726 Kg CO₂-equivalent per 1 BGal

of effluent. Based on the sludge contribution for each plant, 80% of these emissions (flare and cogeneration) can be assigned to WWTP-B and the remaining 20% to WWTP-A (sludge from WWTP-A is processed in WWTP-B accounting for nearly 20% of the total sludge).

The environmental performance of both WWTPs was dominated (100%) by the electrical energy consumption in almost all impact categories but the GWP, for the calendar years 2012-2014. The GWP contribution distribution for WWTP-A was observed to be 83% from electrical consumption, 3% from cogeneration, and 14% from wastewater treatment processes including natural gas consumption and methane flare (20% assignment based on sludge contribution). The GWP contribution distribution for WWTP-B was observed to be 67% electrical energy consumption, 16% cogeneration, and 18% wastewater treatment processes including natural gas consumption and methane flare. The electrical energy consumption dominated all the impact categories by nearly 100%, and the impact of other inventory items was negligible.

Table 3-2 Environmental performance assessment of WWTP-A and WWTP-B.

Global Warming Potential [kg CO ₂ -Equiv.]						
Source	(A) WWTP-A	(A-1) WWTP-A 10 mg/L H ₂ O ₂	(B) WWTP-B	(B-1) WWTP-B 10 mg/L H ₂ O ₂ + 0.5 KWH/m ³	(B-2) WWTP-B 5 mg/L H ₂ O ₂ + 1.0 KWH/m ³	(B-3) WWTP-B 3 mg/L H ₂ O ₂ + 1.5 KWH/m ³
E. Grid	2,567,996	2,567,996	1,518,386	1,610,838	1,703,291	1,795,744
H ₂ O ₂	0	107,457	0	107,457	53,729	32,237
CoGen	88,745	88,745	354,981	354,981	354,981	354,981
Water	126	126	64	64	64	64
WWTP	328,041	328,041	505,107	505,107	505,107	505,107
Total	2,984,909	3,092,366	2,378,537	2,578,447	2,617,171	2,688,132
Acidification Potential [kg SO ₂ -Equiv.]						
Source	(A)	(A-1)	(B)	(B-1)	(B-2)	(B-3)
E. Grid	6,015	6,015	3,557	3,773	3,990	4,207
H ₂ O ₂	0.0	98.4	0.0	98.4	49.2	29.5
Water	0.2	0.2	0.1	0.1	0.1	0.1
Total	6,016	6,114	3,557	3,872	4,039	4,236
Eutrophication Potential [kg Phosphate-Equiv.]						
Source	(A)	(A-1)	(B)	(B-1)	(B-2)	(B-3)
E. Grid	327	327	193	205	217	229
H ₂ O ₂	0.0	16.5	0.0	16.5	8.3	5.0
Water	0.1	0.1	0.0	0.0	0.0	0.0
Total	327	344	194	222	225	234
Freshwater Aquatic Ecotoxicity Pot. [kg DCB-Equiv.]						
Source	(A)	(A-1)	(B)	(B-1)	(B-2)	(B-3)
E. Grid	4,814	4,814	2,847	3,020	3,193	3,367
H ₂ O ₂	0.0	128	0.0	128	64	38
Water	0.5	0.5	0.3	0.3	0.3	0.3
Total	4,815	4,942	2,847	3,148	3,257	3,405
Terrestrial Ecotoxicity Potential [Kg DCB-e]						
Source	(A)	(A-1)	(B)	(B-1)	(B-2)	(B-3)
E. Grid	1,176	1,218	737	737	780	822
H ₂ O ₂	0.0	870	0.0	870	435	261
Water	0.2	0.2	0.1	0.1	0.1	0.1
Total	1,176	2,089	738	1,608	1,215	1,083

SENSITIVITY ASSESSMENT FOR THE ADDITION OF A UV/H₂O₂ AOP IN MUNICIPAL WWTPS

A sensitivity analysis was performed for the environmental impact of using peroxide and UV as an AOP enhancement of the municipal wastewater treatment plants. Three scenarios were considered with peroxide concentrations (3, 5 and 10 mg/L) and corresponding UV dose (1.5, 1.0 and 0.5 Kwh/m³ required energy assuming 15% UV light bulb efficiency). The three combinations were simulated in the GaBi model for WWTP-B (Table 3-2). A sensitivity analysis was performed based on the assessment of environmental impact for H₂O₂ concentration and UV dosage on the selected eco-indicators (GWP, AP, EUP, FAEP, and TEP), and relative differences are listed in Table 3-3.

The three combinations were defined as AOP1 (3 mg/L H₂O₂ and 1.5 Kwhr/m³), AOP2 (5 mg/L H₂O₂ and 1.0 Kwhr/m³) and AOP3 (10 mg/L H₂O₂ and 0.5 Kwhr/m³). The GaBi model was modified to include the H₂O₂ consumption for the additional energy consumption creating a new inventory. Annual inputs of 11,356 Kg, 18,927 Kg and 37,854 Kg H₂O₂ per functional unit and 1,426,529 MJ, 951,019 MJ and 475,509 MJ electrical energy per functional unit were included in the inventory for AOP1, AOP2 and AOP3 respectively. The WWTP-A AOPs (AOP3) modifications resulted in 4%, 2%, 5%, 3%, and 78% increase for GWP, AP, EUP, FAEP, and TEP respectively (Table 3-3). Electrical energy consumption was the factor with the highest environmental impact potential in almost all categories but TEP. Peroxide accounted for 3%, 2%, 5%, 3%, and 42% of the GWP, AP, EUP, FAEP, and TEP, respectively. Energy consumption accounted for 80%, 98%, 95%, 97%, and 58% of the GWP, AP, EUP, FAEP, and TEP, respectively. The Eco-Score of these scenarios for WWTP-A was observed to be 5.9 for 2012-2014 annual average scenario (A) and 6.7 for the scenario for the addition of 10 mg/L

peroxide (AOP scenario) (A-1) as illustrated in Figure 3.4. The score indicates a 13% increase in the overall potential impact by the addition of 10 mg/L peroxide.

The modification of WWTP-B was modeled in GaBi to include the three selected scenarios for this study. It was observed a significantly higher sensitivity of these modifications in all the impact categories, when compared to WWTP-A. The scenario for AOP1 resulted in 13%, 9%, 15%, 11%, and 118% increase in GWP, AP, EUP, FAEP, and TEP, respectively; resulting on Eco-Score of 4.7. The scenario for AOP2 resulted in 15%, 14%, 17%, 14%, and 65% increase in GWP, AP, EUP, FAEP, and TEP, respectively; resulting on Eco-Score of 4.5. The scenario for AOP3 resulted in 18%, 19%, 21%, 20%, and 47% increase in GWP, AP, EUP, FAEP, and TEP, respectively; resulting on Eco-Score of 4.5. The use of peroxide was observed to have a higher effect on the TEP resulting in 54%, 36%, and 24% contribution for AOP1, AOP2, and AOP3 scenarios, respectively.

The relatively low environmental impact for the use of H_2O_2 for AOP applications presents a great opportunity for enhancement of wastewater treatment processes. Especially in the case of WWTP-A, which currently has an UV disinfection system, where a 4% GWP increase, 2% AP increase, 5% EUP increase and 3% increase been determined with the peroxide addition (AOP scenario) (Table 3-3).

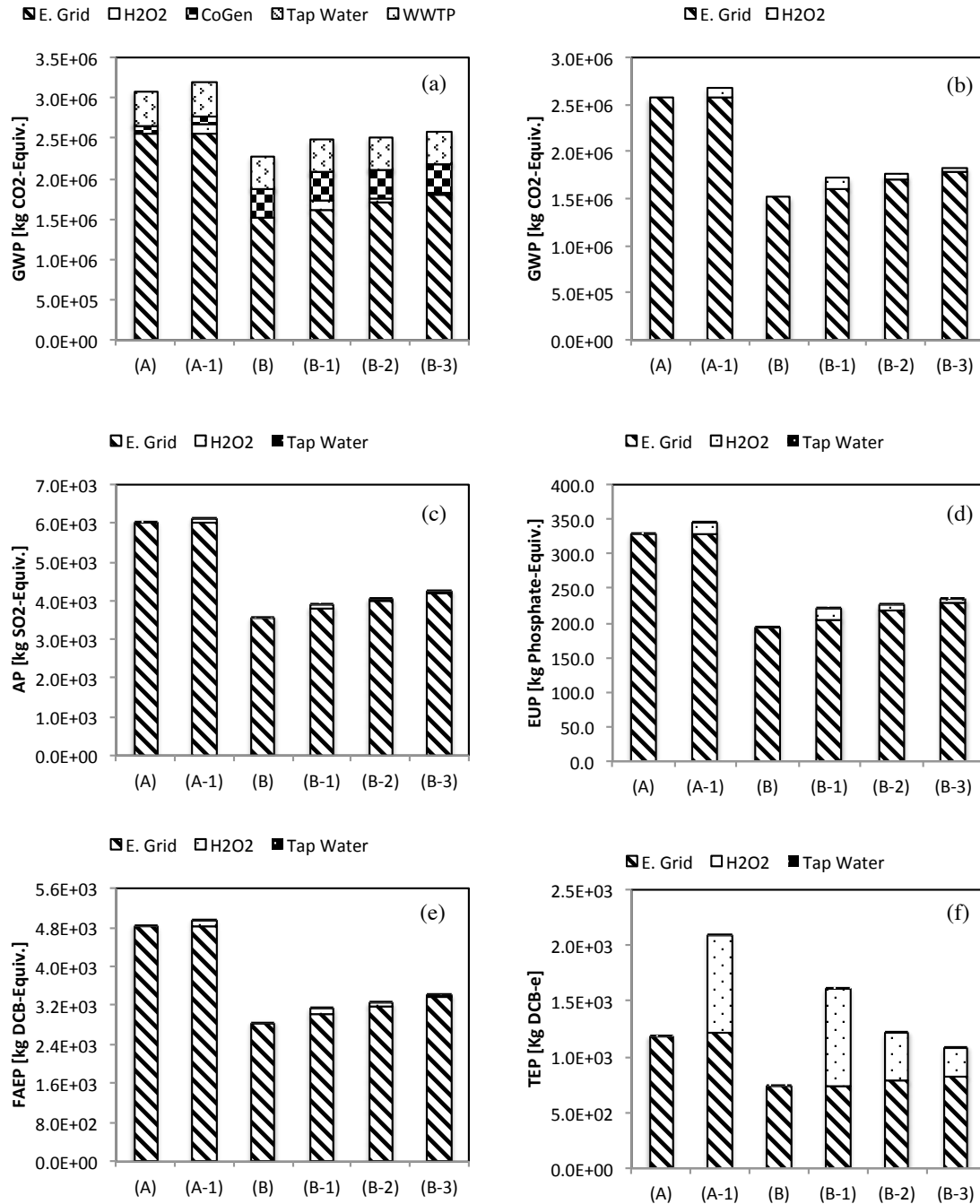


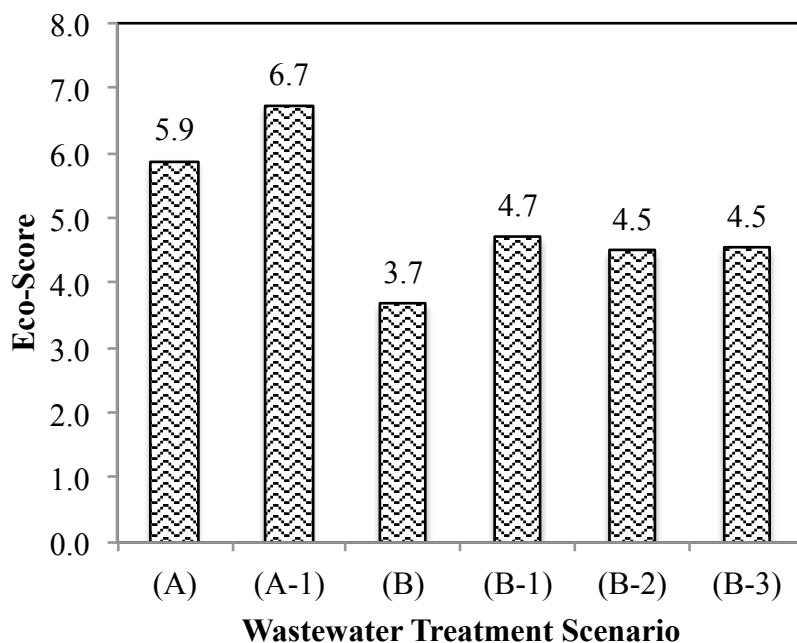
Figure 3.3 Sensitivity analysis for the addition of an AOP system in WWTP-A and WWTP-B, based on global warming potential (a and b), acidification potential (c), eutrofication potential (d), freshwater aquatic ecotoxicity potential (e), and terrestrial ecotoxicity potential (f).

