

# **REMOVAL OF EMERGING CONTAMINANTS FROM AQUEOUS SOLUTION BY OZONE – BASED PROCESSES**

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By  
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## ABSTRACT

The presence of emerging contaminants (ECs) in water and wastewater systems has become a subject of significant concern worldwide. These emerging contaminants are complex organic molecules (e.g. pharmaceuticals) which potentially affect human health and the environment. Conventional wastewater treatment plants are unable to completely remove these contaminants from water and therefore can discharge them into the environment. The need to develop effective methods for ECs removal, the combination of powerful chemical oxidants known as advanced treatment techniques has to be tested. The current study examine the potential of ozone- based advanced oxidation processes (AOPs) to oxidize a number of persistent ECs, using various combinations of ozone with hydrogen peroxide and sodium persulfate. For this study, perfluorinated compounds (PFCs), 1-4, dioxane, N, N-Diethyl-meta-toluamide, and three pharmaceuticals (sulfamethoxazole, trimethoprim and carbamazepine) have been selected. Experiments were conducted in two types of reactor set ups: a batch reactor and a semi batch bubble column reactor. The effect of different process parameters such as reagents dosages, ozone weight percent, and ozone flow rate on destruction of ECs was examined. During ozonation a numbers of reactive species are formed. Basically, the types of oxidation reactions occurring during ozonation processes can be classified as molecular ozone-driven and hydroxyl radical –driven. The experimental results revealed that some of the selected ECs were persistent to direct ozone reaction, however, they were easily oxidized by hydroxyl radical. These reactivity differences may be attributed to the structural differences and process conditions. The operational conditions were optimized for

maximum removal of each compound and their influence on the degradation process is discussed.

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## ABBREVIATIONS

AOP – Advanced oxidation process

DCM – Dichloromethane

DI – Deionized

DO – Dissolved oxygen

EC – Emerging contaminant

EDC – Endocrine disrupting compound

EPA – Environmental Protection Agency

GC/MS – Gas Chromatography – Mass Spectrometry

GC/MS/MS – Gas Chromatography – Tandem Mass Spectrometry

PFC – Perfluorinated compound

PFOA – Perfluorooctanoic acid

PPCPs – Pharmaceuticals and personal care products

SPE – Solid phase extraction

UPLC/MS/MS - Ultra Performance Liquid Chromatography - Tandem Mass

Spectrometry

WWTP – Wastewater treatment plant

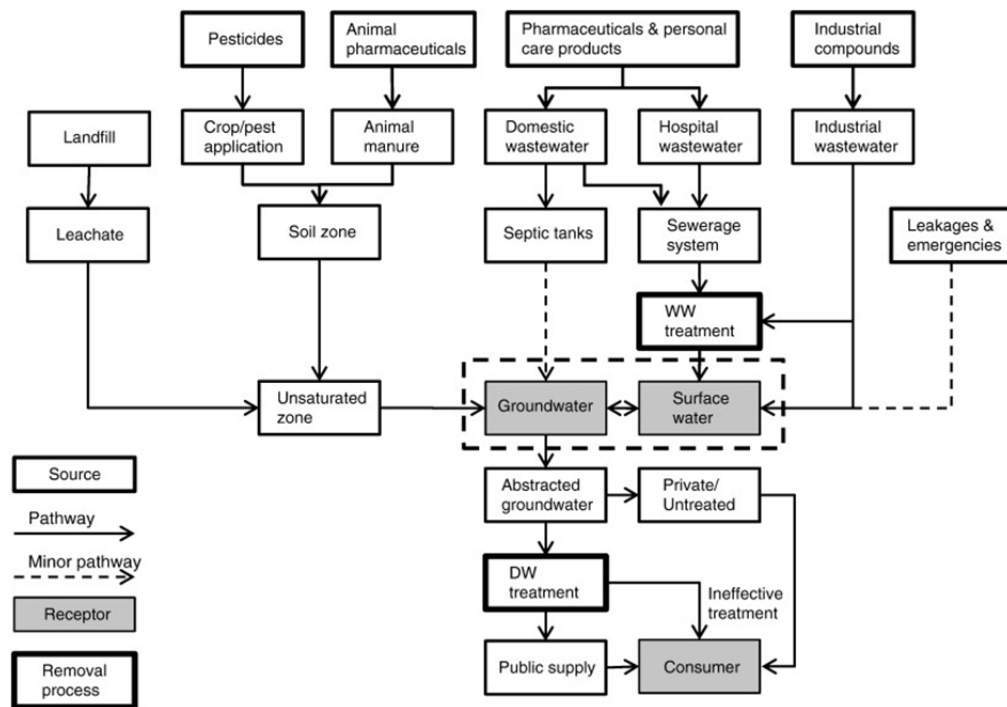
# CHAPTER 1

## INTRODUCTION

The database CAS REGISTRY [[www.cas.org](http://www.cas.org)], produced by Chemical Abstracts Service, at present includes more than 33 million organic and inorganic substances and over 59 million sequences (January 2008). This database is updated daily and, as an average, approximately 4000 new substances are added each day. (Roberto Binetti et al., 2008). Almost every chemical that we use eventually ends up in the environment. Some of them are intentionally released in measured applications, such as pesticides, while others are released through regulated and unregulated industrial discharges to the environment. Some house hold chemicals like surfactants, pharmaceuticals, and other personal care products are released to the environment after passing through waste water treatment processes. These contaminants are commonly referred to as “emerging contaminants (ECs).” These ECs may be persistent and may have potential impacts on the environment and public health. The occurrence of these trace emerging contaminants, have been observed in natural water and municipal wastewater at trace levels (Velicu et al., 2009; Ternes et al., 1999; Vanderford et al., 2003). The release of many ECs to the environment has likely occurred for a long time. As analytical techniques improve, previously undetected ECs are being observed.

A very small amount of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) may cause disruption of endocrine systems and effect the hormonal control of the development in aquatic organism and wild life (Lintelmann et al., 2003). EDCs have been defined by Organization of Economic and Cooperative Development (OECD) as “an exogenous substance or mixture that alters the

function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations” (Lister et al., 2001). Effects of these EDCs in the environment includes reduction in the breakage of eggs of birds, fish and turtles, feminization of male fish, problems in the reproductive system of fish, reptiles, birds and mammals, and changes in the immunologic system of marine mammals. In some cases these effects can lead to declines in populations. Vos et al. (2000) also reported that EDCs are pollutants, which interfere with the normal functioning of the endocrine system resulting in adverse effects on reproduction, development, and immune function. The pathways of these emerging contaminants are not very clear, however the possible routes are depicted in the Figure 1.1



**Figure 1.1: Sources and possible pathways for emerging contaminants to reach various receptors (Stuart, Lapworth, Crane, & Hart, 2012)**

## 1.1 Emerging Contaminants (ECs) of Concern

ECs can be broadly defined as any synthetic or naturally occurring chemical or microorganisms which are being discovered in water and had not being detected or are being detected previously at significant levels than expected. Emerging contaminants include PPCPs, EDCs, polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), nanomaterials, organisms and nonliving pathogens. PPCPs includes pharmaceutical drugs, ingredients in cosmetics, food supplements and other personal care products, and and transformation products (C.G. Daughton et al., 1999).

ECs chosen for this study include, 1,4-dioxane, estrogen hormones in multicomponent system (estrone, 17  $\alpha$  estradiol, 17  $\beta$  estradiol, equilin, 17  $\alpha$ dihydroequilin, estriol, 17 $\alpha$ ethinylestradiol, Medrogestone, Progesterone, Norgestrel)perfluorinated compounds (PFCs) in multicomponent system (perfluoroheptanoic acid, perfluoroundecanoic acid, tricosafuorododecanoic acid, perfluorooctanoic acid, perfluorohexanoic acid, perfluorodecanoic acid, perfluorononanoicacid, heptadecafluorooctane sulfonic acid potassium salt, tridecafluorohexane-1-sulfonic acid potassium salt, perfluorobutanesulfonic acid tetrabutylammonium salt), N,N-diethyl- meta-toluamide, and pharmaceuticals compounds (sulfamethoxaole, trimethoprim and carbamazepine). List of selected compounds and their physical properties are shown in Table 1.1

**Table 1.1: ECs selected for this study**


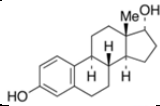
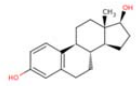
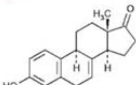
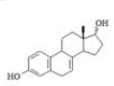
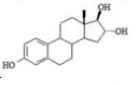
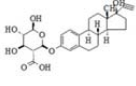
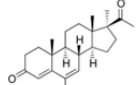
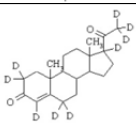
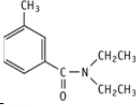
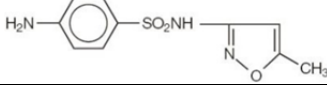
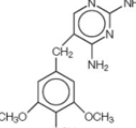
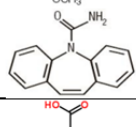

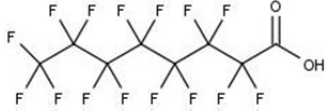
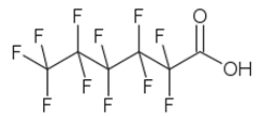

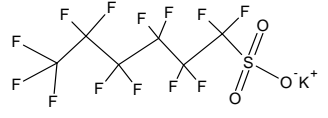
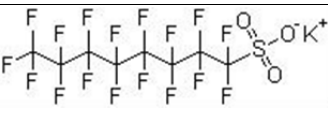

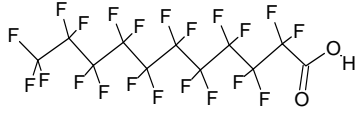
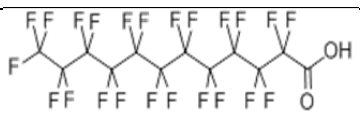

Compounds	Class	Chemical Formula	Chemical Structure	MW (g mol <sup>-1</sup> )
1-4, dioxane	ether	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>		88.11
17 $\alpha$ -estradiol,	Synthetic estrogen	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>		272.38
17 $\beta$ -estradiol, (E2)	Estrogen	C <sub>18</sub> H <sub>24</sub> O <sub>2</sub>		272.38
Equilin,	Estrogen	C <sub>18</sub> H <sub>20</sub> O <sub>2</sub>		268.355
17 $\alpha$ -dihydroequilin,	Estrogen	C <sub>18</sub> H <sub>22</sub> O <sub>2</sub>		270.37
Estriol (E3),	Estrogen	C <sub>18</sub> H <sub>24</sub> O <sub>3</sub>		288.39
17 $\alpha$ -ethinylestradiol (EE2)	Steroid	C <sub>26</sub> H <sub>32</sub> O <sub>8</sub>		472.53
Medrogestone,	Steroid	C <sub>23</sub> H <sub>32</sub> O <sub>2</sub>		340.5
Progesterone,	Steroid	C <sub>21</sub> H <sub>21</sub> O <sub>2</sub> D <sub>9</sub>		323.53
N,N-diethyl-meta-toluamide	Insecticide	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CO N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		191.27
Sulfamethoxazole	antimicrobial	C <sub>10</sub> H <sub>11</sub> N <sub>3</sub> O <sub>3</sub> S		253.279
Trimethoprim	antimicrobial	C <sub>14</sub> H <sub>18</sub> N <sub>4</sub> O <sub>3</sub>		290.3
Carbamazepine	Anticonvulsant	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O		236.269
Para-chloro benzoic acid (p-CBA)		C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>		156.57

Table 1.1 continued

Compounds	Class	Chemical Formula	Chemical Structure	M W (g mol <sup>-1</sup> )
Perfluorooctanoic acid (PFOA)	Surfactants	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>		414.07
Undecafluorohexanoic acid/Perfluorohexanoic acid (PFHXA)	Surfactants	C <sub>6</sub> HF <sub>11</sub> O <sub>2</sub>		314.05
Perfluoroheptanoic acid / (PFHPA)	Surfactants	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>		364.06
Tridecafluorohexane-1-salt (TDFHS)	Surfactants	C <sub>6</sub> F <sub>13</sub> KO <sub>3</sub> S		438.20
Heptadecafluorooctane salt/ Potassium (PFOS) Floral FC 95 Fluorad FC 95	Surfactants	C <sub>8</sub> F <sub>17</sub> KO <sub>3</sub> S		538.22
Perfluorodecanoic acid (NDFDA)	Surfactants	C <sub>10</sub> HF <sub>19</sub> O <sub>2</sub>		514.08
Perfluoroundecanoic acid (PFUNA)	Surfactants	C <sub>11</sub> HF <sub>21</sub> O <sub>2</sub>		564.09
Perfluorododecanoic acid (PFDODCA)	Surfactants	C <sub>12</sub> HF <sub>23</sub> O <sub>2</sub>		614.1
Perfluorotridecanoic acid (PFTRDA)	Surfactants	C <sub>13</sub> HF <sub>25</sub> O <sub>2</sub>		664.11

### 1.1.1 1,4- dioxane

EPA and the International Agency for Research on Cancer (IARC) classified 1, 4-dioxane as a probable (class B) human carcinogen (Kishimoto et al., 2007; USDHHS 2002). It is observed as a water contaminant at sites throughout the United States (USEPA, 2006). 1, 4-dioxane is a cyclic ether containing two symmetrically opposed ether linkage (Table 1.1) with chemical formula of  $C_4H_8O_2$ . It is also known as dioxane, p-dioxane, diethylene ether, diethylene dioxide, and glycol ethylene ether. Its oxygen atoms, each with free electrons, make it hydrophilic and miscible in water (USEPA, 2006). Its relatively high boiling point ( $101.1^\circ C$ ) increases its concentration in solvents during solvent vapor degreasing process (Joshi et al., 1989). Because of its properties, 1,4-dioxane has been shown to migrate rapidly in ground water and dissolve completely. Once dissolved, it is weakly retarded by sorption to soil particles or suspended sediments because of its low  $K_{oc}$  (1.23) (Zenker et al.2003). 1, 4-dioxane is used for a wide variety of industrial purposes. It is used primarily as a solvent stabilizer in paints, varnishes, lacquers, cosmetics, deodorants, cleaning and detergent preparations, and in scintillating fluids and it is also a by-product of many industrial processes. Also, 1, 4-dioxane often has been used with chlorinated solvents, mainly for 1,1,1-trichloroethane (TCA), as a stabilizer and corrosion inhibitor.

Heterocyclic ether structure of 1,4-dioxane makes it is resistant to biodegradation (Howard 1990), and difficult to remove by conventional water treatment methods . Because of its low Henry's Law constant ( $5 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$  at  $20^\circ C$ ) and highly hydrophilic nature ( $\log K_{ow} = -0.27$ ) (Schwarzenbach et al., 2003), dioxane is neither sufficiently volatile for air sparging nor efficiently adsorbed onto activated carbon.

Moreover, due to its small molecular weight of  $88 \text{ g mol}^{-1}$ , low-pressure reverse osmosis membrane may not be able to retain dioxane (Kishimoto et al., 2008). The oxidation with chlorine or permanganate is ineffective and lead to the formation of more toxic compounds (Hoigne and Bader 1983; Kelcka and Gonsoir 1986; Adams et al. 1994; Maurino et al. 1997).

### **1.1.2 Perfluronated compounds (PFCs)**

Perfluorinated chemicals (PFCs) especially perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are stable organic fluorochemical compounds that have wide industrial and consumer applications. They have been detected in several household products such as fabrics, carpets, food packaging, shampoo, nonstick cookware, insecticides, fire-fighting foams, industrial surfactants, food packaging, paper coating, and emulsifiers (Johnson et al., 2008). PFOA is used in the production of fluoropolymers such as PTFE, Teflon, etc. (Robert et al., 2008). The physical and chemical properties of carbon fluorine bonds in these compounds makes them stable and environmentally resistant, bioaccumulative, and potentially harmful (Han et al., 2003).

PFOS has been detected in the Antarctic, the Pacific, and the Arctic oceans (Giesy and Kannan, 2001). PFOS and PFOA have been found in surface water and ground water of several countries including Japan, the USA and Europe (Saito et al., 2004, Hansen et al., 2002, Loos et al., 2007). Studies have been reported presence of PFOA in aquatic environments (approximately 500 ng/L of PFOA has been detected in Tennessee river, the USA (Hansen et al., 2002), approximately 56 µg/L in Alz river Germany (Loos et al., 2008) approximately 25 mg/L has also been observed in ground water well near James

river, Richmond, USA (Du Pont 2007). Several studies have reported presence of PFCs in blood, serum and plasma of humans. Developmental neurotoxic effects in rats and mice have been noticed when exposed to PFOS throughout their pregnancy (Lau et al., 2003).

These compounds are recalcitrant to most conventional water treatment technologies. A review of literature shows that only few technologies were effective in the degradation of PFCs in aqueous solution. Yuan et al. reported that PFOA, with initial concentration of 20mg/L was 80% degraded under the irradiation of 254 nm UV light in the presence of 80  $\mu\text{mol/L}$  Fe (III). Photocatalytic methods, such as under 220-460 nm UV-vis light irradiation and homogeneous photocatalytic heterogeneous heteropolyacid, or by using persulfate as photochemical oxidant (Hori et al., 2004 and 05), ultrasonic irradiation and vacuum ultraviolet light methods have also shown degradation of PFCs (Jie et al., 2009 & Chen et al. 2006).

### **1.1.3 Pharmaceuticals**

Pharmaceuticals constitute a large group of human and veterinary medicines. In recent past, due to frequent use and advanced analytical techniques, a multitude of pharmaceuticals have been detected at trace concentration ( $\text{ng L}^{-1}$ ) in treated waste water, the aquatic environment, drinking and ground water in Europe, Brazil and North America. (Jones, 2001; Cahill et al., 2004). Typical source of pharmaceuticals are sewage effluent, hospital and animal waste (Esplugas et al., 2007). Pharmaceuticals have been detected in drinking water (Ternes et al., 2002; Buffle et al., 2006), ground and surface water, ocean water, sediments and soil (Halling-Sorensen et al., 1998; Andreozzi

et al., 2003a,b; Perez-Estrada et al., 2005), tap water (Halling-Sorensen et al., 1998; Doll and Frimmel, 2003). The potential effects of the compounds are still uncertain but they may cause long term and irreversible change to the organism as they are designed to have a physiological effect on humans and animals in trace concentration. Pharmaceuticals are suspicious of causing development of bacteria resistance to antibiotics (Esplugas et al., 2007; L. Guardabassi et al., 2002; C.D. Miranda et al., 1998). The following three pharmaceutical compounds were included in this study: Sulphamethazole is a sulphonamide type synthetic antibiotic used for the elimination of bacteria causing different illnesses [Merck & Co., 1999]. It has been detected in waste water ( $0.02-0.58 \mu\text{g L}^{-1}$ ). Trimethoprim is an antibiotic, detected in waste water at ( $0.11-0.37 \mu\text{g L}^{-1}$ ). Carbamazepine is used to treat epileptic seizures and bipolar disorder.

#### **1.1.4 DEET**

IUPAC name of DEET is N, N-diethyl-m-toluamide and other isomers, and is a member of the N, N- dialkylamide family of chemicals. It is an active compound in insect repellents and was first introduced in US Army to protect against insect bites in 1946 and has been in market since then (USEPA, 1998). DEET has been detected in ground water, surface water, sea water, effluent from sewage plant and even in drinking water (Barnes et al., 2004; Weigel et al., 2004; Stackelberg et al., 2004; Costanzo et al., 2007; Kolpin et al., 2004) DEET has been reported as potential carcinogen in human nasal mucosal cells (Tisch et al., 2002) and ingestion of even low dosage of DEET has been reported to result in coma and seizures in children (Petrucci et al., 2000). Table 1.1 shows the detailed properties of targeted compounds of this study.

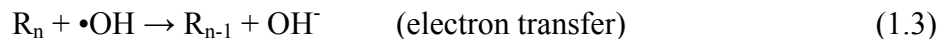
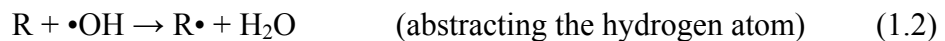
## 1.2 Potential Treatment Technologies for removal of ECs

Existing processes at potable water and wastewater treatment plants are not very effective for the removal of these ECs. Therefore, discussion has been focused on upgrading the treatment processes with additional treatment steps to improve the removal efficiency of these ECs with in the WWTPs. A number of treatment technologies have been tested concentrating on the removal of ECs, including chemical oxidation, activated carbon adsorption, membrane filtration, and others. Of these technologies, chemical oxidation using ozone with or without other oxidizing agents has been observed to be an effective technique (Huber M.M. 2003, 2005, Benitez F. J. 2009). Chemical oxidation using ozone has been proved to be an effective treatment process for a vast number of organic micropollutants during bench, pilot and full scale experiments in both drinking and wastewater (Ternes et al. 2002, 2003; Huber et al. 2005; Westerhoff et al. 2005; Ikehata et al. 2006; Snyder et al. 2006; Hua et al. 2006; Vieno et al. 2007; and Gagnon et al. 2008). Ozone disinfection is a well-known treatment process in drinking water but its benefits for ECs removal in waste water treatment have only been discussed recently. Huber et al. (2005) showed that municipal waste water effluents spiked with 11 selected PPCPs ozonated in a pilot scale, were oxidized up to 90%-99% at ozone dosage ranging from 2-5 mg O<sub>3</sub> L<sup>-1</sup>. The pH, temperature, other water characteristics, ozone dosage and retention time have an impact on the degradation of emerging contaminants. (Yargeau et al. 2008). Ozone (2.5 mg L<sup>-1</sup>) was also observed to be highly effective in 20 drinking water treatment plants (DWTPs) from different locations across United States, while chlorine (2.5 mg L<sup>-1</sup>) and UV (40 mJ cm<sup>-2</sup>) was less efficient (Snyder, 2008).

### 1.2.1 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes use a combination of at least two processes to create hydroxyl radicals ( $\bullet\text{OH}$ ). These radicals greatly enhance the rate of oxidation. AOPs can be categorized into two categories: 1. Photochemical processes, such as UV/ozone, UV/ $\text{H}_2\text{O}_2$ , photo fenton process, and photocatalysis; 2. Non photochemical processes, or chemical oxidation processes, such as hydrogen peroxide, ozone, ozone/ $\text{H}_2\text{O}_2$ , Fenton's reagents ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ ), electrochemical oxidation, and ultrasound (sonolysis).

The suitability of AOPs for contaminant degradation was recognized a few decades ago. AOPs have been used for the treatment of wastewater containing organic compounds such as pesticides, surfactants, coloring matters, pharmaceuticals and endocrine disrupting chemicals. More specifically, they have been used to pretreat wastewater in order to reduce the toxic contaminants that inhibit the biological treatment processes (Stasinakis, 2008). The main mechanism of AOPs is to trigger the generation of  $\bullet\text{OH}$ , which is extremely effective in destroying organic chemicals. Hydroxyl radicals are reactive electrophiles that react rapidly with almost all electron-rich organic compounds. The radicals attack organic species by radical addition, abstracting the hydrogen atom, and/or electron transfer (SES, 1994). These reactions are shown in equations 1.1 through 1.3, where R represents the reacting organic compounds.



As shown in Table 1.3, hydroxyl radicals are the second most powerful oxidizing species,

following fluorine.

