REMOVAL OF TRICLOSAN FROM SURFACE WATERS BY OZONATION: KINETICS & REMOVAL MECHANISM

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

KEMAL BERK ORHON

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

JULY 2014

Approval of the thesis:

REMOVAL OF TRICLOSAN FROM SURFACE WATERS BY OZONATION: KINETICS & REMOVAL MECHANISM

submitted by **KEMAL BERK ORHON** in partial fulfillment of the requirements for the degree of **Master of Science in Environmental Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ___________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. F. Dilek Sanin ___________
Head of Department, **Environmental Engineering**

Prof. Dr. Ülkü Yetiş ___________
Supervisor, **Environmental Engineering Dept., METU**

Prof. Dr. Filiz B. Dilek ___________
Co-Supervisor, **Environmental Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. F. Dilek Sanin ___________
Environmental Engineering Dept., METU

Prof. Dr. Ülkü Yetiş ___________
Environmental Engineering Dept., METU

Prof. Dr. Filiz B. Dilek ___________
Environmental Engineering Dept., METU

Assist. Prof. Dr. Tuba H. Ergüder ___________
Environmental Engineering Dept., METU

Eyüp Kaan MORALI, M.Sc. ___________
Expert, Ministry of Environment and Urban Planning

Date: ___________

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Kemal Berk Orhon

Signature :

ABSTRACT

REMOVAL OF TRICLOSAN FROM SURFACE WATERS BY OZONATION: KINETICS & REMOVAL MECHANISM

Orhon, Kemal Berk
M.Sc., Department of Environmental Engineering
Supervisor: Prof. Dr. Ülkü Yetiş
Co-Supervisor: Prof. Dr. Filiz B. Dilek

July 2014, 115 pages

Triclosan (TCS) has recently attracted the attentions of the researchers from the fields of water treatment due to its existence in water environments as a result of widely usage in the world. This study was conducted to investigate the removal of TCS from Milli-Q and surface water by means of ozonation and to observe ozonation by-product formation. Effects of ozone dose, initial TCS concentration, water matrix and pH were also investigated to comprehend TCS removal by ozonation in different conditions and optimize the treatment system accordingly. Furthermore, kinetics of TCS removal in the aforesaid different conditions were studied to have a clear understanding of the applied technique. Experiments were conducted on lab-scale using ozone generator to supply ozone to the glass reactors containing 1 L samples spiked with TCS. Reactors were exposed to ozone through 30 min. HPLC-UV device was used for TCS measurement of water samples after ozone treatment. Samples were analyzed for TCS at 1, 5, 10, 20 and 30 min. Results have indicated that ozonation is an effective way of TCS removal from water samples with removal efficiency of 99%; however, by-product formation was evident. Three of the five by-products were identified as 2,4-dichlorophenol, 4-chlorocathecol and 2-4 dicholoroanisole which were also observed to be eliminated to a great extent upon further ozonation. Ozone dose, TCS content of the water, water matrix and pH were also found to have significant influences on treatment efficiency and therefore, they should be considered during the design and operation of the ozonation unit.

Keywords: Ozonation, Triclosan, by-product, surface water, kinetics

ÖZ

TRİCLOSANIN YÜZEY SULARINDAN OZON İLE GİDERİMİ: KİNETİK & GİDERİM MEKANİZMASI

Orhon, Kemal Berk
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Ülkü Yetiş
Ortak Tez Yöneticisi: Prof. Dr. Filiz B. Dilek

Temmuz 2014, 115 sayfa

Dünyada yaygın olarak kullanımı neticesinde su kaynaklarında tespit edilen Triklosan (TCS), son yıllarda, su ve atıksu arıtımı konusunda çalışmaları bulunan araştırmacıların dikkatini çekmektedir. Bu çalışma ile TCS enjekte edilmiş ultra saf su ve yüzey suyu örneklerinden ozonlama ile TCS gideriminin incelenmesi hedeflenmiş olup, olası ozonlama yan ürün oluşumu da takip edilmiştir. TCS giderimi; farklı ozon dozları, giriş TCS konsantrasyonları, su komposizyonu ve pH ortamlarında çalışılmış olup, bu değişkenlerin ozonlama ile TCS arıtımına etkisi incelenmiş ve arıtma sisteminin optimizasyonu için öneriler geliştirilmiştir. Ayrıca, bu farklı ortamlardaki TCS arıtım kinetiği üzerine çalışmalar yapılmıştır. Deneyler, laboratuvar ölçeğinde 1 L hacimli ve TCS ile enjekte edilmiş borosilikat cam reaktörler ile gerçekleştirilmiş olup, arıtma için gerekli olan ozon, reaktöre ozon jeneratörü yardımı ile sağlanmıştır. Reaktörler 30 dakika boyunca ozona maruz bırakılmış olup, sırasıyla 1, 5, 10, 20 ve 30 dakikalık arıtma sonrasındaki su örneklerinde TCS analizleri HPLC-UV cihazı ile yapılmıştır. Bu çalışma sonucunda, ozonlamanın suda TCS gideriminde önemli ve etkili bir arıtma yöntemi olduğu ve bu yöntemle %99 oranında arıtma giderim verimine ulaşılabileceği anlaşılmıştır. Ancak, ozonlama sonrasında yan ürün oluşumu da gözlenmiş olup, 5 tane ozonlama yan ürününden 2 tanesinin tayini yapılabilmiştir. Söz konusu yan ürünler 2,4-diklorofenol, 2,4-dikloroanisol ve 4-klorokatekol olarak belirlenmiş ve ozon ile arıtma sonrasında büyük ölçüde giderimleri sağlanmıştır. Ayrıca, ozon dozu, sudaki TCS miktarı, su komposizyonu ve pH'ın arıtma verimi üzerinde önemli etkilerinin olduğu saptanmış olup, bu faktörlerin ozonlama ünitesinin tasarlanması ve işletilmesi esnasında dikkate alınması gerekmektedir.

Anahtar kelimeler: Ozonlama, Triklosan, yan ürün, yüzeysel su, kinetik

To My Family and My Beloved Wife, Aybala

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and deepest gratitude to my supervisor Prof. Dr. Ülkü Yetiş and my co-supervisor Prof. Dr. Filiz Bengü Dilek for their precious guidance, criticism, suggestion and insight about my study.

This study was supported by BIOHYPO (Confronting the Clinical Relevance of Biocide Induced Antibiotic Resistance) Project, funded under the European Commission (FP7-KBBE-227258), which is gratefully acknowledged.

I am, and always will be, grateful to my parents and my sister, for their continuous and unconditional love, encouragement, and support at all stages of my life.

Last but not least, to my beloved wife, Aybala, who always with me and makes me feel happy and confident, especially at the hectic times, and believing in me at all times; thank you for your endless love and support.

TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

ABBREVIATIONS

BOD : Biochemical Oxygen Demand
COD : Chemical Oxygen Demand
DOC : Dissolved Organic Carbon
EC : European Council
EDC : Endocrine Disrupting Compound
EPA : Environmental Protection Agency
GC : Gas Chromatography
HPLC : High Performance Liquid Chromatography
LOD : Limit of Detection
LOQ : Limit of Quantification
MTCS : Methyl-triclosan
NOM : Natural Organic Matter
O_3 : Ozone
PPB : Parts per Billion
PPCP : Pharmaceuticals and Personal Care Products
PPM : Parts per Million
TCS : Triclosan
TOC : Total Organic Carbon
WFD : Water Framework Directive
2,4-DCA : 2,4-dichloroanisole
2,4-DCP : 2,4-dichlorophenol
4-CC : 4-chlorocatechol
4-CR : 4-chlororesorcinol

CHAPTER 1

INTRODUCTION

Since 250 years from the beginning of the Industrial Revolution, human population has increased rapidly and every aspect of human life and life styles has been changed dramatically. It is also considered as a major turning point for Earth’s ecology and human’s relationship with their environment. The use of machinery and factories led to mass production which would afterwards cause numerous environmental problems (URL 1).

Especially over 50 years, with growing technology, humans have degraded the ecosystem more rapidly and extensively than in any comparable period of time in human’s history, largely to meet rapidly demands for food, fresh water, timber and fuel. Although, these efforts have contributed to substantial gains in human well-being and economic development, environment has been neglected and adversely affected. On the other hand, consumers require from the manufacturers better quality of water and food for realizing healthy lifestyle. There is a growing cost in the form of the degradation of many environmental services and this situation would give rise to diminish of the benefits that future generations obtain from the environment (Millennium Ecosystem Assessment Report, 2005).

Water pollution is one of the global problem that threatens future of the humanity hence requires to be evaluated and needs to be taken necessary precautions both in national and international bases. In today’s world, indirect and direct discharges of the contaminants to water bodies without subjected to adequate treatments lead to occur water pollution in all over the world. Triclosan (TCS) is one the emerging substances that has been somehow discharged to the water bodies and pronounced to be adversely affect the environment. It is a broad spectrum antimicrobial and antifungal biocide, widely being used in innumerable numbers of products with the purposes of preservative and controlling the growth of diseases and bacteria by all over the world (Dann and Hontela, 2011).

The widespread use of TCS results in the release of this biocide into the environment via either domestic or industrial discharges. According to the study conducted by Reiss et al. (2002), the great extent (96%) of TCS containing products are eventually rinsed down the drain and discharged with wastewater effluent. In this respect, TCS has been encountered in various type of water environment, such as surface waters, sediments and wastewater treatment plants' influent and effluents, at various concentrations (Singer et al., 2002; Halden and Paul, 2005). It is currently considered to be ubiquitous in the environment and expected to increase as the use of TCS-containing products increases (Perez et al., 2013). This being the case, routine detection of TCS in surface waters has raised the attractions of researchers, public and even policy makers.

Today, TCS brought into prominence due to its adverse health effects. In the literature, TCS is reported to be highly bioaccumulative, induce hormone disruption (Lindström et al., 2002; Fernandes et al., 2011) and cause skin irritation, allergy susceptibility, and also other ecological toxicity to the aquatic and terrestrial environment (Coogan et al., 2007). Besides, it can disrupt the nitrogen cycle in sensitive soils at certain concentrations (Kookana et al., 2011). Cross resistance assertions of TCS against antibiotics lay emphasis on the use of TCS, as well (Dann and Hontela, 2011).

In the light of the growing concerns about the effects and usages of TCS, removal of TCS from water environment became an important issue from the environmental point of view. In this context, several treatment methods have been considered for the removal of it from water environment, such as ozonation (Hernandes-Leal, 2011; Rosal et al., 2010; Snyder et al., 2006), membrane filtration (Yoon et al., 2006; Heberer et al., 2002; Nghiem et al., 2005) and adsorption (Hernandes-Leal et al., 2011; Hartig et al., 2001; Ternes et al., 2002). Among these, ozonation constitutes a more promising technique for the removal of TCS (Larsen et al., 2004; Ikehata et al., 2008) with an increasing acceptation and applicability in drinking water facilities and wastewater treatment plants dealing with pharmaceuticals (Ternes et al., 2003; Vogna et al., 2004; Snyder et al., 2006; Gagnon et al., 2008 and Klavarioti et al., 2009). Regarding this, several studies have been published in the literature indicating considerably high TCS removals by ozone. However, reported figures are quite variable depending on the type of water desired to be treated and the ozone dose applied in the studies: over 99% in the experiment with Milli-Q water where ozone was applied at a rate of 1.22 mg/min.L (Hernandes-Leal et al., 2011); over 87% in the experiment with biologically treated grey water where ozone dose applied was 15 mg/L (Hernandes-Leal et al., 2011); 79% with urban wastewater at ozone dose of 340 μM (Rosal et al., 2010); 94% and 99.9% with aqueous TCS solution at 1:1 and 1:5 TCS:O_3 ratio, respectively (Chen et al., 2012); 98% and 58% with a wastewater containing 7.5 and 12.4 mg /L of DOC, respectively (Suarez et al., 2007); >95% as independent of water quality when the ozone exposure was measurable (0-0.8 mg min/L) (Wert et al., 2009).

In addition to this variability, these studies, except a recent study by Chen et al. (2012), did not consider the possible conversions and by-product formations during the reaction between ozone and TCS. Indeed, it is highly possible that direct ozonation of TCS culminates in the formation of the by-products considering the phenol–ozone reaction mechanisms. In the course of ozonation, reaction of ozone with the hydroxyl group of the phenol ring and oxygen addition to the phenol ring or phenol ring opening (Mvula and von Sonntag, 2003) forms the majority of ozone–TCS reactions. As such, conversions and by-product formations probably occur during the ozonation of TCS. Evidently, Chen et al. (2012) observed that TCS was transformed into different by-products such as 2,4-dichlorophenol, 4-chlorocatechol, 4-chlororesorcinol and conversions as mono-hydroxy-triclosan and di-hydroxy-triclosan. There are some evidences in the literature that these by-products may be more stable and more toxic than the parent compound (Zhang et al., 2005; Canosa et al., 2005; Dann and Hontela, 2011). Accordingly, Chen et al. (2012) claimed about the importance of understanding all possible transformation products in order to enable a full risk assessment when the concern is the treatment of TCS by ozonation. Therefore, taking into consideration of the by-product formation and transformation is substantial within the application of ozonation technique on TCS.

In this study, ozonation was investigated as a removal technique of TCS from surface water, with special emphasis on its by-product formation and factors that may affect it. In this context, a series of tests were run with a lab-scale ozonation system and the effects of ozone applied, initial TCS concentration, pH and water matrix on TCS elimination were sought. Required ozone amount for the removal of TCS was determined as unit basis (mg O_3/ mg TCS). Besides, determination of reaction kinetics of ozone with different compounds in water environment that enables to observe the chemical effect of ozone in waters (Hoigné and Bader, 1983a,b) and provide to evaluate the potential of removing and reactivity of compounds (Jin et al., 2012) is a significant issue that has been also essential to be taken into account.

In brief, the main aim of this study is to provide insight into the removal of TCS by ozonation from surface water and to contribute the optimization of the ozone treatment process with offering appropriate parameters (i.e. ozone dose, retention time) in a way that would be applicable in surface water treatment plants.

CHAPTER 2

LITERATURE REVIEW

2.1 Triclosan

5-chloro-2-(2,4- dichlorophenoxy) phenol, Triclosan (TCS), a chlorinated organic compound, also commercially called as Irgasan, has been produced under the license of Swiss origin chemical company namely “Ciba” (McGinnis, 2008) and used as an antimicrobial and antifungal biocide in numerous numbers of products with the purposes of preservative and controlling the growth of diseases and bacteria since the 1960s especially over the past 25 years in all over the world (Levy et al., 1998).

Dann and Hontela (2011) declare that over 700 antibacterial products the majority of which involves TCS were released to the consumer markets between the years of 1992 and 1999. In one of the market study conducted in 2000, it was found that over 75% of liquid and 30% of bar soaps contained some antibacterial agent and nearly half of those soaps were contained TCS (FSNET, 2000). TCS encountered in personal care products was reached to massive quantities and in Sweden, 1998, 25% of the total amount of toothpaste sold contained TCS which corresponds to nearly 2 tons of TCS consumption per year (Adolfson-Erici et al., 2002). Another study conducted by Singer et al. (2002) indicates that the production of TCS exceeded 1500 tons per year and Europe accounts for 350 tons whereas US is responsible for >300 tons of it. It can be deduced from the data that consumption amount of TCS varies from country to country. As the demand of the consumer products increase, consumption of TCS is anticipated to be increased (Dann and Hontela, 2011).

Today, as a broad spectrum biocide, it has widely being used in innumerable numbers of products especially common consumer products as an ingredient in a good deal of cosmetic and personal care products (e.g. soap, toothpaste, mouthwash, shampoo, deodorant, hair conditioner, creams, gels, body sprays); industrial cleaning products (e.g. detergent, softener, disinfectant, surface cleanser); textile (e.g. shoes, towels, pillows, socks, clothes); plastic manufactures (e.g. kitchenware, toys); first aid materials; computer equipments, and lots of other industrial and household products (Dann and Hontela, 2011; McGinnis D., 2008; NICNAS, 2009).

2.1.1 Physicochemical Properties

TCS (CAS No:3380-34-5) is a hyroxylated tricloro-diphenly ether and more generally categorized as a chlorinated phenol. It is stable, hydrophobic, non-ionic, non-volatile, white to off-white crystalline powder, tasteless, faint aromatic odor and soluble in water (McGinnis, 2008; NICNAS, 2009). Physicochemical properties of TCS are briefly tabulated in Table 1.

Table 1. Physicochemical properties of Triclosan (Reiss et al., 2009; NICNAS, 2009; SCCS, 2009)

Property	**Value**
Molecular formula	$C_{12}H_7Cl_3O_2$
Molecular weight (g/mole)	289.6
Melting point (°C)	57±1
Decomposition temperature (°C)	280-290
Vapor pressure (at 25°C, Pa)	4×10^{-6}
Water solubility (at 25°C, mg/L)	10
Octanol-water partition coefficient (log K_{OW})	4.76
Adsorption to suspended solids (K_{OC}, ml/g)	47,454
Dissociation constant (pK_a)	7.9
Henry's constant (atm-m^3/mole)	$1.5x10^{-7}$
Half-life in surface water (d)	2-2000

As can be depicted from Table 1, TCS has a highly hydrophobic nature having high log K_{OW} value as 4.76 that it is likely to be sorbed to sediment containing high organic carbon content. Also having relatively low water solubility and quite high K_{OC} value, it generally persists in soils and aquatic sediments (Gautam et al., 2014). Moreover, its half-life varies between 2 to 2000 days depending on the latitude and time of the year (Perez et al., 2013).

Its structure could be observed in Figure 1. Allmyer (2009) indicates that TCS has a structural formula similar to the other chemical pollutants such as polychlorinated biphenyls (PCBs) and polybrominated diphenly ethers (PBDEs) (Allmyer, 2009).

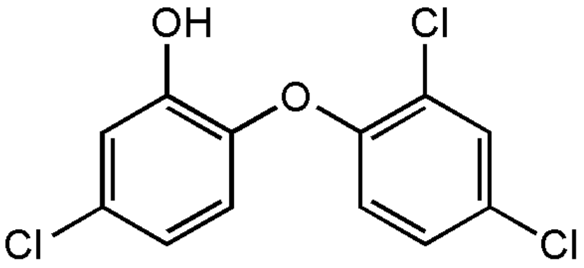


Figure 1. Structural formula of Triclosan

2.1.2 Fate of Triclosan in Water

The widespread use of TCS results in the release of this biocide into the water environment via either domestic and industrial discharges or end-of-life disposal lifecycle stages. TCS has been routinely encountered in various types of water environment, such as surface waters, sediments and wastewater treatment plants' influent and effluents, at various concentrations (Singer et al., 2002; Halden and Paul, 2005; Perez et al. 2013). According to the study conducted by Reiss et al. (2002), the great extent (96%) of TCS containing products are eventually rinsed down the drain and discharged with wastewater effluent. APUA (2011) also indicates that more than 95% of the TCS in consumer products are disposed of in residential drains.

Like many anthropogenic organic contaminants such as detergents and pharmaceuticals, TCS is incompletely removed during the wastewater treatment, as well. Despite high TCS removals (75-99%) are obtained in wastewater treatment plants, the residual untreated TCS has been discharged to the surface waters. NICNAS (2009) pointed out this issue that in sewage treatment plants, influent concentrations of 573-845 ng/L TCS were reduced down to 60-159 ng/L by applying appropriate treatment techniques and eventually discharged to the surface waters. Besides being discharged from the wastewater treatment plants, TCS could directly be released to the surface waters. To illustrate PPCPs, creams or disinfectants containing TCS that have been commonly used for the protection of human skin during recreational activities such as swimming at waterways or beaches may be washed off directly to the surface waters (NICNAS, 2009).

Figure 2 demonstrates the different pathways that TCS pursues from the consumer to its final discharge. As can be seen from this figure, except reuse applications, last destination of TCS becomes either groundwater or surface waters. In this regard, presence of TCS in surface waters is explained in the following Section 2.1.2.1. Right after the discharge of TCS to the waters, it has been exposed to different fate mechanisms mainly such as adsorption, photolysis and biodegradation that are mentioned under the Section 2.1.2.2, as well.

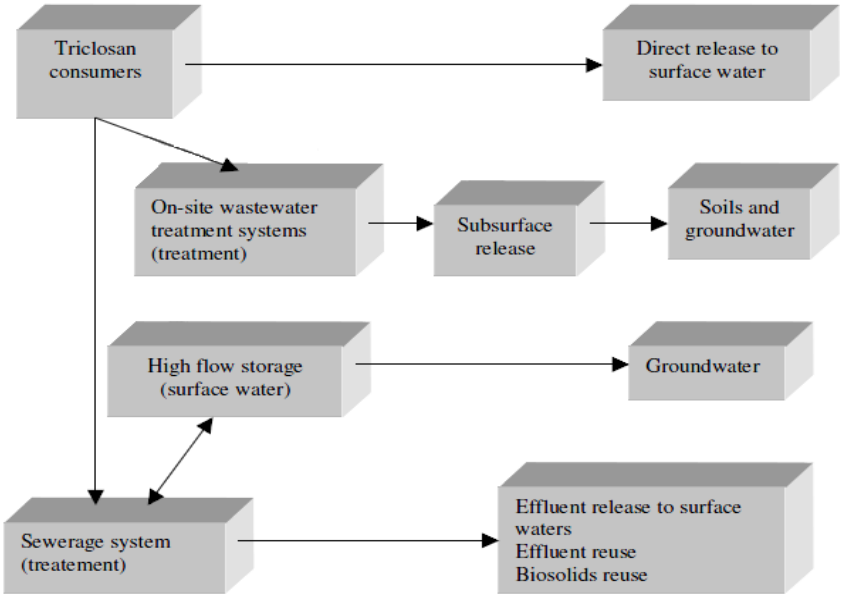


Figure 2. Model for triclosan use, release and disposal (NICNAS, 2009)

Briefly, TCS is currently considered to be ubiquitous in the environment and expected to increase as the use of TCS-containing products increases (Perez et al., 2013). This being the case, routine detection of TCS in surface waters has raised the attractions of researchers, public and even policy makers.

2.1.2.1 Presence in Surface Water

Contaminants emerge yearly somehow find their ways into the aquatic environment via discharges, accidental spills, waste ponds overflow, agricultural and land applications so on (Huang, 2010). As indicated above, following the consumption and passing through the sewer and treatment plants, TCS is eventually discharged to the surface waters. TCS is the antimicrobial biocide that has been most commonly detected anthropogenic organic contaminant in US water resources (Gautam et al., 2014). Several studies have been conducted to investigate the concentration of TCS in surface waters and the TCS levels presented in Table 2 have been reported.

Table 2. TCS levels in surface waters

Measuring area	**Concentration (ng/L)**	**Reference**
Arkansas River, Colorado, USA	3.9-28.3	Gautam et al., 2014
Çamlıdere Reservoir, Ankara, Turkey	0.65-11.15	Yavuz, 2013
Kesikköprü Reservoir, Ankara, Turkey	0.86-48.96	
Eymir Lake, Ankara, Turkey	0.95-757.7	
Stenungsund, Sweden	160	NICNAS, 2009
Australia Estuarine and Fresh Waters	<3-71	Ying and Kookana, 2007
Marine water- Hong Kong	16.2	Wu et al., 2007
Riverine water-Sha Tin, Hong Kong	26	Wu et al., 2007
Germany Freshwater	30-90	Wind et al., 2004
United Kingdom Fresh Water	19-80	Sabaliunas et al., 2003
Norway Marine Water	160	Remberger et al., 2002

Table 2. TCS levels in surface waters (cont'd)

Measuring area	**Concentration (ng/L)**	**Reference**
Switzerland Fresh Water	<3-74	Poiger et al., 2002
	5-100	Singer et al., 2002
United States/Canada Freshwater	2000-300000	Jungclaus et al.,1978
	600-40000	Lopez-Avila and Hites, 1980

As can be deduced from Table 2, TCS levels vary dramatically between 0.65 and 300000 ng/L in different locations of the World. However, except the studies of Junclaus et al. (1978) and Lopez-Avila and Hites (1980), typically TCS has been encountered at ng/L levels in surface waters.

2.1.2.2 Transformation Processes

Following the discharge to the water environment, TCS may undergo some transformation processes such as adsorption, biodegradation, photolysis and volatilization that are described in the following sections.

2.1.2.2.1 Adsorption

In some studies, it has been reported that TCS is sorbed onto the sludge in the wastewater treatment plants (Chu and Metcalfe, 2007; Heidler and Halden, 2007; Yavuz, 2013) and adsorption and desorption kinetics of TCS onto and form biosolids, soils, and biosolids amended solids were studied (Birikorang et al., 2010). NICNAS (2009) also indicates that due to its hydrophobic nature, TCS is expected to have a high affinity for the sediments and soil and major portion of TCS is expected to adsorb on them. In the same study it is also mentioned that once it is adsorbed, it has low mobility and its persistency plays a part on this issue. In this regard, following the discharge of TCS into the surface water, it is highly possible that TCS is sorbed onto the sediment in river, sea and lakes etc.

On the other hand, although several studies related with removal of TCS indicate high TCS removals and mentioned sorption to the sludge, its adsorption possibility onto experimental systems due to its quite high hydrophobicity has not been considered. Almost in all studies, removal of TCS was determined just by taking difference of its influent and effluent concentrations within experimental systems (Koc et al., 2013). Chen et al. (2012), for example, investigated TCS removals based on initial and final TCS concentrations while Hernandes-Leal et al. (2011) and Suarez et al. (2007) reported over 99% TCS removal without considering adsorption phenomena.

To explain more clearly, it is highly possible that TCS in solutions utilized during laboratory experiments might adsorb onto labwares such as beakers, flasks, reactors or any kind of equipments in contact with TCS solution. According to the study conducted by Koc et al. (2013), providing insight into this possibility, TCS was seriously adsorbed onto plastic tubes submerged into the experimental reactor and used with the purpose of supplying ozone into the reactor. In this study, plastic and glass tubes were utilized to supply ozone to the reactor bearing TCS solution and it was found that TCS adsorbed by unit area of plastic tubing was about 100 times greater than glass one. However, in both cases, measuring the effluent of the liquid in reactor, removal of TCS was determined above 98.5% as indicated in the previous studies published in the literature. In the same study, adsorption of TCS to membrane filtration system was also reported and it was mentioned that in experimental studies related with TCS, adsorption onto plastic labware and experimental systems should seriously be taken into account and advised to use glass reactors with glass tubing in the experiments. Otherwise, obtained results might not reflect the truth and mislead the audience.

The study of Kimura et al. (2003) also touch on adsorption phenomena by reporting the adsorption of TCS onto membranes of nanofiltration and reverse osmosis and possibility of overestimation of rejection from membrane system.

2.1.2.2.2 Biodegradation

Biodegradation of TCS by wastewater micro-organisms has been applied as one of the TCS removal techniques from the wastewaters more specifically in wastewater treatment plants. This technique is explained in Section 2.2.2. Apart from that, considering the fate of TCS in surface waters, Huang (2010) mentioned that concentration of TCS could decline through the biodegradation in rivers.

It is mentioned in some of the studies that TCS may transform into methyl-triclosan (MTCS) in water environment which is more stable, hydrophobic and bioaccumulative than the parent compound TCS (NICNAS, 2009); however, its concentration is very low (<1 ng/L) in surface waters (Balmer et al., 2004). Bester (2003) estimated the conversion ratio of TCS to MTCS as 1% in the treatment plants. In another study, it is reported that MTCS is formed as the product of TCS degradation in the nitrification and denitrification processes in wastewater treatment plants.

Available data on MTCS that is directly formed by biotransformation of TCS in surface water environment (i.e. sediment etc.) is still scarce and it has been mostly focused on the situation of wastewater treatment plants (Pintado-Herrera et al., 2014). Since it is the fact, considering the low conversion ratios and lack of reliable data required for the evaluation, biodegradation process of TCS is pale into insignificance among its fate mechanisms in surface water.

2.1.2.2.3 Photolysis

TCS is susceptible to the photolysis process which is considered to be one of the removal pathways from surface waters (Singer et al., 2002; NICNAS, 2009). Mostly, TCS undergoes the photolysis instead of being transported along the water column in proper conditions (Lindström et al., 2002). The study of NICNAS (2009) indicates that photolysis especially during the summer time accounted for 80% depletion of the encountered TCS in surface waters.