Table 3-3 Environmental sensitivity assessment from energy demand and chemical dose for H₂O₂/UV AOP application in municipal WWTPs.

Category	Total increase to impact category			
	WWTP-A	WWTP-B		
	AOP	AOP1	AOP2	AOP3
GWP	4%	13%	15%	18%
AP	2%	9%	14%	19%
EUP	5%	15%	16%	21%
FAEP	3%	11%	14%	20%
TEP	78%	118%	65%	47%
Category	H ₂ O ₂ environmental impact percent contribution			
	WWTP-A	WWTP-B		
	AOP	AOP1	AOP2	AOP3
GWP	3%	4%	2%	1%
AP	2%	3%	1%	1%
EUP	5%	7%	4%	2%
FAEP	3%	4%	2%	1%
TEP	42%	54%	36%	24%
Category	Electric consumption environmental impact percent contribution			
	WWTP-A	WWTP-B		
	AOP	AOP1	AOP2	AOP3
GWP	80%	62%	65%	67%
AP	98%	98%	99%	99%
EUP	95%	92%	96%	98%
FAEP	97%	96%	98%	99%
TEP	58%	46%	64%	76%

Table 3-4 Eco-Score Card evaluation of different wastewater treatment scenarios

Scenario	GWP		AP		EUP		FAEP		TEP		Total Score
	Total	Score	Total	Score	Total	Score	Total	Score	Total	Score	
(A)	3,085,401	1.13	6,016	1.30	327	1.27	4,815	1.29	1,176	0.89	5.9
(A-1)	3,192,859	1.17	6,114	1.32	344	1.33	4,942	1.32	2,089	1.58	6.7
(B)	2,278,285	0.83	3,557	0.77	194	0.75	2,847	0.76	738	0.56	3.7
(B-1)	2,578,447	0.94	3,872	0.83	222	0.86	3,148	0.84	1,608	1.22	4.7
(B-2)	2,617,171	0.96	4,039	0.87	225	0.87	3,257	0.87	1,215	0.92	4.5
(B-3)	2,688,132	0.98	4,236	0.91	234	0.91	3,405	0.91	1,083	0.82	4.5
Average	2,740,049		4,639		258		3,736		1,318		



chong

Figure 3.4 Wastewater treatment scenarios Eco-Scores

CONCLUSIONS

The environmental performance of two municipal wastewater treatment plants was analyzed based on the normalized 3-year average life cycle inventory. It was discovered that WWTP-A has a greater impact in all impact categories, as a result of the current energy demand. The WWTP-A GWP was 35% higher than WWTP-B and more than 60% higher in AP, EUP, FAEP, and TEP. The addition of 10 mg/L peroxide resulted in potential impact increases of 3%, 2%, 5%, 3% and 78% for GWP, AP, EUP, FAEP, and TEP for WWTP-A. The addition of 10 mg/L peroxide resulted in 13% higher Eco-Score, this scenario can be improved by reducing the peroxide addition to 5 mg/L which will result in an Eco-Score of 6.3 (7% higher than no peroxide addition). The scenarios included for WWTP-B resulted in lower Eco-Score values when compared to WWTP-A. The scenarios for WWTP-B and the three proposed scenarios (B-1, B-2, and B-3) resulted in Eco-Score values of 3.7, 4.7, 4.5, and 4.5, respectively. This

proposed modifications resulted in Eco-Score values higher than 20% when compared to current performance of WWTP-B scenario (B). The potential employment of the UV disinfection system as an AOP with relatively low environmental impact leads to the need to investigate the benefits of such modification. Benefits will need to be investigated to include removal of recalcitrant constituents and the potential application for direct portable reuse.

CHAPTER 4: PHOTOCHEMICAL DEGRADATION OF ESTROGENIC EDCS WITH UV AOPS: A COMPARISON OF PEROXIDE AND PERACETIC ACID

ABSTRACT

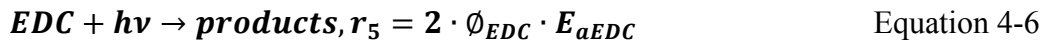
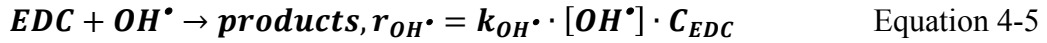
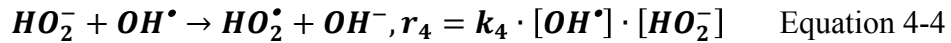
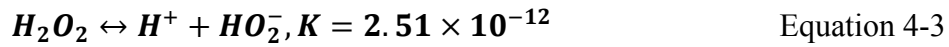
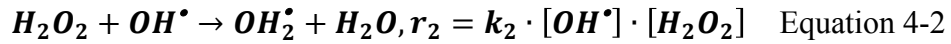
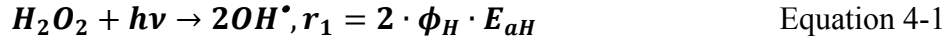
The use of advanced oxidation processes has recently gained worldwide interest for portable water reuse. Here the use of $\text{H}_2\text{O}_2/\text{UV}$ and PAA/UV was investigated to explore potential benefits of PAA/UV for water reuse. The use of PAA/UV and $\text{H}_2\text{O}_2/\text{UV}$ at different UV dosage and initial oxidant concentrations was investigated. The molar absorption coefficients (ϵ) for both H_2O_2 and PAA in DI water were determined at 254nm. The ϵ for H_2O_2 and PAA were 20.04 and 17.69 $\text{M}^{-1} \text{cm}^{-1}$ respectively. Direct UV (1 J/cm^2 , 254 nm) irradiation was found to remove up to 19%, 11% and 61% of the initial concentrations of estradiol, BPA and NP respectively. The UV irradiation of solutions with 10 mg/L initial concentration of H_2O_2 yield removals of 100%, 94% and 84% for estradiol, BPA and NP respectively. The UV irradiation of 5 mg/L initial concentration PAA yield removals of >99.9%, >99.9% and 24% for estradiol, BPA and NP respectively.

INTRODUCTION

The employment of advanced oxidation processes (AOPs) for drinking water treatment purposes have recently gained worldwide interest, especially for the wastewater effluent treatment for direct potable reuse [62]–[70]. One of the most common AOPs water treatment methods currently used in water treatment facilities worldwide is the combination of UV and chemical oxidants; including ozone (O_3), hydrogen peroxide (H_2O_2), and metal oxides (e.g., TiO_2). The estimated specific energy requirement for AOPs in decentralized wastewater treatment plants including the use of O_3 , O_3/UV and $\text{H}_2\text{O}_2/\text{UV}$ are 11.93, 6.15 and 0.23 kWh/m^3 , respectively [33]. In addition, the reported indirect green house gas emissions related to AOPs

employing O₃, O₃/UV and H₂O₂/UV are 10.74, 5.54 and 0.20 Kg CO₂-e/m³ [33]. Based on the estimated energy requirements and greenhouse gas emissions H₂O₂ appears to be a suitable and more sustainable choice for AOP water treatment. Still the developments of more sustainable means for water treatment are needed to further mitigate the operational cost, green house gas emissions and mitigation of environmental impact.

The use of H₂O₂ and UV light produces hydroxyl radicals (OH[•]), which are very reactive species and may be used to degrade endocrine disrupting compounds (EDCs). The reactions and reaction rates in a H₂O₂ photochemical system are represented by the following equations [71]–[75]:



Where,

$$\phi_H = H_2O_2 \text{ quantum yield}$$

$$k_2 = 2.7 \times 10^7 s^{-1}$$

$$k_4 = 7.5 \times 10^9 s^{-1}$$

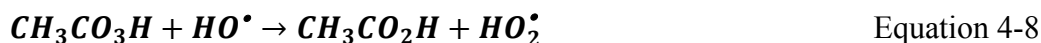
$$E_{aH} = \text{irradiance absorbed by } H_2O_2$$

$$E_{aEDC} = \text{irradiance absorbed by EDC}$$

$$K = \text{equilibrium constant}$$

Hydroxyl radicals will react rapidly with the target EDCs as described above. The reported k_{OH^\bullet} for BPA, estradiol, and nonylphenols (NP) are 8.00×10^9 , 14.10×10^9 , and $8.56 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, respectively [64], [76]. By inspection of the EDC hydroxyl radical reaction rates NP will be the most resistant to UV/H₂O₂ treatment in water.

The presence of these EDCs presents a challenge for current wastewater treatment processes. There is a current need to develop efficient ways of removing these contaminants from wastewater treatment effluents to further mitigate the environmental impact and preserve the quality of future water resources. In recent years, the use of peracetic acid (PAA, CH₃COOH) has gained wide interest for chemical disinfection and enhancement of UV-disinfection in water treatment [77]–[84]. Studies reported significant increase in disinfection efficiency with the use of PAA and UV, as well as comparable log removal as those of hypochlorite (NaOCl) and ozone (O₃) [80]. The UV irradiation of PAA results in the formation of hydroxyl (HO^\bullet) and perhydroxyl (HO_2^\bullet) radicals as described below [85]:



Perhaps the use of UV AOPs could be employed for the removal of EDCs in municipal wastewater treatment effluents to mitigate environmental impacts in the receiving stream or downstream *defacto* reuse. The goal of this study was to compare the use of UV/H₂O₂ and UV/PAA AOPs for the removal of BPA, estradiol, and NP in DI water. In order to achieve this goal three objectives are included: (a) characterize the residence time distribution (RTD) and actinometry of a lab-scale continuous-flow UV reactor, (b) the second objective was evaluate the use of UV/H₂O₂ and UV/PAA as chemical oxidants for the removal of EDCs, (c) the third

objective was to estimate the required UV energy dose and initial chemical concentrations to achieve 90% removal of EDCs in aqueous solutions.

MATERIAL AND METHODS

PHOTOCHEMICAL REACTOR

REACTOR TRACER TEST CHARACTERIZATION

An Ideal Horizons UV reactor (Model IH-1) was employed to carry out the photochemical treatment of water. The reactor consists of a quartz tube aligned in parallel with an 8 W UV lamp (Model # 22001) (Figure 4.1). The quartz tube has a total volume of 147 cm³ and an active volume of 120 cm³ (2.2 cm internal diameter, 31.7 cm length) that is exposed to UV irradiation. The reactor was employed as a continuous flow through system, and feed solutions were pumped with a Cole Parmer (Master Flex L/S digital economy drive) peristaltic pump.