**Table 1.2:** Oxidation potentials of some oxidants

<b>Species</b>	<b>Oxidation Potential (V)</b>
Flourine	3.03
Hydroxyl Radical	2.80
Atomic Oxygen	2.42
Ozone	2.07
Hydrogen Peroxide	1.78
Perhydroxyl Radical	1.70
Permanganate	1.68
Hyprobomous Acid	1.59
Chlorine Dioxide	1.57
Hypochlorous Acid	1.49
Hypoiodous Acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.36

(Source: Legrini et. al., 1993)

## 1.2.2. Ozonation Process

### 1.2.2.1 Ozone

Ozone ( $O_3$ ) is a triatomic molecule, consisting of three oxygen atoms. Ozone molecule is highly reactive having a reduction potential of 2.07 V. Ozone is a highly toxic and very unstable gas. Ozone must be produced onsite, as it cannot be stored and transported like other industrial gases. The structure of molecular ozone and its two extreme forms of resonance are shown in Figure 1.2. The physical and chemical properties of ozone are presented in Table C.1. Due to high reactivity of ozone, only few materials such as stainless steel 316, glass, polytetrafluorethylene, polyvinylidene fluoride and Viton are compatible with ozone. The list of the materials used in the experimental set up and their compatibility with ozone are listed in Table C.3. The molecular structure of ozone allows its reaction through dipole, electrophilic, and nucleophilic pathways. In general, the degradation reactions of organic compounds by ozone occur preferably with unsaturated compound like those with aromatic rings, alkenes, alkynes, etc. (Langlais et al. 1991).

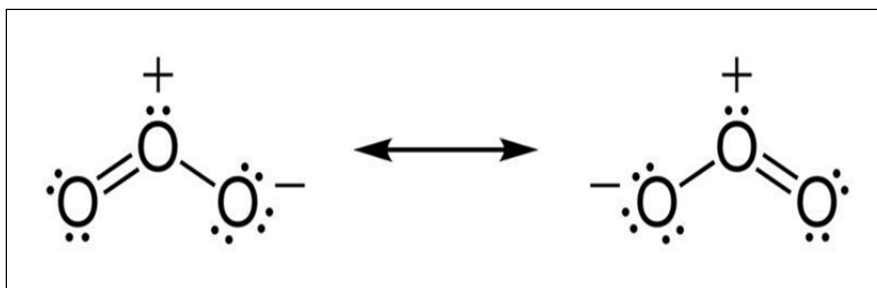
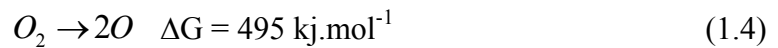


Figure 1.2: Molecular structure of ozone

### 1.2.2.2 Ozone Generation Theory

Ozone can be produced in several ways. Production of ozone by electric discharge (Glaze et al. 1987), UV-illumination of oxygen (Liou et al. 1997; Hashem et al. 1997) and electrolysis are reported in literature. In practical situations ozone is produced from oxygen or air by means of an electric discharge, known as the Siemens process (Masschelein et al. 1998). In this process, a high voltage of high frequency is applied to a flow of oxygen or air passing through a corona discharge tube (Chang et al. 1997; Kaiga et al. 1997). The electric discharge in the tubes results in dissociation of oxygen molecules and recombination of the formed oxygen atoms with oxygen molecules producing ozone.



In the above equations M represents a third collision partner, absorbing the excess energy. The theoretical maximum efficiency of this reaction is 1.22 kg O<sub>3</sub>/kWh (Motret et al. 1998). Part of the energy input is lost due to unavoidable reactions as shown in equations 1.6 and 1.7.



Ozone generators nowadays reach an efficiency of around 0.05 kg O<sub>3</sub>/kWh to 0.125 O<sub>3</sub>/kWh, depending on the quality of the feed gas used for ozone generation (Geering et al. 1999). The most important factors affecting the efficiency of the generation process are operating pressure and temperature, flow velocity, feed gas

humidity, electrical power applied, and frequency of the applied high voltage (Motert 1998; Monge 1997; Peyrous 1998; Diaz 2001). The optimum ozone concentration in the product gas is obtained at a specific power input and a higher than optimal power input will lead to an increased ozone dissociation resulting in lower ozone production. It is possible to reach ozone concentrations of up to 10% in the product gas when using air, and upto 16% when using oxygen (Ishioka 1999)

### **1.2.2.3 Applications of ozone**

Ozone has been shown to be an effective disinfectant and powerful oxidizer (Rakness *et al.* 1993; Janex *et al.* 2000). Ozone has been used for drinking water treatment since 100 years, beginning in France, in 1906 and thereafter throughout the world. Ozone was first used in the united states in 1980, with minimum growth until 1985 (Lepage, 1996). However, within the past two decades more than 40 ozone treatment plants have been designed to accomplish drinking water treatment needs (Tate, 1991). Ozone was first used by municipalities to improve the organic qualities of water with control of taste, odor and color. The use of ozone in wastewater treatment is increasing day by day. Ozone's high reduction potential enables the oxidation of numerous chemical species. Ozonation can be used as a pretreatment to improve the effectiveness of later treatments (Contreras, 2003). The non-introduction of new chemical species in the medium and its strong oxidant nature make ozonation an attractive option for water treatment. The main product of ozone decomposition in water is oxygen, which is a nontoxic compound and is useful for aerobic biological activities (Manahan, 2005).

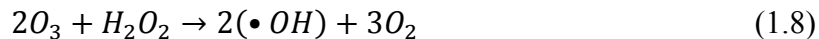
In the ozonation process, ozone reacts with the organic contaminant, either with molecular ozone or through the formation of a hydroxyl radical ( $\text{OH}\cdot$ ). At higher pH, ozone decomposes yielding hydroxyl radicals, which are high oxidizing species that react with a wide range of organic and inorganic compounds in water (Beltran, 2003)

The use of ozone in wastewater treatment includes the removal of,

- Complex organic molecules in order to improve biodegradability
- Pharmaceutically Active Compounds (PAC's) and endocrine disruptors
- Surfactants, detergents from washing centers
- Odor elimination from urban wastewater plants or industrial flue gas
- Cyanides and phenols from chemical waste
- Color from dye work's effluent, paper mills, etc.

### **1.2.3 Peroxone Process**

AOPs using Ozone in combination with hydrogen peroxide (peroxone) can increase the  $\text{OH}\cdot$  concentration for removal of more recalcitrant compounds (Hoigne, 1998). Ozone reacts with organic contaminants through both a direct reaction with molecular ozone or through indirect reaction with free radicals including the hydroxyl radical  $\text{OH}\cdot$  produced by decomposition of ozone (Broseus, 2009). Molecular ozone reacts selectively with unsaturated bonds, aromatic systems and amide groups whereas  $\text{OH}\cdot$  reacts less selectively and faster than ozone (Snyder, 2006). Therefore this process is particularly promising for recalcitrant materials due to its capability to produce high levels of hydroxyl radical  $\text{OH}\cdot$ .



This process has been applied to several toxic non-biodegradable compounds such as methyl-tert-butyl ether, atrazine, and has resulted in significant pollutant removal efficiencies. Several studies examined O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process for the removal of 1,4-dioxane in aqueous solutions. All these studies showed that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> could remove 1,4-dioxane to low ppb levels. Kosaka et al. (1995) also investigated the impact of <sup>•</sup>OH scavengers and observed that dioxane removal was negatively affected by the presence of humic acids in the solution. In addition, Adams et al. (1994) showed that O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process could be used as a pretreatment process to enhance biodegradability of dioxane contaminated water. In this study, with the aim of using O<sub>3</sub>(ozonation) and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (peroxone) processes as treatment of contaminated water with certain ECs and the impact of pH and H<sub>2</sub>O<sub>2</sub> concentration were investigated. Also, a kinetic model has been applied to describe the experimental data and to estimate the rate of 1,4-dioxane oxidation.

## CHAPTER 2

### PROJECT OBJECTIVES

Two technologies involving ozone and Hydrogen peroxide were examined and optimized for the removal of certain ECs from water. The technologies examined were ozonation, and peroxone. The study was divided and performed in two parts,

- 1) In the first part of study, the kinetic rate constants of  $O_3$  and hydroxyl radical with lower 1,4-dioxane were estimated. The ECs of interest for this part of the study were, 1,4-dioxane and 10 estrogen hormones (estrone,  $17\alpha$  estradiol,  $17\beta$  estradiol, equilin,  $17\alpha$  dihydroequilin, estriol,  $17\alpha$  ethinylestradiol, medrogestone, progesterone, norgestrel).
- 2) The second part of this study involved the investigation of removal efficiency of target ECs in bigger (14 L) and semi batch reactor using the two technologies, ozonation and peroxone. The ECs of interest for this part includes: 1,4-dioxane, PFOA, perfluorinated compounds (PFCs) in multicomponent system including, perfluoroheptanoic acid, perfluoroundecanoic acid, tricosafuorododecanoic acid, perfluorooctanoic acid, perfluorohexanoic acid, perfluorodecanoic acid, perfluorononanoic acid, heptadecafluorooctane sulfonic acid potassium salt, tridecafluorohexane-1-sulfonic acid potassium salt, perfluorobutanesulfonic acid tetrabutylammonium salt, 1,4-dioxane, N,N-diethyl- meta-toluamide, and pharmaceuticals compounds sulfamethoxazole, trimethoprim and carbamazepine .

The specific objectives are listed below.

- 1) To examine the removal of 1,4-dioxane by ozonation and peroxone processes
- 1) To examine the impact of different  $O_3/H_2O_2$  ratio on 1,4-dioxane removal
- 2) To estimate the kinetic rate constant of  $O_3$  with lower 1,4-dioxane and lower ozone concentration in milli-Q water.
- 3) To determine the kinetic rate constant with hydroxyl radical with competitor compound *p*-CBA.
- 4) To examine the impact of different ozone concentration and different contact time on removal efficiency of estrogen hormones at very low ozone dosage.
- 5) To examine the impact of initial concentration, salinity and contact time on removal efficiency of 1,4-dioxane during ozonation.
- 6) To examine the removal of 1,4-dioxane by ozonation with persulfate.
- 7) To examine the removal of selected pharmaceuticals by ozonation and peroxone processes.
- 8) To examine the removal of DEET by ozonation and peroxone processes.
- 9) To examine the removal of 10 PFCs in multicomponent system by ozonation and peroxone processes.

## CHAPTER 3

### MATERIAL & METHODS

#### 3.1 Chemicals & Reagents

Most of compounds were obtained from Sigma-Aldrich. The chemicals obtained were: estrone, 17  $\alpha$  estradiol (98%), 17  $\beta$  estradiol (97.1), equilin (99.9%), 17  $\alpha$  dihydroequilin (99.4%), estriol (100%), 17 $\alpha$  ethinylestradiol (99.1%), medrogestone, progesterone (99.6%), trimegestrone (99.3%), Norgestrel and 3-O-methyl estrone (internal standard, 98%). Potassium indigo trisulfonate ( $C_{16}H_7K_3N_2O_{11}S_3$ ), phosphoric acid ( $H_3PO_4$ , 85%), Sodium sulfate ( $Na_2SO_4$ ), 1, 4-dioxane (>99%), 1, 4-dioxane d8 (99%), hydrogen peroxide ( $H_2O_2$ , 35 wt. %) para chloro benzoic acid were obtained from Sigma Aldrich. Methanol ( $CH_3OH$ , HPLC grade), toluene ( $C_7H_8$  ( $C_6H_5CH_3$ ), HPLC grade), dichloromethane, potassium phosphate monobasic ( $KH_2PO_4$ , Laboratory Grade), sodium phosphate monobasic ( $Na_2H_2PO_4$ , certified ACS), sulfuric acid ( $H_2SO_4$ , certified ACS), sodium thiosulfate ( $Na_2S_2O_3 \cdot 5H_2O$ , certified ACS), sodium chloride ( $NaCl$ , certified ACS), sodium persulfate ( $Na_2S_2O_8$ ) were obtained from Fisher Scientific. Potassium iodide (KI, 99+%) and sodium phosphate monobasic ( $KH_2PO_4$ , 99+%) were obtained from Acros Organics. Varian Bond 3ml/500 mg solid phase extraction (SPE) cartridge was obtained from Varian Inc. Filters and amber glassware were obtained from Fisher Scientific. Perfluorochemicals (PFCs) were also purchased from Sigma-Aldrich. PFCs purchased were perfluoroheptanoic acid, perfluoroundecanoic acid, tricosfluorododecanoic acid, perfluorooctanoic acid, perfluorohexanoic acid,

perfluorodecanoic acid, perfluorononanoic acid, heptadecafluorooctane sulfonic acid potassium salt, tridecafluorohexane-1-sulfonic acid potassium salt, perfluorobutanesulfonic acid tetrabutylammonium salt. Genevac EZ-2 Evaporator, Oasis HLB 3cc SPE cartridges from Waters, Aquity ultra performance LC/ MS from Waters has been used for the experiments. All solutions and reagents were prepared with Milli-Q purified water prepared from Millipore Milli-Q Gradient A10 water purification system.

### **3.2 Experimental Set up for ozonation**

Two types of reactor set ups were used to conduct the experiments during the two different parts of the study.

#### **3.2.1 Batch Reactor Setup**

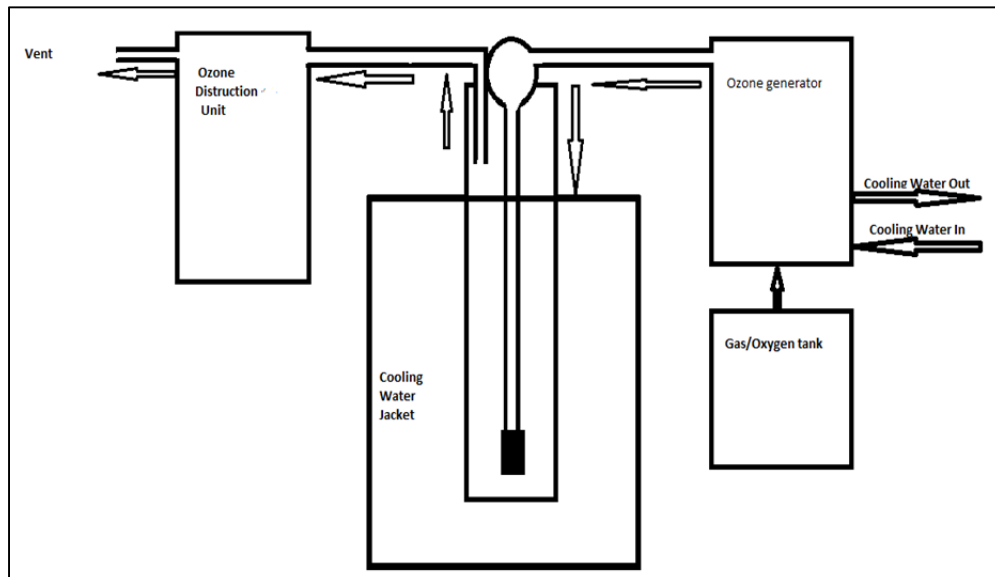
The batch reactor set up used for all kinetic experiments of 1, 4-dioxane and for degradation of estrogen hormones. The setup used for conducting the experiments is shown in Figure 3.1. Gas washing bottle of 250 ml volume equipped with porous gas diffuser, were used to prepare the aqueous ozone solutions. Generated ozone was continuously bubbled through the diffuser. The gas washing bottle was jacketed with cooled iced water beaker to maintain the temperature  $\leq 3^{\circ}\text{C}$  of the ozone aqueous solution to minimize the ozone decomposition.

As a reaction vessel, 500-mL amber glass bottles were used with a teflon coated lid. Aqueous ozone solution was added using glass pipettes to the reaction vessel that contained Milli-Q water spiked with required concentration of the target compounds. The

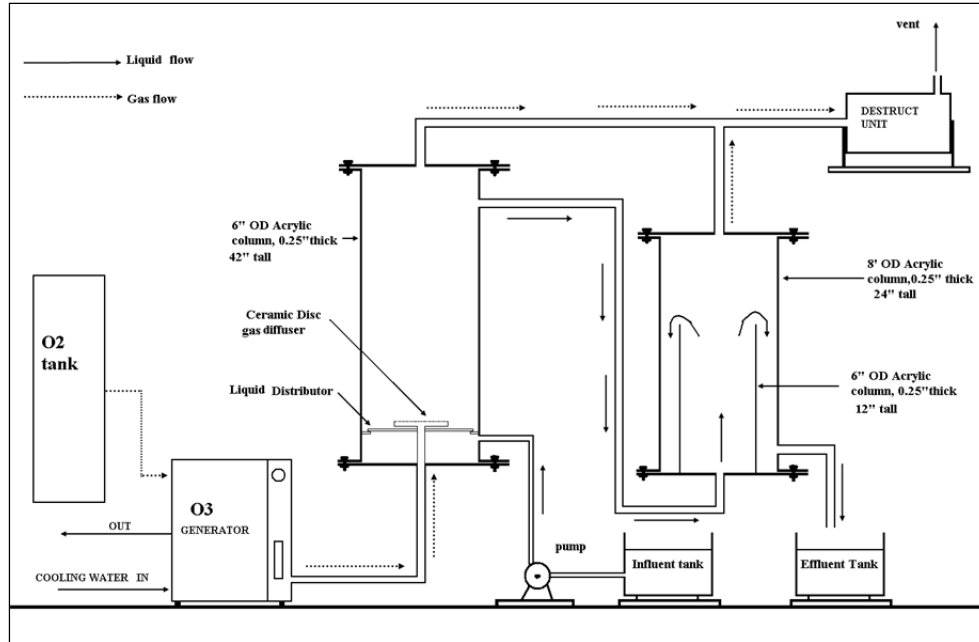
set up used for ozone generation and residual ozone destructor were same as in the bigger semi batch reactor set up (See section 3.2.2).

### 3.2.2 Semi batch reactor set up

The experimental setup used for conducting the experiments is shown in Figure 4.1. The setup comprises of ozone generator, bubble column, degassing unit, and destruct unit. The ozone generator (OZAT CFS-1 2G) was provided by Ozonia Ltd and is shown in Figure A.2. It is capable of generating ozone concentrations of up to 5 wt% in the product gas when using air and, up to 13% when using oxygen. Air and oxygen were supplied from Airgas, Inc. Experimental setup consists of two columns equipped with a porous gas diffuser (pore diameter ranging from 30 to 100 microns). The first column is served for absorption while the second column is served for desorption. Water can be circulated between the two columns. The excess ozone from the reactors is sent to the destruct unit.



**Figure 3.1: Schematic diagram of batch reactor setup for lower ozone concentration experiments**



**Figure 3.2: Schematic diagram of semi batch reactor setup.**

The columns were custom ordered from Marine Technical Concepts Inc. the diffusers were custom built to fit the column. Valves, pressure relief valves and check valves with stainless steel piping was purchased from Swagelok Manufacturing Company.

**Table 3.1: Ozone conditions for all the experiments in semi batch reactor setups**

Feed Gas	Air
Flow rate	5%
Power	90 W
Pressure	3.5 bar
Ozone weight	5

### **3.3 Experimental and Analytical Method**

#### **3.3.1 Glass Ware Cleaning Procedure**

Glassware preparation is an important step before conducting experiments with estrogens. In order to reduce the losses due to sorption of the compounds onto the glassware, a three step cleaning procedure (silanization) was performed to clean and deactivate the glass (Suri et al. 2010). This process was used to chemically bind a thin, water-repellent film to the glass. This layer is neutral, hydrophobic and not oily which creates a nonstick surface to minimize any loss of hormones by sorbing on to the glass.

The three step silanization process of the glassware is as follows:

- Initially glassware was rinsed with toluene containing 5% dichlorodimethylsilane (DCDMS)
- Then the glassware was rinsed with two washes of pure toluene
- In order to remove the toluene, glassware was finally rinsed with methanol three times

After silanizing, glassware was completely dried in the oven at 250°C. All glassware including bottles used for sample collection, beakers, pipettes, test tubes and GC vial inserts were silanized for estrogen experiment.

Glassware for other experiments was meticulously cleaned by the regular cleaning procedure.

### **3.3.2 Solid Phase Extraction**

SPE was carried out using Varian Bond Elute C-18 SPE cartridges, which were initially activated using 3mL of methanol and rinsed with 3 mL of DI water. Samples were passed through these SPE cartridges at a flow rate of 5 mL/min. The cartridges were then rinsed twice with 3mL of DI water and eluted with 6mL of methanol. The eluent was collected in a clean, silanized test-tube and was spiked with 1mL of the internal standard. The spiked eluent was then dried in a Genevac centrifugal evaporator at 40°C and 12mbar vacuum.

### **3.3.3 Gas Chromatography – Tandem Mass Spectrometry Analysis**

GC/MS/MS analysis was performed using a Waters Quattro micro GC coupled with 7890A MS. Auto injections were made using split less mode with a split ratio of 0.1, and an injection volume of 1.0 µL. Injection temperature was 250°C. The initial temperature of the oven was 110°C. The temperature was ramped to 250°C at a rate of 20.0°C/min, and held for 8.0 minutes, then ramped to 265°C at a rate of 1.0°C/min, and finally ramped to 300°C at a rate of 7°C/min and held for 34 minutes. Transfer line temperature to the MS was maintained at 300°C and the electron energy was 70eV.

### **3.3.4 Gas Chromatograph/Mass Spectrometry (GC/MS) Analysis**

Separation and detection of the analytes was performed using an Agilent 6890N GC and Waters Quattro micro GC™ of tandem quadrupole mass spectrometer. The gas chromatograph was coupled a SPB™-624 capillary column (30mx0.25mmx1.4um film; J & W Scientific). The auto injections were made in split less mode and injection volume

used was 1  $\mu$ L. Helium was used as a carrier gas and with flow rate 1 ml/min. Injection temperature was 250 °C and the head pressure was 60 kPa of Helium. The initial oven temperature was 35 °C for 1 min and then ramped to 90 °C at 7 °C/ min. Finally, the oven temperature was ramped to 200 °C at 30 °C/ min and held for 5 min. MS parameters: temperature of transfer line, 250 °C; EI mode; electron energy, 70 eV; ion source temperature, 250 °C.

### **3.3.5. Ultra Performance Liquid Chromatography/ Electro spray Ionization/ Mass Spectrometry/Mass Spectrometry (UPLC/ESI/MS/MS) Analysis**

Analysis was performed using UPLC/ESI/MS/MS consisting of an UPLC (Waters Acquity UPLC™ system) coupled with a Waters Xevo™ mass spectrometer with a Z-Spray™ ESI source. The column used was Acquity UPLC®, BEH C18 column (1.7  $\mu$ m particle size, 1.0  $\times$  50mm, Waters, UK). LC was operated under the following conditions. A gradient mobile phase was used with methanol and water. Mobile phase flow rate was 0.6 ml/min. The injection volume of sample was 10  $\mu$ L. Gradient conditions were initiated with 30% methanol and held for 0.5 min, followed by an increase to 100% (5 min) and held for 0.5min. The proportion of water was then increased to 70% and held for 0.5min. The total run time was in 6.5 min. The mass spectrometer was operated in the negative and positive electrospray ionization mode using multiple reaction monitoring (MRM) for different compounds. The conditions for detection by the mass spectrometer were as follows: capillary voltage, 3.00kV and 3.90 kV; cone voltage, 22V and 27V for negative and positive electrospray ionization mode respectively; multiplier voltage, 650V; desolvation gas flow rate, 1000 Lh<sup>-1</sup>; cone gas flow, 20 L h<sup>-1</sup>; collision gas flow is 0.15

ml/min; desolvation temperature, 600 °C; source temperature, 150 °C. Nitrogen gas was used as desolvation gas and nebulizer gas and argon gas was used as collision gas.