Photolysis of TCS in surface water is dependent on the natural sunlight availability and pH of the water (Tixier et al., 2002; Arnold et al, 2003). The availability of sunlight to surface waters is also affected by several factors such as; latitude, season, time of day, climatic conditions and depth of water. To illustrate, in summer the half-life of TCS at 40° latitude is 2.55 hour while it becomes 5.5 days in winter time. Seasonal changes even cause about 45 fold differences for photolysis of TCS (Arnold et al., 2003). Moreover, rate of photolysis in deeper waters are relatively low due to inability of sunlight to penetrate the deeper levels (NICNAS, 2009). Considering pH, photolysis is relatively greater at alkaline solutions. Half-life of TCS at pH 6 is about 19 times longer than that at pH 10 (NICNAS, 2009). On the other hand, turbidity is an also one of the other points that could be taken into consideration because it adversely affects the photolysis process in surface waters (Perez et al., 2013).

Furthermore, there are likely to be some photolysis by-products of TCS determined by several studies. In this regard, 2,8-dicholorodibenzo-o,dioxin (2,8-DCDD) is the most pronounced compound claimed to be produced by the photochemical conversion of TCS in surface waters (Lopez- Avila and Hates, 1980; Arnold et al., 2003; Latch et al., 2005; Sanchez-Prado et al., 2006; Perez et al., 2013). This dioxin product is mentioned to be further phototransformated to other compounds but not been identified yet (Samsoe-Petersen et al., 2003).

2,4-dichlorophenol, 2,7-dichlorodibenzo-p-dioxin, 4-chlorocatechol and 4-choloro-2,4-dihyroxydiphenyl ether are the other phototransformation by-products of TCS reported in the literature (Latch et al., 2005; Ferrer et al., 2004; Sanchez-Prado et al., 2006).

2.1.2.2.4 Volatilization

TCS is not expected to volatilize from water surfaces and even regarded as non-volatile based on its very low vapor pressure (4×10^{-6} Pa) and low Henry's law constant (1.5×10^{-7} atm-m^3/mole) at the environmentally relevant temperatures of

20°C to 25°C (NICNAS, 2009). Therefore, it is not considered as a significant pathway of TCS encountered within the water environment.

2.1.3 Effects of Triclosan on the Environment

Concerns on the effects of TCS on the environment have been rising with each passing day. Existing researches that conclude its possible adverse health effects on humans also become instigative factor in respect of increasing public concerns and studies on the consumption of TCS (URL 2).

One of the hot topics that have been discussed in great deal of the studies dealing with the effects of TCS, is cross-resistance matter. As commonly known; TCS, being used in pharmaceuticals as antimicrobial and antifungal agent affects the several types of gram-positive and gram negative bacteria and some fungi types (Schweizer, 2001; McAvoy et al., 2002). At low concentrations it is regarded as bacteriostatic (inhibit the growth of the microorganism) while it kills microorganisms at high concentrations and become a bactericidal (APUA, 2011). In the process of TCS between bacteria, TCS blocks the active site of the enoyl-acyl carrier protein reductase enzyme (ENR) which is essential enzyme for fatty acid synthesis in bacteria. By doing so, bacteria could not synthesize the fatty acids which are responsible for growing and building new cell membranes (Levy et al., 1999). However, there are studies with a growing number claiming that by the reason of widespread and extensive usage of it and thereby repetitive exposures; TCS generates cross-resistance in bacteria towards other antimicrobial compounds and antibiotics. It is believed that this may be caused by the bacterial cells developing changes in the intracellular target of TCS and these changes may change a target shared with other clinically important antibiotics. By doing so, TCS may give rise to decrease the susceptibility of the other important antibiotics and consequently may cause undesired environmental and health problems (Saleh et al., 2010). Braoudaki and Hilton (2004) indicate that TCS induces the decrease of *E. coli* O157 strains's susceptibility to range of antimicrobial agents. On the other hand, some of the studies are at the opposite direction regarding the cross-resistance matter. According to one

EU project entitled “Confronting the Clinical Relevance of Biocide Induced Antibiotic Resistance (BIOHYPO)” and finalized in 2012, TCS has no risk of antibiotic resistance in food-grade bacteria and any evidence could not be found regarding the antibiotic resistance in *Enterobacteria*. Also, it does not constitute any hazard for antibiotic resistance in *Staphylococci*. Finally, it was concluded within the results of the project that biocide used in the food-chain is far from the posing a direct risk for promoting clinically relevant antibiotic resistance in pathogens (URL 3). Within this framework, this controversial issue needs to be investigated further and come to light so as to take essential precautions.

Endocrine disrupting potential of TCS is also another matter of concern being investigated by researchers. It is indicated to be causing changes in fin length and sex ratios in fish (Foran et al., 2000). TCS also identified as thyroid disruptive in animals. Crofton et al. (2007) reported that TCS decreased the circulating concentration of thyroxin in rats. As for the study conducted by Veldhoen and Skirrow (2006), TCS can affect the thyroid gland, altering frog metamorphosis in a significant manner at the exposure levels equivalent to those currently detected in environment and human tissues. The researchers also mentioned in the same study that TCS may cause a potential risks to human hormone action, as well. James et al. (2010) also reported that TCS is a potent inhibitor of estradiol and estrone sulfonation in sheep placenta.

Due to its prevalent exposure especially from the common consumer products, TCS has been determined in human body, as well. More than one third of the TCS consumed in the EU countries in 2002 appeared to reach consumers by skin care and oral care products (Allmyr, 2009). It is detected in human blood plasma at the range of <20-300 ng/g (lipid weight) and in human milk (Hovender et al., 2002). In the USA it was found in human urine (Calafat et al., 2008). Under these circumstances, considering the possible health effects of TCS on humans, rising concerns especially of the public within this regard become supportable.

It is also linked to range of environmental and health effects such as allergy susceptibility, skin irritation, depressant effects on the central nervous system of mice (Huang, 2010). Apart from being toxic to the bacteria as its natural usage purpose, it is mentioned to be acutely toxic to grass shrimp and phytoplankton in marine estuarine (DeLorenzo et al., 2008). It also affects earth worms and Japanese medeka fish (Chen et al., 2011; Nassef et al., 2010). Lastly, it is regarded as highly bioaccumulative that concentration of TCS found in fish can be thousands times higher than what is detected in water column (Samsoe-Petersen et al., 2003). Besides, it can disrupt the nitrogen cycle in sensitive soils at certain concentrations (Kookana et al., 2011).

2.1.4 Actions Taken Against Triclosan in the World

As one of the most prevalent antibacterial compound being used in lots of products and said a lot about its effects on environment and living beings, TCS became prominent not only for the researchers but also for large audiences. Public awareness has been increased in virtue of results of the studies conducted on TCS that are increasing with each passing day. Considering the wide range of the effects of TCS that are mentioned in previous section, removal of TCS from the environment and not being used in the formulations or the ingredients of the products become necessity and even obligation. Within this framework, governments, organizations and manufacturers are urged to come into play in this issue. In this regard, some actions have started to be taken against the TCS in the world.

Especially during the recent years, as a result of the pressure of the consumers that has been growing in consequence of the increased public perception by the findings of the researchers regarding its adverse effects in particular to impacts to the thyroid hormone, manufacturers decided to disuse TCS within their products and change their formulations (NICNAS, 2009; Environmental Defense of Canada, 2012).

US State of Minnesota announced that the soaps and other products containing TCS, pollutes water and poison people and then banned the use of TCS in consumer personnel care products by the Triclosan Ban Legislation approved on 16 May 2014 and will take into effect on 1 January 2017 (URL 4). Protector and Gamble (P&G), one of the biggest manufacturers of consumer products, declared to eliminate TCS from its products by 2014 (URL 5). Johnson & Johnson is another company that announced to phase out the use of TCS and will be completed by the end of 2015 (URL 6). Canada declared TCS toxic to the environment and waiting to get enough evidence to ban its use in a range of personnel care products (URL 7). Furthermore, in Japan, permitted amount of TCS in cosmetics is restricted to 0.1% while it is limited as 0.3% in Europe and Canada (NICNAS, 2009). Beyond Pesticides and Food & Water Watch submitted a petition on the ban of TCS and it is currently under evaluation of United States Environmental Protection Agency (EPA) and public review (URL 8). TCS was also determined as specific pollutant in the countries of Norway, Sweden and Switzerland meaning that discharge standards for surface waters will be defined and monitoring activities will be done for TCS in these countries (Republic of Turkey Ministry of Forestry and Water Affairs, 2013).

Considering the situation in Turkey, TCS has been added into the draft specific pollutants list prepared in accordance with Water Framework Directive (WFD-2000/60/EC) in the scope of the projects done in the collaboration with Ministry of Forestry and Water Affairs, Scientific and Technological Research Council of Turkey (TÜBİTAK) and related Universities. In line with the requirements of the WFD, Turkey will first develop environmental quality standards for the surface waters and then accordingly identify discharge standards for TCS. In this regard, monitoring studies will be done for the concentration of TCS in surface waters consistently and necessary precautions and actions will be taken (Republic of Turkey Ministry of Forestry and Water Affairs, 2013).

In order to avoid the exposure of TCS in the environment and humans, beside the bans and limitations for the TCS usage, its removal from the environment especially from waters has also great importance under these conditions. Therefore, there are several treatment techniques being implemented in surface water treatment plants, explained in the following sections of this study, become necessity to be applied properly in this regard (Huang, 2010; NICNAS, 2009).

2.2 Removal Methods for Triclosan from Water Environment

2.2.1 Physical

One way of TCS treatment from water environment is by physical means and the phototransformation is the well-known treatment process applied for the TCS bearing waters among the physical techniques. Tixier et al. (2002) studied the phototransformation of TCS under artificial UV light in Swiss surface waters through different pH conditions between 7 and 9. In this study, they demonstrated that pH and dissolved organic matter content of the water had a significant influence on the phototransformation of TCS from the water bodies.

Membrane filtration processes such as nanofiltration (NF) and reverse osmosis (RO) are the other physical treatment techniques included in the removal of trace organic compounds like TCS (Agenson et al., 2003) and it was reported to be achieved over 95% rejection by way of RO type high pressure membranes (Verliefde, 2008). However, the rejection of trace organic compounds by membrane filtration processes is seriously affected by membrane properties, fouling, pH, natural organic matter content of water, salinity, pressure and temperature affects in different manners (Bellona et al., 2004; Bolong et al., 2009; Steinle-Darling et al., 2010; Verliefde, 2008).

On the other hand, Kimura et al. (2003) stated that adsorption to the membrane is the other undeniable mechanism involved in the removal of trace organics by membrane filtration due to the hydrophobic properties of the compounds of interest and this may result in the overestimations of the exact removal efficiencies leading unreliable results. Adsorption of TCS to the membrane system was also supported by another study conducted by Ogutverici (2012) and focused on the removal of TCS from surface water by NF. Hence, this adsorption issue should be considered and carefully evaluated during the studies conducted for the water treatment of hydrophobic substances like TCS.

Sorption of TCS onto tyre crumb rubber and following removal was the other recent topic of the studies canalized for the treatment of this widely used biocide (Lopez-Morales et al., 2012). Tyre crumb rubber contains rubbers both in natural and synthetic origins, styrene-butadiene polymer, steel, carbon black and zinc and silisium oxides (Amari et al., 1999) and thus includes an attractive surface for the contaminants to adsorb and be removed from the water environment. Considering these properties, tyre crumb rubber was studied for TCS removal from the aqueous solution by means of adsorption and batch mode system was operated within this aim (Lopez-Morales et al., 2012). In this study, they achieved TCS removal efficiency around 89% by TCR adsorption when the pH of the aqueous solution was set to 3 and the removal efficiency declined with the increase in pH directly.

Furthermore, Hernandez-Leal et al. (2011) demonstrated that activated carbon was an effective treatment alternative for the removal of TCS from the water solutions and they reported that 95% TCS removal was achieved at the end of granular activated carbon treatment of aerobically treated grey water at low flow conditions.

2.2.2 Biological

Biological treatment of the wastewaters contaminated with TCS was reported to be the important process for the removal of this chlorinated organic and TCS removal around 79% was accomplished at the end of biological degradation (Singer et al., 2002).

Another study on the biological degradation of TCS was carried out by Chen et al. (2011) and they investigated the biodegradability of TCS in the activated sludge system consisting of enhanced phosphorus removal. During this study, TCS concentration was monitored at aerobic, anoxic and anaerobic conditions by means of GC-MS device and formation of methyl-triclosan was controlled in these conditions. At the end of the analytical measurements, it was observed that aerobic conditions provided higher TCS removal efficiencies compared to the anoxic and anaerobic conditions and almost 75% TCS removal efficiency was achieved under aerobic conditions even in 150 h although TCS was not biodegraded under anoxic and anaerobic conditions within this time schedule. Chen et al. (2011) further stated that only 1% of TCS was transformed into methyl-triclosan at the end of biodegradation under aerobic conditions in the activated sludge system.

Removal of TCS in a biological treatment system was also investigated by Lozano et al. (2013). They found that 97.1% of the initial TCS was removed from the liquid phase of the wastewater treatment system including preliminary treatment, primary treatment, and secondary treatment with nitrogen removal, filtration and disinfection processes respectively. However, when the amount of TCS remaining in the liquid and solid phase are considered together, it was seen that 64.1% of initial TCS was detected in the biosolids due to sorption, and 2.9% of it remained in the effluent water which at the end giving a total 33% removal efficiency as a consequence of biodegradation.

Moreover, Lee et al. (2012) demonstrated that *Sphingopyxis* strain KCY1, one of the wastewater microorganisms, can biologically remove roughly 90% of initial TCS with a concentration of 5 mg/L in one day and after two day, such amount of TCS was wholly biodegraded by this microorganism.

2.2.3 Chemical

Ozone (O_3), agent of the ozonation, is known to react rapidly with wide variety of contaminant in water environment and constitute a promising technique for the removal of TCS which is explained in Section 2.4 thoroughly (Huang, 2010; Mvula and von Sonntag, 2003).

Moreover, chlorination is also the common way of chemical treatment used for the removal of chlorinated organics like TCS. In this regard, Buth et al. (2011)

investigated the chlorine treatment of wastewaters involving TCS for disinfection purposes and the formation of three chlorinated derivatives of TCS (i.e. 4,5-dichloro-2-(2,4-dichlorophenoxy)phenol (4-Cl-TCS), 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol (6-Cl-TCS), and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol (4,6-Cl-TCS)) during the chemical treatment. At the end of the study, they observed that TCS concentration declined dramatically after chlorination; however, there was seen an increase in these chlorinated derivatives of TCS due to the re-formation in the disinfection step. Therefore, the removal of TCS should be considered with the by-chlorination products when the chlorine treatment was utilized as a disinfection process of the treatment plants.

Ferrate (Fe (VI)) oxidation of TCS and corresponding treatment of the aqueous solution was studied by Yang et al. (2011) and complete TCS degradation was accomplished when TCS to ferrate ratio (i.e. stoichiometrically) in the aqueous medium occurred as 1:10. Therefore, ferrate oxidation was said to be the one effective way of eliminating TCS from the waters and wastewaters.

There also exist other researches in the literature focusing on the treatment of TCS by means of permanganate oxidation. The study conducted by Jiang et al. (2009) examined the removal of 10 μg/L TCS from wastewater and river water via permanganate oxidation of different oxidant concentrations in the range of 0.5-4 mg/L during a contact time of 10 min at the natural pHs of the aforesaid water samples. The results of the study indicated that permanganate concentration of 2 mg/L was adequate to achieve TCS removal around 70-80% within a mentioned contact time.

Fenton oxidation is another chemical oxidation option for the treatment of TCS containing waters. It has proven to be an efficient chemical treatment process especially for the cases requiring high removal rates of the contaminants and Munoz et al. (2012) demonstrated in their study that complete degradation of TCS (i.e. initially 10 mg/L) can be reached even in the time period less than 1 h when the temperature of the aqueous solution was 25°C and the concentration of the iron and hydrogen peroxide were 1 mg/L and 5 mg/L, respectively.

Conductive diamond electrochemical-oxidation has been reported to be the recent and effective technology for the removal of chlorinated organic compounds from the aqueous environment (Boye et al., 2006; Brillas et al., 2010; Polcaro et al., 2004; Wang and Li, 2012). When this technology is coupled with ultrasound, it becomes conductive diamond sono-electrochemical oxidation and gives higher removal efficiencies by promoting enhanced mass transfer rate and increasing the rate of decomposition (Lorimer et al., 2004; Sanchez-Carretero et al., 2011). In the recent study conducted by Vidales et al. (2013), conductive diamond electrochemical-oxidation and conductive diamond sono-electrochemical oxidation were investigated for the treatment of TCS including waters within the concentration range between 0.1 mg/L and 100 mg/L. They measured TCS concentration by HPLC device and obtained effluent TCS concentrations lower than the limit of detection value of the device, indicating the entire degradation of TCS thanks to these recent techniques. They also observed the formation of the intermediates of the parent compound; mainly, catechol, chlorohydroquinone, 4-chlorocatechol, acetic acid and dichloroacetic acid during the treatment by conductive diamond electrochemical-oxidation and conductive diamond sono-electrochemical oxidation.

2.3 Ozonation Process

Ozonation is a promising process that has been traditionally applied over the century with the purpose of the removal of wide array of contaminants from the water environment through ozone triatomic molecule consists of three oxygen atoms. (Huang, 2010; Metzger, 2009).

Ozone, agent of the ozonation having very strong oxidizing property, is highly unstable gas that quickly decomposes in water with an average half-life of 20 to 30 min at 20°C. However, half-life of it depends on the ozone reactive impurities in water; therefore, it can be as short as even a second in contaminated water while it can be about an hour in the clean one. In this regard, as it can rapidly decompose and cannot be stored, ozone should be generated at the point of the application (Huang, 2010). Most of the time only the slight part of it reacts with solutes and another part may even decompose before reaction. This decomposition is catalyzed by hydroxide ions or other solutes in solution (Hoigne´ and Bader, 1983). Moreover, ozone dissolves ten times better than oxygen in water and its solubility decrease with an increase of water temperature (Graham, 1997).

Considering the historical development process, ozone was first discovered in 1838 by Friedrich Schonbein and proposed as a chemical substance (Rubin, 2001). It was started to be used for the tap water treatment purposes in Holland (1880's), Nice (1907) and Saint Petersburg (1910). In 1997, following the recognition of safe status for ozone utilization in bottled water by US Food and Drug Administration, investigations on this process has increased and in consequence, its applications for the drinking water treatment increased, as well (Majewski, 2012; Landlais et al., 1991). One of the other reasons that ozone became so popular in water applications within that period was the limitations and even restrictions of using chlorine especially in drinking water treatment processes as a disinfectant due to the trihalomethanes (THMs) formation. As ozone does not cause the formation of any THMs and has high efficiency for killing microorganisms and oxidation of the contaminants, it was preferred to be used instead. In US, 1998, the maximum contaminant level of the THMs were lowered from 100 to 80μg/L by entering into force of a new legislation which induce difficulties for meeting regulatory requirements and impel the researchers to find out new applications. This being the case, in 1997 the number of the drinking water plants using ozone was nearly 150 while it was almost doubled to more than 260 plants in US (Richardson et al., 1999). It was also approved by US Food and Drug Administration to be used as an antimicrobial agent for the storage and processing of meats including meat and poultry in 2001 (Fan et al., 2007). The treatment applications with ozone in drinking water and wastewater treatment plants, especially at the head of treatment plant (pre-oxidation) and after sedimentation, have still been increasing enormously both in number and diversity day by day in worldwide (Huang, 2010; EPA, 1999).

Having said that, ozone applications has begun to be used commonly for drinking and thereby for surface water treatments in 1990s and still continues to be used in a widespread manner throughout the world and attracts researchers’ interest and thereby lots of investigations has been conducted on. Being a strongly powerful oxidant (high redox potential of -2.07 V relative to chlorine having -1.36 V and oxygen -0.40 V) and readily decomposed to the free radicals in aqueous solution which makes it broadly applicable, it has been used traditionally for disinfection applications and for the COD and color removal, taste and odor control and reduction of the suspended solids and turbidity in water (Von Gunten, 2003a; Langlais et al., 1991; Kim et al., 1999; URL 9). Besides, ozone is considered as one of the most effective techniques and preferred to be used for the removal of micropollutants from different structural classes especially for emerging ones (i.e. endocrine disruptor compounds (EDCs), pesticides, persistent organic pollutants (POPs), pharmaceutical and personal care products (PPCPs), antimicrobial and pharmaceutical compounds etc.) from the water environment which are became prominent in the environmental research studies in recent years (Huang, 2010; Wert et al., 2009; Gottschalk et al., 2000)

In the scope of the studies most recently increased to be performed within last decades, Dodd et al. (2009) declares that ozone treatment is popular with rapid oxidation and responsible for the ≥99% deactivation of a wide variety of antibacterial compounds as well as the triclosan (TCS). In one of the study conducted by Fentela et al. (2011) states that most of the pharmaceuticals, which are even regarded as the most persistent ones (i.e. carbamazepine) in the environment and highly resistant to the biodegradation, did not survive after the ozonation treatment and even complete removal (≥99%) are achieved for some compounds (i.e. bisoprolol, betaxolol, salbutamol, losartan) in drinking water treatment. Moreover, pesticides are almost completely degraded with different removal rates by the means of ozonation application (Maldonado et al., 2006; Fontela et al., 2011). According to another study, ozonation removed over 80% of the pesticides, PPCPs and EDCs in natural waters (Broseus et al, 2009). Table 3 summarizes the removal of trace organics during ozonation in drinking water treatment plants.

Table 3. Removal rates of different substances during ozonation process in drinking water treatment plants (Gottschalk et al., 2000)

Substances	**Degree of removal, Range in %**	**Remarks**
Taste and odor	20-90	Source specific
Methylisoborneol geosmin	40-95	Improvements by AOPs: O_3/H_2O_2 and O_3UV
Alkenes	<10	-
Alkenes and chlorinated alkenes	10-100	Chlorine content is important, AOP support oxidation
Aromatics and chloroaromatics	30-100	Highly halogenated phenols are more difficult to oxidize
Aldehydes, alcohols, carbonic acids	Low	Typical products of ozonation, easily biodegradable
N-containing aliphatic and aromatics	0-50	AOP may increase oxidation rate
Pesticides	0-80	Very specific to substance
Polyaromatic hydrocarbons	High, up to 100	-

2.3.1 The Mechanism of Ozone Action

It is well known and considered in a great deal of the studies in the literature that ozone reacts with organic and inorganic compounds through direct reaction with molecular ozone or indirect reaction through free radicals, commonly with hydroxyl radicals ($^{\cdot}OH$), produced by decomposition of molecular ozone during the reaction and immediately react with solutes, or combination of thereof in water. Figure 3 gives the general structure of the mentioned reactions occurs during ozonation process. The oxidation pathway of ozonation is rather complex that could largely regulated by the water matrix especially type and content of naturally organic matters, alkalinity, pH, nature and structure of the reactants and other factors. In general, these two pathways compete for the substrate. Compared to the hydroxyl radical oxidation, direct oxidation with ozone is relatively slow but its concentration is relatively higher (EPA, 1999).

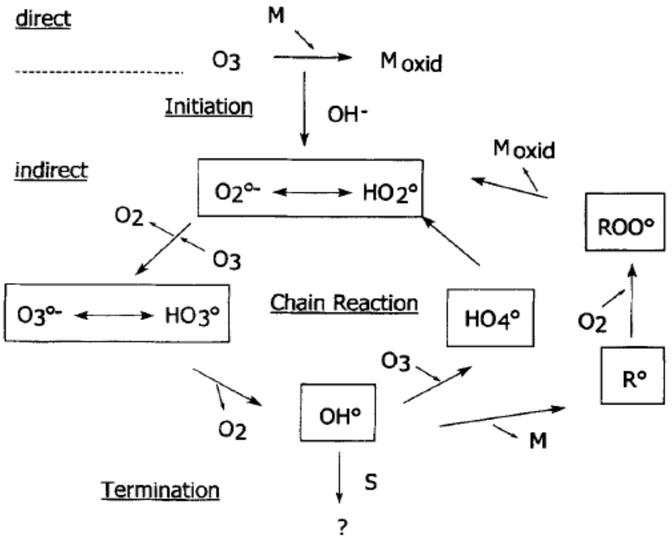


Figure 3. Mechanism of the ozone action (Gottschalk et al., 2000)

The direct oxidation of molecular ozone with solutes occurs selectively with slow degradation kinetics rate constants (1.0-10^3 M^{-1} s^{-1}). It is mainly attributed to react with compounds having unsaturated bonds within its structure (i.e. amino and aliphatic moieties, activated aromatic compounds, sulfides, amines, etc.) (Gottschalk et al., 2000; Hoigne´ and Bader, 1983). Especially, ozone reacts effectively with certain types of electron reach aromatic compounds carrying electron supplying substituent such as hydroxyl group in phenol. As an illustration, the oxidation of the phenol with ozone is depicted in Figure 4. Direct oxidation with molecular ozone dominates the system under acidic conditions (pH<4) (EPA, 1999).

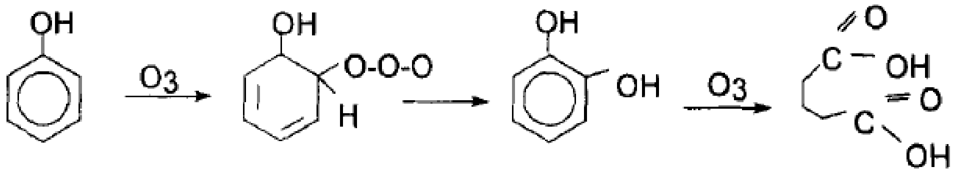


Figure 4. Oxidation of phenol (Gottschalk et al., 2000)

As deducted from Figure 4, extraordinarily reactive OH radical, which is pronounced among the most reactive oxidizing agent in water with the reaction rates on the order of 10^8-10^{13} M^{-1} s^{-1} and characterized by nonselective oxidant, is formed as a secondary oxidant by means of the decomposition of ozone with hydroxide ions and other solutes via radical chain reactions in water (Hoigne´ and Bader, 1983a; Gottschalk et al., 2000). OH radical oxides the compounds indiscriminately and since it is highly reactive, half-life of it is on the order of microseconds and can never reach levels above 10^{-12} M (EPA, 1999; Gottschalk et al., 2000; Von Gunten, 2003a). In general, ozone refractory compounds (i.e. atrazine, diazepam, iopromide etc.) are eliminated by the hydroxyl oxidation in the water.

pH and alkalinity of the solution plays an important role for the formation of OH radicals in ozonation process. In this manner, under the conditions that high pH of water (pH>10), exposure to UV, or addition of hydrogen peroxide (since then can also be called as AOP) the hydroxyl oxidation dominates the ozonation process (EPA, 1999). In drinking water treatment, hydroxyl radical are preferred to oxidize ozone resistant aromatic compounds and chlorinated solvents such as tri- and tetrachloroethane (Von Gunten, 2003a). However, this second pathway oxidation may not work in conditions that ozonation performed at very low pH values or in the presence of high concentrations of solutes that scavenge hydroxyl radicals in competitive reactions (Hoigne´ and Bader, 1983a). Since surface waters have neutral pH (~7-8) direct and indirect oxidations play an important role for the ozonation process (Gottschalk et al., 2000)

Moreover, Von Gunten (2003a) indicates that NOM in water leads to diminish the ozone, and thereby facilitate to formation of OH radicals as well. It is further explained that NOM reacts with OH radicals and forms superoxide radicals that decompose existing ozone in water.

2.3.2 Ozone Production

There are many ways of producing ozone and each has different properties in terms of the sources involved in the ozone production, the principles laid down in their operation and the common usage areas (Gottschalk et al., 2000). Ozone generation methods and their major differences were represented in Table 4.

Table 4. Different ozone production methods and their comparison (Gottschalk et al., 2000)

Ozone Production Method	**Principle of Operation**	**Source of Ozone**	**Usage Area**
Electrical	Electrical discharge	Air or oxygen	Most known method and applicable both in lab-scale and full-scale studies
Electrochemical	Electrolysis	Highly purified water	Mostly for pure water applications both in lab-scale and small industrial scale studies
Photochemical	Irradiation	Air and water which has the quality either as drinking water or is highly purified means	Recent method and applicable both in lab-scale and full-scale studies
Radiation chemistry	Radioactive γ-rays, X-rays	Highly purified water	Not commonly used, applications in experimental studies
Thermal	Light arc ionization	Water	Not commonly used, applications in experimental studies

As indicated in Table 4, electrical discharge is the most common method applied in the ozone production among the other methods and air or oxygen is the potential source of the produced ozone in this method. Electrolysis is the second widespread method after electrical discharge and they are both utilized in the laboratory scale and full scale applications (Gottschalk et al., 2000).