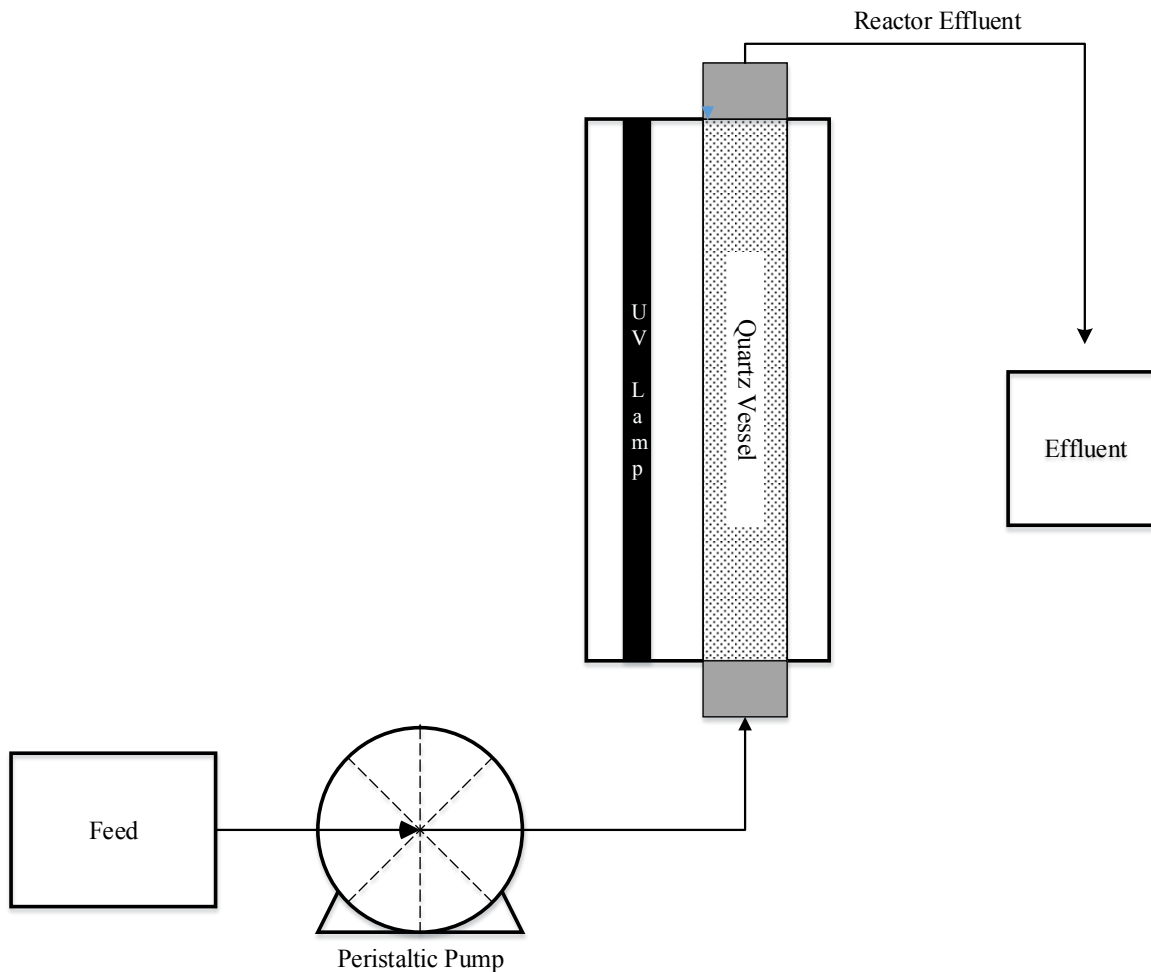


Figure 4.1 Diagram of photochemical reactor apparatus.

A step-function tracer test was performed with DI water and a tracer (dye) to characterize the hydraulic behavior (residence time distribution) of the reactor at flow rates of 50, 95, 150 and 300 mL/min, corresponding to theoretical detention times (τ) of 2.4, 1.3, 0.8 and 0.4 minutes, respectively (based on the active volume of the reactor). The effluent of each of the four tracer tests was sampled periodically, and the tracer concentration was measured with an Agilent Model # 8453 UV spectrophotometer. The mean residence time of the reactor (\bar{t}), normalized time ($\theta = t/\bar{t}$), exit age distribution (E), and cumulative age (F) were calculated following the methods described in MWH [86] and Benjamin and Lawler [87], and the residence time distributions are shown in Figure 4.2.

The exit age distribution of the reactor was modeled using the dispersed flow model (DFM) and tanks-in-series (TIS) model [86], as shown in $E(\theta)_{DFM} = \frac{1}{\sqrt{4\pi\theta(1/Pe)}} e^{-Pe(1-\theta)^2/4\theta}$

Eq. 4-9 and $E(\theta)_{TIS} = \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta}$ Eq. 4-10. The two fitting parameters in the DFM were the mean residence time (\bar{t}) and the dispersion number (d), which is the reciprocal of the Péclet number (Pe). The two fitting parameters in the TIS model were the mean residence time (\bar{t}) and the number (n) of theoretical mixing tanks in series. The best-fit values (by least squares) for each of the two models for each flow are listed in Table 4-1. Based on the tracer test analysis, the reactor behaves similarly to a PFR with relatively low dispersion (or a minimum of 33 tank-in-series) for the flow conditions employed in this study. The effective normalized time (θ_{eff}) was calculated by integrating the normalized time (θ) as a function of the cumulative probability (F), as shown in Eq. 4-11. The effective detention time (τ_{eff}) was calculated by multiplying the effective normalized time by the mean residence time (\bar{t}).

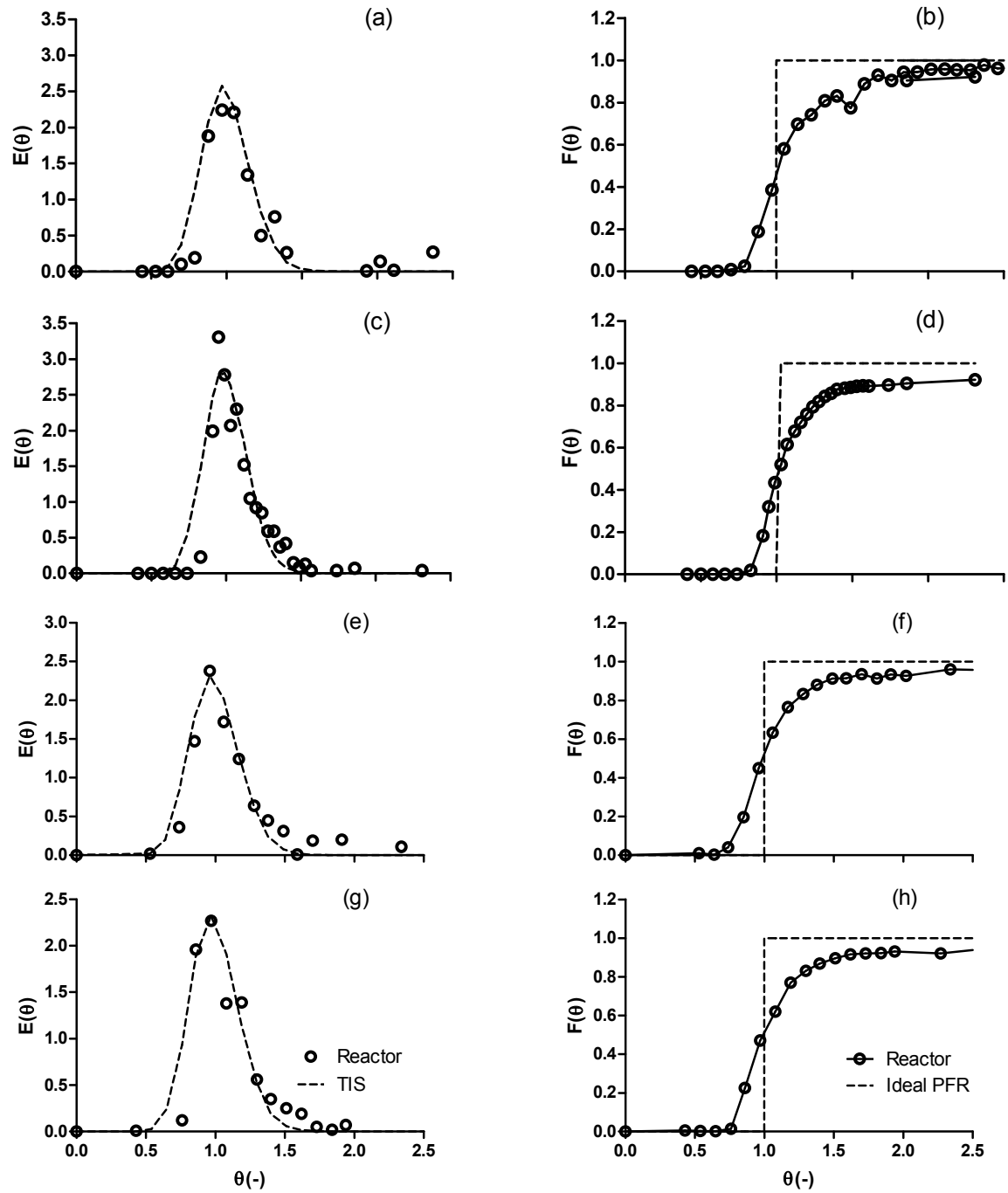


Figure 4.2 Hydraulic characterization (residence time distribution) of the UV reactor at theoretical detention times (τ) of 2.4 min (a and b), 1.3 min (c and d), 0.8 min (e and f) and 0.4 min (g and h).

$$E(\theta)_{DFM} = \frac{1}{\sqrt{4\pi\theta(1/Pe)}} e^{-Pe(1-\theta)^2/4\theta} \quad \text{Eq. 4-9}$$

$$E(\theta)_{TIS} = \frac{n(n\theta)^{n-1}}{(n-1)!} e^{-n\theta} \quad \text{Eq. 4-10}$$

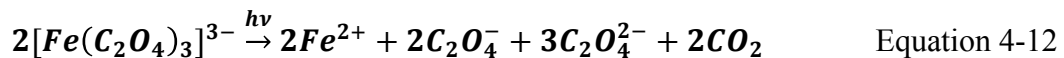
$$\theta_{eff} = \int_0^1 \theta dF \approx \sum_1^n \frac{\theta_{i-1} + \theta_i}{2} (F_i - F_{i-1}) \quad \text{Eq. 4-11}$$

Table 4-1 Exit age distribution model fitting parameters and correlation coefficients for the UV reactor.

Q (mL/min)	\bar{t} (min)	τ (min)	θ_{eff} (-)	τ_{eff} (min)	τ_{eff} / τ (-)	Pe (DFM)	n (TIS)	R^2_{DFM}	R^2_{TIS}
50	2.50	2.40	1.15	2.87	1.20	79.6	41	0.90	0.89
95	1.05	1.26	1.26	1.33	1.05	96.6	49	0.91	0.89
150	0.75	0.80	1.16	0.87	1.09	63.2	33	0.96	0.94
300	0.37	0.40	1.21	0.45	1.12	63.0	33	0.92	0.80

CHEMICAL ACTINOMETRY

Potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$) was used as a chemical actinometer to measure the amount of incident light per unit volume of water passing through the UV reactor. Potassium ferrioxalate is an IUPAC-accepted actinometer [88], [89] introduced in 1953 by Parker and Hatchard [90], [91], and it is a widely used chemical for the measurement of light dosage in UV reactors and UV disinfection systems for water treatment purposes [92]–[98]. This actinometer undergoes photoreduction (Equation 3) when exposed to a wide range of spectrums. The quantum yield (Φ) of the photochemical reaction at 254 nm is 1.25 (moles of Fe^{2+} per mole of photons absorbed) [91], [99].