### **3.3.6 High performance liquid chromatography (HPLC) analysis for *para*-chloro benzoic acid.**

Waters Acquity H-Class UPLC with 30 cm column heater was utilized to perform the analysis of *p*-CBA. The mobile phase consisted of 50% water (0.1% formic acid) and 50% acetonitrile and this was maintained at a 1 mL/min flow rate. More analytical condition used, are as follows; Detector – Water PDA ,Column – Waters, Symmetry C18 5 um, 4.6 x 150 mm, Run time – 5 min, Retention time – 3.58 min, Column temperature - 40C Sample temperature – 4C, Absorbance wavelength – 222 nm, Resolution – 4.8 nm, Injection volume – 50 µl, Calculated LOD – 0.00046, Calculated LOQ – 0.00139

### **3.3.7 Aqueous ozone preparation for the batch reactor experiments**

Stock solutions of aqueous ozone were prepared by continuously bubbling ozone through a gas-washing bottle into Milli- Q water chilled to ~3°C. This stock solution generally contained a steady-state concentration of ozone of 10 mg L<sup>-1</sup>. Lower concentrations were achieved by dilution with Milli-Q water.

The aqueous ozone was transferred into the individual test bottles with glass pipettes. The concentration of ozone was analyzed before and after adding the aqueous ozone solution to the reaction vessels. Care was taken that the aqueous ozone was always handled in exactly the same way, whether it was transferred into samples containing

indigo solution for the analysis of residual ozone or into the reaction vessels. All concentrations of ozone were measured by indigo method. As a reaction vessels, 500-mL amber glass bottle were used with a teflon coated lid(Bader & Hoigne, 1981). The solution was vigorously mixed after adding the aqueous ozone to the reaction vessel. The ozone residual was quenched immediately after the set reaction time by adding 1 mL of sodium thiosulfate (0.1N).The concentration of Initial ozone in aqueous solution and residual ozone in samples were measured by indigo colorimetric method.

### **3.3.8 Analysis of residual ozone in water samples**

The ozone concentration in the aqueous phase was measured using indigo-trisulfonate method (Bader and Hoigne, 1981). Detail is given in next section (3.3.12).

### **3.3.9 Analysis of 1,4-dioxane**

All experiments were conducted in solution containing 50, 100 and 1000 µg/L 1,4-dioxane. For competition kinetic runs, required concentration of *p*-CBA were added to the solution prior to ozonation or peroxone processes. Stock solution of 1, 4-dioxane was prepared at 100mg/L in Milli-Q deionized water and stored in volumetric flask at 4°C. Aqueous solutions of 1-4-dioxane were prepared by spiking 1-4-dioxane stock solution into Milli-Q water. Experiments were conducted in batch mode by adding aqueous ozone into the reaction vessel containing required amount of 1,4-dioxane solution. Tests were conducted for ozonation and peroxone, processes. For peroxone

studies, the oxidant (hydrogen peroxide) was introduced into the solution prior to the ozonation. Effect of pH and initial concentration was also determined. pH of the solution was adjusted using 1M NaOH. These samples were analyzed for both ozone and 1,4-dioxane in water. In samples for 1-4-dioxane analysis,  $\text{Na}_2\text{S}_2\text{O}_3$  was added to quench the ozone. Liquid – Liquid Extraction (LLE) of 1, 4–dioxane was carried out using 20 ml of sample, spiked with a known amount of internal standard. A 10ml sample was placed in clean EPA vial and 20ml of methylene chloride and 2gm of sodium sulfate salt were added. The mixture was vortexed and aqueous layer was extracted out. The remaining 10 ml sample was added to the organic sample, vortexed and the aqueous supernatant layer was discarded. A small amount of sodium sulfate was added to the organic layer to remove any moisture content. The sample was analyzed on GC/MS/MS. For samples with lower concentrations ( $[1,4\text{-D}] = 50\mu\text{g L}^{-1}$ ), solid phase extraction of 1, 4–dioxane was carried out using EPA method 522. In brief, 200 ml of sample was passed through the SPE cartridges. The cartridges were then extracted using 10ml of methylene chloride and a known amount of internal standard was added to the eluent. Small amount of sodium sulfate was added to the mixture to remove any moisture content and the sample was analyzed on GC/MS/MS (Details of GC/MS/MS given in Sec. 3.3.3).

The experimental conditions for 1, 4-dioxane degradation studies in semi batch reactor setup were 5% feed gas flow rate and 5 wt % of ozone.

### **3.3.10 Analysis of estrogens**

Stock solutions of mixture of estrogens were prepared at 100mg/L in methanol and stored in amber volumetric flask at 4°C. Aqueous solutions of mixture of estrogens of

100µg/L individual estrogen concentrations were prepared by spiking estrogens stock solution into water. Estrogens were analyzed using solid phase extraction followed by analysis on UPLC/ESI/MS/MS (Details of UPLC/ESI/MS/MS given in Sec. 3.3.5). During SPE processes for estrogens, a 200 ml of ozonated sample was passed through the Bond Elute C-18 SPE column at a flow rate of 5ml/min. Before loading, the SPE cartridges were activated with 6ml methanol and then rinsed with 6ml of Milli-Q water. After the sample was passed through the SPE column, the column was rinsed with Milli-Q water and then eluted with 6ml of methanol. The methanol eluent was collected in a silanized test tube and a fixed amount of internal standard was added. Eluent was completely dried in a genevac centrifugal evaporator at 45° C and 12 mbar. The completely dried sample were derivatized using bis(trimethylsilyl)- trifluoro- acetamide (derivatization process describe in section 3.3.10). The analysis was performed on GC/MS using a Pursuit DB-225MS capillary column (Details of GC/MS given in Sec. 3.3.4).

### **3.3.11 Derivatization**

Derivatization is a process of chemically modifying a compound in order to produce a compatible compound for GC/MS/MS analysis. After drying, the samples were derivatized by the addition of 25µL of pyridine and 25µL of bis (trimethylsilyl) trifluoro-acetamide (BSTFA). After addition of pyridine and BTM, the sample was left to stand for 20 minutes at 26°C to enable sufficient reaction time. 300 µL of toluene was then added, and the sample was vortexed. The sample was transferred into a 0.25mL silanized GC glass insert and was analyzed on GC/MS/MS.

### **3.3.12 Analysis of residual ozone in water samples of semi batch reactor experiments**

The ozone concentration in the aqueous phase was measured using indigo-trisulfonate method (Bader and Hoigne, 1981). The indigo method is based on the principle that in acidic solution, potassium trisulfonate ( $C_6H_7N_2O_{11}S_3K_3$ ) is discolored by aqueous ozone and the degree of discoloration is compared to a blank solution of the dye. The decrease in the absorbance is linear with increasing ozone concentration.

Indigo solution was prepared by adding distilled water (500ml), concentrated phosphoric acid (1ml), and potassium indigo-trisulfonate (770 mg) to a volumetric flask and diluted to 1L with distilled water. A 1:100 dilution exhibits an absorbance of 0.2(+ or -)  $0.010\text{ cm}^{-1}$  at 600nm, and the solution should be discarded when absorbance falls below 0.16 absorbance units/cm(Bader and Hoigne, 1981). This stock solution is stable for about 4 months when stored in the dark (standard methods). The working solution was made up immediately before use by dilution of 100 ml of the above indigo stock solution to 1L with distilled water and adding 10g of sodium dihydrogen phosphate and 7ml phosphoric acid to it. 100 ml glass bottles were taken and 10 ml of working solution was introduced into each. One bottle was filled with ozone free water and the other with 3ml of ozonated water and filled to the mark with distilled water. The ozone samples were introduced by immersing the pipette to the bottom of the bottle and gently shaking so that no ozone degassing occurred. The difference in absorption of light at 600nm between blank and samples was measured using HACH DR/4000U spectrophotometer. The ozone concentration was then determined using the following equation:

$$C = \frac{V \times \Delta A}{f \times b \times V_t} \quad (3.1)$$

Where C is the concentration of ozone in mg/L;  $\Delta A$  the difference in absorbance;  $f=0.42$  (corresponding to the absorption coefficient for aqueous ozone); b the path length (1 cm);  $V_t$  and V are the total volume (100ml) and volume of sample added (3ml), respectively.

### 3.3.13 Analysis of residual ozone in air phase of semi batch reactor experiments

The ozone concentrations in the air phase are measured using potassium iodide (KI) wet chemistry testing. The KI wet chemistry method is based on the principle that iodide ion is oxidized by ozone to form iodine when ozone gas is bubbled through a solution of KI. When bubbling is stopped, the KI solution is adjusted with sulfuric acid to pH 2, or lower. The liberated iodine is titrated using standardized sodium thiosulfate. The mass of ozone reacted is determined based on a theoretical ozone/iodine stoichiometry of 1.0.



The iodine formed in the above reaction is titrated directly with thiosulfate ion:



Potassium iodide stock reagent (2%) was prepared by dissolving 20g KI, 7.3 g of disodium hydrogen phosphate ( $Na_2HPO_4 \cdot 2H_2O$ ), and 3.5 g of mono potassium dihydrogen phosphate ( $KH_2PO_4$ ) in 1L of distilled water and then stored in brown bottle

and refrigerated. Sulfuric acid (2N) was prepared by adding 56 ml concentrated sulfuric acid to 944 ml distilled water. Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) stock solution was prepared by dissolving 250 g of pentahydrate sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) granules into 1L of distilled water. Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (0.1N) was prepared by adding 100 ml of 1N  $\text{Na}_2\text{S}_2\text{O}_3$  stock solution to 900 ml of distilled water.

A Class A burette was filled with 50 ml of  $\text{Na}_2\text{S}_2\text{O}_3$  (0.1N) titrant. 400 ml of 2% KI solution was added to two gas washing bottles. Ozone was bubbled through the KI solution for a fixed time. After bubbling has stopped, about 10 ml of 2N  $\text{H}_2\text{SO}_4$  was quickly added to each gas washing bottle to lower the pH of the solution below 2. The liquid from each gas washing bottle was then transferred to a 1L flask and titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Mass of ozone trapped in KI is calculated using the formula

$$O_{3_{mass}} = 24 \times V_t \times N_t \quad (3.4)$$

Where  $O_{3_{mass}}$  = mass of ozone trapped in KI, mg

$V_t$  = volume of sodium thiosulfate titrant used, ml

$N_t$  = normality of sodium thiosulfate, mg/meq

### **3.3.14 Study of Removal Efficiencies of Target Compounds in Semi Batch Reactor Set up**

Semi batch experiments were conducted for the study of removal efficiency of all the target compounds selected for this study. For these experiments, only the first column of the reactor set up was used. The ozone generated from the generator was diffused through

the ceramic gas diffuser into the column. The ozone was allowed to pass through the water contained in the column. Aqueous solutions of compounds of required concentration were prepared in a carboy by spiking the compounds into 14 L of Milli-Q water. The reactor was charged with the spiked Milli-Q water before ozonation. Milli-Q purified water was used for investigation of removal efficiency of 1,4-dioxane, PFCs, and DEET while tap water were used to investigate the removal efficiency of pharmaceuticals. The required amount of ozone was used for degradation of compounds while the excess is sent to the destruct unit. During the experiments water samples from the column were collected at regular intervals. These samples were analyzed for both ozone and target compounds in water. Ozone in gas phase samples was collected at a valve near destruct unit. Ozone in water was analyzed using the indigo colorimetric method and ozone in gas phase was analyzed using potassium iodide (KI) wet chemistry method. In Samples for target compound analysis,  $\text{Na}_2\text{S}_2\text{O}_3$  is added to quench the ozone. Air was used as a feed gas for generating ozone.

### **3.3.16 Analysis of PFCs & PFOA**

Single 50 mg L<sup>-1</sup>PFOA and PFCs standard stock solution were prepared in methanol and used for all the experiments. Ozone gas was generated and bubbled through the column containing 12L Milli - Q water spiked with 25ppb PFOA and PFCs for multi component system. All escaping ozone gas was captured and destructed by the ozone destructor. Reaction time for all experiments was from 12 -20 minutes. Ozone in gas phase in the reactor was analyzed by titration standard iodometric method (  $\text{IO}_3^-$  A

method) and ozone in water phase was analysed and calculated by indigo colorimetric method ( US standard method 4500-O<sub>3</sub>B) (Rominder Suri 2008). 14 Liter PFOA/ PFCs water sample was made in 20 liter glass container (carboy) with Milli- Q purified water. Ozonated water samples were collected in 200ml vials and extracted by solid phase extraction (SPE). SPE cartridges were activated with 5 ml of methanol and 5 ml of water at the flow rate of 5ml/min. The sampled water were passed through these cartridges at the same flow rate 5ml/min. Extracted sample were eluted with 6 ml of methanol and spiked with 5 µL of 24ppm PFOA/PFCs Internal standard. The eluted samples were evaporated on evaporator. 2.5ml of methanol followed by 2.5 ml of Milli-Q purified water were added in the evaporated sample. And finally analysis was performed on LC/MS.

### **3.3.17 Analysis of Pharmaceuticals & DEET**

14 L of sample with required concentration were prepared in the carboy. The semi batch reactor was charged with the spiked water. Ozonated samples (200mL) were collected in vials, pH of the samples was adjusted to 2.0 using HCl and 200ng of EDTA were added to the solution. The sample were put on shaker for 1 hour and then extracted by solid phase extraction (SPE). SPE cartridges (HLB Oasis) were activated with 6 ml of methanol and 6 ml of reagent water (Milli-Q water at pH 2.0) at the flow rate of 5ml/min. The sampled water was passed through these cartridges at the same flow rate 5ml/min. Extracted sample were eluted with 8 ml of methanol reagent (0.1 % formic acid in methanol). The eluted samples were evaporated on evaporator. 2ml of reagent methanol

(0.1 % formic acid in methanol) followed by 2 ml of Milli-Q purified water was added in the evaporated sample.

Analysis was performed using UPLC/ESI/MS/MS consisting of an UPLC (Waters Acquity UPLC system) coupled with a Waters Xevo mass spectrometer with a Z-Spray ESI source. The column used was Acquity UPLC<sup>®</sup>, BEH C18 column (1.7 $\mu$ m particle size, 1.0 $\times$ 50mm, Waters, UK). LC was operated under the following conditions. A gradient mobile phase was used with methanol with 0.1 % formic acid and Milli-Q water. Mobile phase flow rate was 0.6 ml/min. The injection volume of sample was 10 $\mu$ L.

## CHAPTER 4

### RESULTS & DISCUSSION

The results and discussion of all target compounds are discussed separately for the both reactor setups used in this study.

#### 4.1 Oxidation of 1,4-dioxane during ozonation and peroxone processes in batch reactor setup

Preliminary experiments of batch reactor setup were performed to optimize the reaction conditions. Results are given in Table 4.1 and Figure 4.1. Ozone decomposition in 15 min of sampling period was <7%. It was assumed that the ozone concentration remained constant during the experiments.

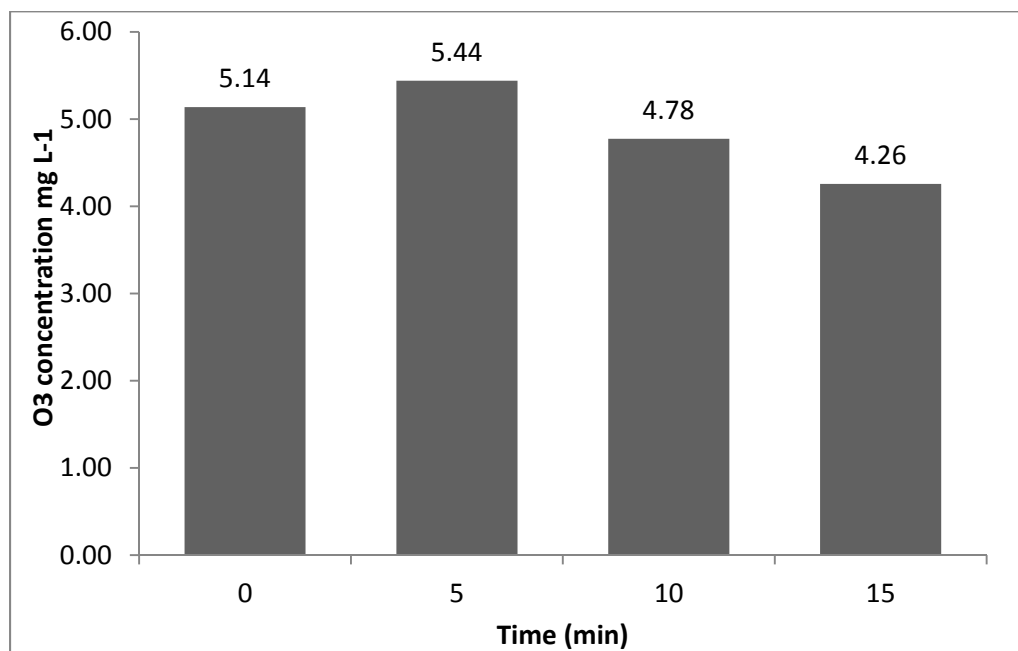


Figure 4.1: Decomposition profile of ozone in transferring the aqueous ozone from gas washing bottle to the reactor vessels during batch reactor experiments,  $[O_3] = 5 \text{ mg L}^{-1}$

**Table 4.1: Decomposition profile of ozone in transferring the aqueous ozone from gas washing bottle to the reactor vessels during batch reactor experiments.**

Set up Conditions	Feed Gas	O <sub>3</sub> conc.(%)		Mean	SD
ozonation ( Flow rate 5, Wt% 9 Retention Time- 5 min)	O <sub>2</sub>	S1 (100%)	41.16		
		S2 (100%)	39.97	39.83	1.401161
		S3 (100%)	38.37		
		50% of S1	15.80		
		50% of S2	19.03	17.43	1.614475
		50% of S3	17.46		
		25% of S1	7.63		
		25% of S2	8.76	7.69	1.041719
		25% of S3	6.68		
Ozone ( Flowrate- 3, Wt%- 9, Retention Time- 5 min)	Air	S1 (100%)	3.27		
		S2 (100%)	3.28	2.72	0.962938
		S3 (100%)	1.61		
		50% of S1	0.64		
		50% of S2	0.58	0.66	0.089576
		50% of S3	0.76		
		25% of S1	0.29		
		25% of S2	0.27	0.27	0.021244
		25% of S3	0.25		
Ozone( Flow rate 0.5, Wt% 9, Retention Time- 10 min)	Air	S1 (100%)	3.27		
		S2 (100%)	3.28	2.72	0.962938
		S3 (100%)	1.61		
		50% of S1	0.62		
		50% of S2	0.58	0.59	0.028816
		50% of S3	0.56		
		25% of S1	0.24		
		25% of S2	0.27	0.20	0.095449
		25% of S3	0.09		

The degradation of 1, 4-dioxane was studied with two ozone based technologies: (1) direct ozonation and (2) peroxone: ozone with hydrogen peroxide.

#### 4.1.1 Ozonation Results

All experiments of semi batch reactor setup were performed in milli-Q water. Experiments were carried out at 20° C. Insignificant 1,4-dioxane percent removal was observed during ozonation process. The results in this study indicated that 1, 4-dioxane is persistent to direct ozone reaction and has low reactivity with ozone ( $k_{O_3} = 0.32 M^{-1} S^{-1}$  by Hoigne and Bader, 1983).

Figure 4.2 shows result of two different initial concentration of 1, 4-dioxane. It shows insignificant change in the removal efficiency during ozonation of two different initial concentration of 1, 4-dioxane solution. Initial concentrations of target compound during these experiments were 0.5 $\mu$ M and 0.9 $\mu$ M (Figure 4.2). Insignificant increase in the removal of 1, 4-dioxane was observed when lower 1, 4-dioxane concentration (0.5 $\mu$ M) was used during ozonation. Approximately 37% removal of 1,4-dioxane was achieved in 15 minute of ozonation process in both the experiments.

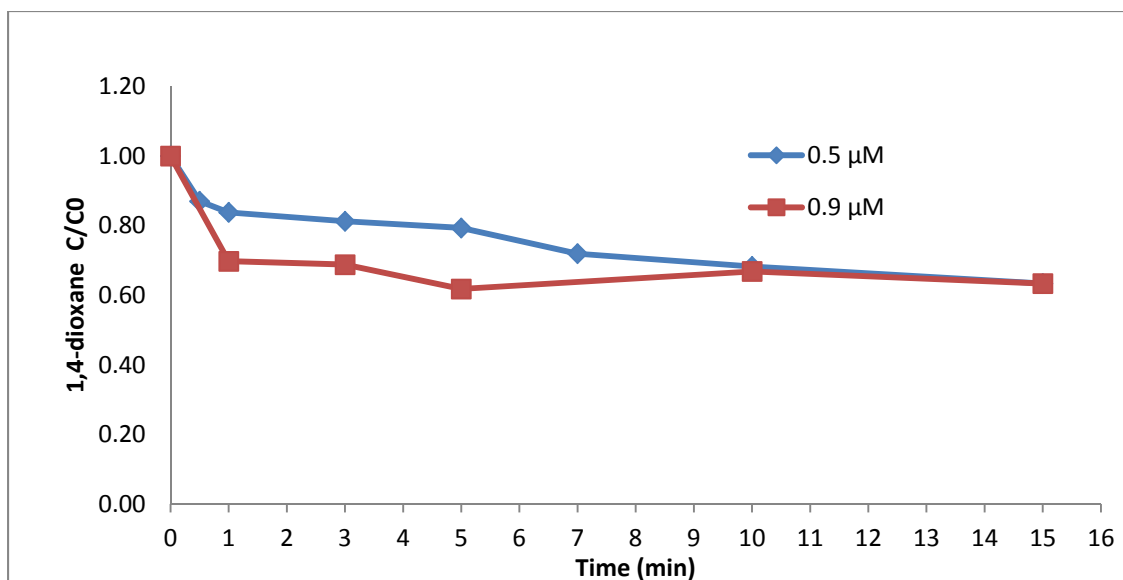


Figure 4.2: Oxidation of 1,4-dioxane during ozonation in batch reactor,  $[O_3] = 0.12 \text{ mM}$  in ( $0.5 \mu\text{M}$  1,4 dioxane) &  $0.1 \text{ mM}$  ( $0.9 \mu\text{M}$  1,4 dioxane),  $[1,4\text{-dioxane}] = 0.5 \mu\text{M}$  and  $0.9 \mu\text{M}$ , reaction volume = 50 ml in both the experiments.