2.3.3 Factors Affecting the Treatment Efficiency of Ozone

As indicated, ozone is quite unstable in water. Its decomposition is a complex process that largely depends on the quality of source water and thereby on water matrix, pH, temperature, organic solutes, inorganic constituents and its alkalinity

(Von Gunten, 2003a; Hoigne´ and Bader, 1975). Half life of it also depends on the ozone reactive impurities in water; therefore, it can be as short as even a second in contaminated water while it can be about an hour in the clean one (Huang, 2010). In this regard, in the scope of the assessment of the treatment efficiency of the ozone in water, mentioned factors needs to be taken into account. The following parts describe the effects of different ozone dose, pH and water matrix on the treatment efficiency.

2.3.3.1 Effects of Ozone Dose on Treatment Efficiency

Efficiency of ozone treatment depends on the applied ozone dose in water. Expectedly, as ozone concentration increase in solution, its oxidation rate of the substrate increases, as well (Gottschalk et al., 2000). To illustrate, Gottschalk et al. (2000) and Adams Randtke (1992) found a linear correlation between the oxidation rate of atrazine (organic substrate) and liquid ozone concentration in drinking water ozonation studies. In similar, Huang (2010), observed higher removal of target chemicals by applying higher ozone doses. In the study of Huang, three different ozone doses (i.e. 5.9, 8.9, 16.6 mg/L) were applied to the four different contaminants and removal rates of 5.9 mg/L ozone (74.4, 74.2, 53.3, 35.6 %) increased to the (97.9, 96.7, 75.9, 44.9 %, respectively) at the 16.6 mg/L ozone dose. It was also considered in the same study that although increase in removal proportional to the increase of the ozone concentration, unlimited increase of ozone could be unwarranted and cost needs to be considered. Therefore, it is crucial to determine required ozone dose properly not only for the removal of the contaminants but also substantial for the economical aspect (Soares et al., 2006).

Beside applied dose, specific ozone amount (mg O_3/mg compound) required to be applied for the removal of target pollutants from water environment has an important role in ozone treatment applications. In this regard, Mozia et al. (2006) indicates the most advisable configuration for the preliminary ozonation with dose of 0.4 mg ozone/ mg TOC. 0.2 to 1.6 mg ozone per mg carbon (Singer et al., 1989; Georgeson and Karimi, 1988) and 2.08 mol ozone to 1 mol phenol at pH 7 are the other values retrieved from the literature.

2.3.3.2 Effects of pH on Treatment Efficiency

Ozone dissolves in water at pH values lower than 7. Under this condition, it does not react with water and stands ready for the reaction as in the form of molecules (Gordon, 1995). It is more stable in the water at low pH values. However, increase of the pH leads to spontaneous decomposition of ozone and thereby the stability of it decrease owing to the fact that hydroxyl ions increases in solution and ozone reacts with them resulting the formation of free hydroxyl radicals by chain reactions that may further react with organic compounds or existing ozone (Chittrakorn, 2008; Gordon, 1995). In this regard, the decomposition of ozone is catalyzed by the hydroxide ion in solution. At lower pH (6-7), molecular ozone predominates over hydroxyl radicals in the ozonation process while at higher pH, hydroxyl radicals dominate the system by the formation of chain reactions. In the study conducted by Hoigne´ and Bader (1983a), half life of the ozone showed about 200-fold decreases when pH changed from 4 to 10. Moreover, at pH 8, about half of the ozone given into the system decomposed to the different forms and to oxygen in 10 min (Gordon, 1995). In another study, ozonation of phenol was performed at pH values of 3, 7 and 10, and reaction rate of ozone with phenol increased as pH increases (Mvula and von Sonntag, 2003). Similarly, Hoigne´ and Bader (1983b) indicates, the reaction rate constants of phenol and phenolic compounds (i.e. p-nitrophenol, o-chlorophenol) increases by a factor of 10 per pH unit increment.

Although decomposition of ozone is increased with the increased pH, it is reported by El-Din et al. (2006) that oxidation of the compounds in solution increased as the formation of hydroxyl radicals, more reactive compared to ozone increased. According to the results represented in the literature related with oxidation of the micropollutants indicates that increasing pH ensures increasing the reaction rate of the micropollutants (Gottschalk et al., 2000). In drinking water treatment, conventional ozonation process is converted to the AOP by increasing the pH in order to increase the oxidation capacity and make it faster. However, increasing pH in the treatment plants could be costly that should also be considered (Von Gunten, 2003a).

Arrangement of the solution pH needs to be done based on the oxidation characteristic of the target compound. If it could be oxidized directly with ozone, treatment could be performed at neutral pH. Otherwise, in the condition that target compound is ozone-resistant, treatment at higher pH could be applied. To illustrate, EDCs and PPCPs is oxidized with both direct (ozone molecule) and indirect oxidation (radicals) at pH value of 7; therefore, ozonation at pH 7 in treatment plants are pronounced as more available preferable choice (Huang, 2010). Furthermore, high oxidation levels of OH radicals could be counteracted by the strong scavenger potential of carbonate when pH increases above 8 (Gottschalk et al., 2000).

2.3.3.3 Effects of Water Matrix on Treatment Efficiency

Presence of inorganic carbon in the water matrix affects the total rate of reaction through the behaving like a scavenger for the hydroxyl radicals in the solution although it does not directly give reactions with ozone (Hoigne´ et al., 1985). The increase in the inorganic carbon content of the wastewater results in the decrease in the available hydroxyl radicals for the oxidation of the desired organic pollutant which then leading to the decrease in the ozone decay and reducing the total rate of the reaction (Gottschalk et al., 2000).

Organic carbon content of water has also effects on the ozone treatment efficiency by acting as a scavenger or a promoter, as well. The type and amount of organic carbon present designates its behavior as either a scavenger or a promoter (Staehelin and Hoigne´, 1983a; Glaze and Kang, 1990; Xiong and Legube, 1991); therefore, the characteristic and available concentration of the organic carbon is of great importance in order to assess its behavior in the water environment. Humic acid is the major organic carbon source existing in natural waters and it influences the treatment efficiency of ozonation process. In the study conducted by Xiong and Graham (1992), it was found that ozone oxidation rate declined seriously with the increase of humic acid concentration in the pure water during the ozonation of atrazine at pH of 7.5. Katsoyiannis et al. (2011) also demonstrated that target micropollutants and dissolved organic matter in the water matrix compete to give reactions with ozone and dissolved organics completely affect the removal of the micropollutants by the applied ozone treatment. Furthermore, another study by Suarez et al. (2007) reported the complete elimination of TCS when the effluent water of conventional wastewater treatment plant having 7.5 mg/L dissolved organic content was treated by ozone with a concentration of 4 mg/L; however, only 58% TCS removal efficiency was achieved when the wastewater with a dissolved organic matter content of 12.4 mg/L was subjected to 6 mg/L ozone dose. That study briefly explains the effect of organic matters in the water matrix on the removal of TCS by ozone treatment.

2.4 Ozonation of Triclosan

Considering the problem posing nature of the micropollutants in water, especially phenolic ones and its derivatives, methods to oxidize these compounds is trend research area and it has been discussed in large number of studies (Mvula and von Sonntag, 2003)

Many investigations show that ozone treatment is effective application for oxidizing activated organic chemicals containing carbon–carbon double bonds, olefinic double bonds, acetylenic triple bonds, aromatic compounds, phenols, polycyclic aromatics, heterocyclics, carbon–nitrogen double bonds, carbon– hydrogen bonds, silicon-hydrogen and carbon-metal bonds (Turhan and Turgut, 2009). Thanks to the chemical structure of the TCS as an aromatic compound including phenol and dichlorophenoxyl moieties, there are various studies that indicates high removal percentages of the TCS (k_{O3}: 1.3×10^{3} M^{-1} s^{-1}) by ozonation (Suarez et al, 2007; von Sonntag and von Gunten, 2012). In the study conducted by Suarez et al. (2007) on the oxidation of TCS by ozone from municipal wastewater, applying 4 mg/L of ozone dose ensured complete depletion of the TCS in respect to the wastewater treatment plants effluents (pH:7.9, DOC:7.5 mg/L) and contribution of $^{\cdot}OH$ oxidation to total observed triclosan losses was accounted for just 35%. It was also concluded in called study that contribution of $^{\cdot}OH$ in the process of triclosan oxidation is low and as the ozone dose applied increased, apparent contribution of OH radical to the overall oxidation of TCS in waters decreased. Moreover, in one of the other study, TCS was attributed as readily degradable by ozonation that at the end of the 24 min ozonation, complete removal of TCS was obtained applying 16.6 mg/L ozone dose to 6.5 mg/L of initial TCS in distilled water (Huang, 2010). In the same study, within another set of experiments, applying 6 min ozone with 8.9 mg/L dose to 8.6 mg/L initial TCS bearing distilled water get >98% removal of TCS. TCS and ozone concentrations and obtained results in respect to these, in the studies relevant with ozonation of TCS are compiled in Table 5.

Table 5. Overview of the ozonation applications for TCS

Initial TCS Concentration	**Applied ozone dose**		**Removal Percentage (%)**	**Measuring Instrument**	**Source**
	(mg/L)	**(mg/h)**			
8.6 mg/L	8.9	5.76	>98.0	GC-MS	Huang, 2010
6.5 mg/L	16.6		100.0		
246 ng/L	16.3	3.49	78.0	GC-MS	Rosal et al., 2010
47 ng/L	7.8	-	99.0	LC-MS/MS	Snyder et al., 2006
48 ng/L	10.0	73.20	87.0	TD-GC-MS*	Hernandes-Leal et al., 2011
150 µg/L	5.0	-	100.0	HPLC-UV	Suarez et al., 2007
1.59 µg/L	3.0	180.0	93.0	-	Drury and Snyder, 2005
	8.0	480.0	95.5	-	
4.5 mg/L	1.1	60.0	94.0	GC-MS	Chen et al., 2012

*Thermal desorption gas chromatography

More generally, in the event that ozone doses applied greater than 1 mg/L at neutral pH, hydroxyl radical oxidation of the TCS was accounted for only 35% of its removal in wastewater treatment (Suarez et al., 2007). These assessments clarifies that oxidation of TCS is governed by primarily via the direct oxidation of ozone molecule. However, as it has indiscriminate reactivity, OH oxidizes not only the phenol but also dichlorophenoxyl ring of the TCS (Dodd et al., 2009).

Mvula and von Sonntag (2003), performed mechanistically-oriented study for the ozonation of the TCS, explains rapid reaction of TCS with ozone by most probably ortho- and para- to the hydroxyl group of phenol ring (Figure 5). Suarez et al. (2007) also support this hypothesis that ozone reacts initially with TCS through it phenol moiety. On the other hand, Levy et al. (1999) indicates that antibacterial activity of the TCS is primarily provided by its phenol ring; therefore, the oxidation of the phenol ring or its deterioration is expected to reduce or eliminate its target-specific antibacterial activity. Moreover, according to the Dodd et al. (2009), ozone reacts rapidly with a wide variety of antibacterial, and it eliminates TCS's antibacterial activity by attacking the phenol ring of it. However, characterization of reaction pathway of ozonation of TCS is still unclear that needs be examined further (Chen et al., 2012).

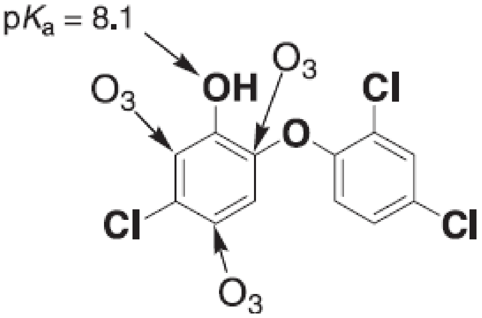


Figure 5. Triclosan structure and probable sites of initial ozone attack (Suarez et al., 2007).

In brief, outcomes of the aforementioned studies appear to constitute particularly promising means of applying the ozonation process for the removal of the TCS from surface water.

2.4.1 Ozonation By-products

Although ozone is being commonly used at many drinking water treatment plants over the world, there have been only few studies examining the by-product formations (Richardson et al, 1999). In the studies done for examining the ozonation of water, it has been mostly focused on the removal ratios of target compounds and its reaction kinetics. However, within the scope of the chemical treatment of drinking waters, oxidation of target compound as well as the matrix components present in water lead to formation of by-products. Being the most efficient chemical and thereby commonly used in the drinking water treatment, ozone is also responsible for the formation of ozonation by-product (Von Gunten, 2003a). In the literature, ozone treatment process is accompanied by the formation of by-products. Sundrarajan et al. (2007) supportively indicates that ozonation does not yield complete mineralization to H_2O and CO_2, it cause to formation of oxidation products such as aldehydes, organic acids and ketones. In another study conducted by Richardsson et al. (1999), it is stated that aldehydes, ketones and carboxylic acids are the major classes of by-products observed. In this regard, bromate is only ozonation by-products regulated in drinking water (IARC, 2009; Von Gunten, 2003b). The European Union and the EPA set a drinking water standard as 10 μg/L (EU, 1998; EPA, 1998).

On the other hand, there is only one study found examining the ozonation by-products of TCS that 2,4 dichlorophenol, 4-chlorocatechol, monohydroxy-triclosan and dihydroxy-triclosan are demonstrated as transformation products of TCS (Chen et al., 2012). Moreover, in another study performed not with TCS but relevant due to dealing with the phenols, hydroquinone, catechol, 1,4-benzoquinone, cis,cis-muconic acid, 2,4-dihydroxybiphenyl and 4,4-dihydroxybiphenyl are the identified ozonation by-products (Mvula and von Sonntag, 2003).

Besides identifying the ozonation by-products, it is also essential to be known whether by-products are more or less harmful than the parent compound. Because it is the well-known fact that, disinfection by-products occurred during oxidation processes such as trihalomethanes (THMs) and haloacetic acid (HAAs) are harmful to the environment, even some of them cause cancer to the animals and regulated by the legislations (Richardson et al., 2007; Komulainen et al., 1997). As indicated before, bromate is regulated by EU and EPA due to its potential carcinogenicity. It attracts the attention and optimization of ozonation process required for minimizing its formation (Sobhani et al., 2012). Therefore, effects of ozonation by-products of

TCS are substantial to be evaluated with respect to the quality of the environment and its health. In this regard, Chen et al. (2012) states that 2,4-dichlorophenol demonstrates lower genotoxic effects than its parent compound TCS but it is classified as toxic to aquatic organism. In the same study, the other transformation by-products could not be evaluated.

2.4.2 Reaction Kinetics

Reaction kinetics of ozone with the organic substances is reported to be bimolecular and can be best described by second-order reaction kinetics (Hoigne´, 1998; Hoigne´ and Bader, 1983b). For instance, reaction kinetics of ozonation of one of the pharmaceutical compounds ranitidine (Rivas et. al., 2009) and one of the pesticides atrazine (Luis et al., 2011) was worked with second-order rate constants. In the study conducted by Suarez et al. (2007), kinetics of TCS with ozone was investigated by using second-order reaction kinetics, as well. Therefore, the reaction kinetics of TCS with ozone is expressed with the Equation 1.

$$\frac{\mathrm{d}\,[\mathrm{triclosan}]}{\mathrm{dt}} = -\mathrm{k}_{\mathrm{app},\mathrm{O3}}[\mathrm{triclosan}][\mathrm{O}_3] \qquad \text{(Eq. 1)}$$

where;

$\mathrm{k}_{\mathrm{app},\mathrm{O3}}$: Apparent second-order rate constant for the reaction at a certain pH (volume/(mass × time))

[triclosan] : TCS concentration (mass/volume)

However, when the ozone concentration in the water solution is much more excess compared to that of target compound, the reaction rate depended mainly on their own concentration in the system thereby follows the pseudo first-order kinetics, as well (Huang, 2010). As ozone was given in excess amount in a continuing manner in the ozonation experiments, pseudo first-order kinetics are eligible to be studied for TCS. Then, the reaction kinetics can be explained by the following formula given in Equation 2.

$$\frac{\mathrm{d}\,[\mathrm{triclosan}]}{\mathrm{dt}} = -\mathrm{k}_{\mathrm{app},\mathrm{O3}}[\mathrm{triclosan}] \qquad \text{(Eq. 2)}$$

where;

$k_{app,O3}$: Pseudo first-order rate constant for the reaction at a certain pH when O_3 is excess in the aqueous solution ($time^{-1}$)

[triclosan] : TCS concentration (mass/volume)

CHAPTER 3

MATERIALS AND EXPERIMENTAL METHODS

3.1 Water Samples and Sample Preparation

Water samples used during the ozonation experiments were Milli-Q water (Millipore ultra-pure water system; Millipore) and natural surface water (pH: 7.3; TDS; 776 mg/L; TOC: 5.2 mg/L) collected from the Kesikköprü Reservoir located near Ankara, Turkey (Figure 6). Milli-Q water served as control source water to understand the factors controlling ozone decomposition by excluding the natural water matrix effect. Surface water was taken into 5 L amber glass bottles that were cleaned prior to sampling to eliminate any associated labware interferences (i.e. impurities). Cleaning was carried out by means of washing the sampling bottles with a powdered, concentrated and anionic detergent called Alconox (Sigma Aldrich), rinsing with hot tap water and then two times rinsing with Milli-Q water, and final rinsing with HPLC grade methanol. Followingly, the sampling bottles were dried at 105°C for one hour before the usage.

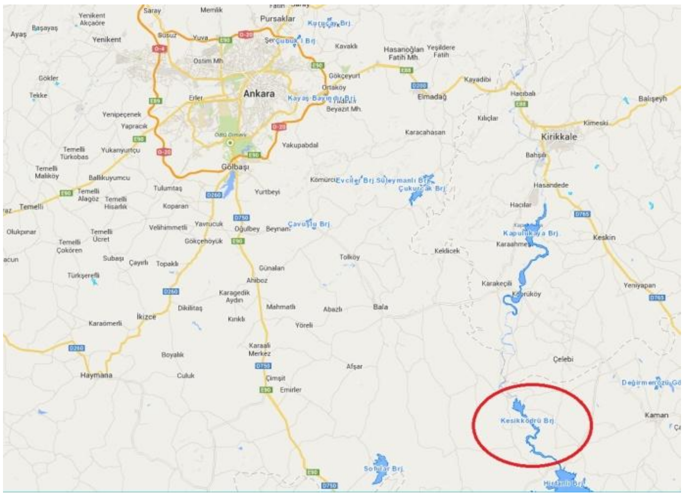


Figure 6. Location of Kesikköprü Reservoir

Following the preparation of the glass bottles for the sampling period, surface water sample was taken into the bottles on-site and brought to the laboratory for further analysis and experiments. Prior to commence each experiments, surface water sample was passed through 0.45 µm pore sized filter via vacuum filtration in order to remove impurities that might lead to clogging of HPLC-UV column and hence to avoid erroneous measurements during the analysis.

During the study, source waters were spiked with the desired amounts of TCS prior to each experiment, using TCS stock solution. TCS stock solution (200 mg/L) was prepared in methanol unless otherwise stated using 100 mL volumetric flask made of borosilicate glass (Pyrex) and stored in refrigerator at +4°C in dark.

3.2 Experimental Set Up

3.2.1 Ozone Generator

Ozone was supplied by means of ozone generator (WEDECO OCS-Modular 4 HC - AirSep AS 12) providing 4 g/h maximum ozone production capacity and having 0.5 bar operation pressure (Figure 7). The width, depth and height of the ozone generator are 600 mm, 210 mm and 600 mm, respectively. Process gas was oxygen and gas flow could be arranged between 10 L/h to 140 L/h with a rated capacity of 4 g/h.

In order to get a desired ozone dose to be supplied through the reactor, gas flow and piezometric buttons were adjusted according to the generator's performance curve given in Appendix A.

Figure 7. Ozone generator

Working principle of this lab-scale ozone generator is based on the Corona Discharge method which is a cost effective method and does not require an oxygen source other than air. In this method, ozone is produced by oxygen by means of electrical discharge. As can be seen from the configuration of the method given Figure 8, oxygen produced by AirSep AS 12 equipment move along the discharge gap and in that area low current electrical discharge and relatively high voltage gradient are provided and in this way oxygen double bond is ruptured and forms two oxygen radicals. And then these radicals combine with oxygen and forms ozone. Electrical discharge is controlled by dielectric bar and excessive heat caused by the process is cooled by cooling water being drilled from the separate water tank (Netzwer and Rice, 1982).

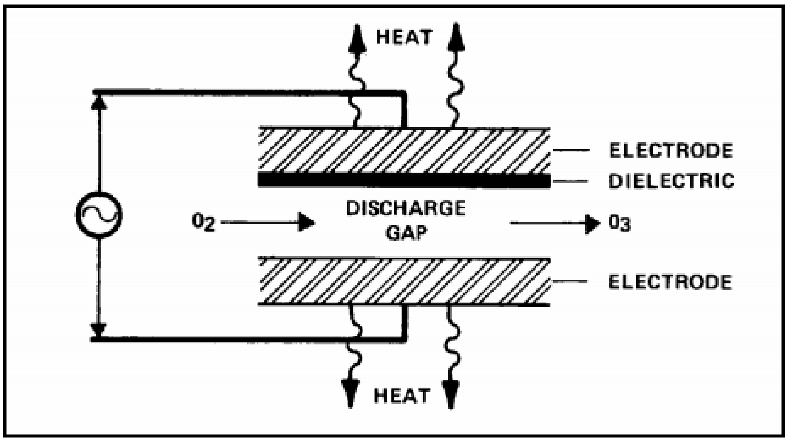


Figure 8. Corona discharge cell configuration (Netzwer and Rice, 1982)

3.2.2 Ozonation Reactor

Ozonation reactor made up of borosilicate glass (Pyrex) (1.2 L), cylinder having 10 cm diameter and 0.8 m length with two ports for inlet and outlet gas flow was used (Figure 9). The glass reactor was dedicatedly preferred to get rid of a potential of adsorption of TCS into the labware due to its highly hydrophobic nature. Ozone gas was given from the top of the reactor through a sintered glass plate diffuser. Ozone concentration supplied to the reactor was adjusted and monitored by means of the potentiometer located on the panel of the ozone generator and the performance curve provided by the manufacturer for the operating pressure of 0.5 bar.

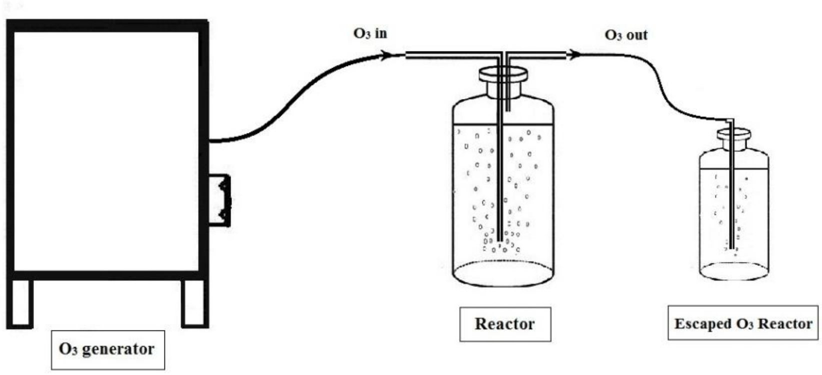


Figure 9. Ozonation set-up

The outlet of the reactor was linked with an another small type glass reactor (500 mL) containing %2 potassium iodide solution (KI) with the purpose of determining the escaped (unreacted ozone) in the system which is crucial for constructing a mass balance and, in a way, for understanding the reaction mechanism. Ozone reactor is also demonstrated in Figure 10.

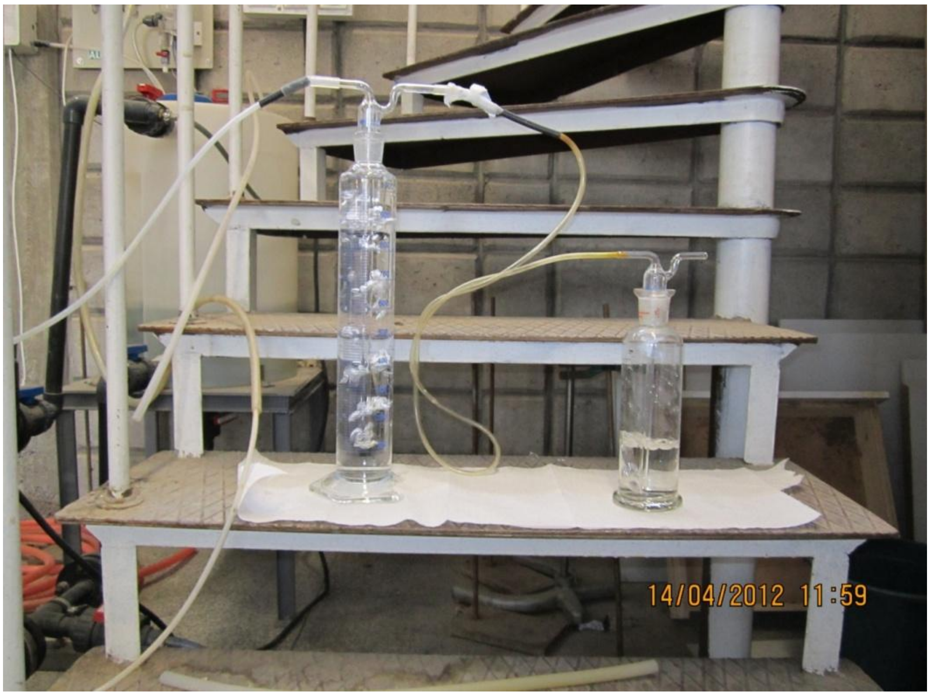


Figure 10. Ozonation reactors

3.3 Experimental Methods

3.3.1 Adsorption Experiments

Prior to commence the ozonation test, considering the highly hydrophobic nature of TCS, it was deemed crucial to investigate and, in a way, to eliminate the effect of its sorption onto the labware, in order to get the true understandings of the reaction going on. In this sense, as a part of ozonation system components, glass reactor, and tubing immersed into the reactor, supposed to sorb TCS during experiments, were examined through series of experiments for their TCS sorption capacities. The description of these experiments is summarized in Table 6.

Table 6. Experimental sets for TCS sorption

Experimental Set	**Reactor**	**Tubing**	**Intention**
1	Glass	Plastic	To observe the behavior of TCS in reactors and sorption onto the inner surface of the reactor
2	Glass	Plastic	To observe the sorption on tubing
3	Glass	Plastic & Glass	To determine the amount of TCS adsorbed onto plastic tubing and find the proper tubing for the subsequent ozonation experiments

During the experiments, Erlenmeyer flasks, made with same material of glass reactor as borosilicate (Pyrex), with 500 mL of volume were used. Instead of ozone, air was supplied either via plastic (PET, polyethylene terephthalate) or glass tubing (Pyrex) by small air pumps in order to simulate mixing condition (e.g. air bubbles, turbulence) apparent in ozonation experiments. Glass tubing had a diameter of 0.5 cm and length of 36 cm, whereas plastic one has 0.6 cm and 72 cm respectively. Length of the each tubing immersed in the Erlenmeyer flasks was set same as 12 cm.

Before starting the each set of experiments, Erlenmeyer flasks and tubing were washed with Alconox detergent and then rinsed five times with tap water and then with Milli-Q water. Later on, they were rinsed with methanol. Erlenmenyer flasks were dried at 105°C in oven.

Firstly, three different initial TCS concentration (i.e. 3, 5 and 10 mg/L) were spiked into three identical Erlenmeyer flasks filled with 500 mL of Milli-Q water (Set 1). Plastic tubings were immersed into each flask and thereby air was supplied to the reactors by air pumps for a duration of 5 h. The flasks were wrapped with aluminum foil in order to prevent possible TCS volatilization and degradation by photolysis. During the 5 h period of experiments, samples were taken from the reactor with 1 hour intervals and then analyzed for their TCS concentration by UV-VIS spectrophotometry. At the end of the experiments, the flasks were completely withdrawn and washed with about 50 mL of methanol with the purpose of analyzing the sorption of TCS onto the inner walls of glass reactors. The aim of this set was to observe the TCS behavior (i.e. abatement in the system and sorption on the inner surface of the flask) in flasks.