Potassium ferrioxalate solutions of 0.006 M in 0.1 N H_2SO_4 were prepared in a 6 L Erlenmeyer flask with DI water. All solutions were prepared and stored in a dark room. Solutions were exposed to UV irradiation in the reactor in batch mode and continuous flow in the dark room. Batch mode reactions were carried out for 30, 62, 120 and 180 seconds; continuous flow reactions were carried out at 300, 150 and 95 mL/min (corresponding to theoretical detention times of 24, 48, and 76 seconds). Collected samples (1 mL) were treated with 0.2% 1,10-phenanthroline (1 mL) and diluted to a 50 mL aqueous solution with DI water to form a colored complex ($\text{Fe}(\text{phen})_3^{2+}$). Treated dilutions were allowed to stand for 30 minutes for color complex development. The $\text{Fe}(\text{phen})_3^{2+}$ complex has a molar absorption coefficient (ϵ) of $11,100 \text{ M}^{-1}\text{cm}^{-1}$ at 510 nm [99]. Standard solutions containing $16 \mu\text{M}$ to $96 \mu\text{M}$ Fe^{2+} were prepared with 0.2% 1,10-phenontraline to prepare a calibration curve based on absorbance at 510 nm using the Agilent 8453 spectrophotometer. The concentration of Fe^{2+} in each sample was calculated from the standard calibration curve and dilution ratio. These concentrations of Fe^{2+} produced by UV irradiation are shown in Figure 4.3 for batch as a function of exposure time and continuous flow as a function of theoretical detention time.

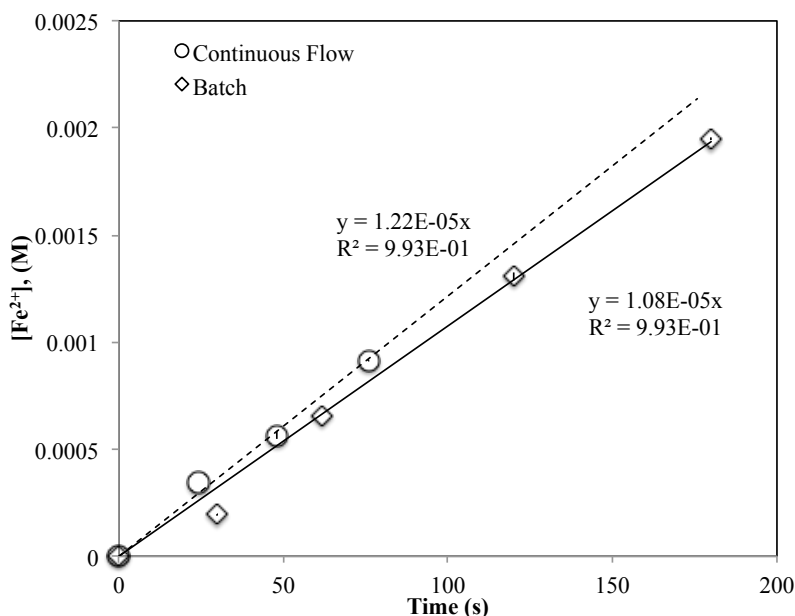


Figure 4.3 Ferrioxalate actinometry for the UV reactor in batch and continuous flow modes.

The UV dose (moles of photons) irradiated per unit volume of solution per unit time can be calculated by dividing the rate of Fe^{2+} produced (*i.e.*, the slope of the regression in Figure 4.3) by the quantum yield. The batch mode yielded a UV dose of 8.61×10^{-6} mol/L per second of exposure time, which correspond to a volumetric UV energy dose of 4.06 mW/cm^3 ($\lambda = 254 \text{ nm}$). The continuous flow experimental setup yield a UV dose of 9.72×10^{-6} mol/L per second of theoretical detention time, which correspond to a volumetric UV power dose of 4.58 mW/cm^3 . Thus, the theoretical detention times of 0.40, 0.80, 1.26, and 4.0 min correspond to volumetric UV energy doses of 110, 220, 346, and 1100 mJ/cm^3 , respectively. It was observed that the UV dose in the continuous flow experiments were an average of 13% higher than the batch mode, which agrees with the average τ_{eff}/τ ratio of 1.11 (Table 4-1).

H₂O₂ AND PAA MOLAR ABSORPTION COEFFICIENTS DETERMINATION

The molar absorption coefficients of H_2O_2 and PAA were determined at 254 nm by preparing dilutions of known concentrations in DI water. The concentrations of the prepared solutions were 0.01, 0.02, 0.03, 0.04, 0.05 and 0.1 M for H_2O_2 and 0.005, 0.02, 0.05 and 0.09 for PAA. Based on the Beers Lambert Law, the light absorption of a chemical species equals the product of its concentration (C), the optical pathlength (l) and the molar absorption coefficient (ϵ). By creating a calibration curve of a compound of interest measuring the absorbance of multiple standard solutions of known concentrations the molar absorption coefficient can be determined by the slope of the calibration curve regression line (Figure 4.4). The molar absorption coefficient of H_2O_2 was observed to be $20.04 \text{ M}^{-1}\text{cm}^{-1}$, which is among the range of reported molar absorptivity [100]–[102]. The molar absorption coefficient determined for PAA

was $17.69 \text{ M}^{-1}\text{cm}^{-1}$; no reported data for the PAA molar absorption coefficient was found in the literature.

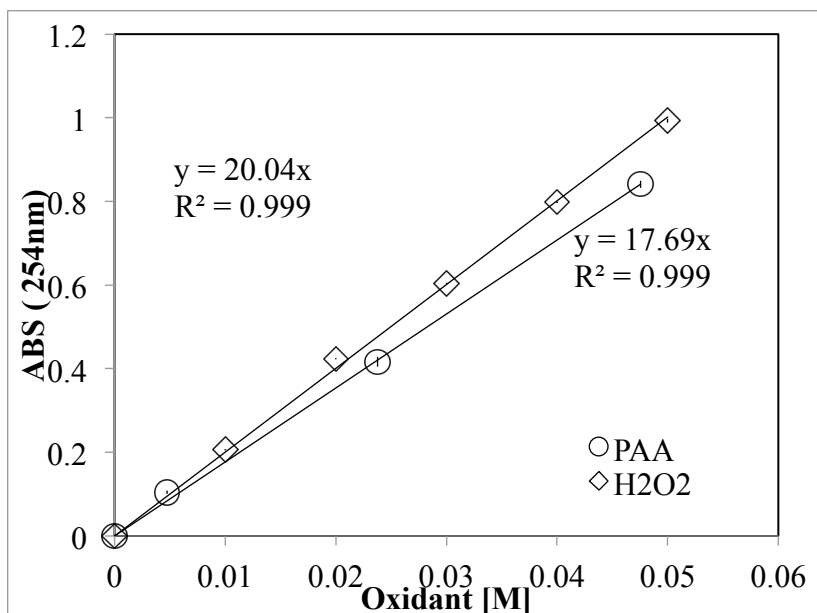


Figure 4.4 Determination of molar absorption coefficient for H_2O_2 and peracetic acid (PAA) in water

PHOTOCHEMICAL DEGRADATION OF EDCS WITH UV AOPS

For the photochemical degradation experiments, a cocktail of EDCs was prepared containing $10 \mu\text{g/L}$ BPA, $20 \mu\text{g/L}$ estradiol, and $17 \mu\text{g/L}$ NPs were prepared in 6 L of DI water. The solutions were exposed to UV doses of 0, 346, and 1100 mJ/cm^3 by adjusting the flow rate of the reactor. In addition PAA and H_2O_2 were used with the previously listed UV doses; oxidant doses were 0, 5, and 10 mg/L for each oxidant. Samples were collected in 100 mL amber jars after a period of time greater than three hydraulic detention times to reach steady state conditions. Reaction was quenched with sodium carbonate and stored in a cool room to follow analysis by GC-MS less than 24 hours after irradiation.

MATERIALS

β -estradiol, Bisphenol A (BPA), and nonylphenol technical mixtures (NP) were purchased from Sigma-Aldrich (MO, USA). BPA (ring 13C12) (ring 13C6) internal standards were from Cambridge Isotope Laboratories, Inc (MA, USA). HPLC grade methanol, acetic acid anhydride and sodium carbonate were purchased from VWR (USA). Stir bars (Twister®, 10 mm×1 mm; coated with polydimethylsiloxane (PDMS) were purchased from Gerstel Inc. (MD, USA). Stock solutions of the individual EDC and a combined working solution for GC/MS were prepared in methanol. Ammonium iron (III) sulfate dodecahydrate, potassium oxalate monohydrate, 1,10-phenontriline monohydrate, ferrous ammonium sulfate, and 32 wt % peracetic acid for chemical actinometry and photochemical reactions were purchased from Sigma-Aldrich (MO, USA). Sodium acetate anhydrous and 30 wt % H₂O₂ for chemical actinometry and photochemical reactions were purchased from Fisher (PA, USA).

GAS CHROMATOGRAPHY MASS-SPECTROMETRY (GC-MS)

After stir bar sorptive extraction, stir bars were loaded into the thermal desorption unit (TDU) (Gerstel, US) under splitless mode. The desorbed chemicals were then cryo-focused in a baffle liner in a cryo-injection system (CIS 4) at -40 °C under liquid nitrogen prior to injection. The gas chromatography separations were performed on a Zebron ZB-5MS capillary column (0.25 mm×30 m×0.25 μ m, Phenomenex, CA). The carrier gas (ultra-pure helium) was set to a constant flow of 1.2 mL/min. The mass spectrometer was operated in the scan mode with electron-impact ionization (ionization voltage, 70 eV). Target compounds were measured based on the following mass to charge ratios (M/Z): 135 and 149 NP, 225 ¹³C-BPA, 213 BPA, and 272 estradiol. A seven-point calibration curve was prepared with concentrations ranging from 0.005 to 22 μ g/L. Method detection limits (MDLs) were calculated as σ *t-value, where σ is the standard deviation of seven standard samples times the t-value of 2.477 [46]. The method detection limits (MDLs) for BPA, NP, lindane, alachlor, chlorpyrifos, estrone, estradiol and 17 α -

ethynylestradiol were 0.010, 0.371, 0.673, 0.107, 0.020, 0.982, 0.135 and 0.538 $\mu\text{g/L}$, respectively.

SAMPLE EXTRACTION AND DERIVATIZATION

Samples were analyzed by means of gas chromatography mass spectrometry (GC-MS) after solid-phase extraction by stir bar sorptive extraction [11]. Stir bar sorptive extraction (SBSE) is a technique that employs the use of a magnetic stir bar coated with a thin film of polydimethylsiloxane (PDMS). The PDMS film provides a surface with low polarity, which extracts low polarity chemicals. Other chemicals with higher polarity could be extracted by chemical modification techniques such as derivatization, allowing the effective extraction of chemicals such as BPA, NPs and estrogens from water samples. The derivatization of BPA, NP, and estrogens was accomplished by adding 200 mg of Na_2CO_3 and 200 μL of acetic acid anhydride into 20 mL of water samples. The stir bars are submerged in the aqueous samples for a period of 2 hours before being loaded into a thermal desorption unit (TDU) to inject extracted organic compounds into the Agilent GC-MS unit.

RESULTS AND DISCUSSION

CHEMICAL DEGRADATION OF EDCS BY H_2O_2 AND PAA (NO UV)

The use of UV AOPs with H_2O_2 and PAA were tested for the removal of estrogenic EDCs in water treatment applications. The addition of these oxidants can produced instant degradation of organic compounds, so a comparison between the initially measured aqueous concentration and the aqueous concentration after the addition of the H_2O_2 or PAA was performed. It observed that NP was not affected by the addition of 10 mg/L H_2O_2 , but only 66% of the initial NP remained after exposure to PAA (Figure 4.5). The addition of 10 mg/L H_2O_2 or PAA reduced the initial aqueous concentration of both BPA (to 85% and 54% of initial, respectively) and estradiol (to 73% and 36% of initial, respectively).