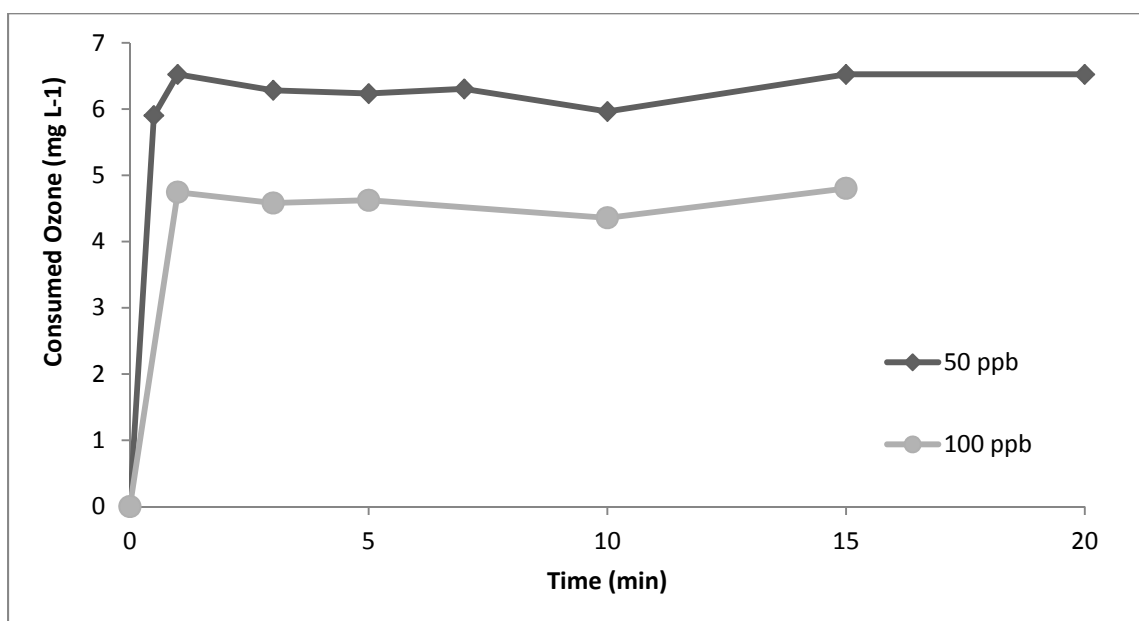


Figure 4.3: Ozone consumption during ozonation of 1,4 dioxane  $[O_3] = 0.12 \text{ mM}$  in ( $0.5 \mu\text{M}$  1,4 dioxane) &  $0.1 \text{ mM}$  ( $0.9 \mu\text{M}$  1,4 dioxane),  $[1,4\text{-dioxane}] = 0.5 \mu\text{M}$  and  $0.9 \mu\text{M}$ , reaction volume = 50 ml in both the experiments.

Ozone consumed during effect of initial 1, 4-dioxane experiments in batch reactor was higher when initial ozone concentration was higher (0.12 mM) and lower when initial ozone concentration was comparatively lower (0.1 mM). Previous Study reported that the initial decomposition rate of ozone depends on the ozone concentration. The first-order rate constant increases by a factor of -1.6 when the O<sub>3</sub> concentration is doubled (Sehested et. al., 1991).

#### **4.1.1.1 Determination of Rate Constant for the reaction of the 1,4-dioxane with ozone in batch reactor**

The kinetic runs were started by adding 25 mL of ozone stock solution to solution containing [1,4-dioxane]= 100 µg L<sup>-1</sup>, yielding a final ozone concentration of 5 mg L<sup>-1</sup> and final [1,4-dioxane]= 50 µg L<sup>-1</sup>. Reaction time for all samples was from 30 sec to 20 minutes. The residual ozone was immediately quenched by adding 1 mL of sodium thiosulfate (0.1M). Preliminary experiments performed under the same conditions showed that ozone decrease is <7% during the sampling period of 5 to 10 min (Figure 4.1). Therefore, it was assumed that the ozone concentration remained constant during the experiments. The samples were extracted by liquid - liquid extraction method and analyzed immediately using GC/MS.

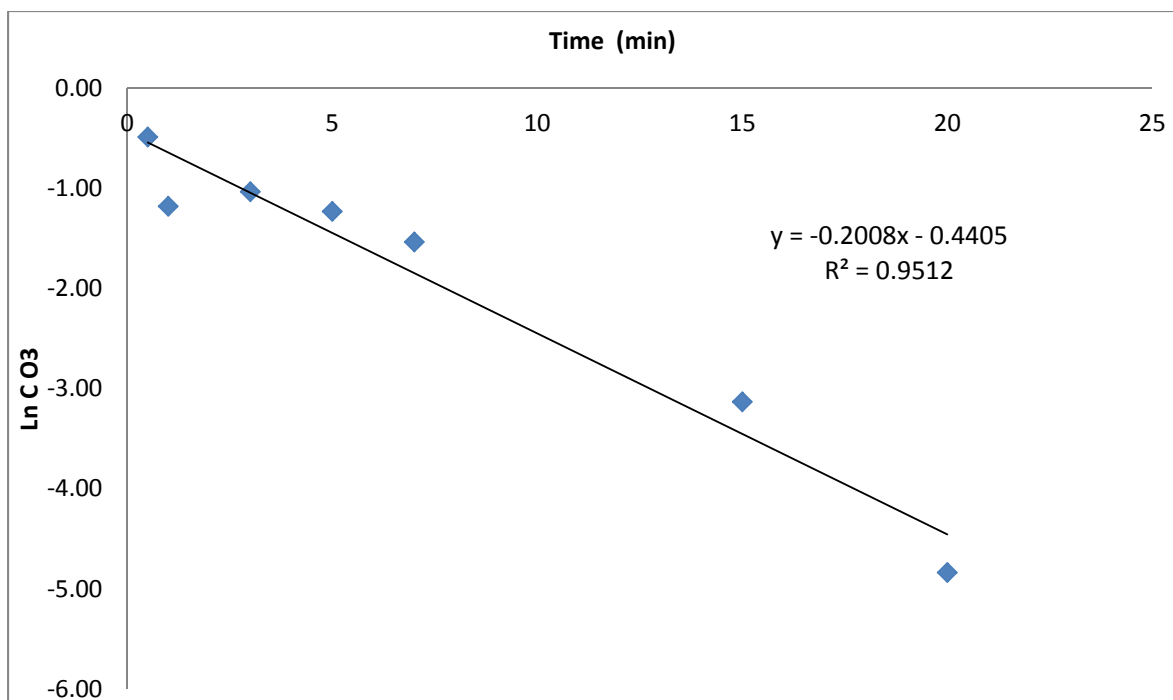


Figure 4.4: Ozonation rate constant  $[O_3]= 5\text{mg L}^{-1}$  ,  $[1,4\text{-dioxane}]= 50\ \mu\text{g L}^{-1}$  , reaction volume = 50 ml

Experimental rate constant ( $k_{exp}$ ) for ozone consumption were evaluated by linear regression of the Ln of the concentration of ozone Vs time. This reflects the first order of reaction and the second order rate constant ( $k_{O_3}$ ) was determined from the added concentration of 1,4-dioxane ( $[M]_0$ ), (Haag et al., 1992, Bader et al., 1983):

$$k_{O_3} = \frac{k_{exp}}{[M]_0} \quad (4.1)$$

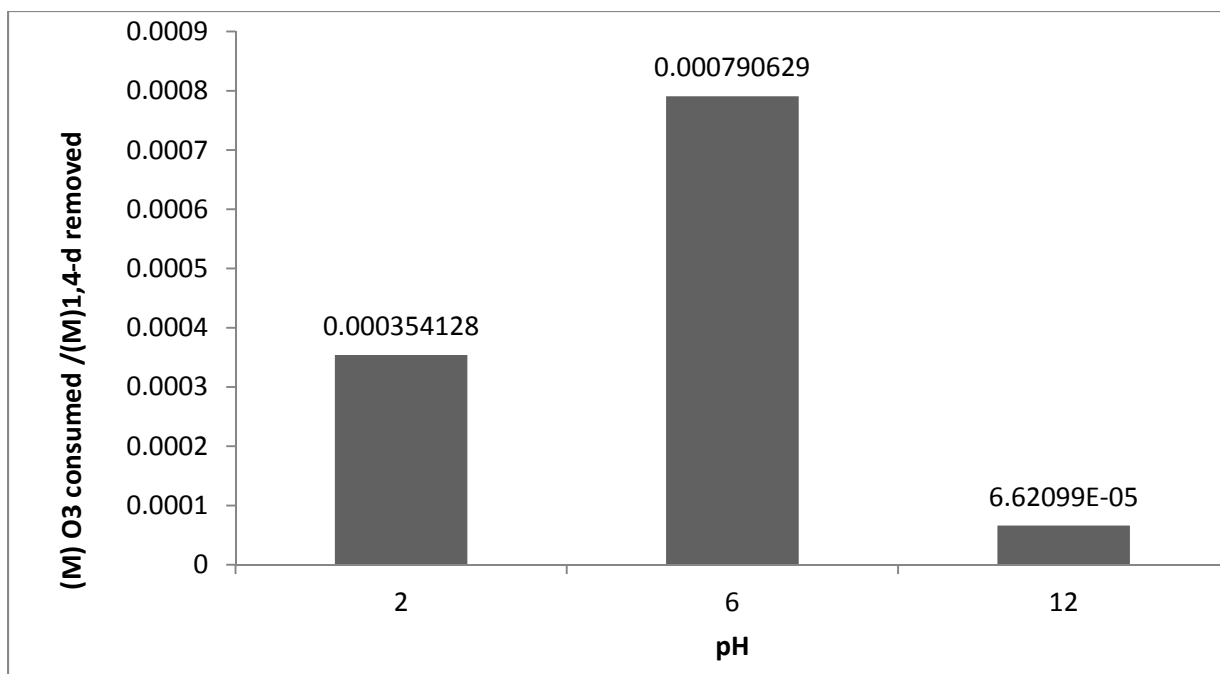
The observed rate constant in this study fall within the ranges expected from previous works ( $k_{O_3} = 0.32\ M^{-1}\ S^{-1}$  by Hoigne and Bader, 1983) which demonstrated that ozone behaves as an electrophilic species (Hoigne and Bader, 1983). The low experimental degradation rate constant for 1,4-dioxane of  $3.54 \times 10^{-1}\ M^{-1}\ S^{-1}$  also shows that 1,4-dioxane has very low reactivity to ozone.

$$k_{O_3} = \frac{k_{exp}}{[M]_0} = \frac{0.2008}{0.56746} = 3.54 \times 10^{-1}\ M^{-1}\ S^{-1} \quad (4.2)$$

Previous studies used hydroxyl radical scavenger t-butanol in (David Yao & Haag, 1991) during ozonation at pH 2 where as no hydroxyl radical scavenger was used in this experiment and all the experiments were performed at neutral pH (No pH adjustment).

#### **4.1.1.2 Effect of pH during ozonation in batch reactor**

The degradation rate of 1,4 dioxane was performed at three different pH values. The initial concentration of 1,4 dioxane and ozone were  $50 \mu\text{g L}^{-1}$  and  $6 \text{ mg L}^{-1}$  respectively. Milli Q water at three different pH values was used to prepare aqueous ozone solutions. This approach resulted in three different concentration of ozone in aqueous solutions. The ozone concentration was constant  $10.5 \text{ mg L}^{-1}$  in neutral pH milli-Q water, and had lower value of  $5.73 \text{ mg L}^{-1}$  at pH 2 and  $1.63 \text{ mg L}^{-1}$  at pH 10. Therefore, due to experimental difficulties, comparison of degradation rate among these three different pH was not possible. However, number of moles of 1,4-dioxane degraded per mole of ozone consumed or decomposed at three different pH were calculated and are presented in Figure 4.5. The rate of 1,4-dioxane degradation increased when pH of the solution was approximately 6 decreased upon increasing the pH value from 6 to 12 or decreasing from 6 to 2 of the reaction solution. The experiment was performed in duplicates.



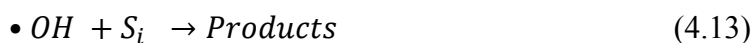
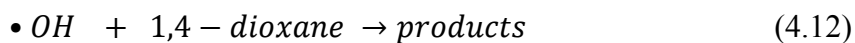
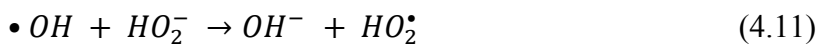
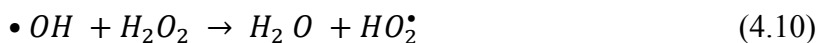
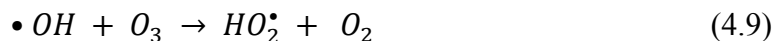
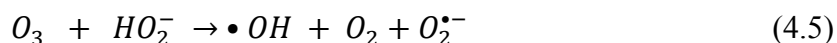
**Figure 4.5: Effect of three different pH on moles of ozone consumed per mole of 1,4-dioxane removed during ozonation pH= 2 , 6 and 12 , [1,4-dioxane]= 50 $\mu$ g L<sup>-1</sup> Reaction time = 5 min, reaction volume = 50 ml**

Previous study reported that ozone decomposition occurs faster in higher pH aqueous solution (Langlais et al.1999). In acidic pH condition the OH radical generation nearly stops, and this appears to have an adverse effect on ozonation. Under this pH condition the direct ozonation reaction dominates, and which involves slow reaction rate with 1,4- dioxane.

Since this experiment was the first attempt (in duplicate analysis), further experiments needs to be done to verify the results (detailed experimental data provided in Table D.6).

### 4.1.2 Peroxone results of batch reactor

The oxidation of 1,4-dioxane with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> involves many reacting species that are formed during the process. However, the principal species reacting with dioxane in O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process are molecular ozone and hydroxyl radicals. Although direct oxidation of dioxane by molecular ozone is not significant ( $k_{O_3} = 0.32 \text{ M}^{-1} \text{ s}^{-1}$ ) (Hoigne and Bader, 1983) as compared to that with hydroxyl radical. The decomposition of ozone, catalyzed by hydroperoxide ( $HO_2^-$ ), generates hydroxyl radicals and contributes to dioxane oxidation (J.Suh et al.2004). According to the basic approaches and mechanism proposed in the literature, the oxidation of 1,4-dioxane can be described by the following simplified reactions (Suh et al.2004).



Where  $S_i$  represents species, e.g. intermediate oxidation products, that compete with 1,4-dioxane for reaction with hydroxyl radical. (Suh et al.2004)

#### 4.1.2.1 Effect of different $\text{H}_2\text{O}_2/\text{O}_3$ molar ratio in batch reactor

These experiments were carried out in two sets by varying the  $\text{H}_2\text{O}_2/\text{O}_3$  molar ratio to achieve the optimum ratio for further experiments. In the first set of experiments three  $\text{H}_2\text{O}_2/\text{O}_3$  molar ratios of 7.0, 11.7 and 23.3 were used. 1, 4- dioxane was readily oxidized at all three  $\text{H}_2\text{O}_2/\text{O}_3$  oxidants ratios upto 86%, 88% and 75% removal respectively was observed at the ozone dosage of 88  $\mu\text{M}$  (4.2mg/L). In the second set of experiment four different  $\text{H}_2\text{O}_2/\text{O}_3$  molar ratios of 1.90, 5.69, 7.59 and 9.49 (less than 11.7) were used. 1, 4- dioxane was readily oxidized at all three  $\text{H}_2\text{O}_2/\text{O}_3$  oxidants ratios up to 92%, 98% and 99% removal respectively was observed at the ozone dosage of 108  $\mu\text{M}$  (5.2mg/L). Maximum  $\mu\text{M}$  1,4-dioxane removed per  $\mu\text{M}$  of ozone observed at 12  $\mu\text{M}$   $\text{H}_2\text{O}_2/\text{O}_3$  molar ratio. At  $\text{H}_2\text{O}_2/\text{O}_3$  ratios of greater than about 12  $\mu\text{M}$ ,  $\text{H}_2\text{O}_2$  brings negative impacts and reduces the amount of 1,4-dioxane removed.  $\text{H}_2\text{O}_2$  may functions as scavenger for hydroxyl radicals and could act as inhibitor when used at high concentrations. The results suggest that the impact of hydrogen peroxide in an  $\text{O}_3/\text{H}_2\text{O}_2$  process is not straightforward and needs to optimize it according to reaction conditions (Detailed result is presented in Table 4.2).

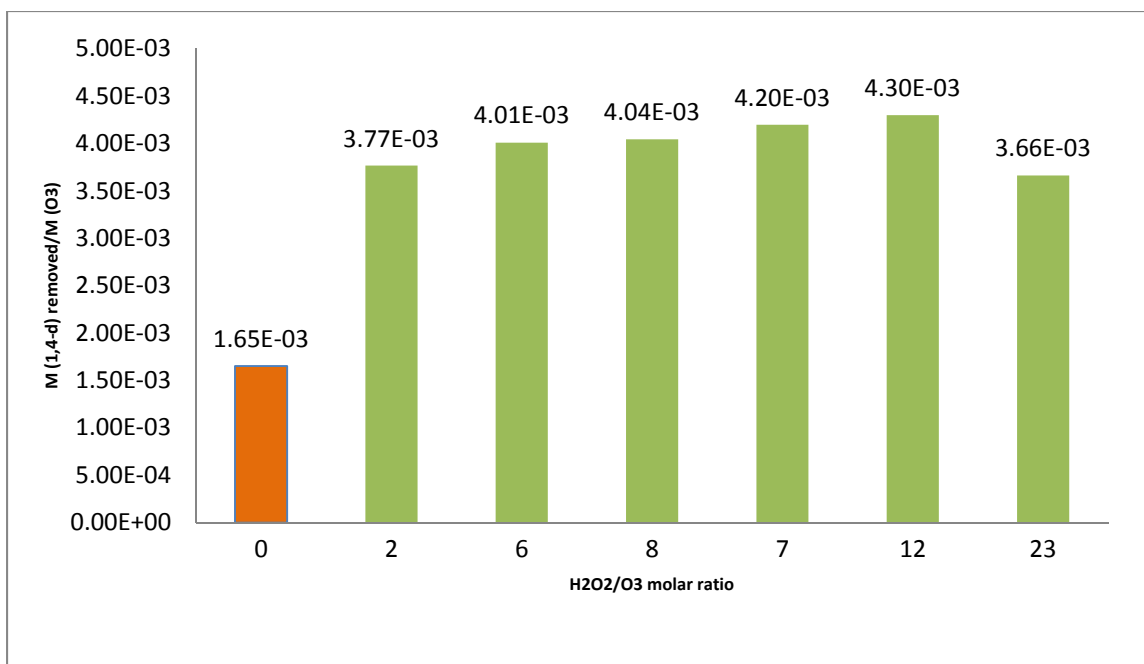


Figure 4.6: 1, 4-dioxane removal at various H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratios during peroxone process [O<sub>3</sub>] = 5 mg L<sup>-1</sup>, [pH] = 5, [1,4-dioxane] = 50 μg L<sup>-1</sup>

Table 4.2: Effect of % 1,4-dioxane removal during peroxone at various H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> ratio

Applied O <sub>3</sub> μM	Applied H <sub>2</sub> O <sub>2</sub> μM	H <sub>2</sub> O <sub>2</sub> /O <sub>3</sub> molar ratio (μM)	In 1,4 dioxane μM	1,4 dioxane removed μM	M 1,4-dioxane removed/M O <sub>3</sub> consumed
<b>Set 1</b>					
88	617	7	0.43	0.37	4.E-03
88	1029	12	0.43	0.38	4.E-03
88	2058	23	0.43	0.32	4.E-03
<b>Set 2</b>					
108	206	2	0.44	0.41	4.E-03
108	617	6	0.44	0.43	4.E-03
108	823	8	0.44	0.44	4.E-03
108	0	0	0.44	0.18	2.E-03

#### 4.1.2.2 Competition kinetics of 1,4-dioxane in batch reactor

It is hard to measure the reaction rate constant with hydroxyl radical by direct methods, therefore competition kinetic approach was used. All kinetic experiments were performed in the presence of *para*-chloro benzoic acid (*p*-CBA) as competitor reference compound. *p*-CBA was chosen as a model organic acid and as a probe compound for hydroxyl radical measurements due to its high reactivity with OH radicals, but very low reactivity with other oxidants (i.e.,  $k_{OH,pCBA} = 5 \times 10^9 \text{ M}^{-1}, \text{ s}^{-1}$ ,  $k_{O_3, pCBA} \leq 0.5 \text{ M}^{-1}\text{S}^{-1}$ , (von Gunten, Driedger, Gallard, & Salhi, 2001).

Under the optimized conditions the kinetic experiments were performed with 1 mg L<sup>-1</sup> of *p*-CBA (competitor compound) as that concentration produced highest percent of 1,4-dioxane oxidation (44%) as well as highest % of *p*-CBA oxidation (77%).

Figure 4.7 shows the experimental rates of dioxane removal as a function of concentration of *p*-CBA. The reaction rates were determined from the amount of dioxane removed in the first minute of the experiment and at various *p*-CBA initial concentrations (between 1 and 2.5 mgL<sup>-1</sup>). The observed rate constant of 1,4-dioxane were evaluated by plotting the equation 4.12 (Haag et al., 1992, Elovitz et al. 2000):

$$k_{OH}^{1,4-d} = \frac{\ln\left(\frac{C_0^{1,4-d}}{C_\infty^{1,4-d}}\right)}{\ln\left(\frac{C_0^{pCBA}}{C_\infty^{pCBA}}\right)} \times k_{OH}^{pCBA} \quad (4.14)$$

$C_0^{1,4-d}$  = Initial concentration of 1,4-dioxane

$C_{\infty}^{1,4-d}$  = Final concentration of 1,4-dioxane

$C_0^{pCBA}$  = Initial concentration of *p*-CBA

$C_{\infty}^{pCBA}$  = Final concentration of *p*-CBA

$k_{OH}^{pCBA}$  = Rate constant of *p*-CBA

The value of  $k_{OH}^{pCBA}$  for *p*-CBA was calculated as ( $5 \times 10^9 M^{-1} s^{-1}$ ) (Park et al. 2004).