Considering the results of the first set, set 2 experiments were conducted in order to observe whether it sorbed on the tubing immersed into the reactor, two identical Erlenmeyer flasks as reactor were prepared and filled with 500 mL of Milli-Q water and spiked with 5 mg/L TCS. One of them was aerated with plastic tubing and the other one was not aerated and so no tubing immersed into it during the entire experiment. TCS in reactors was monitored with 1 hour intervals. At the end of experiment, TCS adsorption onto the inner surfaces of flasks was determined.

In last set of experiments (Set 3) conducted to observe the effect of tubing material on sorption and, in a way, to determine the proper tubing to be used ozonation experiments, two identical Erlenmeyer flasks filled with Milli-Q water bearing 5 mg/L of TCS were used, one of which was aerated with plastic tubing and the other by glass tubing (i.e. glass pipette). At the end of 5 h, flasks were washed with 50 mL of methanol. The inner and outer sides of tubings were also rinsed with methanol. Gathering the rinsed solution into sampling tubes, TCS adsorbed on both wall of flasks and tubings were analyzed.

All the experiments were performed in twice at a room temperature of 20 ± 2°C and average of the results was taken into account.

3.3.2 Photodegradation Experiments

The literature is full of studies indicating the degradation of TCS by the sun and artificial lights. Therefore, photodegradation experiments were conducted with Milli-Q water spiked with 5 mg/L TCS concentration in order to test whether TCS was photodegraded under laboratory condition. For that aim, 3 identical glass reactors (i.e. 1 L Erlenmeyer flasks) of each containing 500 mL Milli-Q water were operated by supplying air into them via small air pumps through plastic tubings and TCS concentration was monitored hourly by UV-VIS spectrophotometer during 5 hour time period. In these experiments, 3 different cases were studied for reactors that were fully coated with aluminum foil, only reactor body coated and its top was open, and without any coating.

3.3.3 Ozonation of Triclosan

In the scope of the ozonation experiments done in this study, although not present in such amounts in surface waters, it was preferred to use relatively high initial TCS concentrations (i.e. 1, 3, 5 mg/L) to sustain its accurate and precise detectability with applied measuring method of HPLC-UV even after 30 min of ozonation and to enable to calculate the removal ratio of TCS and observe its fate, as well. Huang (2010) have an explanation for the effect of high initial concentration of compounds on the removal efficiency that the high initial concentrations nearly 100 times greater than the low initial concentrations had a much less pronounced effect on removal percentages with a difference that was no more than 10%. This situation also support to this study.

In each experiment, glass labwares (i.e. glass reactor with glass tubing etc.) were used to the greatest extent possible so as to inhibit adsorption problem. At the beginning of each experiment, TCS was spiked into the reactors by means of using TCS stock solution and completed to the 1 L of volume with source water (either Milli-Q or surface water). TCS stock solution (200 mg/L) was prepared in methanol unless otherwise stated using 100 mL volumetric flask made of borosilicate glass

(Pyrex). Following the TCS spiking into the reactor, it was exposed to ultrasonic shaker (WiseStir, MSH-20A) for 15 min to obtain sample solution that was homogeneously and fairly mixed. All experiments were run in duplicate and an average of the results was taken into consideration to minimize the experimental errors. The experiments were performed at ambient room temperature (23 ± 2°C).

Ozonation experiments were conducted in three different sets. In the first two sets, Milli-Q water spiked with TCS was used with the intention to exclude the matrix effects and, in a way, to determine the required ozone dose solely for the removal of TCS and then observe the effect of the initial TCS concentration on the removal efficiency. In the last set, Kesikköprü raw water spiked with TCS was subjected to ozonation experiments.

In the first set, initial 5 mg/L TCS was kept constant whereas applied ozone concentration was changed within the experiments with the aim of determining the optimum ozone dose to be used during the further experimentations (i.e. ozonation of surface water, by-product analysis). Optimum ozone dose should have sustained not also the considerably high TCS removal but also enough time to observe the reaction kinetics and its removal mechanism (i.e. by-products formations in different reaction times). Therefore, in the process of determining the optimum ozone dose, removal efficiency and reaction time considered concordantly. In this respect, five different ozone doses (i.e. 5, 10, 15, 24 and 70 mg/L corresponding to 500, 1000, 1500, 1680, 2100 mg/h, respectively) were applied to the reactor full of Milli-Q water for 30 min and samples taken at certain intervals (i.e. 1, 5, 10, 20 and 30 min) were analyzed immediately for their TCS concentration using HPLC-UV. After each experiment, the reactor was washed with Alconox, methanol and then with Milli-Q water in order to make it ready for the next experiment to be performed with a different ozone dose.
In the second set, again with Milli-Q water, ozonation tests were conducted by keeping the ozone dose constant at 5 mg/L, but varying the initial TCS concentration (i.e. 1, 3, and 5 mg/L) within the reactor. The aim was to determine the effect of initial TCS concentration on the removal of TCS. Ozone dose of 5 mg/L (determined as optimum ozone dose in the first set of experiments) was selected based on the

results of the first set of experimentation. Sampling and washing procedures were applied as mentioned above.

Afterwards, the third set of the experiments were performed with surface water by setting ozone dose at 5 mg/L and varying the initial TCS concentration (i.e. 1, 3, 5 mg/L) based upon the results obtained in the first two sets. The reason behind to this set of experiment is to observe the real life ozonation of TCS with the effect of water matrix and monitor the effect of initial compound concentration on the removal efficiency. As mentioned, TCS has been encountered in surface waters at far fewer extents; however, the minimum initial TCS concentration that could be measured by HPLC-UV with the existing method was 1 mg/L and other concentration were chosen as an increasing manner, accordingly.

3.3.4 Ozone Consumption in the System

Determination of the ozone consumption in the system was also substantial for this study. In this respect, the exact amount of ozone used to remove solely TCS in solution was evaluated. System components that would exert an ozone demand are TCS spiked and other organics of the raw water (NOM). Additionally, self-decomposition of ozone is another “out term” for the system. The rest of the ozone entering the system is partly as dissolved (unused) ozone in water and as ozone escaping from the reactor to the ambient air.

Initially, Kesikköprü surface water without spiking TCS was ozonated (5 mg/L O_3, 100 L/h) during 30 minutes and samples were taken at 1, 5, 10, 20 and 30 min. Unused ozone in these samples was measured by using DPD Total Chlorine Reagent by means of pocket colorimeter (Hach). Escaped ozone from the reactor was collected in the separate adjacent glass reactor including 2% KI solution and subsequently measured by iodine titration method. Ozone consumption by the system and organics was found by subtracting the mass of this measured unused ozone and escaped ozone from the known mass of ozone supplied to the reactor (Eq. 3). Later on, same procedure was applied to the Kesikköprü water spiked with 1 mg/L TCS and ozone consumptions by system, organics and TCS were acquired by subtracting the mass of unused ozone and escaped ozone, measured from the samples taken with 1 h intervals during the 5 h experiment, from the known mass of ozone supplied to the reactor. Difference between these two experiments results (i.e. w/o & w/ TCS) gave an opportunity to determine the amount (mg) of ozone that is required to remove 1 mg of TCS for the surface water bearing 1 mg/L TCS.

$$X_{inflow} = X_{organic} + X_{system} + X_{unused} + X_{escaped} + X_{TCS} \qquad \text{(Eq. 3)}$$

where;

X_{inflow} : Ozone inflow to system (mg)

$X_{organics}$: Ozone consumption by organics in solution (mg)

X_{system} : Self-decomposition (mg)

X_{unused} : Dissolved and unused ozone in solution (mg)

$X_{escaped}$: Ozone w/o reacting and escaping from the reactor (mg)

X_{TCS} : Ozone consumption by TCS (mg)

3.3.5 Ozonation By-product Analyses

For the purpose of determining the ozonation by-products of TCS, the chromatograms obtained at the end of ozonation tests were examined. During this, the literature was searched to have an insight about the potential by-products. In this regard, 5 standards namely; 2,4-dichlorophenol (2,4-DCP), 4-chlorocatechol (4-CC), 4-chlororesorcinol (4-CR) (Chen et al, 2012), methyl-triclosan (MTCS) and 2,4-dichloroanisole (2,4-DCA) (McAvoy et al., 2002; Lindstrom et al., 2002), given as the potential ozonation by-product of TCS, were purchased and then spiked directly to surface water and analyzed by means of HPLC-UV with the purpose of identifying their retention times and comparing whether comply with the retention times of the peaks obtained from the chromatograms of ozonated samples of the TCS spiked surface waters.

3.4 Analytical Methods

Analytical methods used in this study are explained below.

3.4.1 TCS Measurement

TCS concentration of the samples taken during experiments was measured using HPLC-UV (Shimadzu, LC-10AT vp) which is equipped with Nucleosil C18 column (4.6 mm×250 mm), LC-10Atvp solvent delivery module, an SCL-10Avp system controller and a SPD-10Avp UV-VIS detector set at 280 nm (Figure 11). Retention time for TCS was obtained as ~5.7 min. Solvents used during the analyses were acetonitrile (75%) and ultra-pure water (25%) at a constant flow rate of 1.5 mL/min. Injection volume of sample was 20 μL.

Analyzes of 2,4-dichlorophenol (2,4-DCP), 4-chlorocatechol (4-CC), 4-chlororesorcinol (4-CR), methyl-triclosan (MTCS) and 2,4-dichloroanisole (2,4-DCA), regarded as potential by-products of ozonation of TCS, were done by means of HPLC-UV with using aforementioned method, as well.

Figure 11. HPLC-UV device

3.4.1.1 Method Development for HPLC

The method to be applied for the analysis of TCS in HPLC was not available readily at the beginning of this study. Therefore, method optimization was of necessity in order to analyze TCS precisely. In this regard, the literature was researched in detail but no specific method that could be directly applied towards TCS was found. Thus, some trials were done in line with related studies published in the literature.

To this purpose, the wavelength in the HPLC detector was set to 280 nm which is suitable for TCS (Tsai et al., 2008), and different mobile phases were tested at different flow rates. Relevant trials conducted are summarized in Table 7. First, Milli-Q water and acetonitrile were tried as two different mobile phases with the mixing ratio of 40:60 and flow rate was set to 2.0 mL/min. As a second attempt, Milli-Q water and acetonitrile together with phosphoric acid and monosodium phosphate (0.03 mol/L) as a buffer was tried as mobile phases with same mixing ration at the same flow rate. Acetonitrile added sodium acetate (0.1 mol/L) and Milli-Q water with mixing ratio of 70:30 respectively and 2.5 mL/min flow rate, and methanol and Milli-Q water containing 0.1% phosphoric acid with ratio of (85:15) and 1.0 mL/min flow rate were the different attempts resulted with poor chromatography results while acetonitrile and Milli-Q water of 70:30 ratio and 1 mL/min flow trial gives relatively good signal performance in the process of method determination. In consequence of these trials, Acetonitrile:Milli-Q water (75:25) as mobile phases and 1.5 mL/min flow rate was determined as the method with which TCS concentrations could be measured precisely.

Table 7. HPLC method optimization-mobile phases, flow rates and corresponding performance

Content of Mobile Phase	**Mobil Phase Mixing ratio**	**Buffer**	**Flow rate of Mobile Phase (mL/min)**	**Signal Performance**
Milli-Q water and acetonitrile	40:60	No	2.0	Poor
Milli-Q water and acetonitrile	40:60	Phosphoric acid and monosodium phosphate (0.03 mol/L)	2.0	Poor
Milli-Q water and acetonitrile	30:70	Sodium acetate (0.1 mole/L)	2.5	Poor
Milli-Q water and methanol	15:85	Phosphoric acid (0.1%)	1.0	Poor
Milli-Q water and acetonitrile	30:70	No	1.0	Good
Milli-Q water and acetonitrile	25:75	No	1.5	Excellent

3.4.1.2 Determination of LOD and LOQ

Limit of Detection (LOD) and Limit of Quantification (LOQ) are one of the fundamental components of experimental studies or analytical measurements and especially substantial for evaluating obtained results. LOD is the lowest quantity of the substance, with a given level of confidence, that can be distinguished from the absence of it in sample but cannot be quantified; whereas, LOQ is lowest quantity of the substance that can be quantified with a given level of confidence (Vial and Jardy, 1999).

LOD corresponds to substance amount for which respond is equal to 3 times of the standard deviation calculated from the responds obtained from the results of 10 times injection of the chosen substance via HPLC-UV measurements. On the other side, LOQ corresponds to amount of substance determined by 10 times of the standard deviation. In this respect, LOD and LOQ were calculated for TCS, 2,4-DCP, 4-CC and 2,4-DCA in surface water individually and listed in Table 8.

Table 8. LOD and LOQ values of TCS and its by-products

Substance	LOD (µg/L)	LOQ (µg/L)
TCS	20.0	76.4
2,4-DCP	1.3	9.8
4-CC	10.0	57.6
2,4-DCA	1.0	6.2

3.4.2 Ozone Measurement

Unused ozone dissolved in water and escaped ozone from the main reactor collected into the adjacent small glass reactor were the ozone components measured in samples taken during ozone consumption experiments.

Unused ozone in samples was measured by the colorimetric N,N-diethyl-p-phenylenediamine (DPD) method which is commonly used for measuring free chlorine in the solution. This method is considered as inexpensive and reliable method for the ozone measurement in solutions (Engelhardt and Malkov, 2013). In this method DPD Free Chlorine Reagent Powder Pillows was used as reagent and it reacts with oxidizers present in water and turn into reddish color which is proportional to the concentration of the oxidizer (Metzger, 2009). Following the reaction with DPD reagent, samples were measured with Hach pocket calorimeter by using method 10069.

On the other hand, escaped ozone from the reactor was measured by iodine titration method. 2% of potassium iodide (KI) and 2 N sulfuric acid (H_2SO_4) was added into the adjacent glass reactor (500 mL) poured with 250 ml of Milli-Q water and following the commence of ozonation process, escaped ozone was pass through the pipes and then get into the adjacent reactor and subsequently water turned into the yellowish color. This solution then titrated with 0.025 M sodium thiosulfate ($Na_2S_2O_3$) and volume of the titrant used for the determining the escaped ozone amount was taken into consideration for the calculations.

3.4.3 pH Measurement

Hach Sension 378 device was used for the pH measurement of the solutions.

3.5 Chemicals Used in the Experiments

Chemicals used during the study were HPLC grade methanol (Merck, >99.9% purity), HPLC grade acetonitrile (Merck), sodium hydroxide (Sigma-Aldrich, ≥97% purity), DPD free chlorine reagent powder pillows (Hach, for 10 mL sample), potassium iodide (Sigma-Aldrich, ≥99% purity), sodium thiosulfate (Sigma-Aldrich), sulfuric acid (Sigma-Aldrich, 95-97% purity) and standards of TCS (Irgasan; Sigma-Aldrich, ≥97% purity), methyl-triclosan (Sigma-Aldrich), 2,4-dichlorophenol (Sigma-Aldrich, 99% purity), 4-chlorocatechol (Sigma-Aldrich, 97% purity), 2,4-dichloroanisole (Sigma-Aldrich, 97% purity) and 4-chlororesorcinol (Sigma-Aldrich, 98% purity).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Adsorption of Triclosan

Adsorption experiments, of which was crucial in the process of true understanding for the fate of TCS and provide insight into its removal mechanism, firstly carried out with three different initial TCS concentration with Milli-Q water in identical glass reactors equipped with plastic tubing, which were the component of lab-scaled ozonation system, with the purpose of observing the behavior of TCS in reactors and sorption onto the inner surface of the reactor.

Although these experiments done without applying any ozone and providing just aeration by plastic pipes via air pumps, Figure 12 demonstrates that TCS concentration in reactors decreases significantly in the process of time. Equilibrium was reached in each reactor at a different TCS concentration level. As TCS has very low vapor pressure (4×10^{-6} Pa at 25°C) (Reiss et al., 2008), it can be considered to be non-volatile. The photodegradation possibility of TCS has also prevented by covering the reactor with aluminum foil just in case not to affect the experimental results. In the light of these results, the eyes were on the results to be obtained with the measurements of TCS adsorbed onto glass reactor.

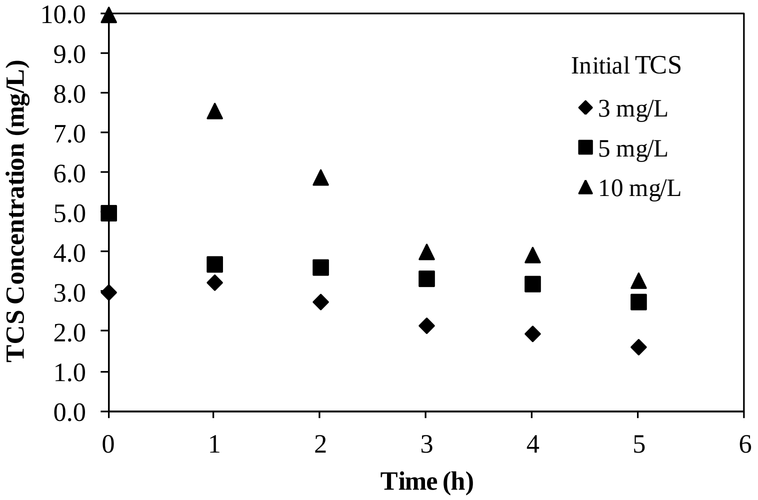


Figure 12. Decrease in TCS concentration in reactors spiked with different initial TCS concentration in Milli-Q water immersed with plastic pipes

In order to determine the TCS amount sorbed onto inner walls of the glass reactors, following the termination of the experiments after 5 h, the reactor was totally emptied, washed with 50 mL of methanol and then TCS in the methanol solution was analyzed for each reactors. Table 9, obtained within this framework, indicates that sorption to the glass reactors was negligible while TCS recovery was never above 60%. Another point that could be interpreted from the Table 9 was the amount of TCS sorbed onto the inner surface of the reactors was almost same indicating the possible saturation of the glass surface by TCS. Mass of TCS sorbed per unit glass area was in range of 0.33-1.06 mg/m^2 (Figure 13).

Table 9. TCS in solution and on the inner surface of glass reactors after 5 h

Initial TCS in reactor		**TCS sorbed onto glass reactor (mg)**	**TCS remaining in solution (mg)**	**Recovery (%)**
mg/L	**mg**			
3	1.500	0.012	0.817	55.24
5	2.500	0.016	1.388	56.17
10	5.000	0.038	1.692	34.59

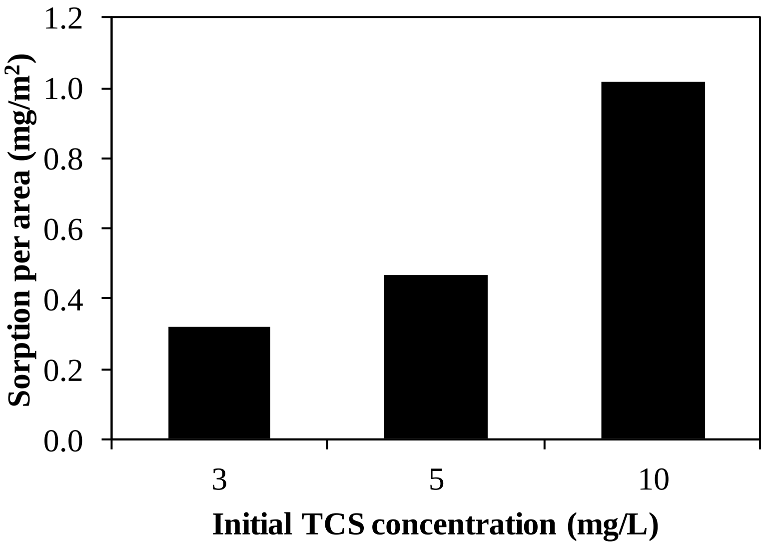


Figure 13. Adsorption on the inner surface area of the reactors after 5 h

As sorption onto glass reactor found as negligible level, the reason of the decrease observed in Figure 12 had not been answered. Therefore, there was only one component of the system left which was most probably responsible for the TCS decrease since then, the tubing. In this regard, two identical erlenmeyer flasks as reactor were prepared and filled with 500 mL of Milli-Q water and spiked with 5 mg/L TCS. One of them was aired with plastic tubing and the other one was not aerated and so no tubing immersed into it. The aim was to clarify whether the sorption was caused due to tubing. Results shown in Figure 14 strengthened and even proved the sorption foresight regarding the plastic tubing that TCS remained almost same in the reactor in which plastic tubing was not immersed whereas it significantly decreased in the case of tubing used.

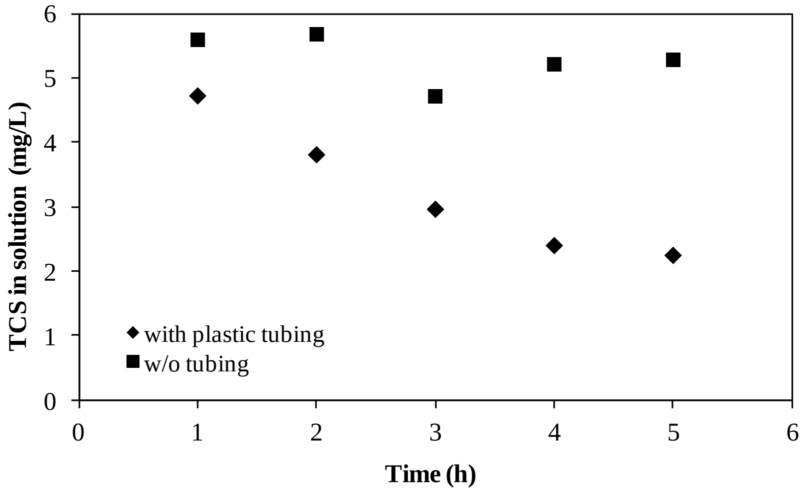


Figure 14. TCS concentration in reactors equipped with plastic tubing and without tubing

This being the case, experiments were canalized to determine the amount of TCS being adsorbed onto plastic tubing and to find alternative tubing for the ozonation experiments to be done subsequently. In this context, two identical Erlenmeyer flasks filled with 500 mL of Milli-Q water were used and 5 mg/L initial TCS was spiked to each. One reactor was aired with plastic tubing while the other was with glass one during 5 h. TCS concentration in solutions were analyzed with 1 hours intervals and sorption on glass reactor and also tubings were analyzed with rinsing of them by methanol at the end of the experiment. Table 10, which represents the data obtained upon the experiment, indicates that TCS was seriously adsorbed to the plastic tubing (about 44% of the initial TCS) while it did not have tendency of adsorb to the glass tubing (<0.4% of the initial TCS) (Figure 15).

Table 10. TCS on glass reactor, plastic and glass tubing after 5 h

Tubing	**TCS on the reactor wall (mg)**	**TCS in solution**		**TCS on tubing**		**Total TCS (mg)**	**Recovery (%)**
		mg/L	**mg**	**mg**	**mg/m^2**		
Plastic	0.016	2.776	1.388	1.090	482.00	2.495	99.8
Glass	0.016	4.879	2.440	0.009	4.86	2.465	98.6

Based on the comparison of TCS adsorbed on glass and plastic tubing, mass of TCS adsorbed on per unit area of plastic tubing was about 100 times greater. Also, above 98.6% of recovery of the experiment was satisfactory in terms of the reliability of the experiments.

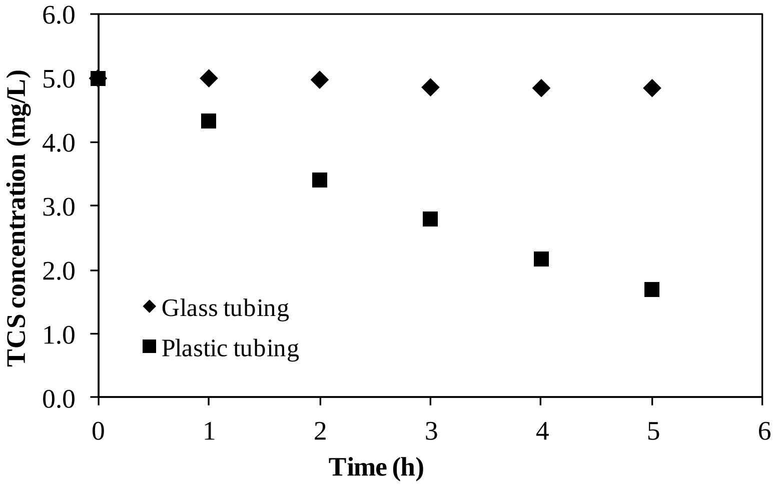


Figure 15. TCS concentration in reactors equipped with plastic tubing and glass tubing

Adsorption experiments proved that labwares and experimental apparatus used in experiments have a significant effect on the results especially in ones dealing with compounds having high hydrophobicity just as TCS. In this manner, results of TCS or of even other compound having high hydrophobic nature, given in the literature, may not indicate the real case due to not taking into account of the this sorption matter and may not reflect the reliable results, and thus may mislead the audience. It is also one possibility that hydrophobic compound may even adsorbed onto the wall of the vessel used to prepare stock solutions in it and thereby erroneous experiments may even commence from the beginning. Therefore, in the experiments to be carried out with high hydrophobic nature, labwares and apparatus made with materials with no affinity to the sorption (i.e. glass) should be preferred and kept away from the plastic ones.

The outputs acquired with these experiments were also crucial for the future of this study and thereby it was definitely decided to use glass materials in the process of the TCS ozonation experiments.

4.2 Photodegradation of Triclosan

Lab-scale photodegradation (or photolysis) of TCS was studied with the experiments performed. This was substantial to be clarified due to photodegradation possibility of TCS mentioned in the literature. Although laboratory experiments were conducted at the point that far from the exposure of the sunlight, the effect of photodegradation on TCS removal was examined through different cases as totally coating the ozonation reactor with aluminum foil, partial coating of the body and without any coating. The results of the called cases are represented in Figure 16.

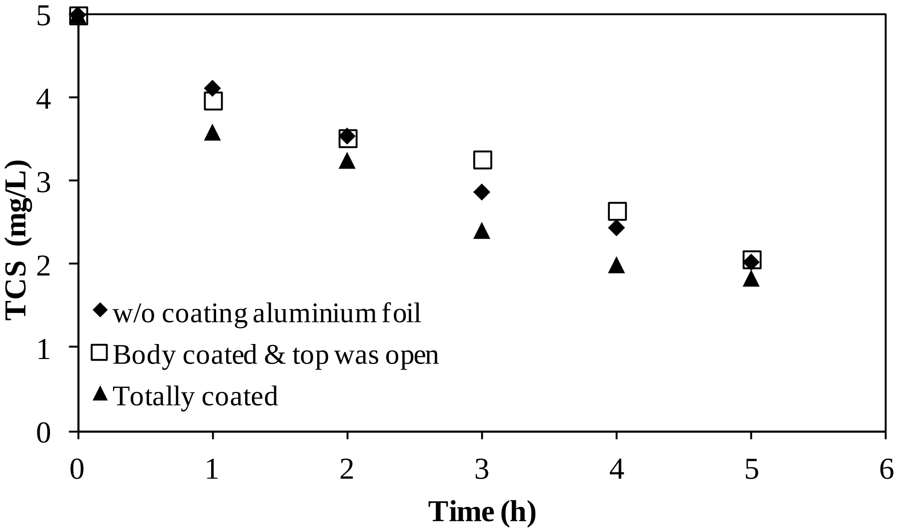


Figure 16. Photodegradation effect on Triclosan concentration in aerobic reactors

As can be seen from the Figure 16, TCS concentration in each case nearly depleted in same manner and after 5 hour aeration period, almost same TCS concentration was observed in each reactor. From this, depletion of TCS was not solely dependent upon the photodegradation and removal can be explained by the adsorption of TCS onto the plastic tubing immersed into the reactors (as explained in previous section) due to its affinity to sorbs on plastic material and its reported high hydrophobicity. Meanwhile, this depletion might be also due to the oxidation of TCS by air continuously supplied into the reactor during 5 h of experiment. In lights of these results, it was evaluated that lab-scale photodegradation does not considerably affect the TCS concentration, at least in our case, and therefore, further experiments were conducted without coating of the ozonation reactors.