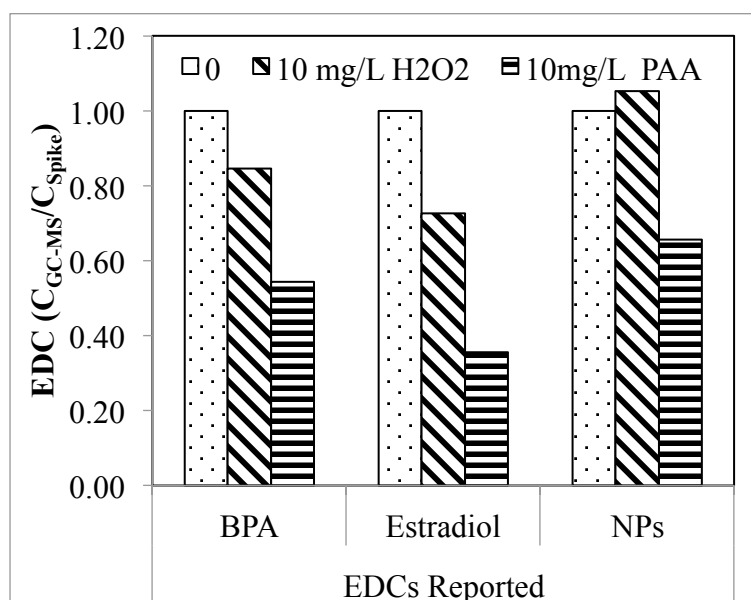


Figure 4.5 EDC degradation by addition of H₂O₂ or PAA

DIRECT PHOTOCHEMICAL DEGRADATION OF EDCS (UV ALONE)

A solution containing a cocktail of BPA (10 ppb), estradiol (20 ppb), NP (17ppb) was irradiated with the lab-scale UV reactor characterized above. UV dosages included 0, 220, 346, and 1100 mJ/cm³. It was observed that UV irradiation alone did not have a significant effect on the degradation of BPA and estradiol, only removing approximately 10-20% of the initial concentrations (Figure 4.6). NP was less resilient to UV irradiation; 40-60% removal of the initial concentration was observed, correlated with increasing UV irradiation. The resiliency of these compounds in UV treatment agrees with other studies [66], [103]–[105].

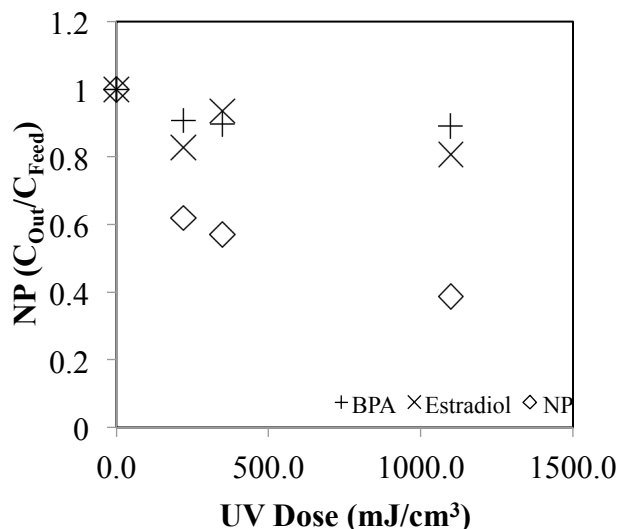


Figure 4.6 Direct photochemical degradation of EDCs in water (UV alone)

INDIRECT PHOTOCHEMICAL DEGRADATION OF EDCs WITH UV/H₂O₂ AOP

A solution containing a cocktail of BPA (10 ppb), estradiol (20 ppb), and NP (17ppb) was irradiated with the UV reactor characterized above. UV dosages included 0, 220, 346, and 1100 mJ/cm³ and H₂O₂ initial concentrations were 0, 5 and 10 mg/L, and effluent concentrations and removal ratios are listed in Table 4-2. The use of 5 mg/L H₂O₂ and 346 mJ/cm³ yielded a partial removal of 45%, 47%, and 59% for BPA, estradiol, and NPs, respectively, as shown inTable 4-2. These AOP conditions nearly doubled the removal of BPA and estradiol as compared to UV alone, but the removal of NPs was only slightly improved. At a greater H₂O₂ concentration of 10 mg/L with the same UV dose, EDC removal of 62%, 80%, and 75% for BPA, estradiol, and NP, respectively (Table 4-2). Based on these results there is an apparent higher sensitivity to the initial H₂O₂ concentration for BPA and estradiol, which agrees with their respective second order reaction rates with hydroxyl radicals [64], [76]. The highest UV dose (1100 mJ/cm³) and initial H₂O₂ concentration (10 mg/L) yielded 94%, 100% and 84% removal for BPA, estradiol, and NP respectively (Table 4-2), which agrees with literature reported trends [64], [66], [103], [104].

Table 4-2 Summary of experimental conditions and results for the direct and indirect photochemical degradation of EDCs with UV, H₂O₂, and PAA

Sample	τ (min)	UV Dose (J/cm ³)	H ₂ O ₂ (mg/L)	PAA (mg/L)	EDCs Reported (PPB)			EDCs Removal (%)		
					NPs	BPA	E2	NPs	BPA	E2
0	0	0.0	0	0	19.59	12.91	22.16	-	-	-
1	0.8	0.2	0	0	12.14	11.71	18.31	38	9	17
2	1.3	0.3	0	0	11.16	11.59	20.73	43	10	6
3	4.0	1.1	0	0	7.56	11.51	17.87	61	10	19
4*	0	0.0	5	0	15.17	13.08	18.55	22	-1	16
5	1.3	0.3	5	0	6.20	7.20	9.81	59	45	47
6	4.0	1.1	5	0	5.29	3.05	2.10	65	77	89
7*	0	0.0	10	0	20.63	10.92	16.09	-5	16	27
8	1.3	0.3	10	0	5.11	4.17	3.26	75	62	80
9	4.0	1.1	10	0	3.39	0.63	n.d.	84	94	>99.4
10*	0	0.0	0	5	24.34	15.60	15.76	-24	-21	29
11	1.3	0.3	0	5	4.27	1.52	0.56	82	90	96
12	4.0	1.1	0	5	3.71	1.95	0.13	85	88	99
13*	0	0.0	0	10	12.86	7.02	7.89	34	46	64
14	1.3	0.3	0	10	3.23	n.d.	n.d.	75	>99.9	>99.4
15	4.0	1.1	0	10	2.32	n.d.	n.d.	80	>99.9	>99.4

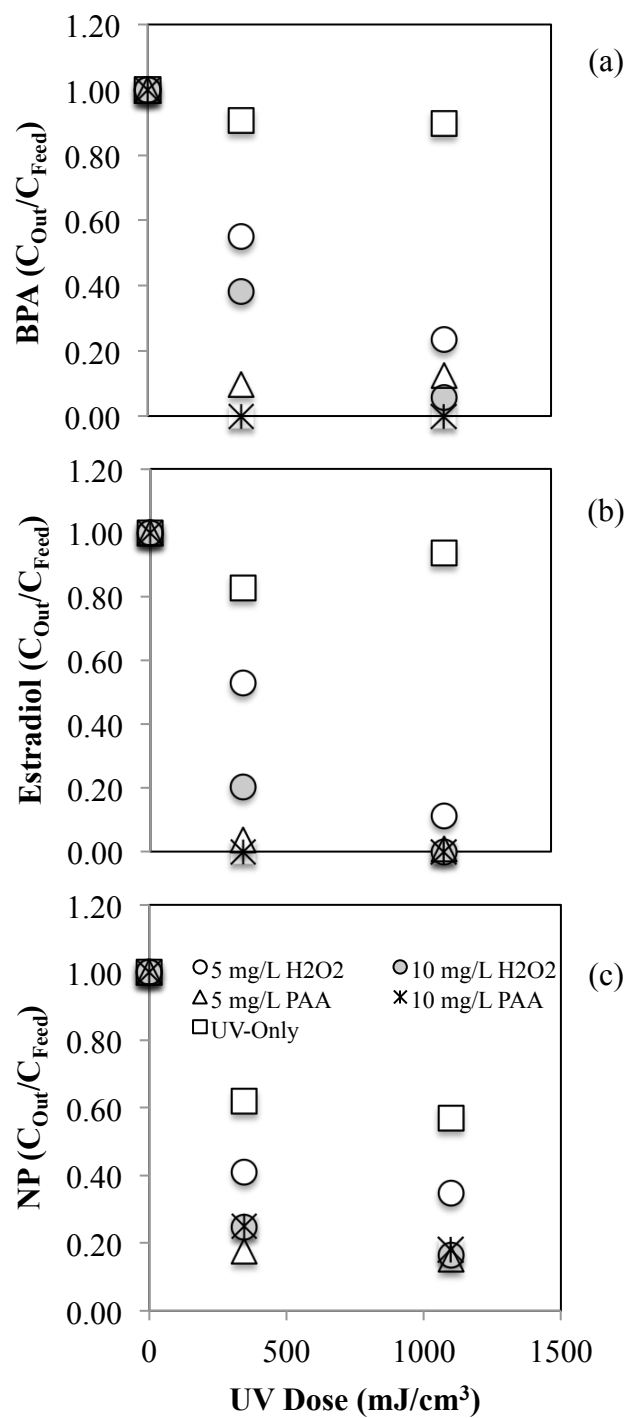


Figure 4.7 Photochemical degradation of aqueous EDCs with UV, UV/ H_2O_2 and UV/PAA

INDIRECT PHOTOCHEMICAL DEGRADATION OF EDCs WITH UV/PAA AOP

The indirect photochemical degradation of BPA, estradiol, and NPs was investigated employing the UV/PAA AOP. The use of UV/PAA demonstrated significant removal for all EDCs (Table 4-2). The addition of an initial concentration of 5 mg/L PAA and 346 mJ/cm³ UV dose resulted in 90% (1 log reduction), 96% (1.5 log reduction), and 82% degradation of BPA, estradiol, and NPs respectively. With an initial concentration of 5 mg/L PAA and the greatest UV dose of 1100 mJ/cm³, slightly higher removals were observed for estradiol and NPs, with removals of 88%, 99% (2 log reduction), and 85% for BPA, estradiol, and NPs, respectively (Table 4-2). With an initial concentration of 10 mg/L PAA and UV dose of 1100 mJ/cm³ removals of >99%, >99%, and 82% were observed for BPA, estradiol, and NPs, respectively (Table 4-2 and Figure 4.7). Lower UV dose (300 mJ/cm³) resulted in similar results but 75% removal of NP as shown in Table 3-2

CONCLUSIONS

The removal of EDCs with UV/H₂O₂ and UV/PAA was investigated for water treatment applications. Both UV/H₂O₂ and UV/PAA achieved significant removal of EDCs at the tested conditions. Greater than 2-log removal of EDCs was achieved at 1100 mJ/cm³ with 10 mg/L H₂O₂ or 10 mg/L PAA. The use of PAA for the removal of EDCs such as BPA and estradiol presents a potential option for the implementation of AOP system with a lower oxidant dosage requirement. This could potentially result in significant mitigation of environmental impact of WWTP effluents at a potentially lower operational cost when compared to other AOPs alternatives [61]. Further investigation should include the environmental impact for the use of PAA, removal efficiencies in wastewater effluents and determination of quantum yields for EDCs in UV/PAA photodegradation.

The employment of PAA for AOP systems needs to be further investigated. The EDC removal with relatively low concentrations presents the opportunity for its use at potential lower environmental impact. The production of reaction byproducts, such as aldehydes need to be investigated further as it can produce disinfection byproducts which might result in adverse environmental impact.