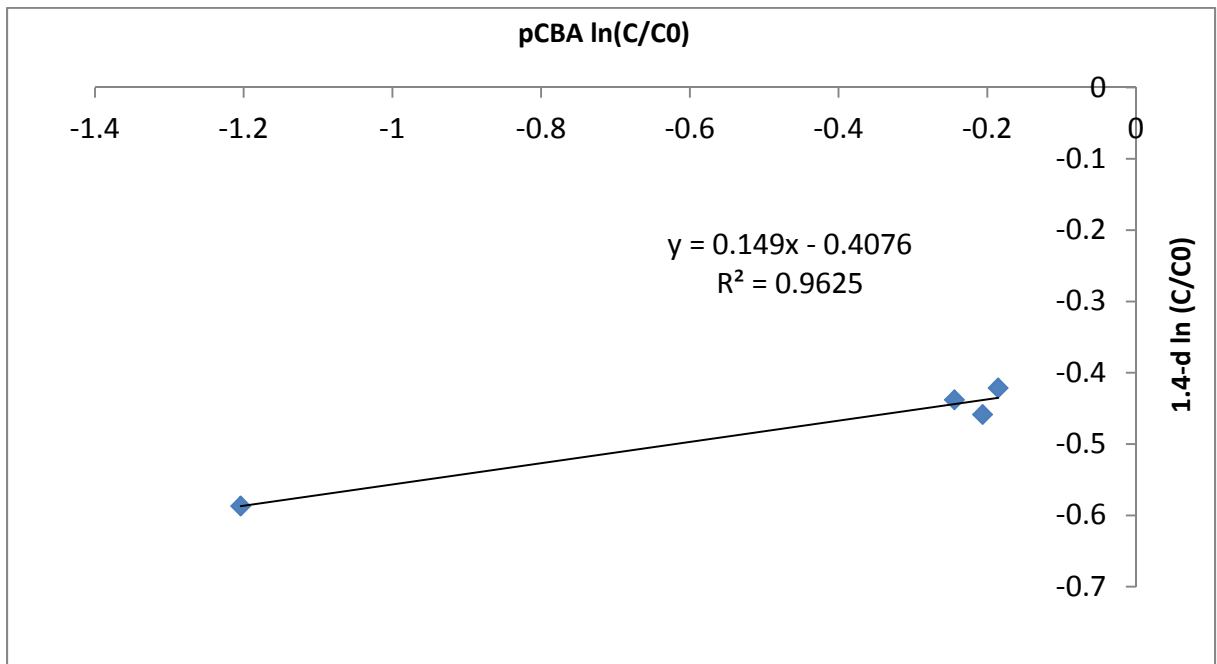


Figure 4.7: The rate of 1,4 dioxane oxidation in the presence of competitor compound *p*-CBA in batch reactor

$$k_{OH}^{1,4-d} = \text{slope} \times k_{OH}^{pCBA} \quad (4.15)$$

$$k_{OH}^{pCBA} = 5 \times 10^9 M^{-1} s^{-1} \quad (\text{Park et al. 2004})$$

$$= 0.149 \times k_{OH}^{pCBA} = 0.149 \times 5 \times 10^9 = 7.45 \times 10^8 M^{-1} s^{-1} \quad (4.16)$$

**Table 4.3: Reaction rate constants of 1,4-dioxane reported in literature**

<b>Oxidizer</b>	<b>Reaction Rate Constant (<i>k</i>)</b>	<b>Reference</b>
Hydroxyl radical	$2.25 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Ghosh et al. 2010
Hydroxyl radical	$1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Anbar et al., 1966
Hydroxyl radical	$2.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Thomas et al., 1966
Hydroxyl radical	$4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Anbar and Neta, 1965
Hydroxyl radical	$(1.1 \times 10^9) - (2.4 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$	Adams et al. 1994
Ozone	$0.32 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 2	Hoigne and Bader, 1983

The reaction rate constant of 1,4-dioxane determined in this study was  $1.57 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , which falls within the ranges reported in previous reports.

## **4.2 Oxidation of estrogen hormones during ozonation processes in batch reactor setup**

Ozonation of 10 estrogen hormones was performed to examine the impact of different ozone concentration at different reaction time on removal efficiency of estrogen hormones at low ozone dosage.

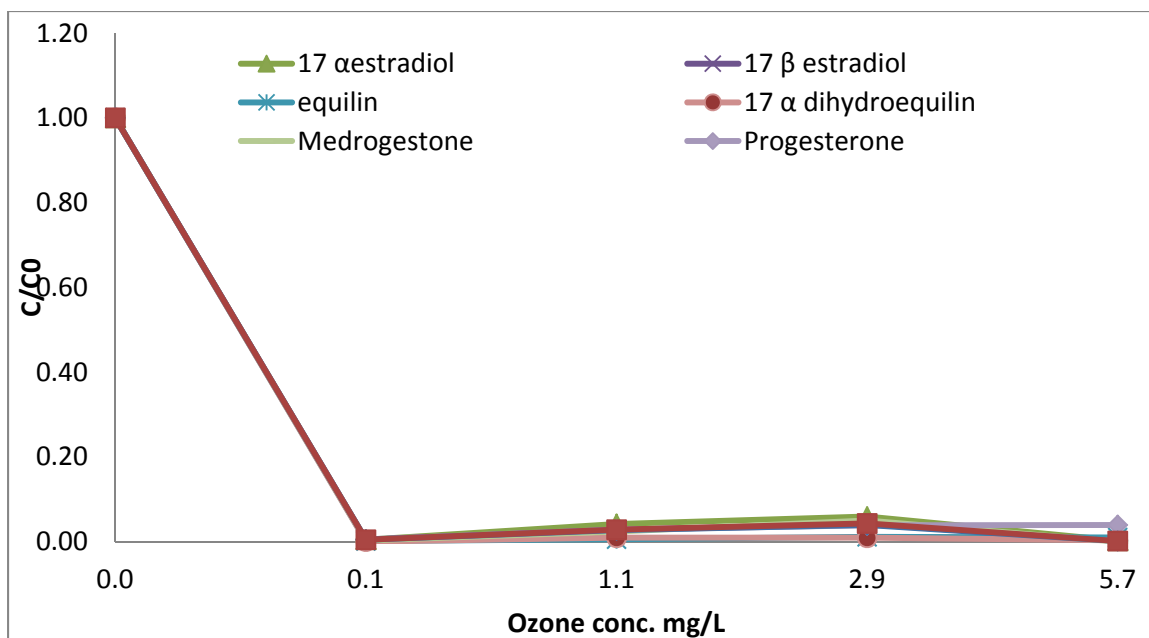


Figure 4.8: Effect of different ozone concentration on removal of estrogens hormones during ozonation process in batch reactor. [Estrogens]=100 µg L<sup>-1</sup>, Reaction time =5 min

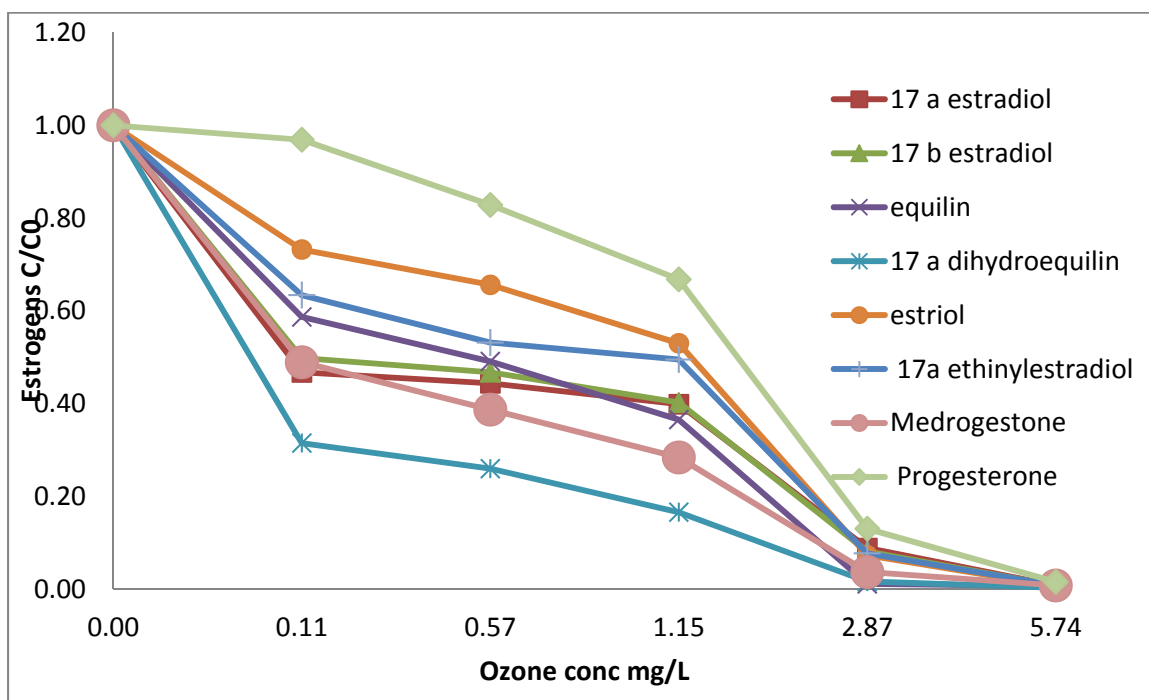


Figure 4.9: Effect of different ozone concentration on removal of estrogens hormones during ozonation process in batch reactor. [Estrogens]=1mg L<sup>-1</sup>, Reaction time =1 min

Estrogen hormones were well removed by ozonation only. Ozonation process was very effective with estrogen the with removal efficiencies up to 99% with in one minute of reaction time. The reaction is extremely fast with half life of few second. The more detailed study of estrogen hormones removal with ozone was accomplished for higher initial concentrations (e.g. 1 mg/L) which slowed down the reaction.

### **4.3 Oxidation of 1,4-dioxane during ozonation and peroxone processes in semi batch reactor**

#### **4.3.1 Effect of initial 1, 4-dioxane concentration on ozonation process**

Ozonation process was tested on 1, 4-dioxane at two different initial contaminant concentrations ( $100\mu\text{g L}^{-1}$  and  $1000\mu\text{g L}^{-1}$ ) in the Milli-Q water (detailed experimental data provided in Table-E.1 and E.2). With the increase in the concentration of 1, 4-dioxane ( $100\mu\text{g L}^{-1}$  to  $1000\mu\text{g L}^{-1}$ ), the percentage removals decreased. At an ozone dosage  $24\text{ mgL}^{-1}$  55% removal of 1, 4-dioxane in 15 minute of reaction time was observed in  $100\mu\text{g L}^{-1}$  solutions. Under similar conditions, only 10% removal was observed at initial 1, 4-dioxane concentration of  $1000\mu\text{g L}^{-1}$  (Figure 4.10). In this case concentration of 1,4-dioxane might be in excess and not enough ozone was present to degrade the compound at higher concentration reaction.

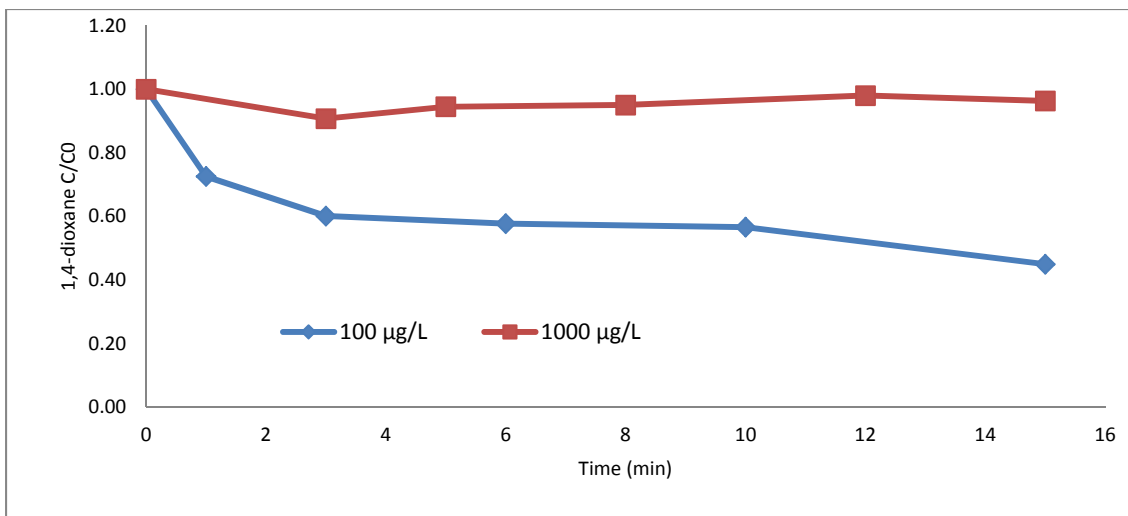
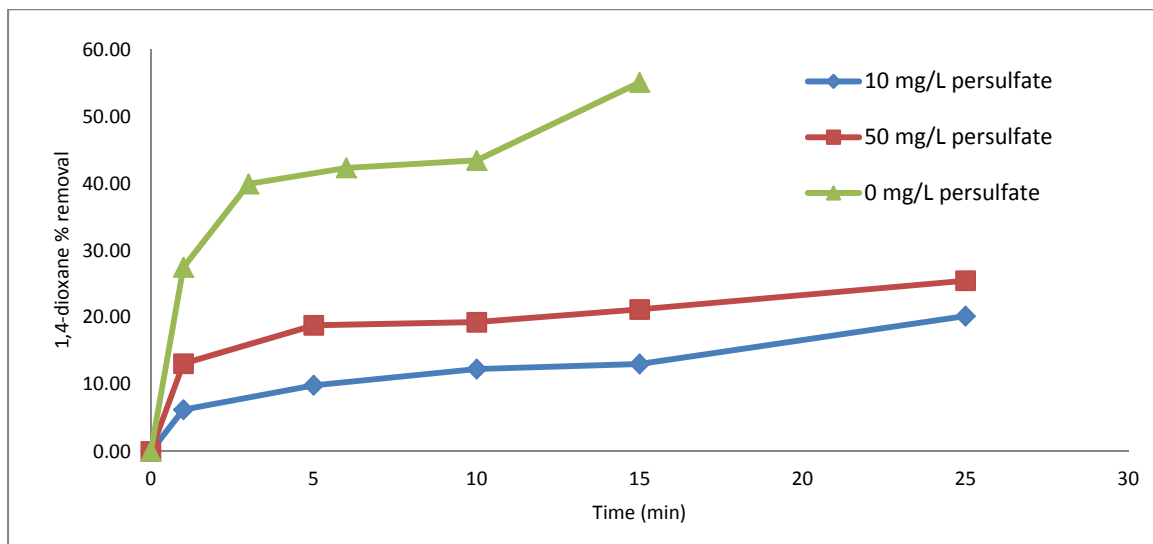


Figure 4.10: Degradation profiles of 1, 4-dioxane in Milli-Q water at two different: initial concentrations in semi batch reactor [1,4-dioxane]= 100µg L<sup>-1</sup> and 1000µg L<sup>-1</sup>, Ozone: 5wt%

### 4.3.2 Effect of persulfate on ozonation process for removal of 1, 4-dioxane

Ozone/persulfate process was tested for the removal of 1, 4-dioxane from aqueous solutions. Degradation of 1, 4-dioxane versus contact time of ozonation at two different concentration of persulfate is shown in Figure 4.11. Tests were conducted for 25 minutes and the ozone dosages increased from 1.5 to 23 mg/L. At persulfate concentration of 10 mg/L and ozone dosage of 10.5 mg/L, only 13% removal of 1, 4-dioxane was observed at 15 min of reaction time and did not show significant increase with the increase in ozone dosage and contact time. At similar conditions, ozonation alone was able to remove 55% of 1, 4-dioxane from aqueous solutions (Figure 4.11). No significant difference in the percentage removal of 1, 4-dioxane was observed with the increase of the concentration of persulfate 15mg/L during ozonation. Previous studies stated that sulfate ions do not react with ozone in acidic solution and in alkaline pH sulfate radical are formed which

has 2.01V oxidation potential which is lower than  $\text{OH}\cdot$  -2.8V and lower than ozone-2.08V.



**Figure 4.11: Degradation profiles of 1,4-dioxane in Milli-Q water during different ozone/persulfate processes in semi batch reactor, [1,4-dioxane]=  $100\mu\text{g L}^{-1}$ , Ozone: 5wt%**

### 4.3.3 Effect of salinity on ozonation process for removal of 1, 4-dioxane

Ozonation process was tested with 1, 4-dioxane at two different concentration of NaCl (50 mM and 75mM). Oxidation of 1, 4-dioxane versus ozonation contact time at the two NaCl concentrations is shown in Figure 4.12. At an ozone dosage of 10mg/L, 14% and 22% removal of 1, 4-dioxane was observed with concentration 50mM and 75 mM of NaCl respectively. With the increase of the salinity of the solution during ozonation significant difference in the percentage removal of 1, 4-dioxane was observed. From the results it may be inferred that, oxidation of 1, 4-dioxane reduced from 55% to 14% and 22% with the presence of salinity. According to reported studies (Muthukumar et al. 2004) Sodium chloride deplete ozone through consumption of  $\text{OH}\cdot$  as well as by direct consumption of dissolved ozone.

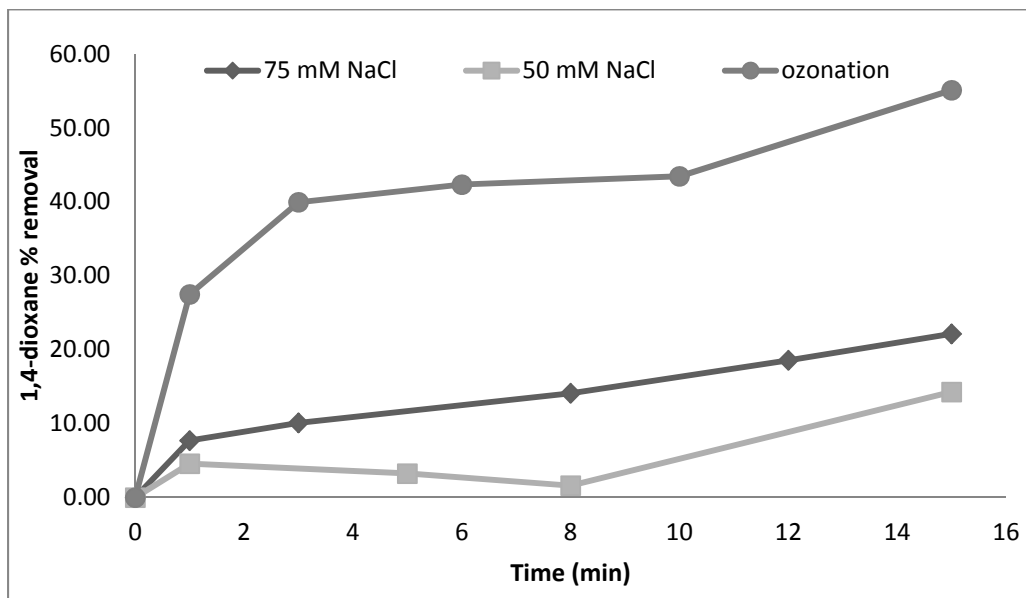


Figure 4.12: Investigation of effect of salinity on the degradation profile of 1,4-dioxane in Milli-Q water with respect to different contact time during ozonation in semi batch reactor ; [1,4-dioxane]=100 $\mu$ g/L, Ozone = 5wt%.

#### 4.4 Oxidation of DEET and pharmaceuticals during ozonation and peroxone processes in semi batch reactor setup

The study of DEET and pharmaceuticals was performed into two different experimental conditions:

- (1) A multiple component mixture of all the pharmaceuticals and DEET
- (2) As a single component of DEET during both the processes.

##### 4.4.1 Removal of DEET and pharmaceuticals in multicomponent system

These experiments were performed in tap water for both ozonation and peroxone processes. The initial concentration of pharmaceuticals and DEET were 100  $\mu$ g L<sup>-1</sup> for all the experiments. Samples were prepared by spiking the stock solution in tap water. For

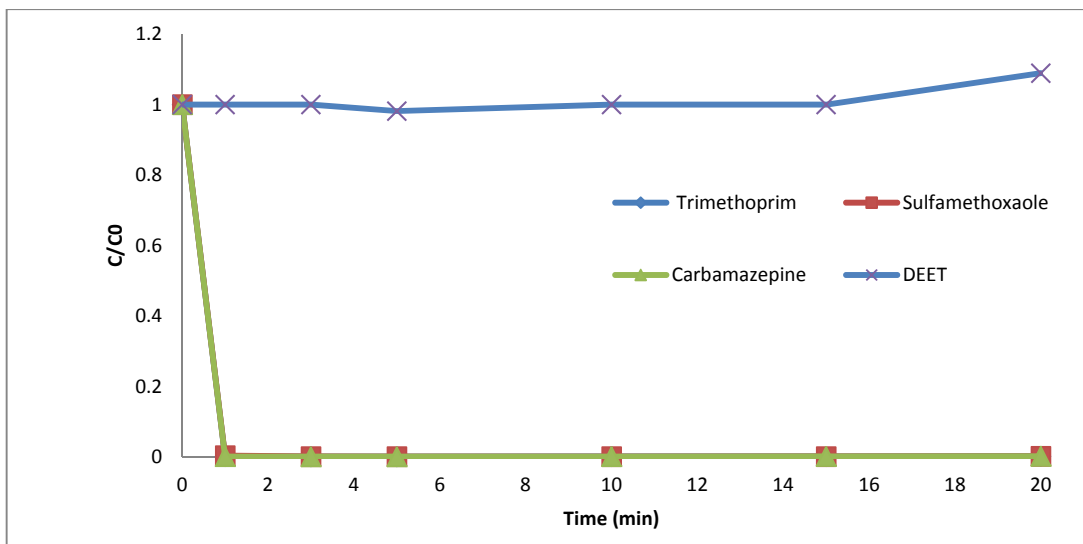
the peroxone processes 5 mg L<sup>-1</sup> and 10 mg L<sup>-1</sup> of hydrogen peroxide were added to the prepared sample before charging into the reactor.

Three experimental conditions were used: (1) ozonation (no hydrogen peroxide added);(2) peroxone with 5 mg<sup>-1</sup>L hydrogen peroxide; and (3) peroxone with 10 mg<sup>-1</sup>L hydrogen peroxide. Trimethoprim, sulfamethoxazole and carbamazepine were oxidized more than 99 % within the first minute during ozonation at applied ozone doses of 2.19mg/L, 2.30mg/L and 2.49 mg/ L.(Figure 4.13.4.14 and 4.15).

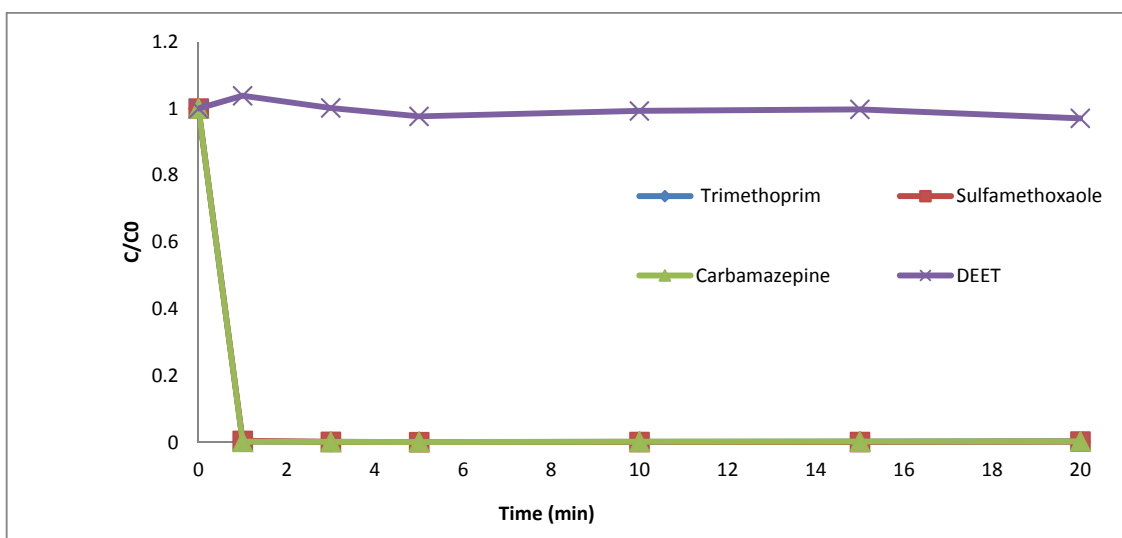
However, DEET showed negligible removal during ozonation and peroxone [5 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>] processes in 20 minute of contact time (Figure 4.13.4.14 and 4.15). The addition of hydrogen peroxide generally resulted in insignificant increase in the removal of DEET. Only 17% removal efficiency was observed in 15 minute of contact time, when higher concentration of hydrogen peroxide (10 mg L<sup>-1</sup>) was used (Figure 4.16). The results are summarized in Table 4.4(detailed experimental data provided in Table F.2 and F.3).