4.3 Ozonation of Triclosan

In this section, it was endeavored to provide insight into the ozonation of TCS by evaluating the results of the experiments done in this study and comparing the gathered results with the ones given in the literature. Within this framework, effects of the ozone dose, initial TCS, pH and water matrix thought to affect the ozonation of the TCS process, are studied and its experimental results are discussed in detail.

4.3.1 Effect of Ozone Dose

In the following part, results obtained from the experiments done with Milli-Q water bearing 5 mg/L of initial TCS and exposed to the different ozone doses (5, 10, 15, 24, 70 mg/L) are discussed. The aim of this work was to observe the effect of ozone dose on the removal of TCS and, in a way to determine optimum dose required for the removal of TCS and to be used during the following experimentations in this study.

Results obtained by applying different ozone doses to the Milli-Q water bearing initial TCS concentration of 5 mg/L showed that after 10 min ozonation, about 99% of TCS was removed with all applied ozone doses (Figure 17). However, as can be seen from Figure 17, the time of achieving this removal efficiency differs for different ozone doses applied. To illustrate, when 70 mg/L O_3 dose was applied, about 98% TCS removal was achieved in only 1 min while it was reached around 10 min at 5 mg/L ozone dose supply. In this respect, expectedly, when applied ozone dose increases, TCS was removed faster from water.

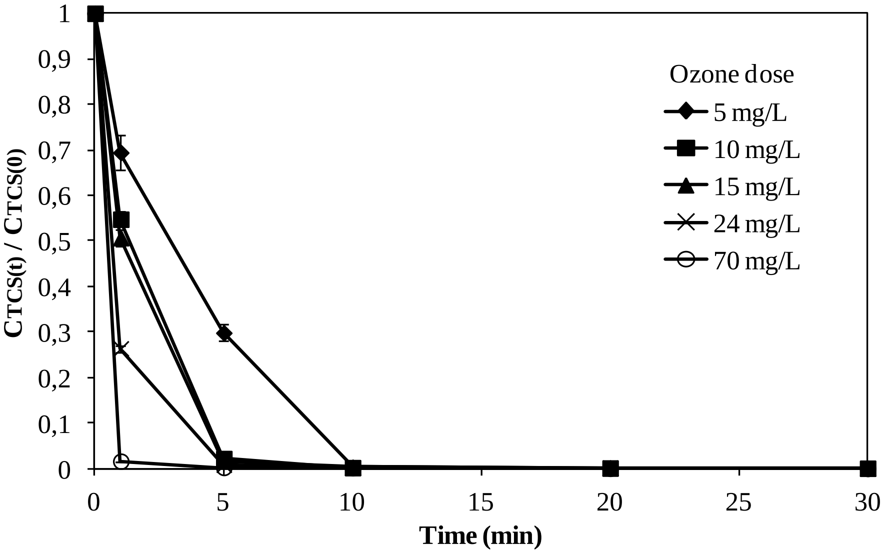


Figure 17. TCS removal from Milli-Q water bearing 5 mg/L initial TCS concentration at different ozone doses applied

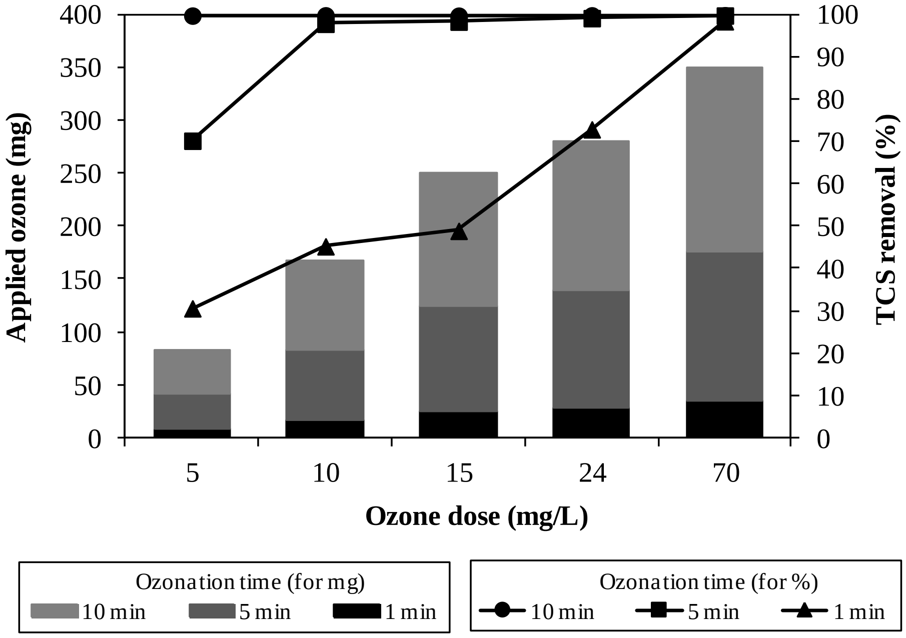


Figure 18. Applied ozone amounts and TCS removals at different ozone doses in different ozonation times

In addition, Figure 18 gives a chance to observe the removal efficiencies in conjunction with the applied ozone amounts in different retention times. Bar diagrams show the applied ozone dose while the line graphs demonstrate the TCS removal. In this respect, it could be deduced from this figure that in the condition of applying ozonation during 1 min, only at 70 mg/L ozone dose achieves the high TCS abatement as 98.4%. On the other hand, applying 5 min ozone at all ozone doses except 5 mg/L, almost complete TCS abatement was achieved. As for 10 min ozonation, nearly complete abatement was observed in all ozone doses, as well. However, applied ozone dose was the key parameter that should be taken into account in company with the removal efficiencies. Optimum ozone dose should have sustained not also the considerably high TCS removal but also enough time to observe the reaction kinetics and its removal mechanism (i.e. by-products formations in different reaction times). Therefore, in the process of determining the optimum ozone dose, removal efficiency and reaction time considered concordantly. In this manner, reaction time was also another crucial parameter evaluated in the process of determining the optimum ozone dose. Thus, in order to be capable of observing the possible by-products and kinetics of the reaction, it was decided to keep reaction time as long as possible. In brief, the ozone dose providing high TCS removal, requiring lower applied ozone amount and sustaining higher reaction times was selected as an optimum ozone dose.

Table 11. TCS concentration at different times with different applied ozone doses ([*]Removal efficiency, [**]Applied ozone amount)

Time (min)	**Applied ozone dose (mg/L)**									
	5		**10**		**15**		**24**		**70**	
	RE[*] (%)	**AO[**] (mg)**	**RE (%)**	**AO (mg)**	**RE (%)**	**AO (mg)**	**RE (%)**	**AO (mg)**	**RE (%)**	**AO (mg)**
1	30.6	8.3	45.3	16.7	48.9	25.0	72.9	28.0	98.4	35.0
5	70.2	41.7	97.8	83.3	98.3	125.0	99.2	140.0	99.8	175.0
10	99.7	83.3	99.8	166.7	99.7	250.0	99.8	280.0	99.8	350.0

By considering the applied ozone amount, the most feasible dose came to the fore is 70 mg/L ozone dose. Because, about 98% abatement was achieved by only applying 1 min ozone with 35 mg (Table 11). Nevertheless, it would not allow observing the any by-product formation and reaction kinetics in such a short time ozonation. Other ozone doses at a 1 min retention time could not achieve desired TCS removals so they were eliminated. Reaction times more than 10 min was also out of scope as almost complete abatement was achieved in 10 min at every ozone doses.

The second option was selecting the dose by considering the dose that removes the TCS in 5 min. In this context, except 5 mg/L, other ozone doses met the high TCS removals. At that time, applied ozone amount step in and 10 mg/L ozone dose with lower ozone amount (83.3 mg) become prominent. However, there was another option that provides 99.7% removal of TCS by the same ozone amount with 10 min reaction time was the dose of 5 mg/L. In this stage, in order to capable of observing the possible by-products and kinetics of the reaction more clearly, by having higher reaction times with TCS, 5 mg/L ozone dose was selected as an optimum dose and hereafter this dose was used in further ozonation experimentation conducted in this study.

4.3.2 Effect of Initial Triclosan Concentration

Effect of initial TCS concentration on TCS removal efficiency was studied first in Milli-Q and then in surface water. As spiked TCS concentration and applied ozone dose were the same in both water cases, results were comparable and thereby this experimentation also served a baseline for the determining the effect of the water matrix on the TCS removal which is explained in Section 4.3.3.

Milli-Q water

Ozonation tests were performed by keeping the ozone dose constant at 5 mg/L, previously determined as optimum dose, to the different initial TCS (i.e. 1, 3, and 5 mg/L) concentration in Milli-Q water. Results of this experimentation are represented in Figure 19. As seen, the more water bears initial TCS concentration, the more time it requires to be exposure to ozone in order to reach reasonable TCS removal. Required exposure time increased as TCS concentration increases in the reactors, as expected; for 1, 3, 5 mg/L TCS bearing reactors, 1, 5, 10 min exposure times were required, respectively.

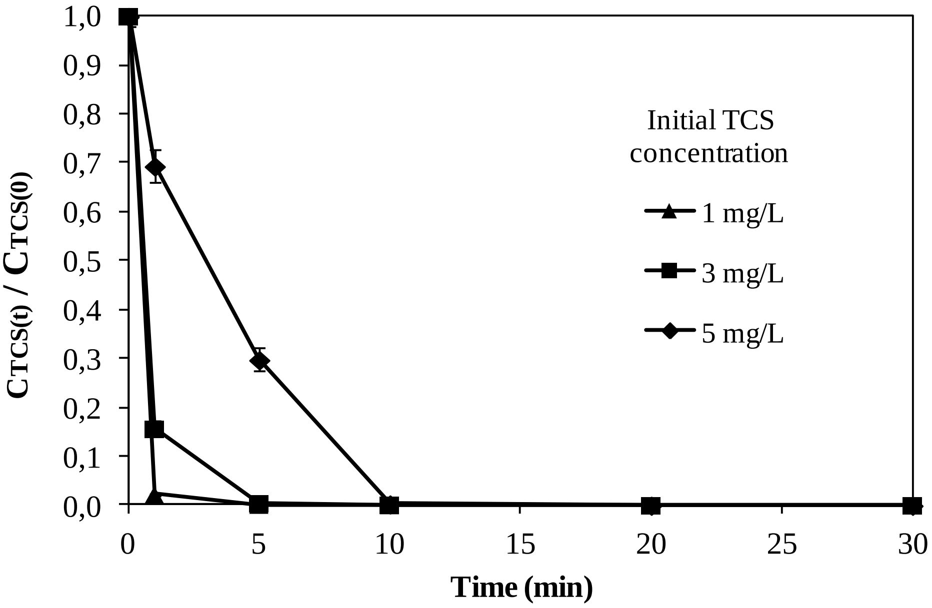


Figure 19. TCS removal from Milli-Q water (initial TCS: 1, 3, 5 mg/L, ozone dose: 5 mg/L)

Another point that can be deduced from Figure 19 is applying 5 mg/L ozone to the 5 mg/L TCS bearing Milli-Q water, 30.6% removal was achieved in 1 min while this ratio became 70.2% and 99.7% at retention times of 5 and 10 min, respectively. In the case that water containing 3 mg/L TCS, after 1 min ozonation 84.4% TCS depletion was monitored. However, at the time of 5 min, 99.7% of it depleted. On the other hand, ozone almost completely deplete (97.8%) the 1 mg/L TCS in just 1 min reaction time.

Surface water

In addition to the ozonation experiments of Milli-Q water, the ozonation experiment was also performed with surface water in order to simulate the real water ozonation case observed in surface/drinking water treatment plants. In this regard, 5 mg/L ozone dose was applied to the reactors including different initial TCS concentration (i.e. 1, 3, 5 mg/L) and Figure 20 represents the results obtained in the scope of this experiments.

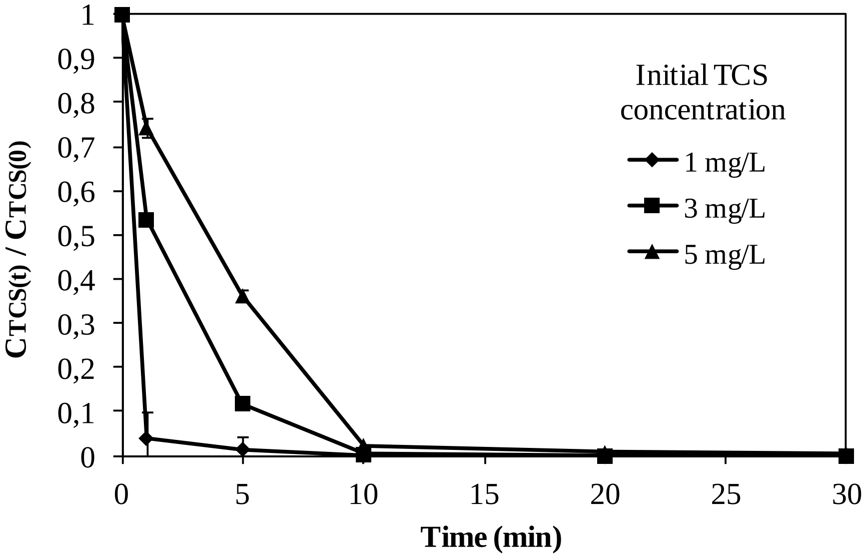


Figure 20. TCS removal from surface water (initial TCS: 1, 3, 5 mg/L, ozone dose: 5 mg/L)

As in the Milli-Q case, expectedly, required exposure time and so required ozone amount for the removal of TCS increase when initial TCS increases. According to Figure 20, it could be interpreted that reaction of ozone with TCS in surface water of which initially spiked with 1 mg/L TCS was so fast that 96% abatement of it was observed in just 1 min while it was observed as 46.5% and 25.6% in the 3 and 5 mg/L bearing ones. On the other hand, removal ratios of the TCS in 3 mg/L TCS bearing surface water were 88.1%, 99.7% at the exposure times of 5 and 10 min. Expectedly, lower ratios were gathered as 63.7% and 97,6% in the surface water spiked with 5 mg/L in that times. Briefly, for the desirable depletion of the TCS in surface water, 1 min of ozonation with 5 mg/L ozone dose is sufficient for the waters bearing 1 mg/L TCS whereas 10 min ozonation is required for the ones containing 5 and 10 mg/L TCS.

When we look at some results given in the literature, more than 98.0% of TCS disappeared within 6 min ozonation (8.9 mg/L ozone dose) from the water initially bearing 8.6 mg/L TCS, and TCS was completely abated when 16.6 mg/L ozone was applied during 24 min to the water containing 6.5 mg/L initial TCS concentration (Huang, 2010). In comparison, applying 5 mg/L ozone to 1,3,5 mg/L initial TCS concentration with obtaining ≥96% TCS removal ratios at the exposure time 10 min is in agreement with the results in the literature, as well.

4.3.3 Effect of Water Matrix

Besides TCS, there are also impurities (i.e. organic and inorganic compounds etc.) in surface water that most probably react with ozone in solution. Therefore, in this case, it is expected that ozone amount that directly react with TCS decreases thus removal ratio of TCS reduced accordingly. In order to clarify this situation, results of the experimentation obtained in ozonation of both Milli-Q and surface waters were combined in a comparable manner in Figure 21.

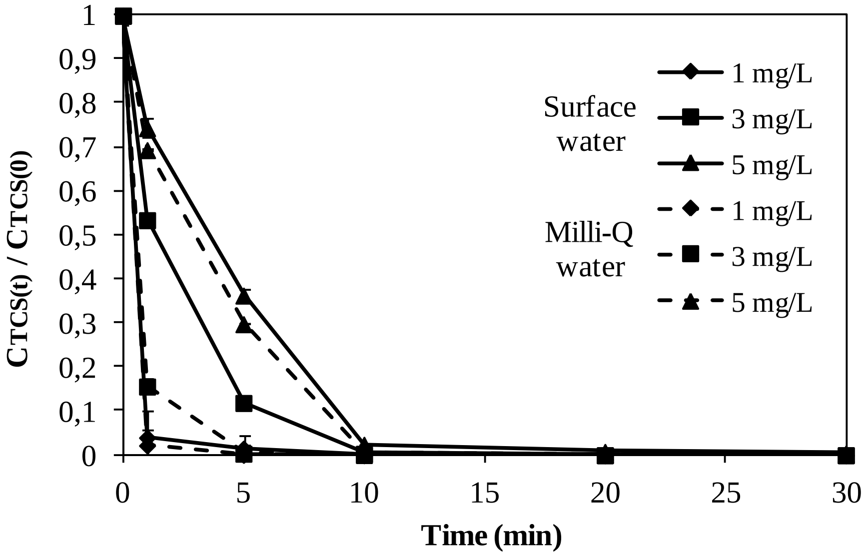


Figure 21. Comparison of TCS removals from Milli-Q and surface waters (initial TCS: 1, 3, 5 mg/L, ozone dose: 5 mg/L)

According to Figure 21, in case of Milli-Q water, the required ozone exposure time to end up with considerably high TCS depletion was 5 min for the one containing 3 mg/L initial TCS concentration while it was 10 min for surface water in the same conditions. On the other hand, in the case of the 1 mg/L and 5 mg/L TCS concentration, not being as much as 3 mg/L, TCS removal ratios decrease in surface water but the required exposure times that reach reasonable TCS depletion amounts were nearly overlapped. To illustrate, for the waters bearing 5 mg/L initial TCS, at 1 min ozonation exposure point, TCS removal ratio in Milli-Q water was calculated as 30.6% while it was 25.6% in surface water. After 5 min ozonation, they were calculated as 70.2% and 63.7%, and 99.7% and 97.6% in the 10 min ozonation, respectively. Although mentioned removal ratios seems to not differ so much, considering the hydrophobic nature and bio-accumulative property of the TCS and its effects on the biota even encountered at very low concentration (Veldhoen and Skirrow, 2006), these ratios become prominent in the surface water treatment plants especially for those have high TCS concentrated inflow.

These results also gave insight to the fact that besides TCS, ozone attacks to the other impurities in surface water and thus, removal efficiency of TCS was reduced. Therefore the more water contains impurities, the more ozonation exposure time or ozone amount is required for the treatment of it.

4.3.4 Effect of pH

In order to study the pH effect on the ozone treatment of TCS, surface water spiked with 1 mg/L TCS concentration was ozonated with 5 mg/L ozone during 30 min for the pH values of 6, 8 and 10. Buffer solutions were used to keep the intended pH constant during the experiments. The samples were taken from the reactor at specified time intervals as 1, 5, 10, 20 and 30 min respectively and they were given to the HPLC-UV so as to identify their TCS and by-products content. Furthermore, result of the experiment done in natural pH (7.3) with surface water spiked 1 mg/L TCS in Section 4.3.2 was taken into consideration in the process of comparison in this chapter, as well.

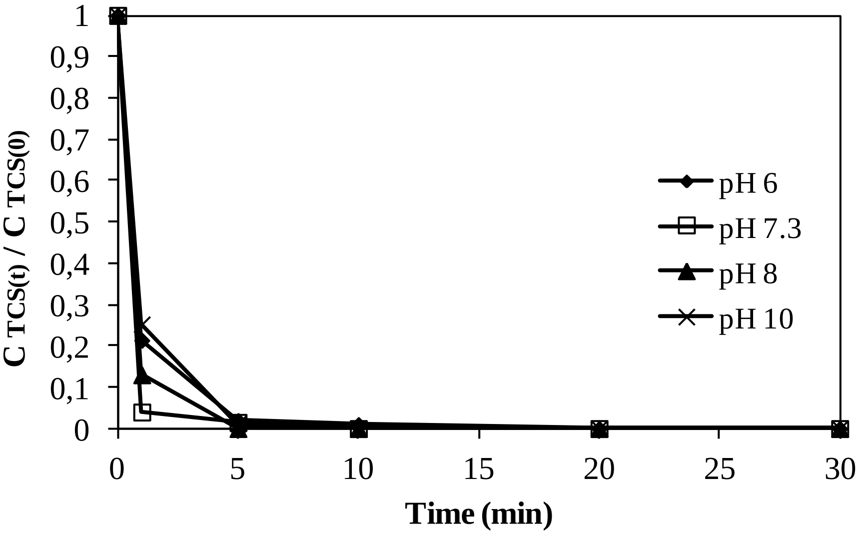


Figure 22. TCS removal during 30 min of ozonation at pH 6, 7.3, 8 and 10

Results of the experimentations done to observe the effect of pH on TCS removal from water are shown in Figure 22 and Table 12. Meanwhile, concentration of the ozonation by-products of TCS identified at different pH and retention times are presented in Table 13, 14, 15, 16, as well.

As can be seen from Table 12, TCS removal was more rapid at pH 7.3 where 96% of the initial TCS was removed within just 1 min. On the other hand, TCS removal was slower for the other studied pH values of 6, 8 and 10 with the removal efficiencies of 52%, 83%, 75%, respectively. TCS removal efficiency greater than 99% was reached in 5 min with the ozonation performed at pH 8 whereas it took 10 min to accomplish the same removal efficiency at pH 6, 7.3 and 10.

Table 12. Effect of pH on TCS removal efficiency (Initial TCS concentration: 1 mg/L)

Time (min)	TCS Removal Efficiency (%)			
	pH=6	pH=7.3	pH=8	pH=10
1	51.5	96.0	83.0	74.8
5	98.0	98.5	>99.0	98.9
10	>98.0	100	100	>99.0
20	100	100	100	>99.0
30	100	100	100	>99.0

Concentration of TCS as well as its ozonation by-products detected at pH values of 6, 7.3, 8 and 10 at different retention times are shown in Table 13, 14, 15 and 16, respectively.

Table 13. Ozonation of 1 mg/L TCS bearing surface water at pH=6 (Ozone dose: 5 mg/L)

Time (min)	**TCS (ppm)**	**4-CC (ppb)**	**2,4- DCP (ppb)**	**U-3.5 (area)**	**U-4.5 (area)**	**2,4-DCA (ppb)**
0	1.03	-	-	-	-	-
1	0.50	103.0	27.0	740.9	-	-
5	0.02	-	26.8	-	-	-
10	<LOD	-	24.8	-	-	-
20	-	-	18.7	-	-	-
30	-	-	-	-	-	-

Table 14. Ozonation of 1 mg/L TCS bearing surface water at pH=7.3 (Ozone dose: 5 mg/L)

Time (min)	**TCS (ppm)**	**4-CC (ppb)**	**2,4- DCP (ppb)**	**U-3.5* (area)**	**U-4.5** (area)**	**2,4-DCA (ppb)**
0	1.00	-	-	-	-	-
1	0.04	50.0	12.6	94.0	3193.0	-
5	<LOD	<LOD	7.0	-	1437.0	<LOD
10	-	<LOD	6.1	-	-	<LOD
20	-	-	-	-	-	-
30	-	-	-		-	-

*U-4.5: Unknown (at 4.5 min); **U-3.5: Unknown (at 3.5 min)

Table 15. Ozonation of 1 mg/L TCS bearing surface water at pH=8 (Ozone dose: 5 mg/L)

Time (min)	**TCS (ppm)**	**4-CC (ppb)**	**2,4- DCP (ppb)**	**U-3.5 (area)**	**U-4.5 (area)**	**2,4-DCA (ppb)**
0	1.00	-	-	-	-	-
1	0.17	184.0	19.6	553.9	348.0	-
5	<LOD	92.6	21.3	-	-	-
10	-	657.0	17.0	-	-	-
20	-	62.3	-	-	-	-
30	-	-	-	-	-	-

Table 16. Ozonation of initially 1 mg/L TCS bearing surface water at pH=10 (Ozone dose: 5 mg/L)

Time (min)	TCS (ppm)	4-CC (ppb)	2,4- DCP (ppb)	U-3.5 (area)	U-4.5 (area)	2,4-DCA (ppb)
0	1.07	-	-	-	-	-
1	0.27	84.4	16.7	390.0	347.9	-
5	<LOD	12.8	13.2	-	-	-
10	<LOD	-	13.0	-	-	-
20	<LOD	-	-	-	-	-
30	<LOD	-	-	-	-	-

According to the foregoing tables, complete removal of TCS and its by-products from the surface water was attained at the end of 20 min at pH value of 7.3 and 30 min for pH value 6 and 8; however, complete removal was still not satisfied at the end of 30 min in the case of pH 10. For that reason, for the alkaline waters (i.e. pH 10), ozone exposure time may need to be increased in order to achieve complete removal of the contaminant of concern from the water environment.

Another implication from these tables that among the identified ozonation by-products of TCS during this study, 4-CC and 2,4-DCP were detected in the all pH values (i.e. 6, 7.3, 8 and 10) and 2,4-DCA was only detected at pH 7.3 in samples taken at the end of 5, 10 and 20 min of ozone exposure. After 20 min, 2,4-DCA was completely lost from the water environment.

4-CC was formed just in 1 min at each studied pH values and it was entirely removed in 5 min, 20 min and 10 min for the pH 6, 7.3 and 10, respectively (Table 17). At pH 8, after formation in 1 min, its concentration decreased steadily and it was wholly removed from the surface water thanks to 30 min of ozone treatment. In this sense, it was clear that it was easier to remove 4-CC with ozonation by setting and arranging the pH of 6 in the existing situations.

Table 17. Comparison of 4-CC formation at different pH values (pH=6, 7.3, 8 and 10; 1 mg/L initial TCS concentration)

Time (min)	**Concentration of 4-CC (ppb)**			
	pH=6	**pH=7.3**	**pH=8**	**pH=10**
1	103.0	50.0	184.0	84.4
5	-	5.0	92.6	12.8
10	-	<10	657.0	-
20	-	-	62.3	-
30	-	-	-	-

2,4-DCP was also generated just in 1 min at all pH values and it was observed to be in a tendency to be degraded with further ozone supply (Table 18). The times of ozone supply needed to achieve complete removal of this transformation product were found as 30 min for pH 6 and 20 min for the rest. From this point of view, it can be said that basic pH values are more preferable in terms of 2,4-DCP removal from the system.

Table 18. Comparison of 2,4-DCP formation at different pH values (pH=6, 7.3, 8 and 10; 1 mg/L initial TCS concentration)

Time (min)	**Concentration of 2,4-DCP (ppb)**			
	pH=6	**pH=7.3**	**pH=8**	**pH=10**
1	27.00	12.62	19.60	16.68
5	26.84	7.00	21.34	13.17
10	24.78	6.10	17.03	13.01
20	18.67	-	-	-
30	-	-	-	-

These experiments also demonstrated that the operating conditions of the reactor such as pH value sustained during the study have a significant effect on the ozone treatment of TCS. According to the existing pH, some transformation products of TCS may and may not be formed at the end of ozonation. This was entirely related with the chemical nature of the products and their tendency to be generated in the existing situation. Therefore, the key point while trying to remove TCS or TCS like substances by means of ozone reaction was the investigation of the actual quality of waters including pH and so, and then making the necessary arrangements in order to end up with the desired effluent contaminant and its potential by-products concentration.

4.4 Ozonation By-products of Triclosan

Though almost complete removal of TCS was achieved through ozonation (i.e. 5 mg/L ozone dose to 1 mg/L initial TCS for 5 min and to 3 and 5 mg/L initial TCS for 10 min in surface water, pH:7.3), transformation by-products of this removal during the ozonation process needs to be assessed in order to be able to consider this removal as complete, indeed. Considering the possibility of by-product formation during the ozonation of TCS and their potential to be more toxic, bioaccumulative and persistent than the parent compound, the monitoring of the by-products was considered essentially important. Hence, ozonation by-products of TCS, if any, were sought by comparing the surface water chromatograms obtained with HPLC-UV before, during and after the ozonation tests.

Figure 23 represents the chromatograms obtained following the ozonation with 5 mg/L ozone dose of surface water bearing initially 1 mg/L TCS during 30 min. As seen from Figure 23, apart from TCS peak which was revealed at 5.7 min, five major peaks with retention times of 2.0, 2.7, 3.5, 4.5 and 5.0 were identified. This observation confirmed the formation of oxidation by-products of TCS upon ozonation. In an attempt to identify these by-products, considering the studies done for the by-products of the TCS, compounds expected to be formed based on the possible reactions of TCS with ozone and the contents of solution were determined as 2,4-dichlorophenol (2,4-DCP), 4-chlorocatechol (4-CC) (Chen et al., 2012), methyl-triclosan (MTCS), 4-chlororesorcinol (4-CR), 2,4-dichloroanisole (2,4-DCA) and were sought, accordingly. To this purpose, standards of these compounds were bought and subsequently analyzed by the HPLC-UV.