CHAPTER 5: CONCLUSIONS

The goal of this study was to investigate the environmental performance of municipal wastewater treatment for the removal of EDCs and explore the environmental impacts for the removal enhancement of EDCs by modifying a UV disinfection system into an AOP. First, an assessment for the detection of EDCs in municipal wastewater treatment was performed through collecting and analyzing samples by GC-MS. The analysis was complemented by a biological yeast assay to screen for estrogenic potential in the wastewater samples. Second, a sustainability analysis was developed to assess the environmental impact of the modification of a WWTP UV disinfection system into an AOP for EDC removal. Third, the introduction of peracetic acid (commonly used for disinfection) was tested in an bench-scale UV AOP system for the removal of BPA, estradiol and NP.

ENDOCRINE DISRUPTING COMPOUNDS (EDCS) AND ESTROGENICITY IN MUNICIPAL WASTEWATER TREATMENT

The goal of this study was to assess EDC removal in municipal wastewater treatment processes. The municipal WWTPs selected for this study have different unit treatment processes; WWTP-B includes both primary sedimentation and an anoxic basin before aeration, but WWTP-A does not include either. Analysis of WWTPs revealed that the biological treatment in WWTP-A provided better removal efficiency of BPA than WWTP-B, but the biological treatment in WWTP-B (including anoxic treatment) provided better removal efficiency of NP. Overall removal was observed to be 96% and 99% for BPA and 97% and 99% for NP for WWTP-A and WWTP-B, respectively (Table 2-1 and Figure 2.3). Bioassays revealed much greater estrogenic activity in the influent of WWTP-A than WWTP-B, but both WWTP-A and WWTP-B produced a final effluent with near-blank estrogenic activity (Figure 2.3). It was found for NP to be more resilient to current municipal wastewater treatment, making it a good surrogate for enhancement of treatment technologies.

LIFE CYCLE IMPACT ASSESSMENT (LCIA) OF AOPS IN MUNICIPAL WASTEWATER TREATMENT

The environmental performance of two municipal wastewater treatment plants was analyzed based on the normalized 3-year average life cycle inventory. It was discovered that WWTP-A has a greater impact in all impact categories, as a result of the current energy demand. The WWTP-A GWP was 35% higher than WWTP-B and more than 60% higher in AP, EUP, FAEP, and TEP. The addition of 10 mg/L peroxide resulted in potential impact increases of 3%, 2%, 5%, 3% and 78% for GWP, AP, EUP, FAEP, and TEP for WWTP-A. The addition of 10 mg/L peroxide resulted in 13% higher Eco-Score, this scenario can be improved by reducing the peroxide addition to 5 mg/L which will result in an Eco-Score of 6.3 (7% higher than no peroxide addition). The scenarios included for WWTP-B resulted in lower Eco-Score values when compared to WWTP-A. The scenarios for WWTP-B (B) and the three proposed scenarios (B-1, B-2, and B-3) resulted in Eco-Score values of 3.7, 4.7, 4.5, and 4.5, respectively. This proposed modifications resulted in Eco-Score values higher than 20% when compared to current performance of WWTP-B scenario (B). The use of new chemical oxidants such as PAA presents a potential opportunity for the use of UV disinfection systems for AOP. The relatively lower environmental impact leads to the need to investigate the benefits of such modification. Benefits will need to be investigated to include removal of recalcitrant constituents and the potential application for direct portable reuse.

PHOTOCHEMICAL DEGRADATION OF ESTROGENIC EDCS WITH UV AOPS

The introduction of the chemical disinfectant PAA as an oxidant for AOPs wastewater treatment was analyzed and compared to $\text{H}_2\text{O}_2/\text{UV}$ in this study. For the comparison, the removal performance of EDCs with $\text{UV}/\text{H}_2\text{O}_2$ and UV/PAA was investigated. Both $\text{UV}/\text{H}_2\text{O}_2$ and UV/PAA achieved significant removal of EDCs at the tested conditions. Greater than 2-log removal of EDCs was achieved at $1100 \text{ mJ}/\text{cm}^3$ with 10 mg/L H_2O_2 or 10 mg/L PAA. PAA performed better than H_2O_2 for the removal of EDCs achieving 1 log removal at lower

concentrations than peroxide. The use of PAA for the removal of EDCs such as BPA and estradiol presents a potential option for the implementation of AOP system with a lower oxidant dosage requirement. This could potentially result in significant mitigation of environmental impact of WWTP effluents at a potentially lower operational cost when compared to other AOPs alternatives [61].

CONCLUDING REMARKS

The analysis of wastewater treatment samples as cohorts provided an opportunity to assess the relative removal performance of EDCs. It was found that municipal wastewater treatment removes most of the targeted EDCs, but NPs were not removed effectively. The biological yeast assay results agreed with this finding, which includes any non-targeted EDCs that might be present in the wastewater samples. The fate and transport of these EDCs needs to be investigated further for the WWTPs included in this study, especially since WWTP-A sludge constitutes 20% of the total sludge treated in WWTP-B. The effluent NP concentrations in WWTP-A present a potential long term adverse effect to the environment which could compromise the water resource quality for future generations. The assessment of a sustainability model for the modification of the UV disinfection system in WWTP-A resulted in promising application for AOP, by the addition of H_2O_2 . The sustainability assessment revealed that the addition of H_2O_2 in WWTP-A AOP scenario (A-1) was the contributed a relatively small increment in the GWP, AP, EUP, and FAEP impact categories, significant higher impact was observed in TEP impact category. Future work should include the investigation of several concentrations of H_2O_2 as well as other potential chemicals such as chlorine and PAA. The introduction of PAA/UV for AOP resulted in higher EDCs removal at lower PAA initial concentration when compared with H_2O_2 . Future work should include the analysis for the combination of PAA/ H_2O_2 /UV at several ratios for EDC removal in wastewater effluent as well as the use of different UV lamps including several light intensities.

REFERENCES

- [1] C. Stavrakakis, R. Colin, C. Faur, V. Hequet, and C. Le Pierre., “Analysis and behavior of endocrine disrupting compounds in wastewater treatment plant.,” *Eur. J. Water Qual.*, vol. 39, no. 2, pp. 145–155, 2008.
- [2] J. Nelson, F. Bishay, A. van Roodselaar, M. Ikonomou, and F. C. P. Law, “The use of in vitro bioassays to quantify endocrine disrupting chemicals in municipal wastewater treatment plant effluents.,” *Sci. Total Environ.*, vol. 374, no. 1, pp. 80–90, 2007.
- [3] H. Siegrist, A. Joss, T. Ternes, and J. Oehlmann, “Fate of EDCS in wastewater treatment and EU perspective on EDC regulation.,” in *WEFTEC.05, Conf. Proc., Annu. Tech. Exhib. Conf., 78th*, 2005, pp. 3142–3165.
- [4] H. Ogawa, N. Miyata, and K. Iwahori, “Assessment of endocrine disrupting chemicals from domestic wastewater treatment facility (Gappei-shori Johkasou) and night soil treatment facility to public waters.,” *Yosui to Haisui*, vol. 48, no. 2, pp. 161–168, 2006.
- [5] Z. S. Can, M. Firlak, A. Kerç, and S. Evcimen, “Evaluation of different wastewater treatment techniques in three WWTPs in Istanbul for the removal of selected EDCs in liquid phase,” *Environ. Monit. Assess.*, vol. 186, no. 1, pp. 525–539, 2014.
- [6] J. Zhang, M. Tomanek, H. Dong, R. G. Arnold, W. P. Ela, D. M. Quanrud, and A. Eduardo Saez, “Fate of Polybrominated Diphenyl Ethers, Nonylphenol, and Estrogenic Activity during Managed Infiltration of Wastewater Effluent.,” *J. Environ. Eng. (Reston, VA, United States)*, vol. 134, no. 6, pp. 433–442, 2008.
- [7] M. Auriol, Y. Filali-Meknassi, R. D. Tyagi, C. D. Adams, and R. Y. Surampalli, “Endocrine disrupting compounds removal from wastewater, a new challenge,” *Process Biochem.*, vol. 41, no. 3, pp. 525–539, Mar. 2006.
- [8] B. L. L. Tan, D. W. Hawker, J. F. Mueller, L. A. Tremblay, and H. F. Chapman, “Stir bar sorptive extraction and trace analysis of selected endocrine disruptors in water, biosolids and sludge samples by thermal desorption with gas chromatography-mass spectrometry.,” *Water Res.*, vol. 42, no. 1–2, pp. 404–412, 2008.
- [9] L. B. Barber, J. E. Loyo-Rosales, C. P. Rice, T. A. Minarik, and A. K. Oskouie, “Endocrine disrupting alkylphenolic chemicals and other contaminants in wastewater treatment plant effluents, urban streams, and fish in the Great Lakes and Upper Mississippi River Regions,” *Sci. Total Environ.*, vol. 517, pp. 195–206, 2015.
- [10] X. Ye, X. Guo, X. Cui, X. Zhang, H. Zhang, M. K. Wang, L. Qiu, and S. Chen, “Occurrence and removal of endocrine-disrupting chemicals in wastewater treatment plants in the Three Gorges Reservoir area, Chongqing, China,” *J. Environ. Monit.*, vol. 14, no. 8, p. 2204, 2012.

- [11] H. A. Balsiger, R. de la Torre, W.-Y. Lee, and M. B. Cox, "A four-hour yeast bioassay for the direct measure of estrogenic activity in wastewater without sample extraction, concentration, or sterilization.," *Sci. Total Environ.*, vol. 408, no. 6, pp. 1422–1429, 2010.
- [12] Z. Qiang, H. Dong, B. Zhu, J. Qu, and Y. Nie, "A comparison of various rural wastewater treatment processes for the removal of endocrine-disrupting chemicals (EDCs).," *Chemosphere*, vol. 92, no. 8, pp. 986–992, 2013.
- [13] M. P. Fernandez, I. D. Buchanan, and M. G. Ikonomou, "Seasonal variability of the reduction in estrogenic activity at a municipal WWTP," *Water Res.*, vol. 42, pp. 3075–3081, 2008.
- [14] J. E. Drewes, J. Hemming, S. J. Ladenburger, J. Schauer, and W. Sonzogni, "An assessment of endocrine disrupting activity changes in water reclamation systems through the use of bioassays and chemical measurements.," *Water Environ. Res.*, vol. 77, no. 1, pp. 47–65, 2004.
- [15] V. Belgiorno, L. Rizzo, D. Fatta, and C. Della, "Review on endocrine disrupting-emerging compounds in urban wastewater : occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse," vol. 215, no. June 2006, pp. 166–176, 2007.
- [16] D. P. Mohapatra, S. K. Brar, R. D. Tyagi, and R. Y. Surampalli, "Physico-chemical pre-treatment and biotransformation of wastewater and wastewater Sludge - Fate of bisphenol A.," *Chemosphere*, vol. 78, no. 8, pp. 923–941, 2010.
- [17] J. M. Hemming, H. J. Allen, K. a Thuesen, P. K. Turner, W. T. Waller, J. M. Lazorchak, D. Lattier, M. Chow, N. Denslow, and B. Venables, "Temporal and spatial variability in the estrogenicity of a municipal wastewater effluent.," *Ecotoxicol. Environ. Saf.*, vol. 57, no. 3, pp. 303–10, Mar. 2004.
- [18] L. B. Barber, K. E. Lee, D. L. Swackhamer, and H. L. Schoenfuss, "Reproductive responses of male fathead minnows exposed to wastewater treatment plant effluent, effluent treated with XAD8 resin, and an environmentally relevant mixture of alkylphenol compounds.," *Aquat. Toxicol.*, vol. 82, no. 1, pp. 36–46, 2007.
- [19] E. Oberdorster and A. O. Cheek, "Gender benders at the beach : endocrine disruption in marine and estuarine organisms," *Environ. Toxicol. Chem.*, vol. 20, no. 1, pp. 23–36, 2001.
- [20] C. Staples, E. Mihaich, J. Carbone, K. Woodburn, and G. Klecka, "A Weight of Evidence Analysis of the Chronic Ecotoxicity of Nonylphenol Ethoxylates, Nonylphenol Ether Carboxylates, and Nonylphenol," *Hum. Ecol. Risk Assess. An Int. J.*, vol. 10, no. 6, pp. 999–1017, 2004.
- [21] J. L. Carwile and K. B. Michels, "Urinary bisphenol A and obesity: NHANES 2003–2006," *Environ. Res.*, vol. 111, no. 6, pp. 825–830, 2011.