**Table 4. 4:Details of experimental conditions during ozonation and peroxone processes for oxidation of pharmaceuticals (sulphamethaxazole, trimethoprim and carbamezapine) and DEET in multicomponent scheme.**

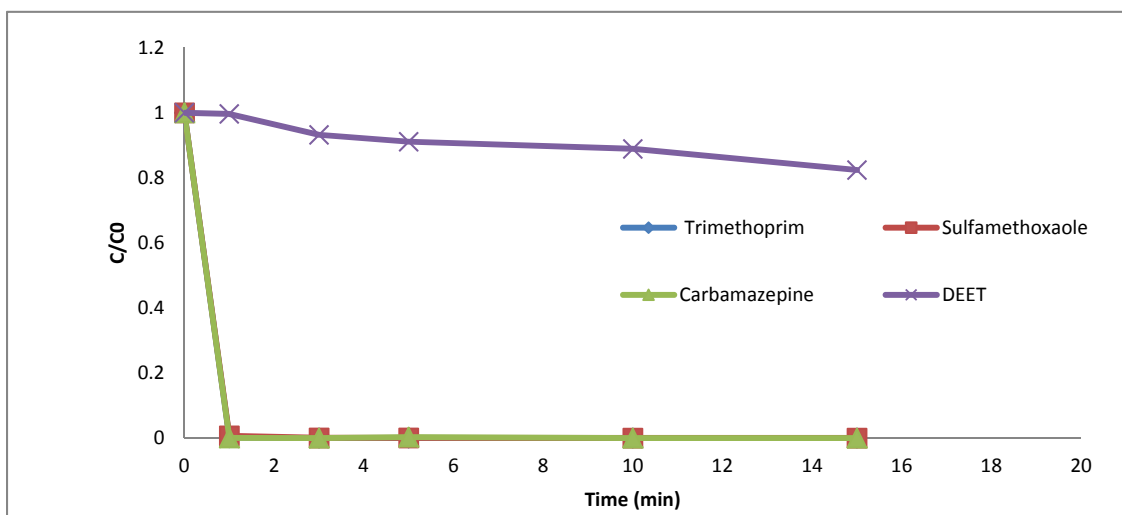
Compounds	Initial concentration (µg L <sup>-1</sup> )	Matrix	H <sub>2</sub> O <sub>2</sub> (mg L <sup>-1</sup> )	Consumed O <sub>3</sub> dosage (mg L <sup>-1</sup> )	Contact time (min)	Removal Efficiency (%)
Pharmaceuticals (multi component)	100	Tap water	0	2.09	20	> 99
Pharmaceuticals (multi component)	100	Tap water	5	2.30	20	> 99
Pharmaceuticals (multi component)	100	Tap water	5	2.49	15	> 99
Pharmaceuticals (multi component)	100	Tap water	10	2.39	15	> 99



**Figure 4.13: Removal efficiency of pharmaceuticals & DEET during ozonation in semi batch reactor [pharmaceuticals]= 100µg L<sup>-1</sup>, [DEET]= 100µg L<sup>-1</sup>, ozone = 5%**



**Figure 4.14: Removal efficiency of pharmaceuticals & DEET during peroxone process using 5 mg/L hydrogen peroxide ozonation in semi batch reactor [pharmaceuticals]= 100µg L<sup>-1</sup>, [DEET]= 100µg L<sup>-1</sup>, ozone = 5%**



**Figure 4.15: Removal efficiency of pharmaceuticals & DEET during peroxone process using 10 mg/L hydrogen peroxide in semi batch reactor. [pharmaceuticals] = 100 µg L<sup>-1</sup>, [DEET] = 100 µg L<sup>-1</sup>, ozone = 5%**

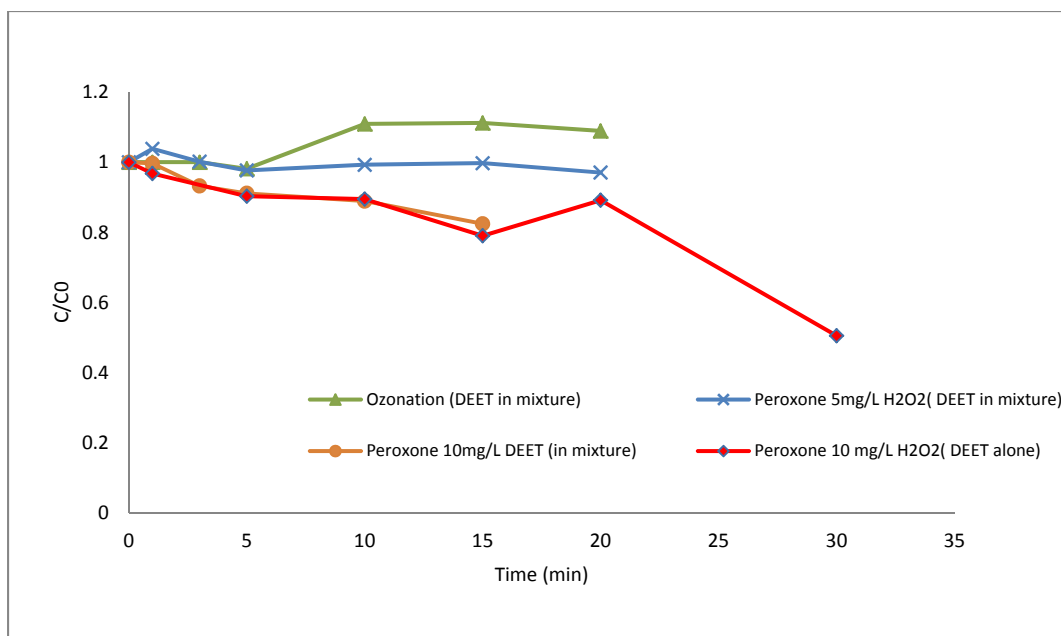
#### 4.4.2 Removal of DEET in single component system

Since DEET showed negligible removal efficiency in the multi component scheme in both processes, another set of experiments was performed using single component of DEET. These were done to investigate if negligible and low removal of DEET was due to any competition occurring among the compounds for ozone and hydroxyl radicals. For this experiment Milli-Q water was used to avoid any matrix interference. There was no significant increase in the removal of DEET was observed in single component system during ozonation. Increasing the dosage of hydrogen peroxide (10 mg/L) did not show any significant increase in the removal of DEET (18%). However as shown in Fig 4.16, the concentration of DEET slowly decreased up to 49% with the increase of reaction time (30 min) during peroxone process.

**Table 4.5: Details of experimental conditions during ozonation and peroxone processes for oxidation of DEET in multicomponent and single component scheme.**

	Initial conc. ( $\mu\text{g L}^{-1}$ )	Matrix	H <sub>2</sub> O <sub>2</sub> dosage ( $\text{mg L}^{-1}$ )	Consumed O <sub>3</sub> dosage ( $\text{mg L}^{-1}$ )	Contact time (min)	Removal Efficiency (%)
DEET	100	Milli-Q water	10	77	30	49
DEET (multi component)	100	Tap water	0	43	20	0
DEET (multi component)	100	Tap water	5	46	20	3
DEET (multi component)	100	Tap water	10	47	15	17

There is no difference observed in the removal efficiency of DEET in single component system and in multicomponent system, with 10 mg L<sup>-1</sup> of hydrogen peroxide for 15 minute of reaction time. (Detailed information is provided in table F.4,5 and 6). DEET was not very reactive with ozone and peroxone. Previous study reported 42% removal of DEET (100 mM initial concentration) in 400 min at 5 mg/min ozone dosage (Masten et al. 2001 and 2003).

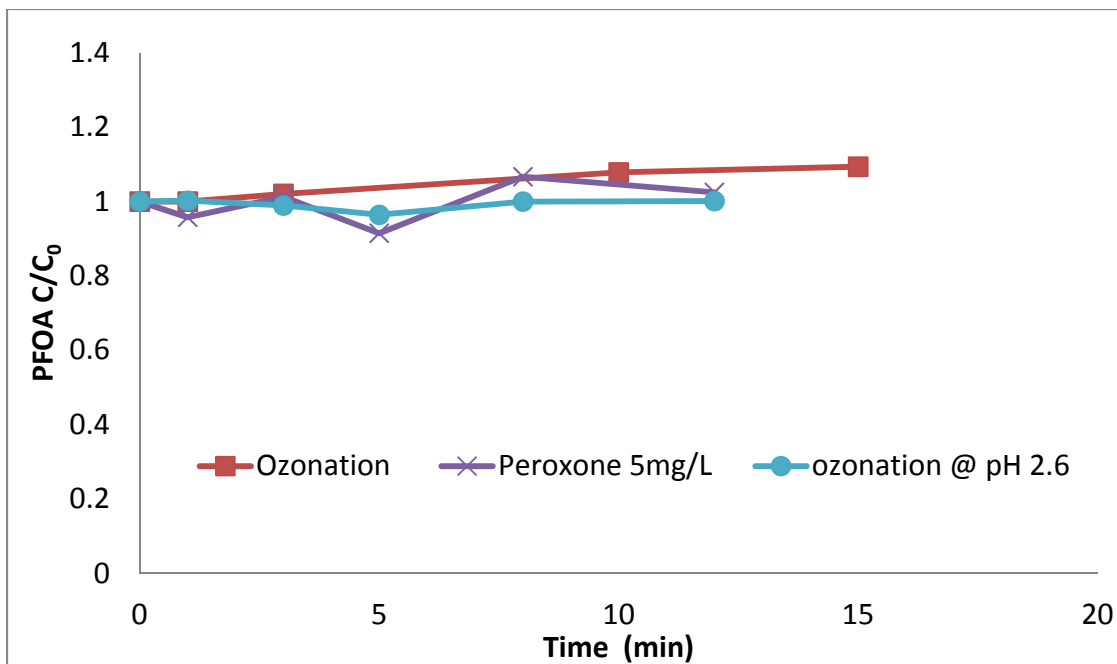


**Figure 4.16: Comparison of removal efficiency of DEET as multicomponent during ozonation & peroxone processes in semi batch reactor. [Pharmaceuticals]=  $100\mu\text{g L}^{-1}$ , [DEET]=  $100\mu\text{g L}^{-1}$ , ozone = 5%**

## 4.5 Oxidation of PFCs during ozonation and peroxone processes in semi batch reactor setup

### 4.5.1 Removal of PFOA in single component system

Ozonation of PFOA under different reaction conditions: (1) ozonation, (2) peroxone and (3) ozonation at high acidic condition (at 2.67 pH), showed negligible degradation of the compound. Ozone consumption/decomposition increased with the increase of reaction time. Summarized data of the initial concentration of ozone generated and concentration of ozone consumed are shown in Table G.1. PFOA removed under different reaction conditions is shown in Figure 4.17.



**Figure 4.17: Removal efficiency profile of PFOA in single component system under different reaction conditions. [PFOA]=25 $\mu$ g L<sup>-1</sup>, [O<sub>3</sub>]=18mg L<sup>-1</sup>**

#### 4.5.2 Removal of PFCs in multicomponent system

Similar experimental system was used to conduct semi batch ozonation experiment with a mixture of 10 PFCs: Perfluoro octanoic acid (PFOA) , Undecafluorohexanoic acid, Perfluoroheptanoic acid, Tridecafluorohexane-1-salt, Heptafluorooctane salt, Perfluorodecanoic acid, Perfluoroundecanoic acid, Perfluorododecanoic acid, Perfluorotridecanoic acid, Tridecafluorononanoic acid, Heptafluorooctane salt. The ozonation processes was ineffective in removing most of the PFCs. However, among 10 PFCs tridecafluorononanoic acid, perfluoroundecanoic acid, perfluorotridecanoic acid and perfluorododecanoic acid showed some removal during peroxone process as shown in Figure 4.18 and 4.19.

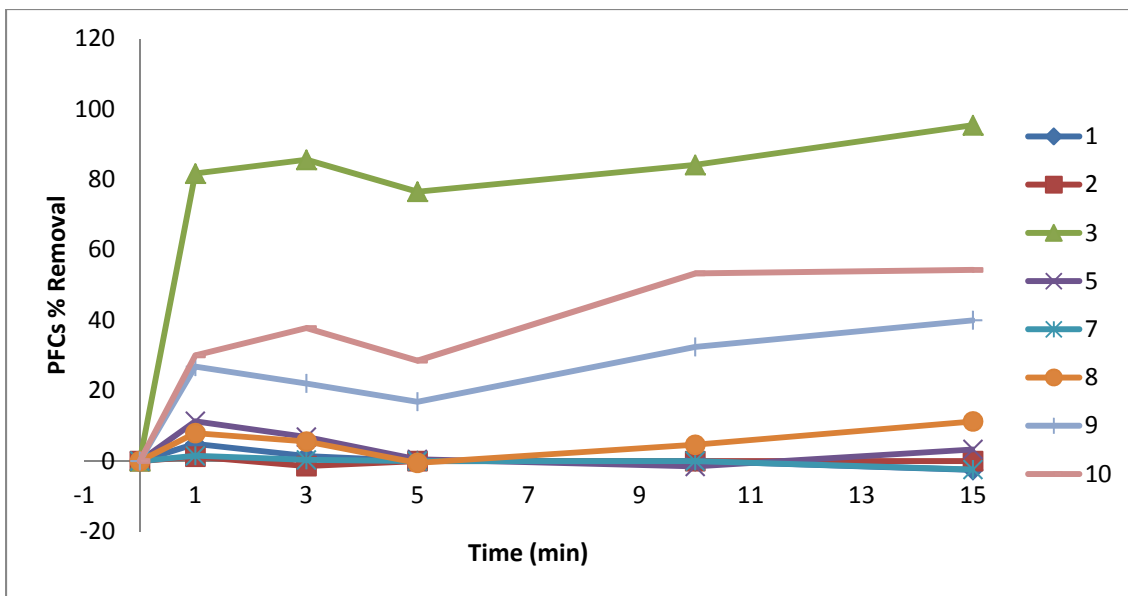


Figure 4.18: Removal efficiency profile of PFCs in multi component system in semi batch reactor;  $[PFCs]_0=25\mu\text{g L}^{-1}$ ,  $[O_3]=30.5\text{mg L}^{-1}$ . 1.Undecafluorohexanoic acid 2.Perfluoroheptanoic acid, 3.Trifluorononoic acid 4.Tridecafluorohexane-1-salt, 5.Perfluoro octanoic acid (PFOA), 7.Heptafluorooctane salt, 8.Perfluorodecanoic acid, 9.Perfluoroundecanoic acid, 10.Perfluorododecanoic acid, 9. Perfluorotridecanoic acid

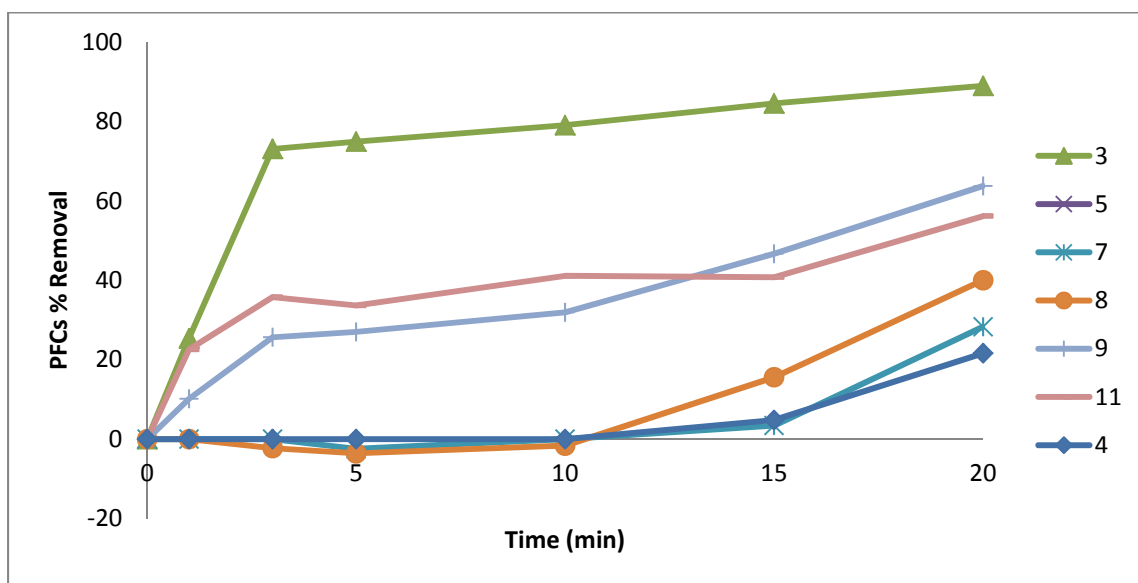


Figure 4.19: Removal efficiency profile of PFCs in multi component system in semi batch reactor;  $[PFCs]_0=25\mu\text{g L}^{-1}$ ,  $[O_3]_0=25\text{mg L}^{-1}$ . 1.Undecafluorohexanoic acid 2.Perfluoroheptanoic acid, 3.Trifluorononoic acid 4.Tridecafluorohexane-1-salt, 5.Perfluoro octanoic acid (PFOA), 7.Heptafluorooctane salt, 8.Perfluorodecanoic acid, 9.Perfluoroundecanoic acid, 10.Perfluorododecanoic acid, 9. Perfluorotridecanoic acid

The reason for the low removal of these PFCs may be attributed to the properties of these compounds, which contain one of the strongest chemical bonds (C-F) and their longest-chained structure. Other factors may also play important roles such as size and presence of functional groups. It may be concluded that either of the processes (ozonation or peroxone) is not an effective technique for PFOA and PFCs removal for the conditions of this study. More research needs to be performed to verify the results of the three PFCs that showed degradation during ozonation.

## CHAPTER 5

### CONCLUSION

#### 5.1 1,4-Dioxane degradation studies

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> based advanced oxidation process is a promising technology for the removal of 1,4-dioxane. The results of the experiments suggest that ozonation alone is not an effective treatment process for 1,4-dioxane, as only 40 % removal in batch reactor setup and 55% removal in semi batch reactor setup were achieved in 15 min of reaction time. Retention time exceeding 15 minutes would make the ozone process impractical due to the high consumption of ozone. Peroxone, on the other hand, is an effective technology for the removal of 1, 4-dioxane as it removed more than 90% within 10 minutes, at the H<sub>2</sub>O<sub>2</sub> / O<sub>3</sub> ratio of 12 in batch reactor setup. The experimental degradation rate constant of 1, 4-dioxane  $5.80 \times 10^{-2} M^{-1}S^{-1}$  was observed, which is one order of magnitude lower than previous study  $k_{O_3} = 0.32 M^{-1} S^{-1}$  by Hoigne and Bader(1983). The reaction rate constant of 1,4-dioxane with hydrogen peroxide determined in the current research was  $7.45 \times 10^8 M^{-1} s^{-1}$ , which is consistent with previously reported results.

Addition of sodium per sulfate during ozonation impacted the removal of 1,4-dioxane from aqueous solution. The removal of 1, 4-dioxane in ozone/peroxide process is primarily through the reaction with hydroxyl radicals though the principal species reacting are molecular ozone and hydroxyl radicals during peroxone process.

Furthermore, the ozonation processes were tested in presence of salinity in semi batch reactor setup. Significant decrease from 55% (during ozonation) to 14% and 22%

in 1,4-dioxane removal was observed with the addition of 50 mM and 75 mM NaCl, respectively in clean water. It is concluded that environmental saline conditions can cause adverse effects to the ozonation system as sodium chloride deplete ozone through consumption of OH• as well as by direct consumption of dissolved ozone.

Increase in the initial concentration of 1,4-dioxane showed significant decrease in removal efficiency from 55% in  $100\mu\text{g L}^{-1}$  to 9% in  $1000\mu\text{g L}^{-1}$  during ozonation. This may be due to low ozone concentration in the system.

## **5.2 Pharmaceuticals and DEET degradation studies**

Ozonation process was very effective for the removal of pharmaceuticals in aqueous solutions. All the three compounds: Trimethoprim, sulfamethoxazole and carbamazepine were removed more than 99 % within the first minute during ozonation at applied ozone doses of 2.19mg/L, 2.30mg/L and 2.49 mg/ L.

DEET showed negligible removal efficiency in the multi component as well as in single component system during ozonation. Only up to 49% of removal was observed during peroxone process after 30 min of peroxone process ( $77\text{ mg L}^{-1}$  ozone dosage). The result of this study is consistent with that obtained in previous studies (Masten et al., 2001) in which DEET was found to be slowly reactive with ozone. The concentration of DEET slowly but continuously decreased to 42% of the original concentration after 400 min (6.5 hours) of ozonation. Despite DEET's apparent low reactivity with ozone, during ozonation, the concentration of ozone at the outlet of the system remained nearly zero. That shows there was not enough ozone. This may be

concluded that DEET can be removed by higher concentration of ozone and for longer period of reaction time.

### **5.3 Degradation of PFCs**

The results of the experiments suggest that ozonation and peroxone under different reaction conditions in semi batch reactor do not provide sufficient removal of PFOA. It is concluded that PFOA is recalcitrant to ozone and peroxone degradation. Out of ten PFCs compounds examined in system, tridecafluorononanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid, showed significant removal. However, more research is needed.