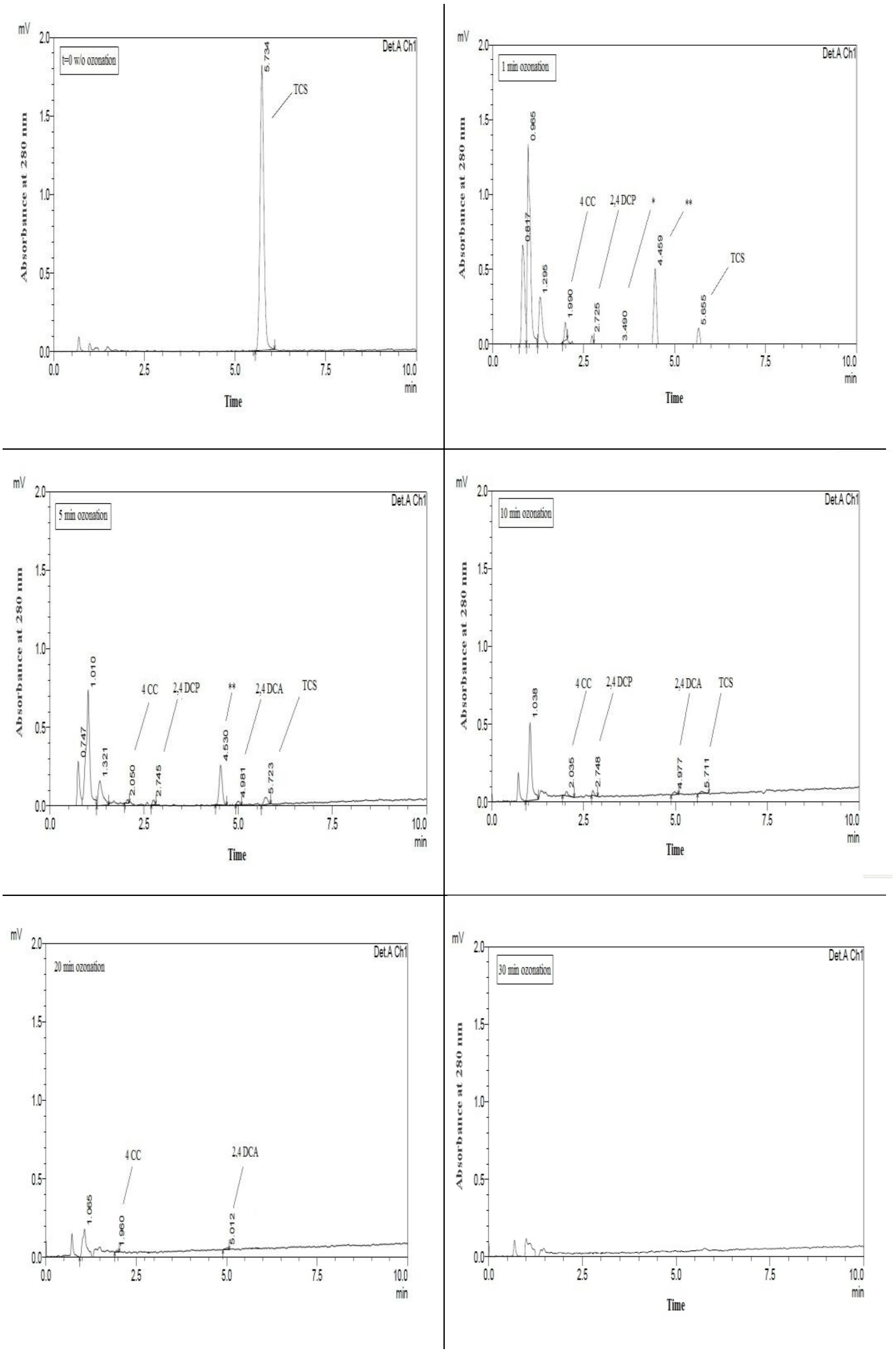
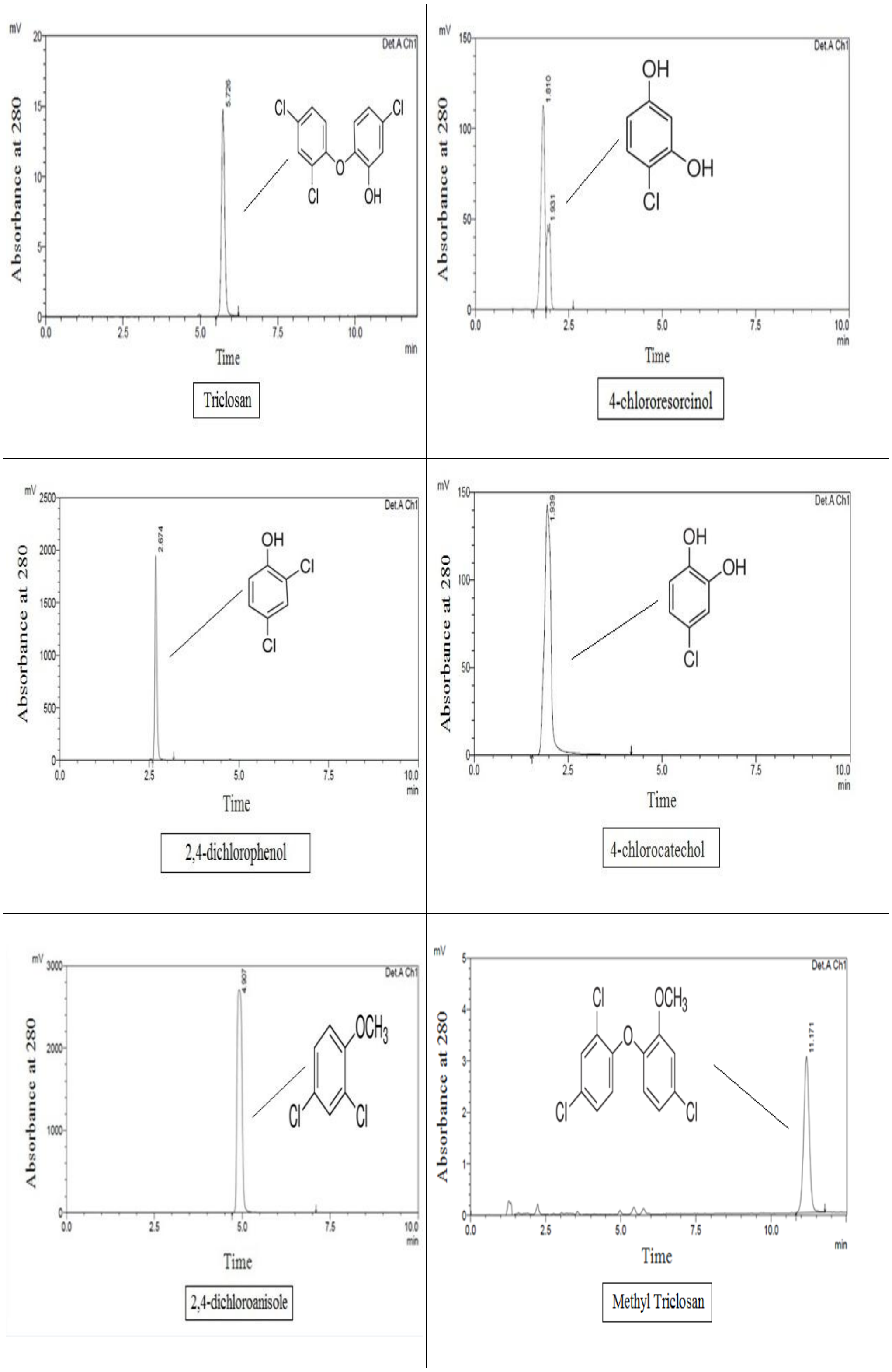


Figure 23. The chromatograms obtained following the ozonation of TCS (initial TCS conc.:1 mg/L; applied ozone concentration: 5 mg/L to surface water; * Unknown (at 3.5 min); ** Unknown (at 4.5 min))

Figure 24 presents the chromatograms purely obtained by direct measurement of the standard solutions of these possible products without any ozonation and adding TCS in surface water by means of HPLC-UV. It was observed that peaks revealed at 2.7 min (2,4-DCP) in both ozonation of TCS (Figure 23) and in direct standard analyzes (Figure 24) were overlapped. In addition, it was also identified that retention times of the 4-CC (2.0 min) and 2,4-DCA (5.0 min) complied with the retention times of the major peaks illustrated, as well. Thus, it could be interpreted that 2,4-DCP, 4-CC, 2,4-DCA are the ozonation by-products of the TCS. The first two were also observed in the study by Chen et al. (2012), but not the latter one.

On the other hand, as it is seen from the Figures 23 and 24, retention times of MTCS (11.2 min) and 4-CR (≈ 1.85 min) were not overlapped or not correlated with the retention times of any by-products' peak. As such, they could not be confirmed and seemed not to be an ozonation by-product of TCS. Peaks appearing in ozonation of TCS with retention times of 3.5 and 4.5 minutes (Figure 23) could not be matched with the peaks of standard solutions checked and therefore could not be identified. In addition, peaks observed before 1.9 min corresponds to impurities coming from solvents used for the TCS standard solutions (i.e. methanol and sodium hydroxide).



Triclosan

4-chlororesorcinol

2,4-dichlorophenol

4-chlorocatechol

2,4-dichloroanisole

Methyl Triclosan

Figure 24. The chromatograms of surface waters spiked with standards

Furthermore, regarding the by-product of 2,4-DCA which has a methyl moiety within its structure, it was suspected that this by-product might be formed owing to methanol used for TCS stock solution. In an attempt to clarify this possibility, this time TCS stock solution prepared with sodium hydroxide solution used for the spiking 1 mg/L TCS into the surface water before ozonation (5 mg/L ozone dose). Subsequent ozonation performed with this surface water sample revealed that 2,4-DCA was not formed as illustrated in the chromatograms in Figure 25. As seen from Figure 25, there is not any peak having retention time of 5 min designated for 2,4-DCA previously. This result brought into open the suspected issue that 2,4-DCA is formed in the presence of methanol in water. Therefore, in ozonation studies being worked with any methyl containing solutions or solvents, this issue should be considered cautiously.

As can be depicted from Figures 23 and 25, in the case of ozonation of surface water initially spiked 1 mg/L TCS, as TCS is eliminated with time from water, reaction by-products start to appear. Their peaks first increase in size (at ozonation time of 5 min) then decrease substantially with the ozonation time (30 min). This indicates that the products formed are further oxidized by the ozone. However, they are not completely removed until exposed 20 min ozonation, except the unknown by-products belonging to the retention times of 3.5 and 4.5 min. Therefore, not only in this study but also in a good deal of study in the literature, TCS removal attained by ozonation does not refer to the complete removal, but to the conversion. In this respect, besides identifying the by-products, their quantitative assessments were also considered substantial with regard to the determination of the ozone concentration and exposure times to be implemented for the complete removal of TCS and its by-products from surface waters as well as for the evaluation of their environmental effects. For this purpose, the data gathered from the experiments conducted with 1 mg/L, 3 mg/L and 5 mg/L TCS bearing surface waters ozonated with 5 mg/L ozone was utilized. Table 19 summarizes the time course variation of the concentration of the aforementioned by-products.

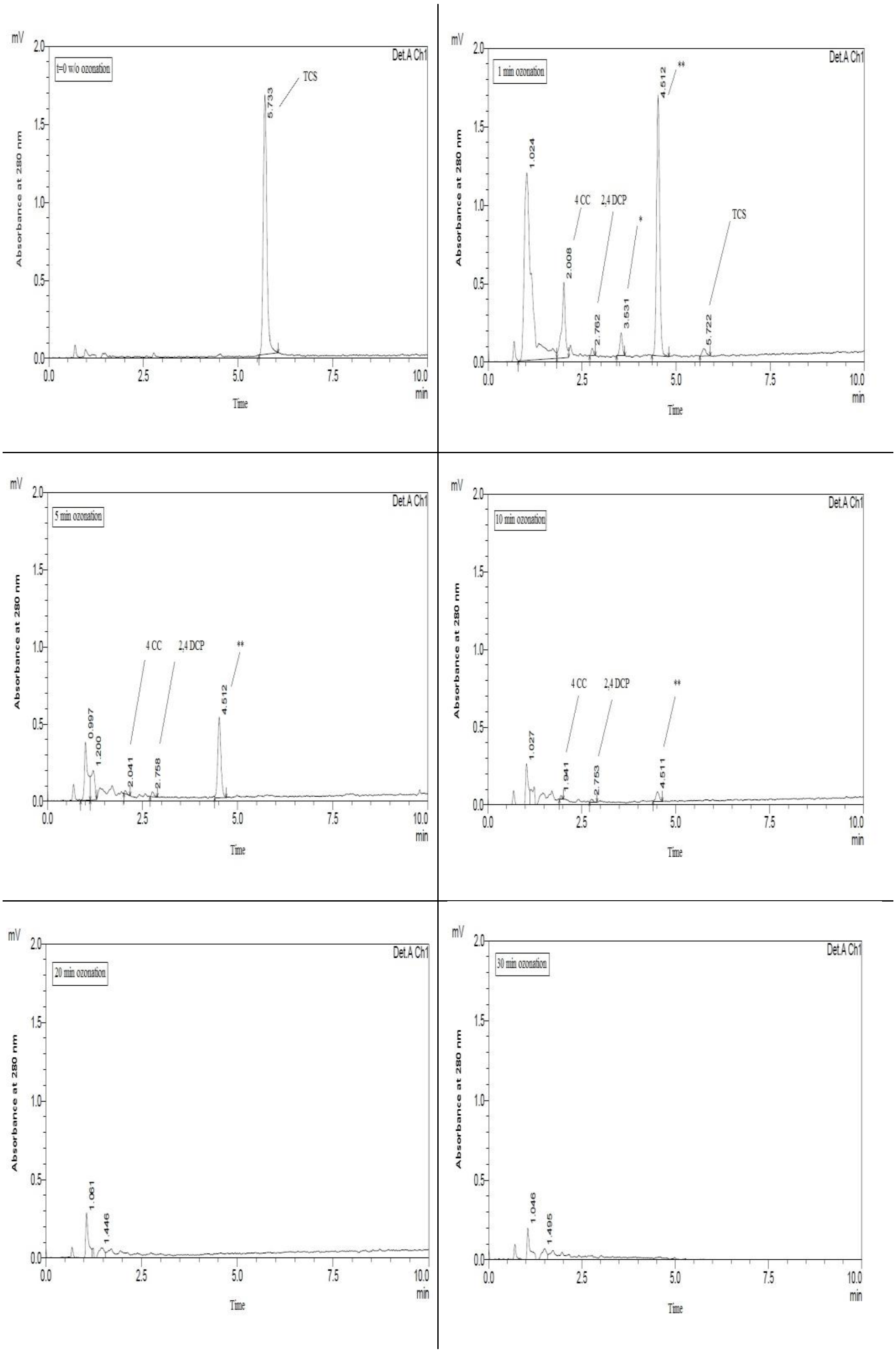


Figure 25. Chromatograms obtained as a result of the ozonation of TCS containing samples prepared with sodium hydroxide (Initial TCS=1 mg/L; ozone at 5 mg/L).

Table 19. Concentrations of by-products measured following the ozonation of TCS

Time (min)	Concentration of TCS and Transformation by-Products, ppb[*]																	
	Initial TCS concentration: 1 mg/L						Initial TCS concentration: 3 mg/L						Initial TCS concentration: 5 mg/L					
	TCS (ppm)	4-CC (ppb)	2,4- DCP (ppb)	U-3.5[**] (area)	U-4.5[***] (area)	2,4-DCA (ppb)	TCS (ppm)	4-CC (ppb)	2,4 DCP (ppb)	U-3.5 (area)	U-4.5 (area)	2,4-DCA (ppb)	TCS (ppm)	4-CC (ppb)	2,4 DCP (ppb)	U-3.5 (area)	U-4.5 (area)	2,4-DCA (ppb)
0	1.00	-	-	-	-	-	3.03	-	-	-	-	-	5.04	-	-	-	-	-
1	0.04	50	12.62	94	3193	-	1.62	342	32.8	256	4163	<LOD	3.75	246	42.50	608	8087	<LOD
5	<LOD	<10	7.00	-	1437	<LOD	0.36	378	16.7	101	8970	<LOD	1.83	261	18.90	374	10421	<LOD
10	-	<10	6.10	-	-	<LOD	<LOD	<LOD	16.6	-	3983	<LOD	0.12	-	16.30	-	13028	<LOD
20	-	-	-	-	-	-	-	<LOD	15.1	-	-	<LOD	0.04	-	12.70	-	1865	<LOD
30	-	-	-	-	-	-	-	-	-	-	-	-	0.02	-	-	-	-	-

[*] as chromatogram area for Unknowns ; [**]U-4.5: Unknown (at 4.5 min); [***]U-3.5: Unknown (at 3.5 min)

As seen from Table 19, retention times and concentration of the reaction products are variable. Time to reach to their peak amounts also showed an alteration in different initial TCS concentrations. To illustrate, U-4.5 reached its peak amount at 10 min in 5 mg/L initial TCS case while it was reached at 5 min in 3 mg/L and 1 min in 1 mg/L initial TCS. In addition, in 3 mg/L and 5 mg/L initial TCS cases, concentration of 4-CC have an increase between 1 and 5 min retention times while it had its peak in 1 min and then decreased in 1 mg/L initial TCS. Furthermore, apart from U-4.5 and 4-CC, quantity of each reaction products showed increase from the beginning to 1 min retention time and decrease with a time. As it can be deduced from these results, considering not only the solely removal of TCS but also the by-products, in order to remove the TCS and eliminate the ozonation reaction by-products from water, at least 20 min ozonation is required for 1 mg/L TCS bearing surface waters while it is required 30 min ozonation for both 3 and 5 mg/L TCS bearing surface waters with 5 mg/L ozone dose.

Since TCS has not been encountered at mg/L levels but encountered at μg/L levels in surface waters, it would be better and make sense to define the required ozone to TCS ratio with respect to the aforementioned contact time and ozone doses. In this respect, considering the applied ozone dose 8.33 mg/min (5 mg/L) and 1 L of ozonation reactor, 166.6 mg ozone to 1 mg TCS and 249.9 mg ozone to both 3 and 5 mg TCS bearing surface waters are required so as to remove the TCS and its reaction by-products completely.

From the foregoing discussion, it is clear that applying the ozonation technique eliminates TCS from surface water samples; however, it leads to the formation of some by-products. Although further ozonation eliminates them as well to a great extent, their toxicity needs to be explored. In this respect, Chen et al. (2012) reported that 2,4-DCP shows lower genotoxic effects than TCS at the tested concentrations, however this compound is classified as toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Accordingly, other possible transformation products should be cautiously taken into consideration for their possible genotoxic effect at their appeared concentrations on ozonation. In this regard, their general physical and chemical properties regarding their environmental fate, and responsible for their effects on the environment are presented in Table 20.

Table 20. Physical and chemical properties of TCS and its ozonation by-products (Johnson et al., 2012; Melnick, 1989; NICNAS, 2009; Kondo et al., 2005; URL 10; URL 11)

Parameter	**TCS**	**2,4-DCP**	**4-CC**	**2,4-DCA**
CAS No	3380-34-5	120-83-2	2138-22-9	553-82-2
Molecular formula	$C_{12}H_7Cl_3O_2$	$C_6H_4Cl_2O$	$C_6H_5ClO_2$	$C_7H_6Cl_2O$
Solubility in water (at 25°C, mg/L)	10	4,500	1,126	76.44
pK_a	7.9	7.85	-	-
Henry's constant (atm-m^3/mol)	4.99×10^{-9}	5.50×10^{-6}	4.32×10^{-11}	1.75×10^{-4}
Log K_{oc}	4.265	2.42-2.82	-	2.499
Log K_{ow} (at 20°C)	4.76	3.06-3.25	1.68	3.36
EDC	Most probably	Unclear	-	-
LC_{50}	0.288 mg/L (rainbow trout)	2.2-3.1 mg/L (rainbow trout) 1.6-2.6 mg/L (Bluegill)	1.58 mg/L (fathead minnow)	-
EC_{50}	0.7-1.4 µg/L (freshwater algae)	9.2 mg/L (freshwater algae)	-	-
BCF	905-10,779	3.8-100	24.02	-

- no data available

Table 20 provides an opportunity to assess the chemical and physical properties of TCS and its ozonation by-products in a comparable manner so as to determine their toxicity, bio-accumulation, and persistency on the environment. In this respect, with a lowest water solubility amount, TCS has less tendency to stay in water phases. Therefore, hydrolysis process is not expected to be important mechanism for TCS's self degradation while it probably works for the by-products. Besides, TCS is more hydrophobic and has more affinity to remain or adsorb solid phases due to its highest organic carbon partition coefficient (log K_{oc}) and octanol–water partition coefficient (log K_{ow}) values. Therefore, removal of TCS is more complex and difficult due to being highly adsorbed to the sediment/soil. Also it may have relatively high detrimental effects on organisms living in sediment and soil. Considering the Henry's constant values, except from 4-CC, TCS has lowest value compared to the by-products indicating that its by-products are more volatile from the water which is desirable condition in terms of removal mechanism for the aforementioned by-products. From the point of environmental toxicity, TCS is clearly more toxic compound than the rest of the compounds of interest since it has about 7-10 fold higher median lethal concentration (LC_{50}) values and approximately 1000 fold higher half maximal effective concentration (EC_{50}) values. Furthermore, TCS is more bio-accumulative substance by having quite higher bio-concentration factor (BCF) values. Lastly, TCS has been started to be pronounced among one of the endocrine disruptors in the literature (NICNAS, 2009) whereas there is not yet proved scientific study on the endocrine disrupting chemicals (EDCs) effect of the other called compounds. In this context, TCS is more hydrophobic, less soluble in water, more bio-accumulative, more toxic and endocrine disrupter among its ozonation by-products. Although it seems that being encountered of TCS in water environment poses higher threats to the environment, it is obvious that its ozonation by-products, considering their environmental parameters, also have certain risks to the aquatic environments as an hazardous compounds when they are present in these systems. As such, the ozone dose and contact time should be adjusted so well that TCS and its by-products are removed completely or at least decreased to desirable concentration not to cause to any toxicity in the environment.

4.5 Ozone Demand of Triclosan

In the course of decision making to apply the right ozone dose and its contact time for the removal of TCS from the waters, removal of its by-products has also great importance. As indicated earlier in this study, considering the results obtained from the experiment done with ozonation (5 mg/L ozone dose) of the Kesikköprü surface water spiked with 1, 3 and 5 mg/L TCS (Table 19), it could be interpreted that retention times and concentrations of the by-products are variable.

Besides applied dose and contact time, specific ozone consumption (mg O_3/mg compound) by the target pollutant has an important role in ozone treatment applications. Since that is the fact, amount of ozone that was solely consumed by TCS was calculated by considering the results obtained from two different experiments done with spiking 1 mg/L TCS and without spiking TCS into the surface water applying 5 mg/L ozone. In these experiments, whole conditions were kept same and the only difference was TCS; therefore, the differences of calculated amounts gave the ozone amounts that were solely consumed for TCS. The results of these experiments are represented in Table 21.

Table 21. Ozone consumptions in different experiments done with surface water bearing TCS (1 mg/L) and free of TCS

Time (min)	**1**	**5**	**10**	**20**	**30**
Experiment done for surface water bearing 1mg/L TCS					
O_3 dosed into the system (mg)	8.33	41.67	83.33	166.67	250.00
Unused O_3 (mg) (-)	0.68	1.22	2.30	2.57	2.57
Escaped O_3 (mg) (-)	0.54	2.58	5.34	13.74	23.94
O_3 consumed by Organics +System +TCS (mg)	7.12	37.87	75.69	150.36	223.49
Experiment done for surface water w/o TCS					
O_3 dosed into the system (mg)	8.33	41.67	83.33	166.67	250.00
Unused O_3 (mg) (-)	1.49	1.89	2.57	3.11	3.25
Escaped O_3 (mg) (-)	2.04	5.94	11.46	23.04	36.30
O_3 consumed by Organic +System (mg)	4.81	33.83	69.30	140.52	210.45
Difference					
O_3 consumed by TCS (mg)	2.31	4.04	6.39	9.84	13.04

- Consumption

Taking into account of the results obtained for ozone consumption for only TCS (Table 21) and also by-product formation in the conditions that surface water bearing 1 mg/L TCS were ozonated with 5 mg/L ozone (Table 19), although 10 min ozonation provides almost complete abatement for TCS, two by-products (2,4-DCP and 4-CC) still encountered in solution and therefore it needs to be 20 min of ozonation for their elimination. In the light of these results, for the removal of the TCS and elimination of its by-products from the surface water having 1 mg/L TCS, 20 min of ozonation with 5 mg/L ozone dose is required and within this framework, in line with the results in Table 19, amount of ozone required was found as 9.84 mg ozone for per mg TCS. Ozone consumption amounts with respect to time and obtained removal ratios are can be deduced from Table 22, as well.

Table 22. Timely variation in ozone consumption by TCS and TCS removal rate (5 mg/L ozone to 1 mg/L TCS bearing surface water)

Time (min)	O_3 consumption of TCS (mg)	Removal (%)
1	2.311	96.0
5	4.036	98.5
10	6.390	100
20	9.841	100
30	13.036	100

Ozone demand or ozone consumed per unit mass TCS is also substantial for the determination of the critical parameters (i.e. ozone dose, contact time) of the ozonation process to be applied especially in surface water and drinking water treatment plants. This ratio could also be used for the optimization of the ozonation treatment processes. In this scope, Figure 26 enables to observe the ozone consumption per TCS removed ratio with graphical manner. As can be seen from Figure 26 (a), considerably high removal rates (98.5%) were obtained after 5 min ozonation of initially 1 mg/L TCS bearing surface water and almost whole TCS was depleted in water, thereby in the process of time, removal of TCS was reached up to 100% depletion or at least undetectable levels. Although, 98.5% of it was depleted in 5 min ozonation and then almost completely depleted at the time of 10 min ozonation, ozone consumption for TCS was increased even between 10 and 30 min ozonation time (Table 22 & Figure 26 (b)). This could only be explained by the presence of its ozonation by-products (i.e. 2,4-DCP, 4-CC, 2,4-DCA) being transformed during ozonation process. In fact, mentioning to ozone consumed by solely TCS is not correct approach in this regard. This being the case, considering the already complex ozonation process and its ozonation by-products being formed in different times with inconsistent amounts, it can be stated that it is highly difficult to define the required ozone amount which corresponds only for the removal of TCS in water. In this respect, 9.84 mg ozone to 1 mg TCS ratio, previously determined by taking into account of the removal of its by-products as well, can be attributed not only for the TCS removal but also required for the complete removal of its transformation by-products.