- [22] L. Trasande, T. M. Attina, and J. Blustein, "Association between urinary bisphenol A concentration and obesity prevalence in children and adolescents," *JAMA - J. Am. Med. Assoc.*, vol. 308, no. 11, pp. 1113–1121, 2012.
- [23] T. Wang, M. Li, B. Chen, M. Xu, Y. Xu, Y. Huang, J. Lu, Y. Chen, W. Wang, X. Li, Y. Liu, Y. Bi, S. Lai, and G. Ning, "Urinary bisphenol A (BPA) concentration associates with obesity and insulin resistance," *J. Clin. Endocrinol. Metab.*, vol. 97, no. 2, pp. 223–227, 2012.
- [24] R. Rezg, S. El-Fazaa, N. Gharbi, and B. Mornagui, "Bisphenol A and human chronic diseases: Current evidences, possible mechanisms, and future perspectives," *Environ. Int.*, vol. 64, pp. 83–90, 2014.
- [25] T. Anumol, S. Dagnino, D. R. Vandervort, and S. A. Snyder, "Chemosphere Transformation of Polyfluorinated compounds in natural waters by advanced oxidation processes," *Chemosphere*, vol. 144, pp. 1780–1787, 2016.
- [26] A. A. Nogueira, J. P. Bassin, A. C. Cerqueira, and M. Dezotti, "Integration of biofiltration and advanced oxidation processes for tertiary treatment of an oil refinery wastewater aiming at water reuse," 2016.
- [27] V. K. Gupta, I. Ali, T. A. Saleh, A. Nayak, and S. Agarwal, "Chemical treatment technologies for waste-water recycling—an overview," *RSC Adv.*, vol. 2, no. 16, p. 6380, 2012.
- [28] N. Asif, S. S. Ali, Z. Bhatti, and R. Zafar, "Chemically Enhanced Primary Wastewater Treatment (CEPT) in Conjunction with H₂O₂ / UV Technology in Controlled Atmosphere," vol. 5, no. 3, pp. 153–159, 2013.
- [29] N. N. Mahamuni and Y. G. Adewuyi, "Ultrasonics Sonochemistry Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment : A review with emphasis on cost estimation," *Ultrason. - Sonochemistry*, vol. 17, no. 6, pp. 990–1003, 2010.
- [30] Y. Yang, J. J. Pignatello, J. Ma, and W. A. Mitch, "Effect of matrix components on UV / H₂O₂ and UV / S₂O₂ 8 advanced oxidation processes for trace organic degradation in reverse osmosis brines from municipal wastewater reuse facilities," *Water Res.*, vol. 89, pp. 192–200, 2016.
- [31] T. Yonar, K. Kestioglu, and N. Azbar, "Treatability studies on domestic wastewater using UV / H₂O₂ process," vol. 67, pp. 223–228, 2006.
- [32] M. Ksibi, "Chemical oxidation with hydrogen peroxide for domestic wastewater treatment," *Chem. Eng. J.*, vol. 119, no. 2–3, pp. 161–165, 2006.
- [33] M. Chong, A. Sharma, C. Saint, and S. Burn, "Advanced oxidation technologies for wastewater treatment and reuse: Where to from here for decentralized sytems?," *Water*, no. March, pp. 3–6, 2012.

- [34] Y. I. Weng, P. Y. Hsu, S. Liyanarachchi, J. Liu, D. E. Deatherage, Y. W. Huang, T. Zuo, B. Rodriguez, C. H. Lin, A. L. Cheng, and T. H. M. Huang, "Epigenetic influences of low-dose bisphenol A in primary human breast epithelial cells," *Toxicol. Appl. Pharmacol.*, vol. 248, no. 2, pp. 111–121, 2010.
- [35] J. T. Wolstenholme, E. F. Rissman, and J. J. Connelly, "The role of Bisphenol A in shaping the brain, epigenome and behavior," *Horm. Behav.*, vol. 59, no. 3, pp. 296–305, 2011.
- [36] M. Kundakovic and F. A. Champagne, "Epigenetic perspective on the developmental effects of bisphenol A," *Brain. Behav. Immun.*, vol. 25, no. 6, pp. 1084–1093, Aug. 2011.
- [37] F. S. vom Saal, S. C. Nagel, B. L. Coe, B. M. Angle, and J. A. Taylor, "The estrogenic endocrine disrupting chemical bisphenol A (BPA) and obesity," *Mol. Cell. Endocrinol.*, vol. 354, no. 1–2, pp. 74–84, 2012.
- [38] L. Balest, G. Mascolo, I. Di C., and A. Lopez, "Removal of endocrine disrupter compounds from municipal wastewater by an innovative biological technology.," *Water Sci. Technol.*, vol. 58, no. 4, pp. 953–956, 2008.
- [39] M. E. Karpuzcu, D. Fairbairn, W. a Arnold, B. L. Barber, E. Kaufenberg, W. C. Koskinen, P. J. Novak, P. J. Rice, and D. L. Swackhamer, "Identifying sources of emerging organic contaminants in a mixed use watershed using principal components analysis.," *Environ. Sci. Process. Impacts*, vol. 16, no. 10, pp. 2390–9, 2014.
- [40] D. P. Weston, H. L. Ramil, and M. J. Lydy, "Pyrethroid insecticides in municipal wastewater," *Environ. Toxicol. Chem.*, vol. 32, no. 11, pp. 2460–2468, 2013.
- [41] M. C. Larsen, P. A. Hamilton, and W. H. Werkheiser, *Water Quality Status and Trends*. Elsevier B.V., 2013.
- [42] R. G. Luthy, D. L. Sedlak, M. H. Plumlee, D. Austin, and V. H. Resh, "Wastewater-effluent-dominated streams as ecosystem-management tools in a drier climate," *Front. Ecol. Environ.*, vol. 13, no. 9, pp. 477–485, 2015.
- [43] Q. Sui, J. Huang, S. Deng, W. Chen, and G. Yu, "Seasonal Variation in the Occurrence and Removal of Pharmaceuticals and Personal Care Products in Different Biological Wastewater Treatment Processes," *Environ. Sci. Technol.*, vol. 45, pp. 3341–3348, 2011.
- [44] Y. Yu, L. Wu, and A. C. Chang, "Seasonal variation of endocrine disrupting compounds, pharmaceuticals and personal care products in wastewater treatment plants.," *Sci. Total Environ.*, vol. 442, pp. 310–316, 2013.
- [45] Metcalf and Eddy, "Wastewater Flowrates and Constituents Loading," in *Wastewater Engineering Treatment and Resource Recovery*, 5th ed., McGraw-Hill Education, 2013, p. 222.

- [46] E. W. Rice, R. B. Baird, A. D. Eaton, and L. S. Clesceri, "Quality Control," in *Standard Methods for the Examination of Water and Wastewater*, 22nd ed., American Public Health Association, American Water Works Association and Water Environment Federation, 2012, pp. 1–8.
- [47] J. W. Liu and D. Picard, "Bioactive steroids as contaminants of the common carbon source galactose," *FEMS Microbiol. Lett.*, vol. 159, no. 2, pp. 167–171, 1998.
- [48] D. Picard, B. Khursheed, M. J. Garabedian, M. G. Fortin, S. Lindquist, and K. R. Yamamoto, "Reduced levels of hsp90 compromise steroid receptor action in vivo.," *Nature*, vol. 348, no. 6297, pp. 166–168, 1990.
- [49] D. Balabanič and A. Krivograd Klemencič, "Presence of Phthalates , Bisphenol A , and Nonylphenol in paper mill wastewaters in Slovenia and efficiency of aerobic and combined aerobic- anaerobic biological wastewater treatment plants for their removal," *Fresenius Environ. Bull.*, vol. 20, no. 1, pp. 86–92, 2011.
- [50] A. Laganà, A. Bacaloni, I. De Leva, A. Faberi, G. Fago, and A. Marino, "Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters," *Anal. Chim. Acta*, vol. 501, pp. 79–88, 2004.
- [51] A. D. Vethaak, J. Lahr, S. M. Schrap, A. 'lique C. Belfroid, G. B. J. Rijs, A. Gerritsen, J. De Boer, A. S. Bulder, G. C. M. Grinwis, R. V Kuiper, J. Legler, T. A. J. Murk, W. Peijnenburg, H. J. M. Verhaar, and P. De Voogt, "An integrated assessment of estrogenic contamination and biological effects in the aquatic environment of The Netherlands," *Chemosphere*, vol. 59, pp. 511–524, 2005.
- [52] B. Dong, A. Kahl, L. Cheng, H. Vo, S. Ruehl, T. Zhang, S. Snyder, A. E. Sáez, D. Quanrud, and R. G. Arnold, "Fate of trace organics in a wastewater effluent dependent stream.," *Sci. Total Environ.*, vol. 518–519, pp. 479–90, 2015.
- [53] H. Asakura, T. Matsuto, and N. Tanaka, "Analytical study of endocrine-disrupting chemicals in leachate treatment process of municipal solid waste (MSW) landfill sites.," *Environ. Sci. (Tokyo, Japan)*, vol. 14, no. 2, pp. 79–87, 2007.
- [54] H. E. Nice, D. Morritt, M. Crane, and M. Thorndyke, "Long-term and transgenerational effects of nonylphenol exposure at a key stage in the development of *Crassostrea gigas*. Possible endocrine disruption?," *Mar. Ecol. Prog. Ser.*, vol. 256, pp. 293–300, 2003.
- [55] N. Ademollo, F. Ferrara, M. Delise, F. Fabietti, and E. Funari, "Nonylphenol and octylphenol in human breast milk," *Environ. Int.*, vol. 34, no. 7, pp. 984–987, 2008.
- [56] M. J. Lopez-Espinosa, C. Freire, J. P. Arrebola, N. Navea, J. Taoufiki, M. F. Fernandez, O. Ballesteros, R. Prada, and N. Olea, "Nonylphenol and octylphenol in adipose tissue of women in Southern Spain," *Chemosphere*, vol. 76, no. 6, pp. 847–852, 2009.