## **CHAPTER 6**

### **RECOMMENDATIONS**

Based on the experimental investigations conducted for the removal of 1,4-dioxane, pharmaceuticals, DEET and PFCs, using ozone/H<sub>2</sub>O<sub>2</sub> advanced oxidation process, following recommendations are proposed:

- Study the effect of process parameters including salinity, alkalinity, initial concentration, solution pH, and natural organic matter, for the removal of pharmaceuticals using ozonation.
- Study the removal of pharmaceuticals during ozonation in batch reactor setup to find out minimal ozone concentration required
- Study the rate constant of pharmaceuticals using batch reactor approach since the reaction observed was very fast
- Study the effect of peroxone with higher H<sub>2</sub>O<sub>2</sub>/ozone ratio for the removal of Tridecafluorononanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid
- Study the effect of tap water, ground water, and wastewater matrices on the removal of 1,4-dioxane, pharmaceuticals during ozonation and peroxone processes
- Perform pilot testing and cost analysis for the removal for all the contaminants
- Examine by-product formation for all the contaminants

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**APPENDIX A**  
**ADDITIONAL**  
**INFORMATION ON EXPERIMENTAL SETUP**



**Figure A.1: Semi batch ozone reactor setup**

## APPENDIX A CONTINUES



Figure A.2: ozone generator (OZAT CFS-1 2G)

## APPENDIX B

### ADDITIONAL INFORMATION ON GAS FLOW RATES

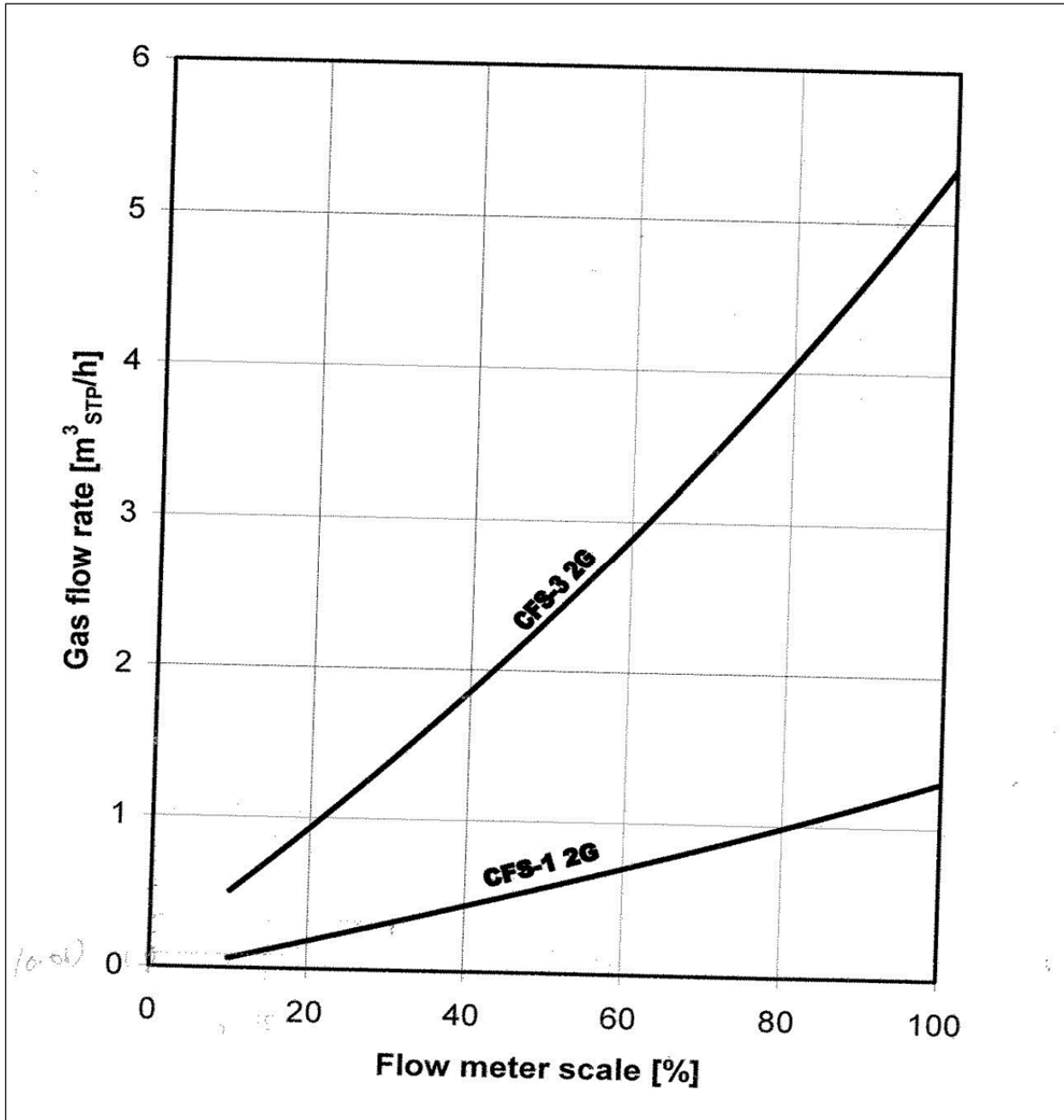


Figure B.1: Gas flow diagram for feed gas as air

APPENDIX B, CONTINUED

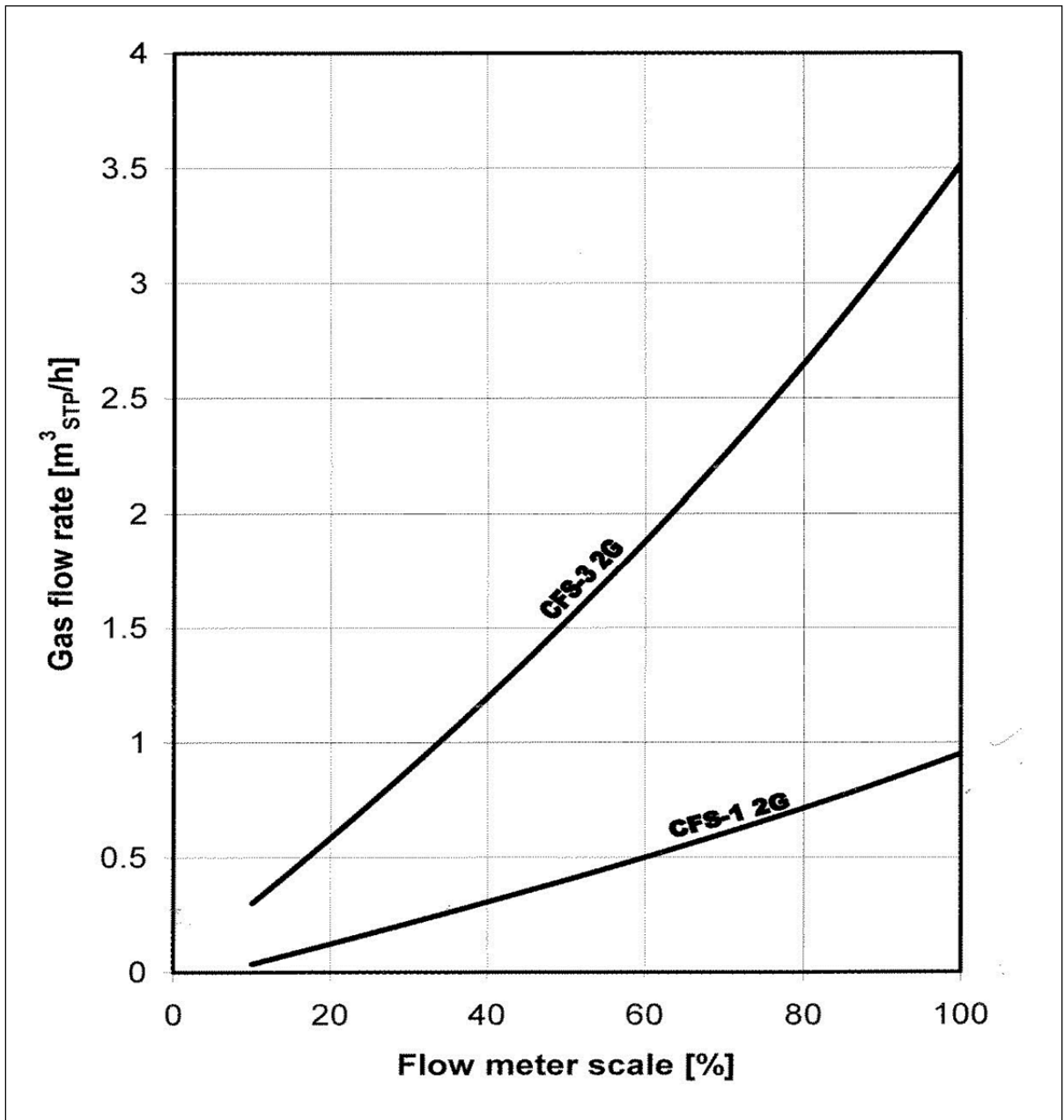


Figure B.2: Gas flow diagram for feed gas as oxygen

## APPENDIX B, CONTINUED

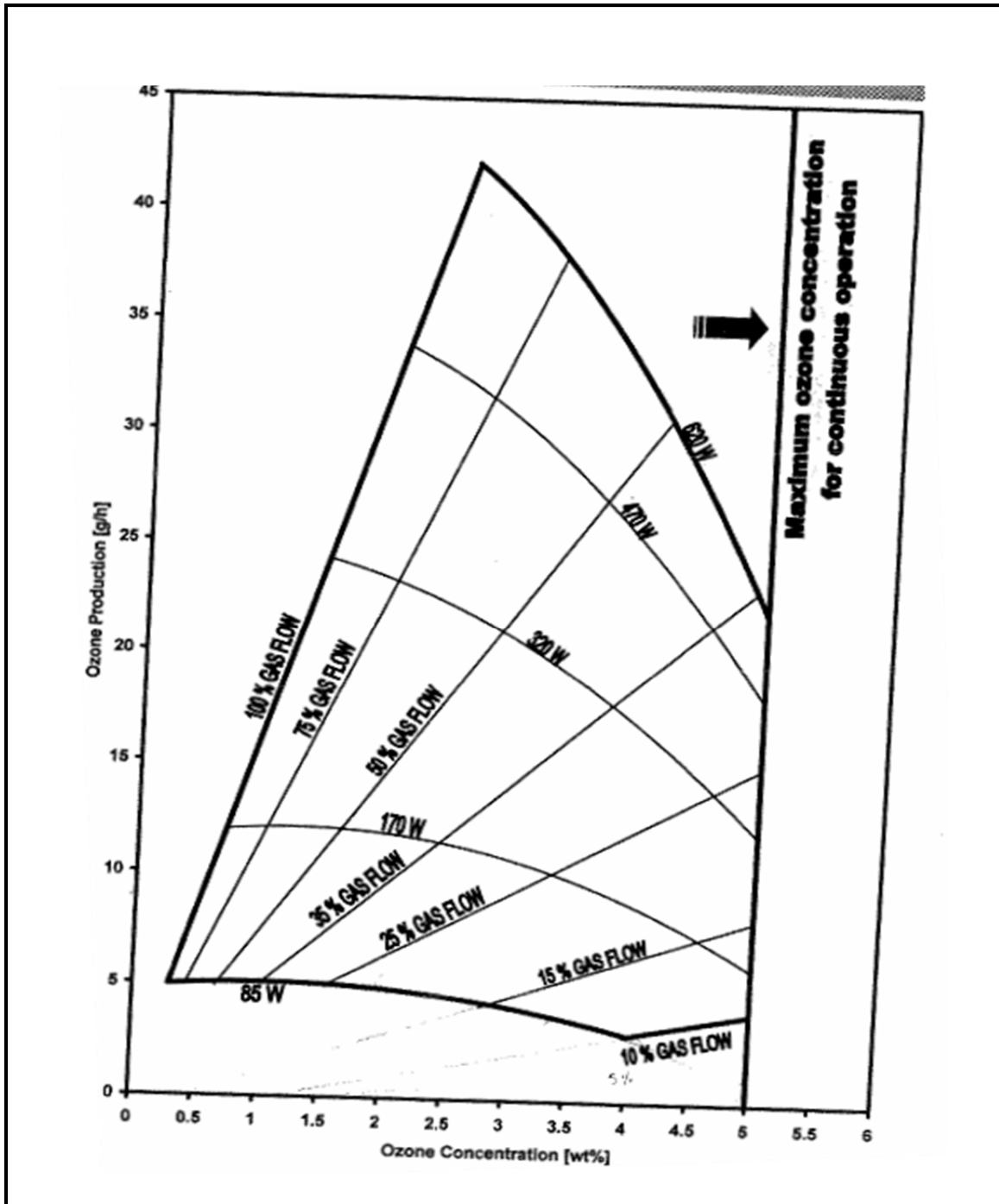


Figure B.3: Setting curves for feed gas as Air

## APPENDIX B, CONTINUED

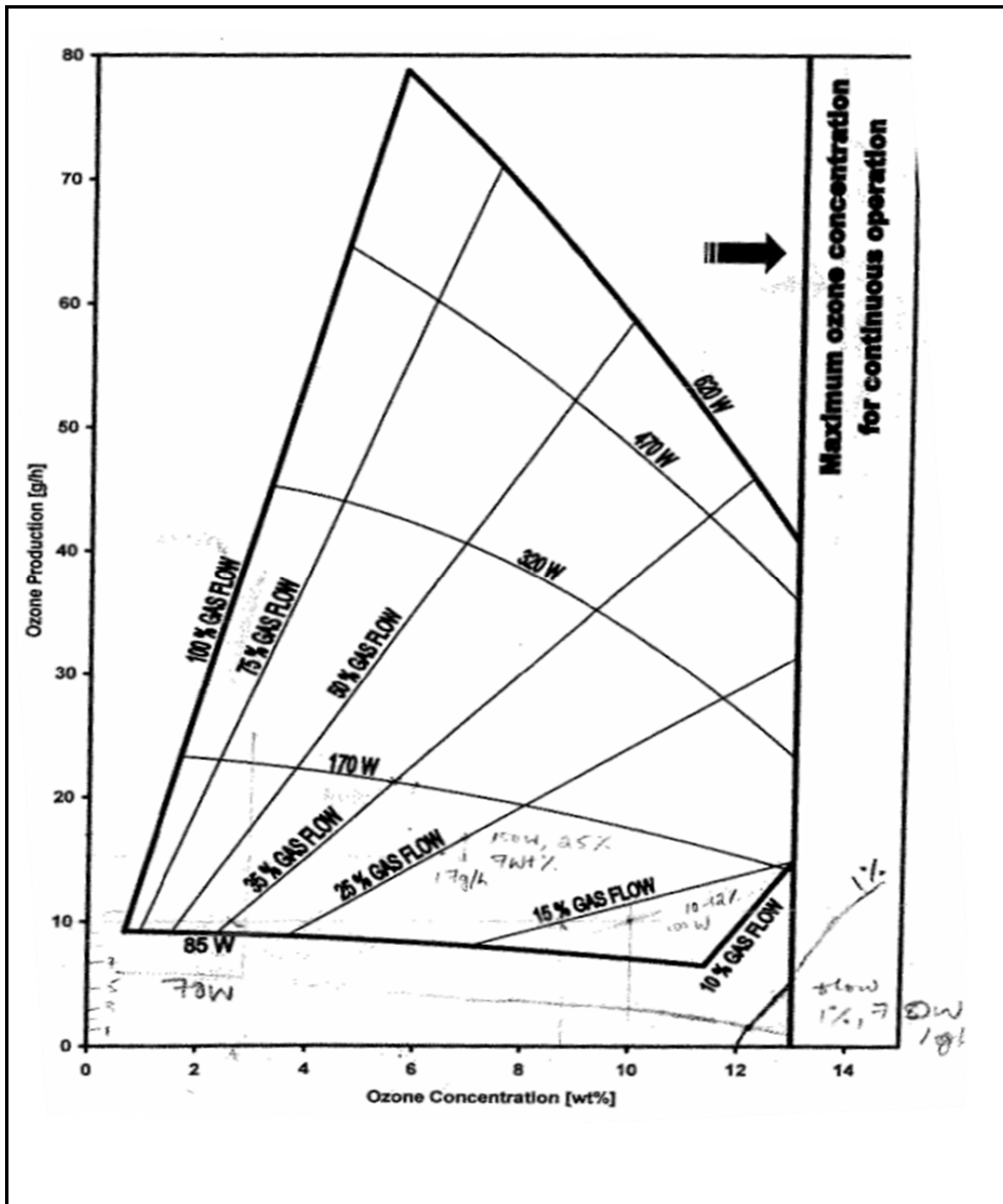


Figure B.4: Setting curves for feed gas as Oxygen

**APPENDIX C**  
**ADDITIONAL DATA ON OZONE**

**Table C.1: Selected Properties of Ozone**

Characteristic	Property
Molecular weight	48.00
Specific gravity of gas (air =1.0)	1.66
Boiling point at 1 atm	-111.9 <sup>0</sup> C
Melting point at 1 atm	-192.5 <sup>0</sup> C
Critical temperature	-12.1 <sup>0</sup> C
Critical pressure	5,460 kPa (abs)
Critical density	540 kg/m <sup>3</sup>
Latent heat of gas at boiling point and at 1 atm	297 kJ/kg
Specific heat of gas at 32 <sup>0</sup> F (0 <sup>0</sup> C)	0.767 kJ/kg (°C)
Solubility in water, vol/vol at 32 <sup>0</sup> F (0 <sup>0</sup> C)	0.64
Weight of liquid at boiling point	1,352 kg/m <sup>3</sup>

Source: Compressed Gas Association, Inc. Publication CGA P-34, 2001.

## APPENDIX C, CONTINUED

**Table C.2: Personal Exposure Effects and Limits for Ozone – United States**

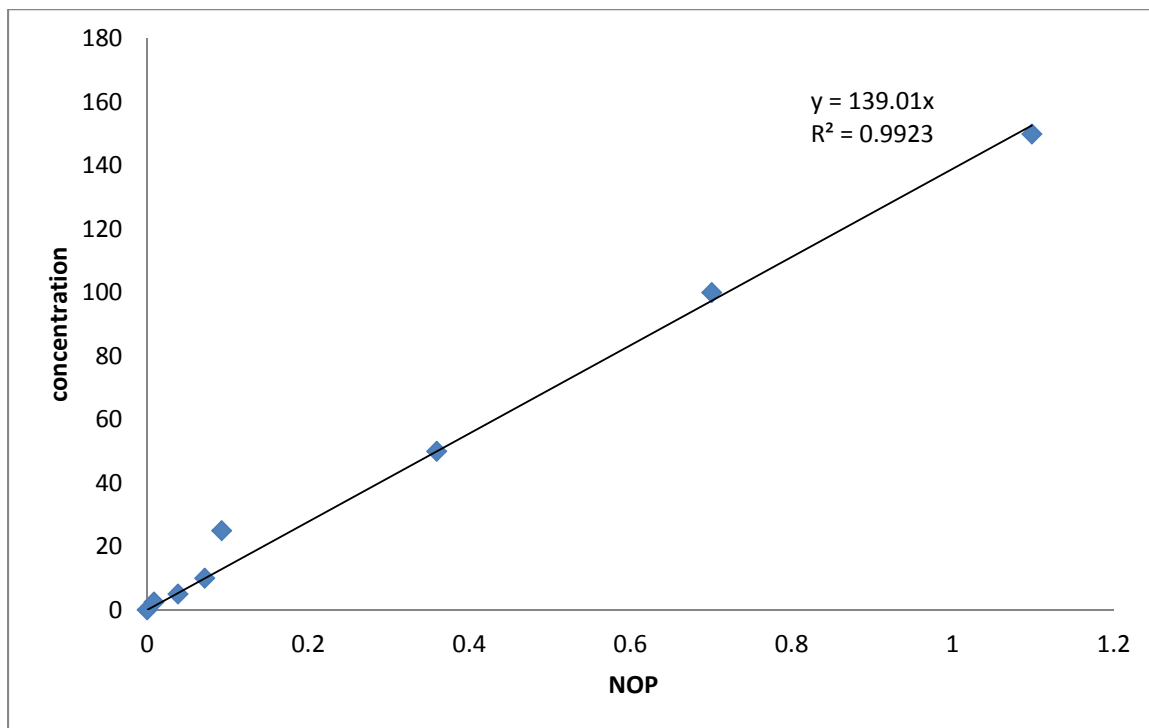
Observed effects	Concentration, ppm <sub>v</sub>
Threshold odor detection, normal person	0.01-0.04
Maximum 8-hour average personal exposure limit	0.1
Minor eye, nose, and throat irritation; shortness of breath	>0.1
Breathing disorders, reduction in oxygen consumption, lung irritation, severe fatigue, chest pain, dry cough	0.5-1
Headache, respiratory irritation, and possible coma; possibility of severe pneumonia at higher levels of exposure	1-10
Lethal to small animals within 2 hours	15-20
Lethal in few minutes	>1,700

Source: Compressed Gas Association, Inc. Publication CGA P-34, 2001.

**Table C.3: Ozone compatibility of the materials used in the setup**

Parts	Materials used	Ozone compatibility
Tubing (gas flow)	PVDF, 316 Stainless Steel	Excellent
Tubing (water flow)	PVDF, PVC	Excellent
Influent and effluent tanks	Glass	Excellent
Valves and seals	316 Stainless Steel and Teflon	Excellent
Columns	Polycarbonate (plexiglass)	Excellent
Distributor	Polycarbonate	Excellent
Diffuser	Ceramic	Excellent

**APPENDIX D**  
**EXPERIMENTAL DATA FOR 1, 4-DIOXANEDURING**  
**OZONATION AND PEROXONE PROCESSES IN BATCH**  
**REACTOR SETUP**



**Figure D.1: Calibration curve of 1,4 dioxane using LLE method for batch reactor setup**

## APPENDIX D CONTINUED

**Table D.1: Results of percent removal of 1,4-dioxane during ozonation at different reaction time**  
 $[O_3] = 6.5 \text{ mg L}^{-1}$ ,  $[1,4\text{-dioxane}] = 50 \text{ } \mu\text{g L}^{-1}$ , reaction volume = 50 (used in fig 4.2)

50 ppb initial concentration of 1,4-dioxane				
Time (min)	Con ( $\mu\text{g/L}$ )	% removal	Residual $O_3$	$O_3$ consumed
0	45.38	0	6.52	0.00
0.5	39.49	13	0.62	5.90
1	38.04	25	0.00	6.52
3	36.88	19	0.24	6.28
5	36.00	21	0.29	6.23
7	32.65	28	0.22	6.30
10	30.98	32	0.56	5.96
15	28.76	37	0.00	6.52

**Table D.2: Results of percent removal of 1,4-dioxane during ozonation at different reaction time**  
 $[O_3] = 5 \text{ mg L}^{-1}$ ,  $[1,4\text{-dioxane}] = 100 \text{ } \mu\text{g L}^{-1}$ , reaction volume = 50 (used in fig 4.2)

100 ppb initial concentration of 1,4-dioxane					
Time (min)	Con ( $\mu\text{g/L}$ )	$C/C_0$	% removal	Residual $O_3$	$O_3$ consumed
0	80.94	1.00E+00	0.00	5.12	0.00
1	56.46	6.98E-01	12.99	0.38	4.74
3	55.68	6.88E-01	25.00	0.54	4.58
5	50.02	6.18E-01	18.74	0.50	4.62
10	54.10	6.68E-01	20.68	0.76	4.36
15	51.27	6.33E-01	28.06	0.32	4.80

## APPENDIX D CONTINUED

**Table D.3: Results of 1,4-dioxane degradation during ozonation at different reaction time to analyze reaction rate  $[O_3] = 5 \text{ mg L}^{-1}$ ,  $[1,4\text{-dioxane}] = 100 \text{ } \mu\text{g L}^{-1}$ , reaction volume = 50 (used in Figure 4.4)**

Time	Avg of (Ao - Af)	Ozone Concentration	Ln (O3Concentration)
0.5	0.00776	0.615873016	-0.48471448
1	0.00388	0.307936508	-1.17786166
3	3	0.356349206	-1.031844112
5	0.00369	0.292857143	-1.228070356
7	0.00272	0.215873016	-1.533064934
10	0.007	0.555555556	-3.597861034
15	0.00055	0.043650794	-3.131533815

## APPENDIX D CONTINUED

**Table D.4: Results of 1,4-dioxane degradation during ozonation at different pH in batch reactor experiment: [1,4-dioxane] = 50  $\mu\text{g L}^{-1}$ , reaction volume = 50 (used in 4.5)**