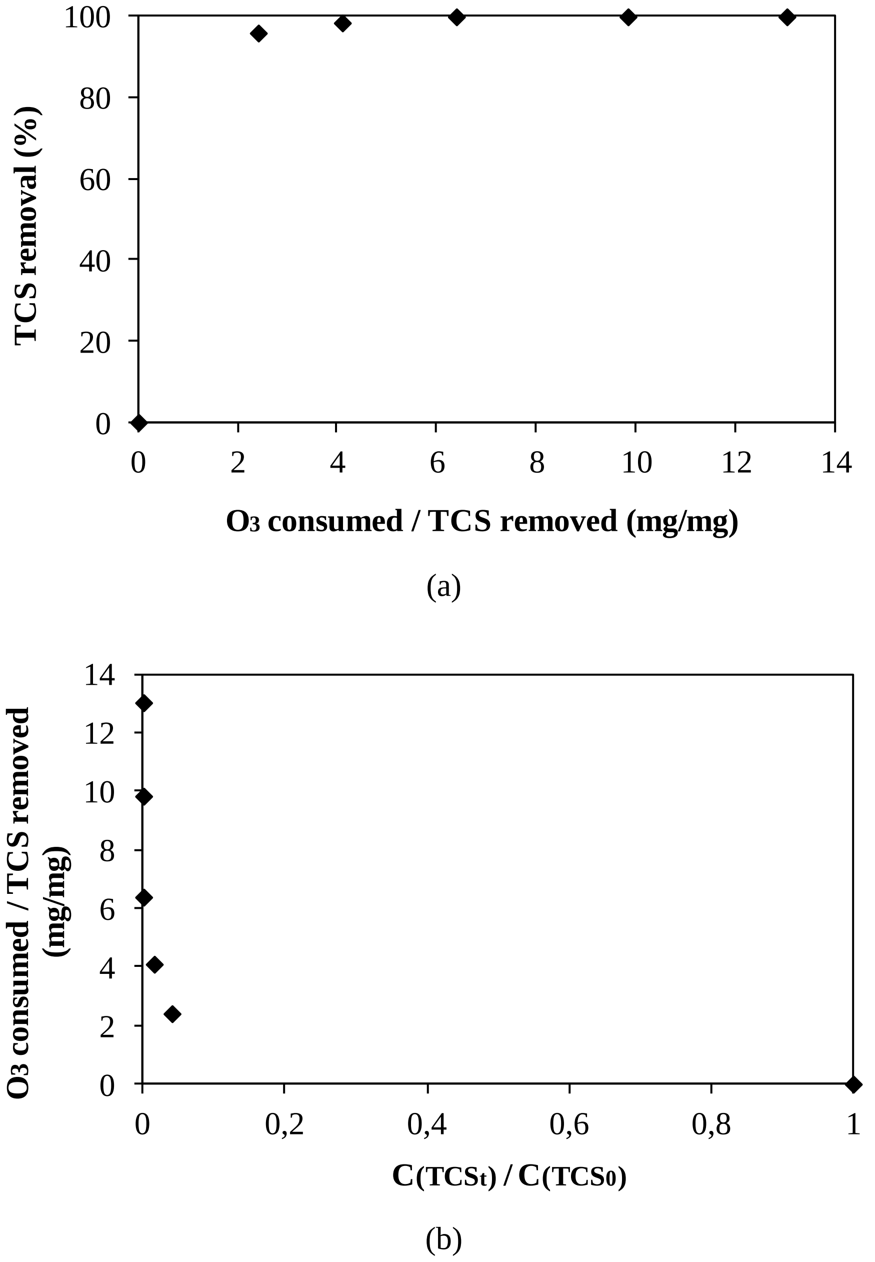


Figure 26. Ozone consumption amounts per TCS removed and TCS removal ratios (1 mg/L initial TCS in surface water, 5 mg/L ozone dose)

4.6 Reaction Kinetics

When the ozone concentration in the water solution is much more excess compared to that of target compound, the reaction rate depended mainly on their own concentration in the system thereby follows the pseudo first-order kinetics (Huang, 2010). As ozone was given in excess amount in a continuing manner in the ozonation experiments done in this study, pseudo first-order kinetics was applied by considering following Equation (2) within the scope of the determination of ozonation reaction rate constants of TCS. In this respect, effects of ozone dose, initial TCS concentration and pH were studied in order to observe reaction kinetics under different conditions.

$$\frac{\mathrm{d}\,[\mathrm{triclosan}]}{\mathrm{dt}} = -\mathrm{k}_{\mathrm{app},\mathrm{O3}}[\mathrm{triclosan}] \qquad \text{(Eq. 2)}$$

where;

k_{app,O_3} : Pseudo first-order rate constant for the reaction at a certain pH when O_3 is excess in the aqueous solution (time^{-1})

[triclosan] : TCS concentration (mass/volume)

4.6.1 Effect of Ozone Dose

Effects of different ozone doses on the ozonation kinetics of TCS were examined by plotting ln C/C_0 vs time transformation of means of applying 5 different ozone concentration (i.e. 5, 10, 15, 24, 70 mg/L) to the 5 mg/L TCS bearing Milli-Q water. Results obtained are represented in Figure 27 and 28.

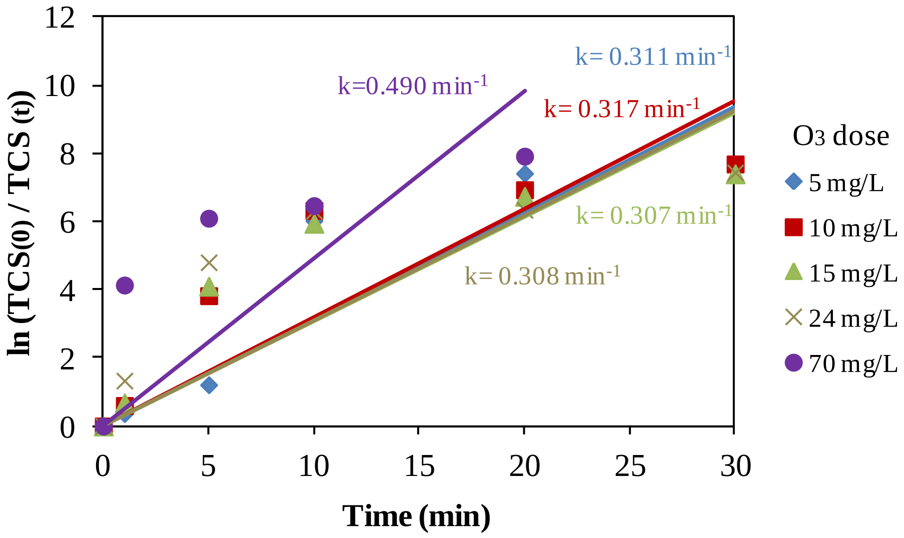


Figure 27. Reaction kinetics at different ozone doses

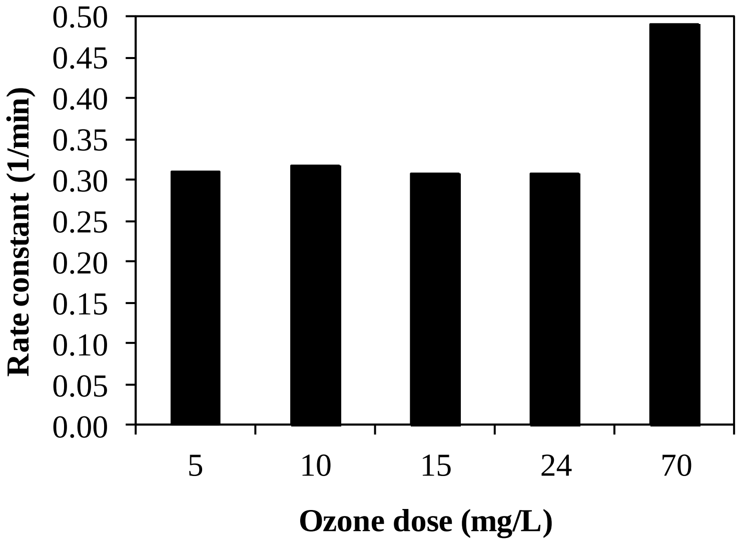


Figure 28. Ozonation rate constants at different ozone doses

As can be deduced from the Figure 27 and Figure 28, different ozonation rate constants were found at different ozone doses. The reaction rate constants calculated for each ozone dose were varied between 0.307 min^{-1} and 0.490 min^{-1}. It was observed that reaction rate constants of TCS during ozonation experiments did not differ as much for the ozone doses between 5 and 24 mg/L which were calculated as between 0.307 min^{-1} and 0.317 min^{-1} although ozone to TCS ratio in the aqueous

Milli-Q water solution increased by nearly 5 fold as in the case of 5 mg/L to 24 mg/L ozone application and there were not any other ozone depleting substance in the solution.

In this respect, it can be said that rate of oxidation of TCS was not entirely dependent on the ozone concentration applied to the system when the ozone concentration was between 5 and 24 mg/L, and the effect was minimal compared to that of 70 mg/L ozone dose. Furthermore, with the increase of ozone dose to the 70 mg/L, reaction rate constant increased and calculated as 0.490 min^{-1}. This can also comply with the obtained TCS removal efficiencies at these aforementioned ozone doses that complete removal of TCS was achieved in 30 min of ozonation for the ozone doses between 5-24 mg/L whereas 20 min of ozone exposure was adequate to remove the same amount of TCS from the Milli-Q water for the ozone dose of 70 mg/L which at the end manifesting the reaction proceeding faster with that higher ozone dose compared to the rest.

One other output of these finding was that although the same TCS removal efficiencies were reached in short period of time especially in 10 min of ozonation during the experiments performed with higher ozone doses, the overall rate of the reaction of TCS with ozone did not change significantly verifying the assumption made initially on the reaction pursuing the pseudo first-order kinetics which was independent from ozone supplied to the system due to its being at excessive amount over TCS.

Moreover, after 10 min of ozone exposure, effluent with nearly same TCS content was obtained for each ozone dose applied indicating the independency of removal efficiency with the ozone dose after that exposure time which also affecting the overall rate constants. It was also found that not all of the ozonation by-products of TCS were removed from the aqueous solution within 10 min which requiring longer period of ozone treatment to be completely removed. From this finding, the choose of ozone dose to be applied in the treatment process is more of the consideration either the ultimate aim is to deal with only TCS or the concern is also including both TCS and its ozonation by-products from the water environment.

4.6.2 Effect of Initial Triclosan Concentration

Effects of initial TCS concentration in the aqueous solution to be treated, on the oxidation kinetics were investigated by keeping the ozone dose constant (i.e. 5 mg/L) and altering the initial TCS concentration (i.e. 1, 3 and 5 mg/L). Aqueous solution was the surface water in this case and TCS was spiked to this medium to observe ozonation reaction rate constant based upon the amount of TCS involved in the aqueous medium. Results obtained within this scope of the experiments are given in Figure 29 and 30.

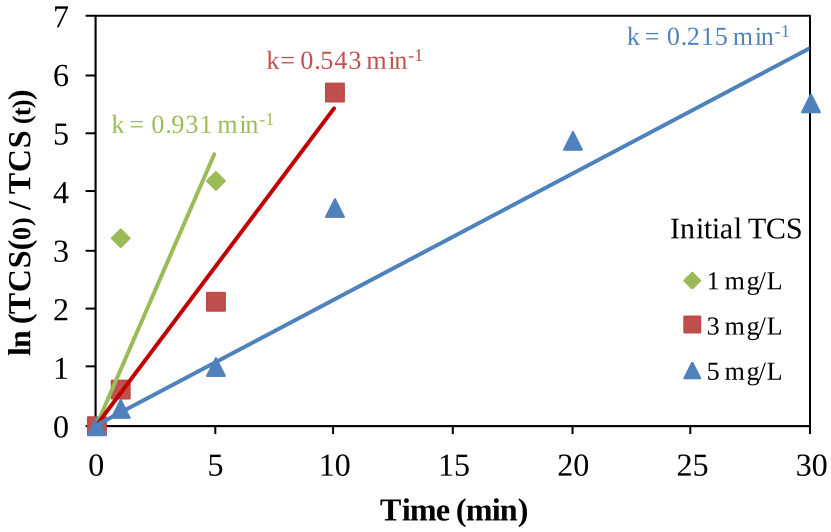


Figure 29. Reaction kinetics at different TCS concentration

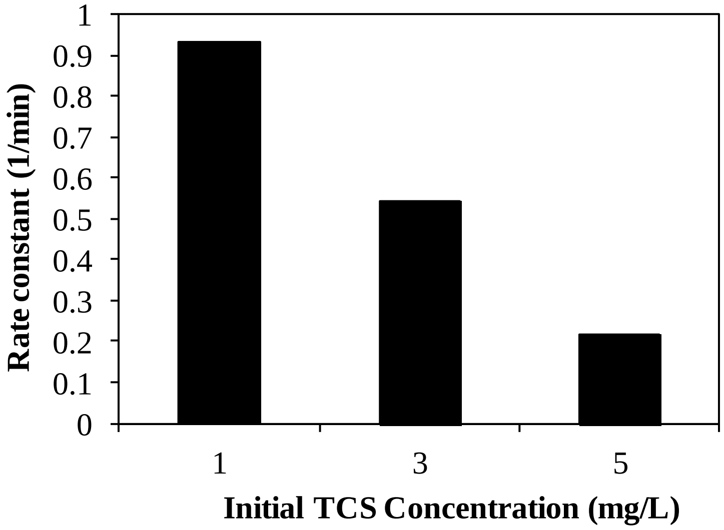


Figure 30. Ozonation rate constants at different initial TCS concentration

As can be seen from Figure 29 and Figure 30, ozonation reaction rate constant of TCS changed significantly based upon the initial TCS concentration in the surface water and it decreased dramatically with the increase in the initial TCS concentration. Reaction rate constants were determined as of 0.931 min^{-1}, 0.543 min^{-1} and 0.215 min^{-1} for the initial TCS concentration of 1, 3 and 5 mg/L respectively. Actually, this was an expected situation since available ozone in the solution more easily attacked and gave more rapid reactions with the surface water bearing lesser amount of TCS.

Furthermore, there obtained a high linear correlation between the initial TCS concentration and the ozonation reaction rate constant with a R^2 value of 0.9977 which demonstrating the reaction strongly dependent on the contaminant concentration desired to be removed by means of ozone treatment.

The findings were also supported by the effluent TCS concentration after 5 mg/L ozone exposure that complete removal was achieved in 10 min of ozonation for 1 mg/L TCS involving surface water while it was accomplished in 20 min and more than 30 min for 3 mg/L and 5 mg/L TCS including surface water respectively. Hence, the reaction proceeded faster for the first case, as well.

Another comparison can be made with the result obtained in the ozone dose effect on kinetic constants for the initial TCS concentration of 5 mg/L and ozone dose of 5 mg/L within the scope of which the ozonation reaction rate constant was calculated as 0.311 min^{-1}, as well. The rate constant (i.e. 0.215 min^{-1}) was obtained lower than that value since the former kinetic study was conducted with Milli-Q water whereas the latter one was performed with surface water which including various components beyond TCS that were oxidisable with ozone. This output also demonstrated the importance of water matrix on the determination of kinetic constants for the desired contaminants.

4.6.3 Effect of pH

Effects of aqueous solution pH on the ozonation reaction rate constants of TCS were studied by keeping the ozone dose (i.e. 5 mg/L) and initial TCS concentration (i.e. 1 mg/L) constant and altering the surface water pH (i.e. pH 6, 7.3, 8 and 10). The kinetic constants were observed both in acidic and alkaline conditions by setting the pH; however, it was given importance to study with the highly possible pH values encountered naturally in the water mediums. Results obtained within this scope of the experiments are summarized in Figure 31 and 32.

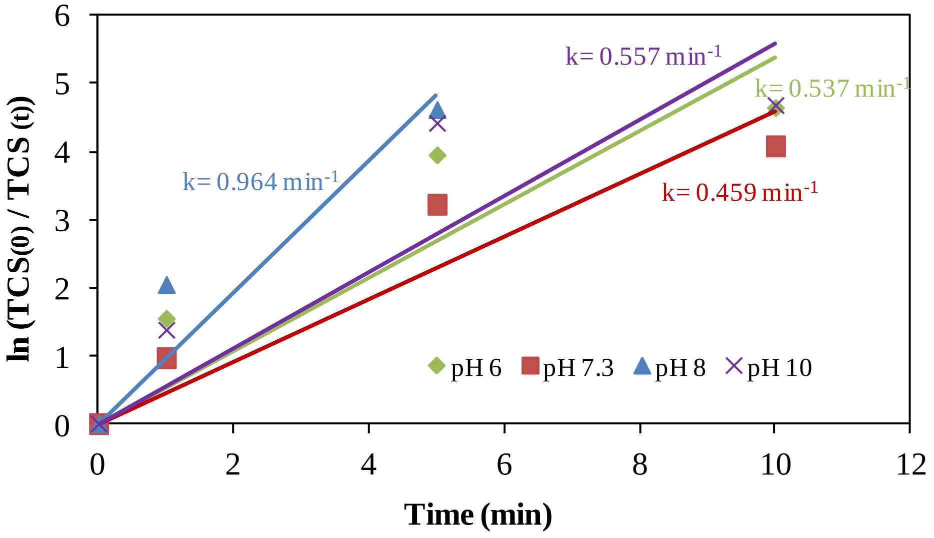


Figure 31. Reaction kinetics at different pH values

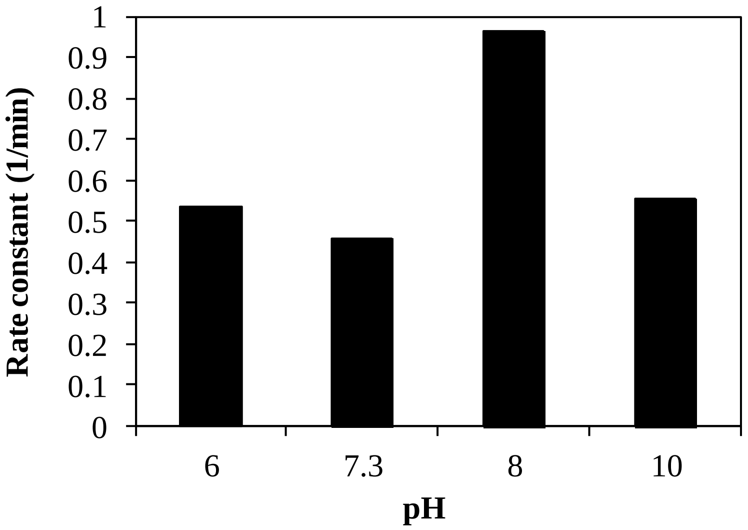


Figure 32. Ozonation rate constants at different pH values

As can be inferred from Figures 31 and 32, the ozonation reaction rate constant varied with the pH of the surface water; however, there was no linear trend between the obtained values of the rate constants. The reaction rate constants calculated for each pH changed between 0.459 min^{-1} and 0.964 min^{-1}.The highest rate constant (i.e. 0.964 min^{-1}) was observed for the condition where the pH of the solution was 8 whereas the lowest one (i.e. 0.459 min^{-1}) was determined at pH 7.3. The rate constants obtained at pH 6 an pH 10 were nearly same, a bit greater of the former one and found as 0.537 min^{-1} and 0.557 min^{-1} respectively.

The pH of the water solution has also influences on the composition of the water environment and it can lead to the dominancy of the various compounds based on the ionization and solubility properties. Thus, since the changes in pH directly or indirectly affects the content of the water, the effect on the kinetic constants become more complex and the interpretations go beyond the real cases. Moralı (2010) also demonstrated in his study that there was no observable trend between the pH of the wastewater and the reaction rate constants of COD and color removal at the end of ozone treatment and indicating the most suitable pH of 4 for the highest rate of the reactions. This situation supports the variability of the ideal pH values in different water mediums and the finding of not interpretable relationship between the pH data sets covered in the corresponding researches.

Although the concrete conclusion could not be made regarding the pH effect on the ozonation reaction rate constant of TCS, it was demonstrated that kinetic constants were differed with the pH of the water environment and therefore, it should be seriously considered during the studies conducted for the determination of the kinetic constants.

CHAPTER 5

CONCLUSION

Emerging pollutants like TCS have recently been encountered in lots of receiving waters necessitating the studies on the determination of their actual abundances in these water ecosystems and upcoming removal techniques in order to achieve the good water qualities in these environmental systems and as a consequence protect the environment and humanity. In this context, ozone treatment of TCS spiked Milli-Q water and surface water was investigated in this thesis study and the factors affecting the ozone treatment was taken into consideration in detail in order to shed light into the removal of TCS by ozone and to optimize the treatment process that could be applied in surface or drinking water treatment plants and achieve higher removal efficiencies within the laboratory-scale experiment. High removal efficiencies were obtained at the end of ozone treatment and the obtained removal efficiencies were changed based upon the time of ozone supply. Almost complete elimination of TCS from the Milli-Q water and surface water were satisfied after 10 min treatment with 5 mg/L continuous ozone exposure.

Effects of ozone dose, initial TCS concentration, water matrix and pH were studied during the study and each was found to be the major factors influencing the ozone treatment of TCS containing waters and removal of TCS kinetics within the system. Different ozone doses between 5-70 mg/L were investigated and the time of achieving the same removal efficiency lessened with the higher doses. TCS level of the water of interest was also observed to be important for the removal of TCS by means of ozonation since the time to achieve complete elimination was not same for the different contaminant concentration and it increased in parallel to the concentration of the compound to be treated from the system. Moreover, impurities in the surface waters such as organic and inorganic compounds were demonstrated to be involved in the ozone treatment since ozone attacks and gives reactions with them by reducing the available ozone in solution and lowering the removal efficiency of TCS. In other words, the more water contains impurities, the more ozone exposure time or ozone amount is required for the treatment of TCS within the system. Water quality in terms of pH was the other factor affecting the ozone treatment of TCS and it was found that optimal conditions changes with the water of concern and thus, different pH values have to be investigated in order to designate the ideal condition giving the higher removal efficiency for the applied ozone dose.

Furthermore, it was clear that ozone application eliminated TCS from surface water samples; however, it leaded to the formation of some transformation by-products such as 2,4-DCP and 4-CC. In addition, 2,4-DCA was formed as ozonation by-product of TCS in the presence of methane group in water, as well. There were also other two transformation products detected at 3.5 and 4.5 minutes on the chromatograms but they could not be identified in this study. The major conclusion from these findings is that the previous studies reporting the higher removal efficiencies of TCS at the end of ozone treatment was not completely reliable since none of them considered the possible by-product formation and followed the fate of these by-products within the system. Therefore, taking into account not only the solely removal of TCS but also the by-products, it was found that at least 20 min treatment was required for 1 mg/L TCS bearing surface waters treated with 5 mg/L continuous ozone dose in order to remove TCS and eliminate its ozonation by-products from the water. Although further ozonation eliminated the aforesaid by-products as well to a great extent, their toxicity and bio-accumulation profiles were explored in order to understand their behaviors in the environmental water samples. In this manner, the physical and chemical properties of the identified by-products were compared with those of TCS and it was observed that TCS is more hydrophobic, more bio-accumulative, more toxic and endocrine disrupter among its ozonation by-products and that is why the priority should be given to TCS during the studies conducted for the ozone treatment of this biocide. However, it was also found that these ozonation by-products, considering their environmental parameters, have still certain risks to the aquatic environments as hazardous compounds due to their outlined risk and bio-accumulation profiles when they are present in these systems. Thus, the ozone dose and exposure time should be adjusted so well that TCS and its by-products are removed completely or at least decreased to desirable concentration not to cause to any harms in the environment.

CHAPTER 6

RECOMMENDATIONS

Recommendations, compiled in line with the scope and results of this study, that are thought to be useful for the further studies and essential to be taken into consideration for the better environment and prosperity of humankind are listed as follows;

- Alternative compounds should be preferred instead of TCS in the ingredients and formulations of the products.

- In studies to be worked with high hydrophobic nature, labwares and apparatus made with materials with no affinity to the sorption (i.e. glass) should be preferred and kept away from the plastic ones.

- In the ozonation studies, it should be canalized to the not only TCS removal but also its potential ozonation by-products in order to evaluate the fate of TCS in a complete manner.

- By-products which could not identified in this study should be identified by further studies in order to be done proper risk assessment evaluation of ozonation of TCS in surface waters towards humanity and environment.

- Further studies should be done to clarify the EDC and cross-resistance issues of TCS.

- As incorporated in the specific pollutant list of Turkey and other 3 countries, TCS should be monitored in waters and necessary precautions should be taken not to be discharge to the water bodies in watershed basis in line with the requirements of WFD.

- More studies should be done for the ozonation of TCS bearing surface waters especially on treatment plant basis that would better reflect the real situation and enable to observe the effects on the ozonation of TCS on-site.

- In further studies, considering the fact that TCS has been encountered at very low concentrations (i.e. ng/L and µg/L) in surface waters, it would be suitable to use devices such as HPLC-MS/MS, LC-MS/MS or GC-MS/MS giving the more sensitive measurement results.

REFERENCES

Adams C.D., Randtke S.J., 1992. Ozonation byproducts of atrazine in synthetic and natural waters. Environmental Science and Technology 26, 2218-2227.

Adolfsson-Erici, M., Petersson M., Parkkonen, J. and Sturve J., 2002. Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. Chemosphere 46:1485-1489.

Agenson, K.O., Oh, J.I. and Urase, T., 2003. Retention of a wide variety of organicpollutants by different nanofiltration/reverse osmosis membranes: controlling parameters of process. Journal of Membrane Sciences, 225 (1-2), 91-103.

Aiello, E.A., Larson, E.L., Levy, S. B., 2007. Consumer Antibacterial Soaps:Effective or Just Risky?. Clinical Infectious Diseases, 45, 137-147.

Allmyr, M., 2009, On the Fate Of Triclosan in Humans, Department of Dental Medicine, Karolinska Institute, Stockholm, Sweden.

Amari, T., Themelis, N. and Wernick, I., 1999. Resource recovery from used rubber tires. Resource Policy. 25, 170.

APUA, 2011, White Paper prepared the Alliance for the Prudent Use of Antibiotics.

Arnold, W.A., McNeill, K., Packer, J.L., Latch, D.E. and Boreen, A.L., 2003. Photochemical fate of pharmaceutical compounds discharged and detected in natural waters. Department of Chemistry, University of Minnesota, USA.

Bellona, C., Drewes, J.E., Xu, P. and Amy, G., 2004. Factors affecting the rejection of organic solutes during NF/RO treatment-a literature review. Water Research. 38 (12), 2795-2809.

Bester, K., 2003. Triclosan in a sewage treatment process-balances and monitoring data. Water Research, 37(16), 3891-3896.

Birikorang, S.A., Miller, M., O’Connor, G.A., 2010. Retention-release characteristics of triclocarban and triclosan in biosolids, soils and biosolids-amended solids, Environmental Toxicology and Chemistry, 29 (5), 1925-1933.

Bolong, N. Ismail, A.F., Salim, M.R. and Matsuura, T., 2009. A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination. 239 (1-3), 229-246.

Boye, B., Brillas, E., Marselli, B., Michaud, P.A., Comninellis, Ch., Farnia, G. et al., 2006. Electrochemical incineration of chloromethylphenoxy herbicides in acid medium by anodic oxidation with boron-doped diamond electrode. Electrochimica Acta. 51, 2872–2880.

Braoudaki, M. and Hilton A.C., 2004. Low level of cross-resistance between triclosan and antibiotics in Escherichia coli K12 and E. coli 055 compared to E. coli O157. FEMS Microbiology Letters, 235, 305-309.

Brillas, E., Garcia-Segura, S., Skoumal, M. and Arias, C., 2010. Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes. Chemosphere. 79, 605–612.

Broseus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauve, S., Barbeau, B., Prevost, M., 2009. Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. Water Research, 43, 4707-4717.

Buth, J.M., Ross, M.R., McNeill, K. and Arnold, W.A., 2011. Removal and formation of chlorinated triclosan derivatives in wastewater treatment plants using chlorine and UV disinfection. Chemosphere. 84, 1238-1243.

Calafat, A.M., Ye, X., Wong, L.Y., Reidy, J.A., Needham, L.L., 2008. Urinary concentrations of triclosan in the U.S. population: 2003-2004. Environment Health Perspective, 116, 303-307.

Canosa, P., Morales, S., Rodriguez, I., Rubi, E., Cela, R., Gomez, M., 2005, Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. Analytical & Bioanalytical Chemistry 383 (7-8), 1119-1126.

Chen, X., Richard, J., Liu, Y., Dopp, E., Tuerk, J., Bester, K., 2012, Ozonation products of triclosan in advanced wastewater treatment. Water Research 46 (7), 2247-2256.

Chen, X., Nielsen, J.L., Furgal, K., Liu, Y., Lolas, I.B. and Bester, K., 2011. Biodegradation of triclosan and formation of methyl-triclosan in activated sludge under aerobic conditions. Chemosphere. 84 (4), 452-456.

Chu, S., Metcalfe, C.D., 2007. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry, Journal of Chromatography A, 1164 (1-2), 212-218.

Coogan, M.A., Edziyie, R.E., La Point, T.W., Venables, B.J., 2007. Algal bioaccumulation of triclocarban, triclosan, and methyltriclosan in a North Texas wastewater, treatment plant receiving stream. Chemosphere 67 (10), 1911–1918.

Crofton, K.M., Paul, K.B., Hedge, J.M., DeVito, M.J., 2007. Short-term in vivo exposure to the water contaminant triclosan: evidence for distruption of tyroxine. Environmental Toxicology and Pharmacology, 24, 194-197.