- [57] J. E. Schneider, J. M. Brozek, and E. Keen-Rhinehart, "Our stolen figures: The interface of sexual differentiation, endocrine disruptors, maternal programming, and energy balance," *Horm. Behav.*, vol. 66, no. 1, pp. 104–119, 2014.
- [58] A. Kumar and I. Xagorarakis, "Pharmaceuticals, personal care products and endocrine-disrupting chemicals in U.S. surface and finished drinking waters: A proposed ranking system.," *Sci. Total Environ.*, vol. 408, no. 23, pp. 5972–5989, 2010.
- [59] B. D. Stanford and H. S. Weinberg, "The impact of co-contaminants in septic effluents on the transport of steroid estrogens through soil-water treatment.," *Proc. - Water Qual. Technol. Conf. Expo.*, pp. stanf1/1–stanf1/8, 2007.
- [60] B. Applebaun, "Water & Sustainability: U.S. Electricity Consumption for Water Supply & Treatment - The Next Half Century, EPRI, Palo Alto, CA: 2000. 1006787.," 2000.
- [61] L. Høiby, J. Clauson-Kaas, H. Wenzel, H. F. Larsen, B. N. Jacobsen, O. Dalgaard, L. Høiby, J. Clauson-Kaas, H. Wenzel, H. F. Larsen, B. N. Jacobsen, and O. Dalgaard, "Sustainability assessment of advanced wastewater treatment technologies," *Water Sci. Technol.*, vol. 58, no. 5, pp. 963–968, 2008.
- [62] G. Bertanza, R. Pedrazzani, V. Zambarda, G. Dal M., F. Icarelli, L. Baldassarre, M. Dal Grande, F. Icarelli, and L. Baldassarre, "Removal of endocrine disrupting compounds from wastewater treatment plant effluents by means of advanced oxidation.," *Water Sci. Technol.*, vol. 61, no. 7, pp. 1663–1671, 2010.
- [63] S. Carbonaro, M. N. Sugihara, and T. J. Strathmann, "Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: Activity, inhibition, and deactivation of TiO₂ photocatalysts in wastewater effluent," *Appl. Catal. B Environ.*, vol. 129, pp. 1–12, 2013.
- [64] E. Felis and K. Miksch, "Nonylphenols degradation in the UV, UV/H₂O₂, O₃ and UV/O₃ processes - Comparison of the methods and kinetic study," *Water Sci. Technol.*, vol. 71, no. 3, pp. 446–453, 2015.
- [65] D. Gerrity, S. Gamage, J. C. Holady, D. B. Mawhinney, O. Quinones, R. A. Trenholm, and S. A. Snyder, "Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection.," *Water Res.*, vol. 45, no. 5, pp. 2155–2165, 2011.
- [66] K. G. Linden, E. J. Rosenfeldt, and S. W. Kullman, "UV/H₂O₂ degradation of endocrine-disrupting chemicals in water evaluated via toxicity assays," *Water Sci. Technol.*, vol. 55, no. 12, pp. 313–319, 2007.
- [67] E. Rosenfeldt, "UV and UV/H₂O₂ degradation of endocrine disrupting chemicals in water," 2001.

- [68] S. Sarkar, S. Ali, L. Rehmann, G. Nakhla, and M. B. Ray, "Degradation of estrone in water and wastewater by various advanced oxidation processes," *J. Hazard. Mater.*, vol. 278, pp. 16–24, 2014.
- [69] E. J. Rosenfeldt, P. J. Chen, S. Kullman, and K. G. Linden, "Destruction of estrogenic activity in water using UV advanced oxidation," *Sci. Total Environ.*, vol. 377, no. 1, pp. 105–113, 2007.
- [70] U. Schulze-Hennings and J. Pinnekamp, "Response surface method for the optimisation of micropollutant removal in municipal wastewater treatment plant effluent with the UV/H₂O₂ advanced oxidation process," *Water Sci. Technol.*, vol. 67, no. 9, pp. 2075–2082, 2013.
- [71] D. Błędzka, D. Gryglik, and J. S. Miller, "Photodegradation of butylparaben in aqueous solutions by 254nm irradiation," *J. Photochem. Photobiol. A Chem.*, vol. 203, no. 2–3, pp. 131–136, 2009.
- [72] D. Błędzka, D. Gryglik, M. Olak, J. L. Gebicki, and J. S. Miller, "Degradation of n-butylparaben and 4-tert-octylphenol in H₂O₂/UV system," *Radiat. Phys. Chem.*, vol. 79, no. 4, pp. 409–416, 2010.
- [73] H. Christensen, K. Sehested, and H. Corfitzen, "Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures," *J. Phys. Chem.*, vol. 86, no. 9, pp. 1588–1590, 1982.
- [74] M. S. Elovitz and U. von Gunten, "Hydroxyl Radical/Ozone Ratios During Ozonation Processes. I. The Rct Concept," *Ozone Sci. Eng.*, vol. 21, no. 3, pp. 239–260, 1999.
- [75] O. Legrini, E. Oliveros, and A. M. Braun, "Photochemical processes for water treatment," *Chem. Rev.*, vol. 93, no. 2, pp. 671–698, 1993.
- [76] B. A. Wols and C. H. M. Hofman-Caris, "Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water," *Water Res.*, vol. 46, no. 9, pp. 2815–2827, 2012.
- [77] C. Drosou, A. Coz, N. P. Xekoukoulotakis, A. Moya, Y. Vergara, and D. Mantzavinos, "Peracetic acid-enhanced photocatalytic and sonophotocatalytic inactivation of E. coli in aqueous suspensions," *J. Chem. Technol. Biotechnol.*, vol. 85, no. 8, pp. 1049–1053, 2010.
- [78] A. González, R. Gehr, M. Vaca, and R. López, "Disinfection of an Advanced Primary Effluent with Peracetic Acid and Ultraviolet Combined Treatment: A Continuous-Flow Pilot Plant Study," *Water Environ. Res.*, vol. 84, no. 3, pp. 247–253, 2012.
- [79] R. Gehr, M. Wagner, P. Veerasubramanian, and P. Payment, "Disinfection efficiency of peracetic acid, UV and ozone after enhanced primary treatment of municipal wastewater," *Water Res.*, vol. 37, no. 19, pp. 4573–4586, Nov. 2003.

- [80] V. Mezzanotte, M. Antonelli, S. Citterio, and C. Nurizzo, "Wastewater Disinfection Alternatives: Chlorine, Ozone, Peracetic Acid, and UV Light," *Water Environ. Res.*, vol. 79, no. 12, pp. 2373–2379, Nov. 2007.
- [81] M. Kitis, "Disinfection of wastewater with peracetic acid: a review," *Environ. Int.*, vol. 30, no. 1, pp. 47–55, Mar. 2004.
- [82] J. B. da Costa, S. Rodgher, L. A. Daniel, and E. L. G. Esp?ndola, "Toxicity on aquatic organisms exposed to secondary effluent disinfected with chlorine, peracetic acid, ozone and UV radiation," *Ecotoxicology*, vol. 23, no. 9, pp. 1803–1813, 2014.
- [83] B. K. Biswal, R. Khairallah, K. Bibi, A. Mazza, R. Gehr, L. Masson, and D. Frigon, "Impact of UV and peracetic acid disinfection on the prevalence of virulence and antimicrobial resistance genes in uropathogenic escherichia coli in wastewater effluents," *Appl. Environ. Microbiol.*, vol. 80, no. 12, pp. 3656–3666, 2014.
- [84] F. Zanetti, G. De Luca, R. Sacchetti, and S. Stampi, "Disinfection efficiency of peracetic acid (PAA): inactivation of coliphages and bacterial indicators in a municipal wastewater plant.," *Environ. Technol.*, vol. 28, no. 11, pp. 1265–71, 2007.
- [85] C. Caretti and C. Lubello, "Wastewater disinfection with PAA and UV combined treatment: A pilot plant study," *Water Res.*, vol. 37, no. 10, pp. 2365–2371, 2003.
- [86] J. C. Crittenden, Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous, *MWH's Water Treatment: Principles and Design: Third Edition*. John Wiley and Sons, 2012.
- [87] Mark M. Benjamin and D. F. Lawler, *Water Quality Engineering: Physical / Chemical Treatment Processes*. Wiley & Sons, 2013.
- [88] H. J. Kuhn, S. E. Braslavsky, and R. Schmidt, "Chemical actinometry (IUPAC Technical Report)," *Pure Appl. Chem.*, vol. 76, no. 12, pp. 2105–2146, 2004.
- [89] M. Montalti, A. Credi, L. Prodi, and M. T. Gandolfi, "Chemical Actinometry," *Handb. Photochem.*, pp. 601–616, 2006.
- [90] C. Parker, "A new sensitive chemical actinometer. I. Some trials with potassium ferrioxalate," ... *R. Soc. London. Ser. A ...*, vol. 220, no. 1140, pp. 104–116, 1953.
- [91] C. G. Hatchard and C. a. Parker, "A New Sensitive Chemical Actinometer. II. Potassium Ferrioxalate as a Standard Chemical Actinometer," *Proc. R. Soc. A Math. Phys. Eng. Sci.*, vol. 235, no. 1203, pp. 518–536, 1956.
- [92] T. Aillet, K. Loubiere, O. Dechy-Cabaret, and L. Prat, "Accurate measurement of the photon flux received inside two continuous flow microphotoreactors by actinometry," *Int. J. Chem. React. Eng.*, vol. 12, no. 1, pp. 257–269, 2014.
- [93] G. Harris and V. D. Adams, "Potassium ferrioxalate as chemical actinometer in ultraviolet reactors," *J. Environ. Eng.*, vol. 113, no. 3, pp. 612–627, 1987.

- [94] G. G. D. Harris, V. Dean Adams, W. M. Moore, D. L. Sorensen, and V. D. Adams, "Potassium Ferrioxalate as Chemical Actinometer in Ultraviolet Reactors," *J. Environ. Eng.*, vol. 113, no. 3, pp. 612–627, 1987.
- [95] R. Ilinsky and A. Ulyanov, "Fluence rate in UV photoreactor for disinfection of water: Isotropically radiating cylinder," *Int. J. Chem. Eng.*, vol. 2014, 2014.
- [96] R. L. Romero, O. M. Alfano, and A. E. Cassano, "Radiation field in an annular, slurry photocatalytic reactor. 2. Model and experiments," *Ind. Eng. Chem. Res.*, vol. 42, no. 12, pp. 2479–2488, 2003.
- [97] A. B. Silva, N. M. Lima Filho, M. A. P. F. Palha, and S. M. Sarmento, "Kinetics of water disinfection using UV-C radiation," *Fuel*, vol. 110, pp. 114–123, 2013.
- [98] F. Solari, G. Girolimetti, R. Montanari, and G. Vignali, "A New Method for the Validation of Ultraviolet Reactors by Means of Photochromic Materials," *Food Bioprocess Technol.*, vol. 8, no. 11, pp. 2192–2211, 2015.
- [99] L. Prodi, M. T. Gandolfi, and F. Group, "Handbook of Photochemistry, 3rd Ed.," p. 609, 2006.
- [100] M. S. Morgan, P. F. Van Trieste, S. M. Garlick, M. J. Mahon, and A. L. Smith, "Ultraviolet molar absorptivities of aqueous hydrogen peroxide and hydroperoxyl ion," *Anal. Chim. Acta*, vol. 215, no. C, pp. 325–329, 1988.
- [101] W. H. Glaze, Y. Lay, and J.-W. Kang, "Advanced Oxidation Processes. A Kinetic Model for the Oxidation of 1,2-Dibromo-3-chloropropane in Water by the Combination of Hydrogen Peroxide and UV Radiation," *Ind. Eng. Chem. Res.*, vol. 34, no. 7, pp. 2314–2323, Jul. 1995.
- [102] J. M. Barazesh, T. Hennebel, J. T. Jasper, and D. L. Sedlak, "Modular Advanced Oxidation Process Enabled by Cathodic Hydrogen Peroxide Production," *Environ. Sci. Technol.*, vol. 49, no. 12, pp. 7391–7399, 2015.
- [103] E. Felis, S. Ledakowicz, and J. S. Miller, "Degradation of bisphenol A using UV and UV/H₂O₂ processes.," *Water Environ. Res.*, vol. 83, no. 12, pp. 2154–2158, 2011.
- [104] G. Li Puma, V. Puddu, H. K. Tsang, A. Gora, and B. Toepfer, "Photocatalytic oxidation of multicomponent mixtures of estrogens (estrone (E1), 17 β -estradiol (E2), 17 β -ethynylestradiol (EE2) and estriol (E3)) under UVA and UVC radiation: Photon absorption, quantum yields and rate constants independent of photon abso," *Appl. Catal. B Environ.*, vol. 99, no. 3–4, pp. 388–397, 2010.
- [105] E. J. Rosenfeldt and K. G. Linden, "Degradation of Endocrine Disrupting Chemicals Bisphenol A, Ethinyl Estradiol, and Estradiol during UV Photolysis and Advanced Oxidation Processes.," *Environ. Sci. Technol.*, vol. 38, no. 20, pp. 5476–5483, 2004.

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