Experimental results with different pH during ozonation							
Initial pH	Final pH	1,4-dioxane Final Conc. ( $\mu\text{g/L}$ )	1,4-dioxane Ave Conc. ( $\mu\text{g/L}$ )	% Removal	initial ozone concentration mg/L	Residual $\text{O}_3$ concentration mg/L	Consumed $\text{O}_3$ concentration mg/L
6	6	45.38352			0		
5.6	5.6	45.38352			0		
2.4	2.6	41.2382	38.74991	14.61678	2.87	0.14	2.72
2.3	2.5	36.26162			2.87	0.89	1.98
5.5	4.2	33.58341	33.03882	27.20084	5.26	0.82	4.44
5.4	4.2	32.49423			5.26	0.59	4.67
12.2	11.8	35.78041	39.62347	12.69193	0.82	0.00	0.82
12.2	11.9	43.46653			0.82	0.00	0.82

**Table D.5: Results of percent removal of 1,4-dioxane during peroxone at different ozone: hydrogen peroxide ratio,  $[\text{O}_3] = 5 \text{ mg L}^{-1}$ ,  $[\text{pH}] = 5$ ,  $[\text{1,4-dioxane}] = 50 \mu\text{g L}^{-1}$**

Time (min)	$\text{H}_2\text{O}_2/\text{O}_3$ molar ratio ( $\mu\text{M}$ )	% 1,4-dioxane removal
5	0	32
5	2	92
5	6	98
5	8	99
5	7	86
5	12	88
5	23	75

## APPENDIX D CONTINUED

**Table D.6: Investigation of competition kinetics of 1,4-dioxane with *p*-CBA (different concentrations of *p*-CBA) during peroxone Process (contact time 15 min), Initial concentration of 1,4-dioxane was 50 µg/L (used in Figure 4.7)**

Objective - Investigation of competition kinetics of 1,4-dioxane with different <i>p</i> -CBA conc during peroxone process								
Initial <i>p</i> -CBA conc (ppm)	H <sub>2</sub> O <sub>2</sub> conc (ppm)	1,4-dioxane F conc µg/L	1,4-dioxane% degradation	1,4-dioxane C/C <sub>0</sub>	<i>p</i> -CBA Final conc mg/L	<i>p</i> -CBA% degradation	Final Ozone conc	Ozone consumed
0	28	51.92	0.00	1.00	0.00	0.00	0	0.00
1	28	28.86	44.40	0.56	0.3	70.00	1.11	4.89
1.5	28	33.50	35.46	0.65	1.175	21.67	1.56	4.44
2	28	32.82	36.78	0.63	1.627	18.65	0.95	5.05
2.5	28	34.07	34.38	0.66	2.077	16.92	0.17	5.83

**APPENDIX E**  
**EXPERIMENTAL DATA FOR 1,4-DIOXANE IN SEMI BATCH REACTOR**  
**SET UP**

**Table E.1: Investigation the effect of initial concentrations on the removal efficiency of 1,4 dioxane in semi batch reactor during ozonation process: [1,4-dioxane]= 100 $\mu\text{g L}^{-1}$  (Used in Figure 4.10)**

100 $\mu\text{g/L}$ 1,4-dioxane (ozonation)				
Contact time (min)	Initial 1,4-dioxane Conc. ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)	ozone dosage (mg/L)
0	84.99	0	0.00	0.00
1	61.64	27	0.58	1.61
3	51.05	40	2.24	4.82
6	49.02	42	4.60	9.64
10	48.07	43	7.31	16.07
15	38.17	55	9.88	24.10

**Table E.2: Investigation the effect of initial concentration on the removal efficiency of 1,4 dioxane in semi batch reactor during ozonation process concentrations: [1,4-dioxane]= 1000 $\mu\text{g L}^{-1}$  (Used in Figure 4.10)**

1000 $\mu\text{g/L}$ initial concentration of 1,4-dioxane			
Contact time (min)	Initial Conc. ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)
0.00	1027.38	0.00	0.00
3.00	932.02	3.71	2.24
5.00	970.77	2.02	3.12
8.00	976.23	4.98	4.82
12.00	1006.58	5.51	6.73
15.00	989.25	9.28	8.01

## APPENDIX E CONTINUED

**Table E.3: Investigate effect of sodium persulfate on the removal efficiency of 1,4 dioxane in semi batch reactor during ozonation process [1,4-dioxane]= 100 $\mu\text{g L}^{-1}$ , (Used in figure 4.11)**

10 mL/ l sodium persulfate			
Contact time (min)	Initial Conc ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)
0	109.47	0.00	0.00
1	102.67	6.21	0.64
5	98.68	9.86	4.25
10	96.02	12.29	7.99
15	95.21	13.03	10.35
25	87.37	20.19	12.63
50 mL/ l sodium persulfate			
Contact time (min)	Initial Conc. ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)
0	117.66	0.00	0.00
1	102.26	13.09	0.50
5	95.52	18.82	3.39
10	94.98	19.28	6.29
15	92.73	21.19	8.41
25	87.68	25.48	12.08

## APPENDIX E CONTINUED

**Table E.4: Investigate the effect of salinity on the removal efficiency of 1,4 dioxane in semi batch reactor during ozonation process (Used in figure 4.12)**

75 mM NaCl			
Contact time (min)	Initial Conc ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)
0	108.11	0	0.00
1	99.78	7.70	1.23
3	97.20	10.09	2.95
8	92.87	14.09	6.80
12	88.06	18.54	9.32
15	84.18	22.13	10.86
50 mM NaCl			
Contact time (min)	Initial Conc. ( $\mu\text{g/L}$ )	1,4-dioxane % removal	ozone consumed (mg/L)
0	100.12	0	0
1	95.54	4.57	0.57
5	96.88	3.24	2.42
8	98.51	1.60	5.26
15	85.83	14.27	9.17

# APPENDIX F

## EXPERIMENTAL DATA FOR PHARMACEUTICALS & DEET IN SEMI BATCH REACTOR SET UP

Compound name: Carbamazepine  
Correlation coefficient:  $r = 0.985620$ ,  $r^2 = 0.971446$   
Calibration curve:  $13399.4 * x + 14460.6$   
Response type: External Std, Area  
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

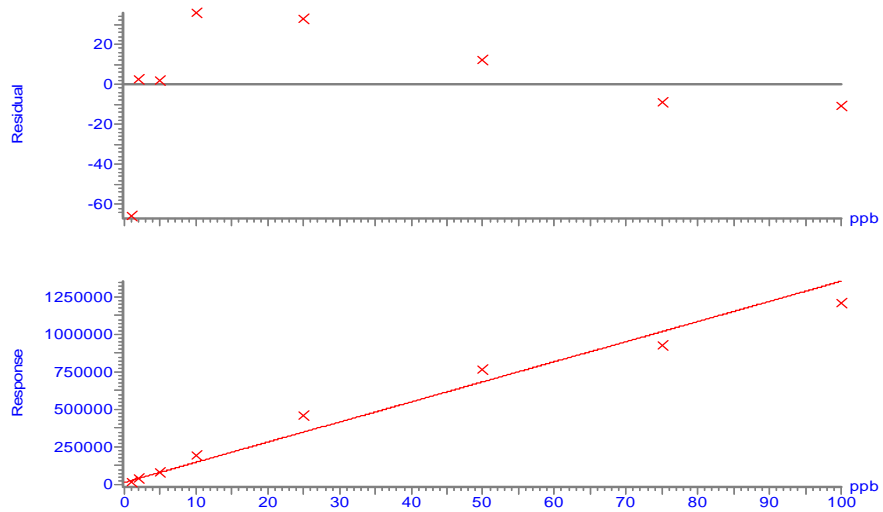


Figure F.1: Calibration curve of carbamazepine using SPE method

Compound name: Sulfamethoxazole  
Correlation coefficient:  $r = 0.968835$ ,  $r^2 = 0.938642$   
Calibration curve:  $23268.5 * x + -27017.4$   
Response type: External Std, Area  
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

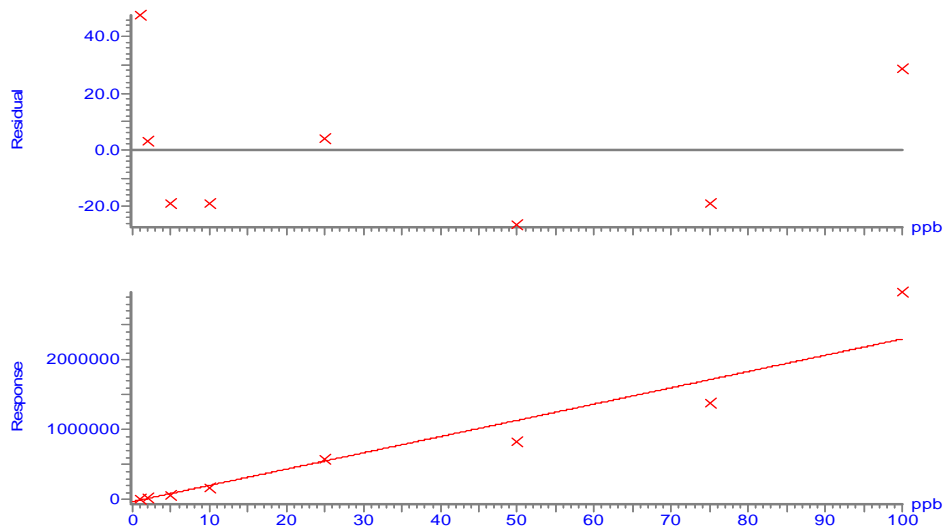


Figure F.2: Calibration curve of sulfamethoxazole using SPE method

## APPENDIX F CONTINUED

Compound name: Trimethoprim  
Correlation coefficient:  $r = 0.981987$ ,  $r^2 = 0.964299$   
Calibration curve:  $53546.2 * x + -27162.6$   
Response type: External Std, Area  
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

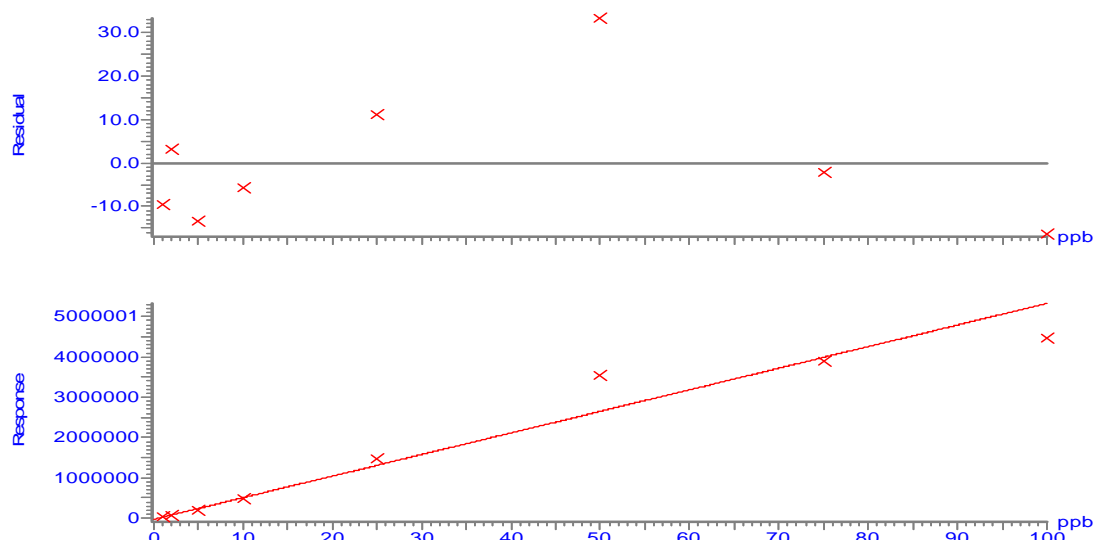


Figure F.3: Calibration curve of trimethoprim using SPE method

Compound name: DEET  
Correlation coefficient:  $r = 0.988568$ ,  $r^2 = 0.977266$   
Calibration curve:  $6022.06 * x + 14535.8$   
Response type: External Std, Area  
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

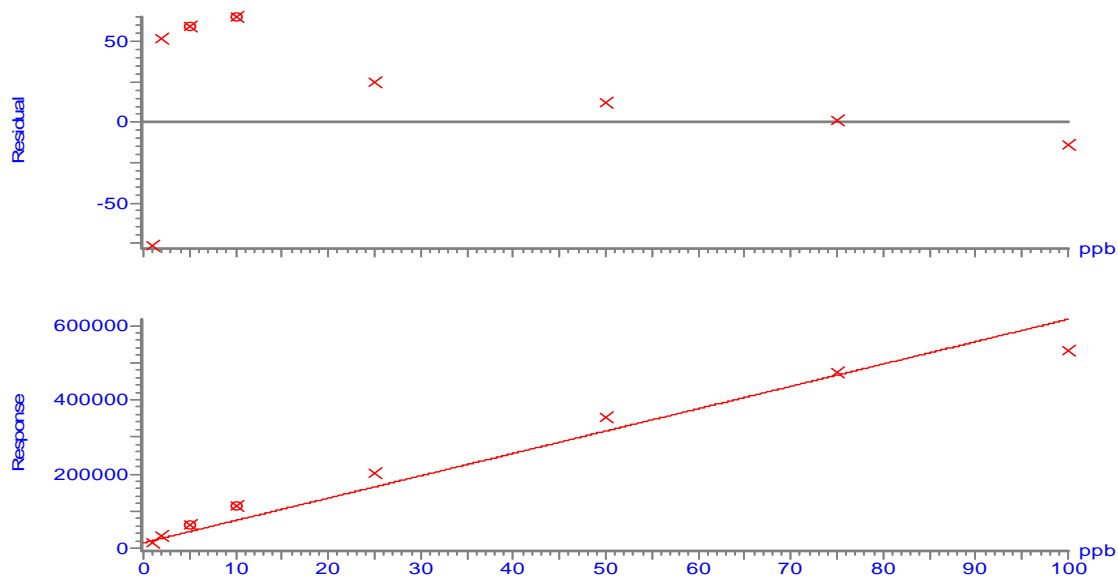


Figure F.4: Calibration curve of DEET using SPE method

## APPENDIX F CONTINUED

**Table F.1: Concentration of pharmaceuticals and DEET in tap water in multicomponent system in semi batch reactor during ozonation [pharmaceuticals]= 100 $\mu\text{g L}^{-1}$ , [DEET]= 100 $\mu\text{g L}^{-1}$ , (Used in figure 4.13)**

Ozonation in tap water				
Time (min)	Trimethoprim $\mu\text{g/L}$	Sulfamethoxazole $\mu\text{g/L}$	Carbamazepine $\mu\text{g/L}$	DEET $\mu\text{g/L}$
Initial	112.18	110.74	82.85	79.42
1.00	0.06	0.35	0.04	94.03
3.00	0.04	0.07	0.03	93.83
5.00	0.03	0.05	0.02	77.96
10.00	0.07	0.06	0.05	88.12
15.00	0.09	0.09	0.07	88.33
20.00	0.14	0.14	0.11	86.51

**Table F.2: Removal efficiency of pharmaceuticals in tap water in multicomponent system in semi batch reactor during ozonation [pharmaceuticals]= 100 $\mu\text{g L}^{-1}$ , [DEET]= 100 $\mu\text{g L}^{-1}$ , (Used in figure 4.14)**

% removal ozonation in tap water				
Time (min)	Trimethoprim	Sulfamethoxazole	Carbamazepine	DEET
Initial	0.00	0.00	0.00	0.00
1.00	99.95	99.68	99.96	-18.40
3.00	99.97	99.94	99.97	-18.14
5.00	99.97	99.95	99.98	1.84
10.00	99.94	99.94	99.94	-10.95
15.00	99.92	99.92	99.91	-11.22
20.00	99.87	99.87	99.87	-8.93

## APPENDIX F CONTINUED

**Table F.3: Concentrations of pharmaceuticals and DEET in tap water in multicomponent system in semi batch reactor during peroxone process ,  $[H_2O_2]= 5mg L^{-1}$ [pharmaceuticals]=  $100\mu g L^{-1}$ ,  $[DEET]= 100\mu g L^{-1}$ , (Used in figure 4.5)**

Peroxone in tap water ( 5mg/L H <sub>2</sub> O <sub>2</sub> )				
Time (min)	Trimethoprim $\mu g/L$	Sulfamethoxazole $\mu g/L$	Carbamazepine $\mu g/L$	DEET $\mu g/L$
Initial	148.03	134.17	96.43	92.54
1.00	0.30	0.58	0.16	96.08
3.00	0.16	0.17	0.11	92.69
5.00	0.12	0.10	0.08	90.36
10.00	0.19	0.14	0.14	91.87
15.00	0.29	0.12	0.19	92.30
20.00	0.37	0.31	0.26	89.82

**Table F.4: Removal efficiency of pharmaceuticals and DEET in tap water in multicomponent system in semi batch reactor during peroxone process ,  $[H_2O_2]= 5mg L^{-1}$ [pharmaceuticals]<sub>0</sub>=  $100\mu g L^{-1}$ ,  $[DEET]= 100\mu g L^{-1}$ , (Used in figure 4.5)**

% Removal of Peroxone in tap water ( 5mg/L H <sub>2</sub> O <sub>2</sub> )				
Time (min)	Trimethoprim	Sulfamethoxazole	Carbamazepine	DEET
Initial	0.00	0.00	0.00	0.00
1.00	99.80	99.56	99.83	-3.83
3.00	99.89	99.88	99.89	-0.17
5.00	99.92	99.93	99.92	2.35
10.00	99.87	99.89	99.85	0.73
15.00	99.81	99.91	99.80	0.26
20.00	99.75	99.77	99.73	2.94

## APPENDIX F CONTINUED

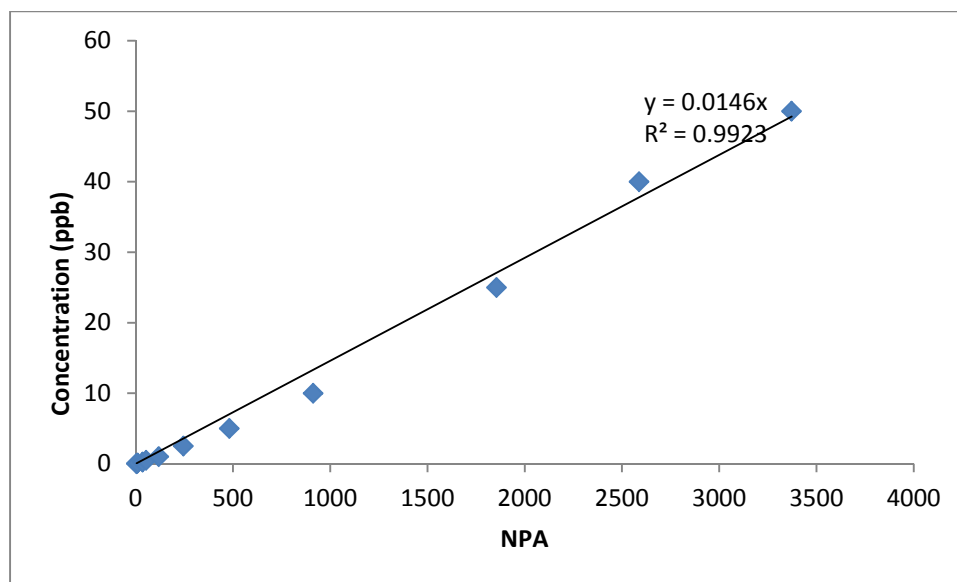
**Table F.5: Concentration of pharmaceuticals in tap water in multicomponent system in semi batch reactor during ozonation process peroxone process,  $[H_2O_2]= 10mg L^{-1}$ [pharmaceuticals]=  $100\mu g L^{-1}$ , [DEET]=  $100\mu g L^{-1}$ , (Used in figure 4.6)**

Ozone in tap water ( 10mg/L H2O2)				
Time (min)	Trimethoprim $\mu g/L$	Sulfamethoxazole $\mu g/L$	Carbamazepine $\mu g/L$	DEET $\mu g/L$
Initial	<b>124.71</b>	<b>88.76</b>	<b>105.24</b>	111.53
1.00	0.17	0.62	0.05	111.15
3.00	0.03	0.08	0.02	104.00
5.00	0.06	0.07	0.32	101.63
10.00	0.02	0.03	0.02	99.16
15.00	0.03	0.03	0.00	91.93

**Table F.6: Removal efficiency of pharmaceuticals in tap water in multicomponent system in semi batch reactor during peroxone process peroxone process,  $[H_2O_2]= 10mg L^{-1}$ [pharmaceuticals]=  $100\mu g L^{-1}$ , [DEET]=  $100\mu g L^{-1}$ , (Used in figure 4.6)**

% Removal Peroxone in tap water ( 10 mg/L H <sub>2</sub> O <sub>2</sub> )				
Time (min)	Trimethoprim	Sulfamethoxazole	Carbamazepine	DEET
Initial	0.00	0.00	0.00	0.00
1.00	99.86	99.30	99.95	0.34
3.00	99.98	99.91	99.98	6.75
5.00	99.95	99.93	99.70	8.87
10.00	99.99	99.96	99.98	11.09
15.00	99.97	99.97	100.00	17.57

**APPENDIX G**  
**EXPERIMENTAL DATA FOR PFCs IN SEMI BATCH REACTOR SET UP**



**Figure G.1: Calibration curve of PFOA using SPE method**

## APPENDIX G CONTINUES

**Table G.1: Detailed results of PFOA in different experimental conditions (H1, H2, H3 & H4) in semi batch reactor during ozonation and peroxone processes (Used in figure 4.17)**

TableH1

Time (min)	PFOA Peak	IS Peak	NPA	Final Conc	% removal
Control	3262125	1872	1742.59	23.50	
1	4358099	2194	1986.37	27.34	0
3	4408159	2243	1965.30	27.00	0
5	4514981	2195	2056.94	28.47	0
10	4614584	2147	2149.32	29.95	0
15	4703660	2355	1997.31	27.51	0
20	4650934	2181	2132.48	29.68	0

Table H2

25ppb PFOA Ozonation (1ppm H <sub>2</sub> O <sub>2</sub> )					
Time (min)	PFOA Peak	IS Peak	NPA	Final Conc	% removal
Control	1059	1773772	1674.95	35.37	
0	921	1752806	1903.16	40.61	0
1	881	1865231	2117.17	45.56	0
3	997	1739815	1745.05	36.97	0
5	915	1687318	1844.06	39.24	0

Table H3

25ppb PFOA Ozonation (5 ppm H <sub>2</sub> O <sub>2</sub> )					
Time (min)	PFOA Peak	IS Peak	NPA	Final Conc	% removal
Control	4350	1937312	445.36	26.77	
0	4130	1958076	474.11	28.49	0
1	4181	1898445	454.06	27.29	0
3	3947	1895387	480.21	28.86	0
5	4062	1761453	433.64	26.06	0
8	3969	2007615	505.82	30.40	0
12	3911	1899912	485.79	29.20	0

Table H4

9 ppb PFOA ozonation @ pH 2.67 (NO H <sub>2</sub> O <sub>2</sub> )					
Time (min)	PFOA Peak	IS Peak	NPA	Final Conc	% removal
Control	12691	2033810	160.26	9.37	
0 @2.67pH	12324	1979320	160.61	9.39	0
3	12781	2027027	158.60	9.27	0
5	12562	1943777	154.73	9.04	0
8	12424	1990797	160.24	9.37	0
12	12183	1954875	160.46	9.38	0