Dann, A., Hontela, A., 2011. Triclosan: environmental exposure, toxicity and mechanisms of action. Journal of Applied Toxicology 31 (4), 285-311.

Dodd, M.C., Kohler, H.-P.E., von Gunten, U., 2009. Oxidation of antibacterial compounds by ozone and hydroxyl radical: elimination of biological activity during aqueous ozonation processes. Environmental Science & Technology 43 (7), 2498-2504.

DeLorenzo, M.E., Keller, J.M., Arthur, C.D., Finnegan, M.C., Harper, H.E., Winder, V.L., Zdankiewicz, D.L., 2008. Toxicity of the antimicrobial compound triclosan and formation of the metabolite methyl-triclosan in estuarine systems. Environmental Toxicology, 23(2), 224-232.

Drury, D., Snyder, S., (2005). Use of ozone for disinfection and EDC removal at CCWRD.

Elovitz, M.S., Shemer, H., Peller, J.R., Vinodgopal, K., Sivaganesan, M., Linden, K.G., 2008. Hydroxyl radical rate constants: comparing UV/H2O2 and pulse radiolysis for environmental pollutants. Journal of Water Supply Research and Technology 57 (6), 391-401.

Engelhardt, T.L., Malkov, V.B., 2013. Chlorination, Chloramination and Chlorine Measurement, Hach Company.

Environmental Defense of Canada, 2012. The trouble with triclosan. Toronto, Canada.

EPA, 1999, Alternative Disinfectants and Oxidants Guidance Manual, Office of Water.

European Commission, Scientific Committee on Emerging and Newly Identified Health Risks (EC-SCENIHR), 2009. Assessment of the Antibiotic Resistance Effects of Biocide (SCCP/1192/08). Directorate General for Health and Consumers.

European Union (EU), 1998. Official J. Eur. Community L330: Directive 98/83/EG.

Fan, L., Song, J., McRae, K.B., Walker, B.A., Sharpe, D., 2007. Gaseous ozone treatment inactivates Listeria innocua in vitro. Journal of Applied Microbiology 103, 2657-2663.

Fernandes, M., Shareef, A., Kookana, R., Gaylard, S., Hoareb, S., Kildeaa, T., 2011. The distribution of triclosan and methyl-triclosan in marine sediments of Barker Inlet, South Australia, Journal of Environmental Monitoring 13 (4), 801-806.

Ferrer, I., Mezcua, M., Jose Gomez, M., Thurman, M.E., Aguera, A., Hernando M.D. and Fernandez-alba AR, 2004. Liquid chromatography/time-of-flight mass spectrometric analyses for the elucidation of the photodegredation products of triclosan in wastewater samples. Rapid Communications in Mass Spectrometry, 18, 443-450.

Fontela, M. H., Galceran, M. T., Ventura, F., 2011. Occurance and removal of pharmaceuticals and hormones through drinking water treatment. Water Research, 45, 1432-1442.

Foran, C.M., Bennett, E.R., Benson, W.H., 2000. Development evaluation of a potential non-steroidal estrogen: triclosan. Marine Environmental Research, 50, 153-156.

FSNET. 2000. Survey of U.S. Stores reveals widespread availability of soaps containing potentially harmful antibacterial agents. Centre for Safe Food, University of Guelph.

Georgeson D.L., Karimi A.A., 1988. Water quality improvements with the use of ozone at the Los Angeles water treatment plant. Ozone science and engineering. 10(3), 255-276.

Glaze, W.H. and Kang, J.W., in Proc. Symposium on Advanced Oxidation Processes and Treatment of Contaminated Water and Air. Burlington, Ontario, Canada, 1990.

Gordon G., 1995. The chemistry and reactions of ozone in our environment. Progr. Nuclear Energy, 29, 89–96.

Gottschalk, C., Libra, J.A., Saupe, A., Ozonation of Water and Wastewater, Wiley-VCH, 2000.

Gautam, P., Carsella, J. S., Kinney C. A., 2014.Presence and trasport of the antimicrobials triclocarban and triclosan in a wastewater dominated stream and freshwater environment. Water Research, 48, 247-256.

Haag, W.R., Yao, C.C.D., 1992. Rate constants for reaction of hydroxyl radicals with several drinking-water contaminants. Environmental Science & Technology 26 (5), 1005-1013.

Halden, R.U., Paul, D.H., 2005. Co-occurence of Triclocarban and Triclosan in U.S. water resources. Environmental Science & Technology 39 (6), 1420–1426.

Hartig, C., Ernst M., and Jekel M., 2001. Membrane Filtration of Two Sulphonamides in Tertiary Effluents and Subsequent Adsorption on Activated Carbon, Water Research 35(16): 3998–4003.

Heidler, J., Halden, R. U., 2007. Mass balance assessment of triclosan removal during conventional sewage treatment, Chemosphere, 66 (2), 362-369.

Heberer, T., D. Feldmann, K. Reddersen, H.J. Altmann, and T. Zimmermann, 2002, Production of Drinking Water from Highly Contaminated Surface Waters: Removal of Organic, Inorganic and Microbial Contaminants Applying Mobile Membrane Filtration Units, Acta hydrochimica et hydrobiologica 30 (1), 24–33.

Hernández-Leal, L., Temmink, H., Zeeman, G., Buisman, C.J. 2011. Removal of micropollutants from aerobically treated grey water via ozone and activated carbon, Water Research 45 (9), 2887-96.

Hoigne´, J., Bader, H., 1975. Identification and kinetic properties of the oxidizing decomposition products of ozone in water and its effect on water purification. 2nd Ozone World Congress, Montreal, Ashton, MD: International Ozone Association. 271.

Hoigné J., and H. Bader. 1983a. Rate Constants of Reaction of Ozone with Organic and Inorganic Compounds in Water - I. Non-dissociating Organic Compounds. Water Research 17, 173-183.

Hoigne´, J., Bader, H., 1983b. Rate constants of reactions of ozone with organic and inorganic compounds in water-II: dissociating organic compounds. Water Research 17, 185–194.

Hoigne´, J., Bader, H., Haag, W.R. and Staehelin, J. 1985. Rate constants of reactions of ozone with organic and inorganic compounds in water - III. inorganic compounds and radicals. Water Research. 19, 993-1004.

Hoigne´ , J., 1998. In: Hrubec, J. (Ed.), The Handbook of Environmental Chemistry. Springer, Berlin, Germany, 83–141.

Huang, Y., 2010. Degradation of waterborne contaminants by ozone and hydrogen peroxide, Department of Civil and Environmental Engineering, The University of Utah.

Huber, M.M., Gobel, A., Joss, A., Hermann, N., Loffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A., von Gunten, U., 2005. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study. Environmental Science & Technology 39 (11), 4290–4299.

Ikehata, K., Gamal El-Din, M., Snyder, S.A., 2008. Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater. Ozone: Science and Engineering 30 (1), 21–26.

IARC, 2009. International Agency for Research on Cancer. Summaries & Evaluations: Potassium Bromate (Group 2B). Canadian Centre for Occupational Health and Safety.

James, M.O., Li, W., Summerlot, D.P., Rowland-Faux, L. and Wood, C., 2010. Triclosan is a potent inhinitor of estradiol and estrone sulfonation in sheep placenta. Environment International, 36, 942-949.

Jiang, J., Pang, S.Y. and Ma, J. Oxidation of triclosan by permanganate (mn(vıı)): importance of ligands and in situ formed manganese oxides. Environmental Science & Technology. 2009, 43, 8326-8331.

Jin, X., Peldszus, S., Huck, P.M., 2012. Reaction kinetics of selected micropollutants in ozonation and advanced oxidation processes Water Research, 46 (17), 6519-6530.

Johnson, I., Atkinson, C., Hope S-J and Sorkin N., 2012. Proposed EQS for Water Framework Directive Annex VIII substances:2,4-dicholorophenol. Water Framework Directive-United Kingdom Technical Advisory Group (WFD-UKTAG).

Jungclaus, G.A., Lopez-Avila V., and Hites R.A., 1978. Organic compounds in an industrial wastewater: a case study of their environmental impact. Environmental Science and Technology. 12 (1), 88-97.

Katsoyiannis, A., Sweetman, A.J. and Jones, K.C. 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environmental Science & Technology. 45 (20), 8897-8906.

Kim J. G., Yousef, A.E., Dave S., 1999. Application of ozone for enhancing the microbiological safety and quality of foods: A review. Journal of Food Protect, 62, 1071-1087.

Kimura, K., Amy, G., Drewess, J., Watanabe, Y., 2003. Adsorption of hydrophobic compounds onto NF/RO membranes: An artifact leading to overestimation of rejection, Journal of Membrane Science, 221 (1-2), 89-101.

Koc, A., Orhon, K.B., Ogutverici, A., Yilmaz, L., Furi, L., Oggioni, M.R., Dilek, F.B., Yetis, U., 2013. Is adsorption an artifact in experimentation with Triclosan?, Desalination and Water Treatment, 1 (7).

Kondo, T., Yamamoto, H., Tatarazako, N., Kawabe, K., Koshio, M., Hirai, N.,Morita, M., 2005. Bioconcentration factor of relatively low concentrations of chlorophenols in Japanese medaka. Chemosphere 61, 1299-1304.

Kookana, R.S., Ying, G.G., Waller, N.J., 2011. Triclosan: its occurrence, fate and effects in the Australian environment, Water Science and Technology 63 (4), 598-604.

Langlais, B., Reckhow, D.A., Brink, D.R., 1991. Ozone in water treatment:application and engineering. Lewis Publishers, 3-8.

Larsen, T.; Lienert, J., Joss, A.; Siegrist, H., 2004. How to avoid pharmaceuticals in the aquatic environment. Journal of Biotechnology 113 (1-3), 295-30.

Latch, D.E., Packer, J.L., Arnold, W.A. and McNeill, K., 2003. Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution. Journal of Photochemistry and Photobiology A: Chemistry, Short Communication, 158: 63066.

Lee, D.G., Zhao,F., Rezenom, Y.H., Russell, D.H. and Chu, K.H. Biodegradation of triclosan by a wastewater microorganism. Water Research. 2012, 46, 4226-4234.

Levy, C.W., Roujeinikova, A., Sedelnikova, S., Baker, P.J., Stuitje, A.R., Slabas, A.R., Rice, D.W., Rafferty, J.B., 1999. Molecular Basis of Triclosan Activity. Nature. 398 (6726), 383-384.

Lindström, A., Buerge, I., Poiger, T., Bergqvist,P., Rudolfbuser, H., 2002. Occurrence and Environmental Behavior of the Bactericide Triclosan and Its Methyl Derivative in Surface Waters and in Wastewater. Water Science and Technology, 36 (11), 2322-2329.

Lopez-Avila, A. and Hites, R.A., 1980. Organic compounds in an industrial wastewater. Their transport into sediments. Environmental Science and Technology, 14, 1382-1390.

Lopez-Morales, J., Perales-Perez, O. and Roman-Velazquez, F., 2012. Sorption of triclosan onto tyre crumb rubber. Adsorption Science and Technology, 30 (10), 831-845.

Lorimer, J.P., Mason, T.J., Plattes, M., Phull, S.S., Iniesta, J. and Walton, D.J., 2004. Sonovoltammetric studies on copper in buffered alkaline solution. Ultrason Sonochem, 11, 223–226.

Lozano, N., Rice, C.P., Ramirez, M. and Torrents, A., 2013. Fate of triclocarban, triclosan and methyltriclosan during wastewater and biosolids treatment processes. Water Research, 47, 4519-4527.

Luis, P., Saquib M., Vinckier, C., Bruggen, B.V., 2011. Effect of membrane filtration on ozonation efficiency for removal of atrazine from surface water. Industrial & Engineering Chemistry Research, 50, 8686-8692.

Majewski, J., 2012. Methods for measuring ozone concentration in ozone-treated water. Lublin University of Technology, Faculty of Electrical Engineering and Informatics. Electrical Review, ISSN 0033-2097, R. 88.

McAvoy, D.C., Schatowitz, B., Jacob, M., Hauk, A., Eckhoff, W.S., 2002. Measurement of triclosan in wastewater treatment systems. Environmental Toxicology and Chemistry 21 (7), 1323-1329.

McGinnis D., 2008. Toxicological Profile of Triclosan in the Aquatic Environment. Department of Marine and Environmental Systems. Florida Institute of Technology.

Melnick, R., 1989. Toxicology and Carcinogenesis Studies of 2,4-Dicholorophenol in Rats and Mice (Ph. D. Thesis) U.S. Department of Health and Human Services

Metzger, M., 2009. Ozone Applications and Measurements. Water Conditioning & Purification.

Millennium Ecosystem Assessment Report, 2005. Ecosystem and Human Well-Being; Synthesis. World Resources Institute, Island Press, Washington DC.

Moralı, E.K., 2010. Ozonation of a denim producing textile industry wastewater-process optimization, (M.S. Thesis). Middle East Technical University, Faculty of Sciences, Department of Environmental Engineering.

Mozia, S., Tomaszewska, M., Morawski, A. W., 2006. Application of an ozonation–adsorption–ultrafiltration system for surface water treatment. Desalination. 190, 308-314.

Munoz, M., Pedro, Z.M., Casas, J.A. and Rodriguez, J.J. Triclosan breakdown by fenton-like oxidation. Chemical Engineering Journal. 2012, 198-199, 275-281.

Mvula, E., von Sonntag, C., 2003. Ozonolysis of phenols in aqueous solution. Organic and Biomolecular Chemistry 1 (10), 1749–1756.

Nassef, M., Matsumoto, S., Seki, M., Khalil, F., Kang, I.J., Shimasaki, Y., Oshima, Y. and Honja, T., 2010. Acute effects of triclosan, diclofenac and carbamazepine on feeding performance of Japanese medaka fish oryzias latipes. Chemosphere, 80, 1095-1100.

Netswer, A., Rice, G., 1982. Handbook of ozone technology and applications-Volume 1. Ann Arbor Science Publishers.

Nghiem, L.D., A.I. Schafer, and M. Elimelech, 2005. Pharmaceutical Retention Mechanisms by Nanofiltration Membranes, Environmental Science & Technology 39 (19), 7698–7705.

NICNAS (National Industrial Chemicals Notification and Assessment Scheme), 2009,Priority Existing Chemical Assessment Report No.30, Triclosan, Australian Government.

Ogutverici, A., 2013. Triclosan removal by nanofiltration from surface water, (M.S. Thesis). Middle East Technical University, Faculty of Sciences, Department of Environmental Engineering.

Perez, A.L., De Sylor, M.A., Slocombe, A.J., Lew, M.G., 2013. Triclosan occurrence in freshwater systems in the united states (1999-2012): a meta analysis. Environmental Toxicology and Chemistry, 32 (7), 1479-1487.

Pintado-Herrera, M.G., Gonzalez-Mazo, E., Lara-Martin, P.A., 2014. Determining the distribution of triclosan and methyl triclosan in estuarine settings. Chemosphere, 95, 478-485.

Poiger, T., Lindstrom, A., Buerge, I. J., Buser, H., Bergvist, P. A. and Muller, M.D., 2003. Occurance and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. Chimia, 57(1-2), 765-774.

Polcaro, A.M., Mascia, M., Palmas, S. and Vacca, A., 2004. Electrochemical degradation of diuron and dichloroaniline at BDD electrode. Electrochimica Acta, 49, 649–656.

Richardson, S., Thruston A., D., Caughran, A., D., Chen, P. H., Collette, T.W., Floyd, T. L., 1999. Identification of new ozone disinfection byproducts in drinking water. Environmental Science and Technology 33 (19), 3368-3377.

Richardson S.D., Plewa M.J., Wagner E.D., Schoeny R., Demarini D.M. 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. Mutation Research. 636(1-3):178-242.

Reiss, R., Mackay, N., Habig, C., Griffin, J., 2002. An ecological risk assessment for triclosan in lotic systems following discharge from wastewater treatment plants in the United States. Environmental Toxicology and Chemistry 21 (11), 2483–2492.

Remberger, M., Sternbeck, J., Strömbeg, K., 2002. Screening of triclosan and some brominated phenolic substances in Sweden. Sweedish Environmental Research Institute, Stocholm, Sweeden.

Republic of Turkey Ministry of Forestry and Water Affairs. Project on the Control of the Pollution Caused by Hazardous Substances-Final Report, 2013.

Rivas, J., Gimeno, O., Encinas, A., Beltran, F., 2009. Ozonation of the pharmaceutical compound ranitidine: reactivity and kinetic aspects. Chemosphere 76(5), 651-656.

Rosal, R., Rodriguez, A., Perdigon-Melon, J.A., Petre, A., GarciaCalvo, E., Gomez, M.J., Aguera, A., Fernandez-Alba, A.R., 2010. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. Water Research 44 (2), 578-588.

Rubin B. M., 2001, The History of Ozone. The Schonbein Period, 1839-1868. Bulletin for the History of Chemistry, 26-(1), 40-56.

Sabaliunas, D., Webb, S. F., Hauk, A., Jacob, M., Eckhodd, W.S., 2003. Environmental fate of Triclosan in the River Aire Basin, UK, Water Research, 37 (13), 3145-3154.

Saleh, S., Haddadin, R. N. S., Baillie, S. and Collier, P.J., 2010. Triclosan-an update. Letters in Applied Microbiology, 52, 87-95.

Samsoe-Petersen, L., Winther-Nielsen, M. and Madsen, T., 2003. Fate and effects of Triclosan. Danish Environmental Protection Agency. Environmental Project No.861.

Sanchez-Carretero, A., Saez, C., Canizares, P., Cotillas, S. and Rodrigo, M.A., 2011. Improvements in the electrochemical production of ferrates with conductive diamond anodes using goethite as raw material and ultrasound. Industrial & Engineering Chemistry Research, 50, 7073–7076.

Sanchez-Prado, L., Llompart, M., Lorez, M., Fernandez-Alvarez, M., Garcia-Jares, C. and Cela, R., 2006. Further research on the photo-SPME of triclosan. Analytical and Bioanalytical Chemistry, 384 (7-8), 1548-1557.

Schweizer, H.P., 2001, Triclosan: a widely used biocide and its link to antibiotics. FEMS Microbiology Letters 2002,1-7.

Singer, P.C., Ken Robinson & Robert A. Elefritz, 1989. Ozonation at Belle Glade, Florida : A Case History. Ozone: Science & Engineering: The Journal of the International Ozone Association. 12 (2), 199-215.

Singer, H., Muller, S., Tixier, C., Pillonel, L., 2002. Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. Environmental Science & Technology. 36 (23): 4998–5004.

Snyder, S.A., Wert, E.C., Rexing, D.J., Zegers, R.E., Drury, D.D., 2006. Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. Ozone: Science and Engineering 28 (6), 445–460.

Snyder, S.A., Adham, S., Redding, A.M., Cannon, F.S., DeCarolis, J., Oppenheimer, J., Wert, E.C., Yoon, Y., 2007. Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals. Desalination 202, 156-181.

Soares, O.S.G.P., Orfao, J.M.J., Portela, D., Vieira, A., Pereira, M.F.R., 2006. Ozonation of textile effluents and dye solutions under continuous operation: Influence of operating parameters. Journal of Hazardous Materials B137, 1664–1673.

Sobhani, R., Mcvicker, R., Spangengber, C., Rosso, D. 2012. Process analysis and economics of drinking water production from coastal aquifers containing chromophoric dissolved organic matter and bromide using nanofiltration and ozonation. Journal of Environmental Management. 93, 209-217.

SSCS, 2010. Scientific Committee on Consumer Safety, Opinion on triclosan-antimicrobial resistance, European Union.

Staehelin, J. and Hoigne, J. 1983. Mechanism and kinetics of decomposition of ozone in water in the presence of organic solutes. Vom Wasser. 61, 337-348.

Steinle-Darling, E., Litwiller, E. and Reinhard, M., 2010. Effects of sorption on the rejection of trace organic contaminants during nanofiltration. Environmental Science and Technology, 44, 2592-2598.

Suarez, S., Dodd, M.D., Omil, F., Gunten, U., 2007. Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity: Relevance to municipal wastewater ozonation. Water Research 41 (12), 2481–2490.

Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.J., Haist Gulde, B., Preuss, G., Wilme, U., and Zulei-Seibert N., 2002. Removal of Pharmaceuticals During Drinking Water Treatment. Environmental Science & Technology 36 (17), 3855–3863.

Tixier, C., Singer H.P., Canonica S. and Muller, R.S., 2002. Phototransformation of Triclosan in Surface Waters: A Relevant Elimination Process for This Widely Used Biocides Laboratory Studies, Field Measurements, and Modeling. Environmental Science and Technology, 36, 3482-3489.

Tsai, S., Shih, M., Pan, Y., 2008. Determinations and residual characteristics of triclosan in household food detergents of Taiwan, Chemosphere, 72, 1250-1255.

Turhan, K., Turgut, Z., 2009, Decolorization of direct dye in textile wastewater by ozonation in a semi-batch bubble column reactor, Desalination, 242, 256-263.

United States Environmental Protection Agency - EPA, 1998. Federal Register, 63, 241, 69390-69476.

Veldhoen, N., Skirrow, R.C., Osachoff, H., Wigmore, H., Clapson, D.J., Gunderson, M.P., Van Aggelen, G. and Helbing, C.C., 2006. The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development. Aquatic Toxicology, 80 (3), 217-227.

Verliefde, A.R.D., 2008. Rejection of organic micropollutants by high pressure membranes (NF/RO). Delft, Netherlands: Water Management Academic Press, 281.

Vial J., Jardy A., 1999. Experimantal comparison of the different approaches to estimate LOD and LOQ of an HPLC method. Analytical Chemistry 71 (14), 2672-2677.

Vidales, M.J.M., Saez, C., Canizares, P. and Rodrigo, M.A., 2013. Removal of triclosan by conductive-diamond electrolysis and sonoelectrolysis. J Chem Technol Biotechnology, 88, 823-828.

Von Sonntag, C., von Gunten, U., 2012. Chemistry of ozone in water and wastewater treatment. IWA Publishing.

Von Gunten, U., 2003a. Ozonation of drinking water: part I. oxidation kinetics and product formation. Water Research, 37, 1443-1467.

Von Gunten, U., 2003b. Ozonation of drinking water: part II. disinfection and byproduct formation in presence of bromide, iodide or chlorine. Water Research. 37 (7), 1469-1487.

Wang, J. and Li, X., 2012. Electrochemical treatment of wastewater containing chlorophenols using boron-doped diamond film electrodes. Advanced Materials Research, 356–360,1418–1422.

Wert, E.C., Rosario-Ortiz, F.L., Snyder, S.A., 2009. Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater. Water Research 43 (4), 1005–1014

Wind, T., Werner, U., Jacob, M., Hauk, A., 2004. Environmental concentrations of boron, LAS, EDTA, NTA and Triclosan simulated with GREAT-ER in the River Utter. Chemosphere, 54, 1135-1144.

Wu, J. L., Lam, N. P., Martens, D., Kettrup, A. abd Cai, Z., 2007. Triclosan determination in water related to wastewater treatment. Talanta, 72,1650-1654.

Xiong, F. and Legube, B. 1991. Enhancement of radical chain reactions of ozone in water in the presence of an aquatic fulvic acid. Ozone Science &. Engineering. 13, 349-361.

Xiong, F. and Graham, N. J. D. 1992. Research Note: Removal of atrazine through ozonation in the presence of humic substances. Ozone Science & Engineering.,14, 283-301.

Yang, B., Ying, G.G., Zhao, J.L., Zhang, L.J., Fang, Y.X. and Nghiem, L.D., 2011. Oxidation of triclosan by ferrate: Reaction kinetics, products identification and toxicity evaluation. Journal of Hazardous Materials, 186, 227-235.

Yavuz, M., 2013. M.S. Thesis. Investigation of occurence and fate of biocides in wastewater treatment plants and surface waters. Middile East Technical University, Department of Environmental Engineering.

Ying G. G., and Kookana R. S., 2007. Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. Environment International, 33(2), 199-205.

Yoon, Y., Westerhoff, P., Synder, S.A., Wert, E.C., 2006. Nanofiltration and ultrafiltration of endocrine disrupting compounds, pharmaceuticals and personal care products. Journal of Membrane Sciences 270 (1-2), 88–100.

Zhang, J.F., Liu, H, Sun, Y.Y., Sun, Y.Y., Wang, X.R., Wu, J.C., Xue, Y.Q., 2005. Responses of the antioxidant defenses of the Goldfish Carassius auratus exposed to 2,4-dichlorophenol. J. Environmental Toxicology and Pharmacology, 19: 185–190.

URL 1. http://www.ecology.com/2011/09/18/ecological-impact-industrial-revolution/ (Accessed on 9 April 2014)

URL 2. http://www.beyondpesticides.org/antibacterial/triclosan.php
(Accessed on 25 May 2014)

URL 3. http://ec.europa.eu/research/bioeconomy/food/projects/food_quality /biohypo_en.htm (Accessed on 25 May 2014)

URL 4. http://www.beyondpesticides.org/dailynewsblog/?p=13318 (Accessed on 25 May 2014)

URL 5. http://www.beyondpesticides.org/dailynewsblog/?p=11848 (Accessed on 25 May 2014)

URL 6. http://www.beyondpesticides.org/dailynewsblog/?p=7913 (Accessed on 25 May 2014)

URL 7. http://www.beyondpesticides.org/dailynewsblog/?p=7151 (Accessed on 25 May 2014)

URL 8. http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2010-0548-0625 (Accessed on 7 April 2014)

URL 9. http://water.me.vccs.edu/courses/ENV149/ozonation.htm (Accessed on 7 April 2014)

URL 10 http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid= 16496#x332 (Accessed on 12 May 2014)

URL 11 http://www.chemspider.com/Chemical-Structure.15638. html (Accessed on 12 May 2014)

APPENDIX A

OZONE GENERATOR PERFORMANCE CURVE

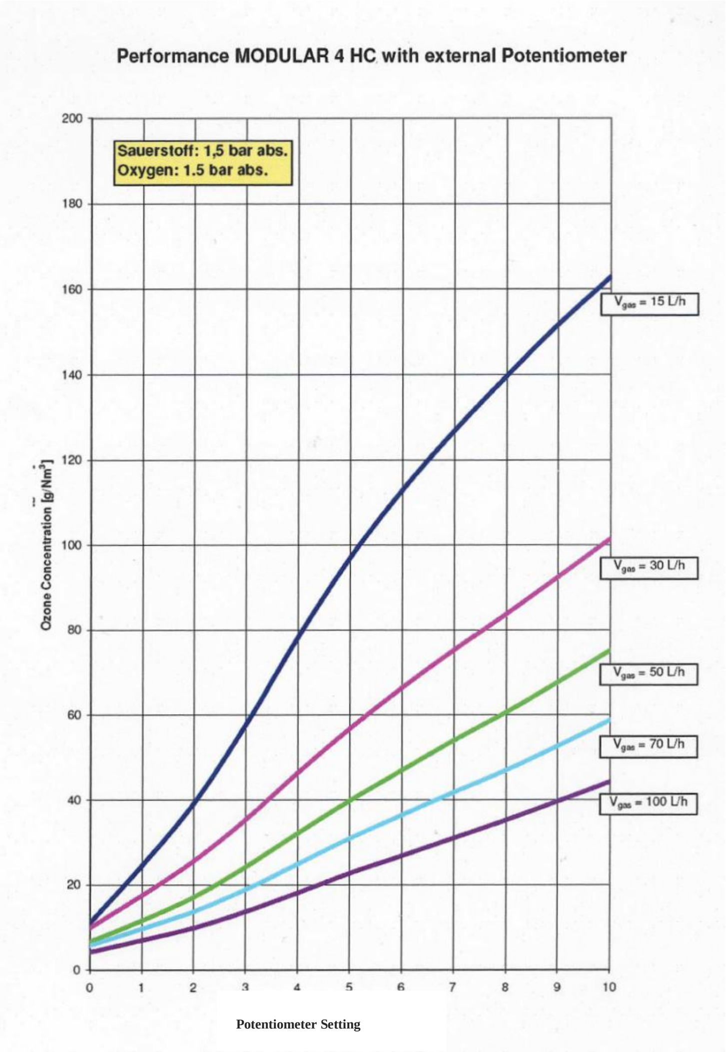


Figure 33. Ozone generator performance curve