DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

TREATMENT OF TRICLOSAN USING ADVANCED OXIDATION PROCESSES

by

Merve ÖZTAMER

February, 2016

İZMİR

TREATMENT OF TRICLOSAN USING ADVANCED OXIDATION PROCESSES

A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of Science in
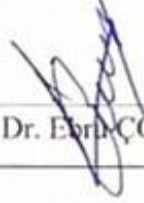Environmental Engineering

by
Merve ÖZTAMER

February, 2016

İZMİR

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"TREATMENT OF TRICLOSAN USING ADVANCED OXIDATION PROCESSES"** completed by **MERVE ÖZTAMER** under supervision of **ASSIST. PROF. DR. EBRU ÇOKAY** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

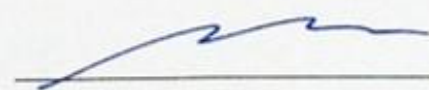Assist. Prof. Dr. Ebru ÇOKAY

Supervisor

(Jury Member)

Assist. Prof. Dr. Mesut AK

(Jury Member)

Prof.Dr. Ayşe OKUR
Director
Graduate School of Natural and Applied Sciences

ACKNOWLEDGEMENTS

TREATMENT OF TRICLOSAN USING ADVANCED OXIDATION PROCESSES

ABSTRACT

Triclosan is one of the most used active ingredients in antibacterial personal care products and usage of triclosan increases in recent years. Also, triclosan have endocrine-disrupting properties. It can easily detect in wastewater effluent water and it is discharged from wastewater treatment plant effluents into the natural environment.

The purpose of this study is compare the removal of triclosan from aqueous solution by advanced oxidation processes (photo-Fenton and photo-Fenton like oxidation) using Box-Behnken statistical experiment design. Effects of triclosan, hydrogen peroxide and ferrous ion concentrations on the extent of triclosan removal, was investigated. Samples taken from the reactor in different reaction time, have been analyzed with HPLC device that previously is defined of triclosan and its by-products.

In addition to Triclosan removal efficiency, 2,4-Dichlorophenol and 2,4,6-Trichlorophenol concentrations were analyzed as byproducts that are expected formation. Complete removal of triclosan was accomplished within one hour, also complete mineralization was not occurred even within sixty minutes indicating formation of some intermediate compounds such as 2,4-Dichlorophenol and 2,4,6-Trichlorophenol.

Optimum reagent concentrations yielding the highest triclosan and its by-products removals were determined using Box-Behnken method. In photo-Fenton treatment, the highest triclosan removal (ninety nine percent) was obtained and 2,4-Dichlorophenol formation was observed as a by-product while in photo-Fenton like treatment yielded higher triclosan removal (ninety seven percent) and both of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol formations were observed as by-products.

Photo-Fenton treatment and photo-Fenton like treatment are resulted greater than ninety five percent removal efficiency of triclosan. In photo-Fenton treatment, the highest triclosan removal was obtained with a H_2O_2/Fe (II)/triclosan ratio of 50/2/0.1. In photo-Fenton like treatment, the highest triclosan removal was obtained with a H_2O_2/Fe (III)/triclosan ratio of 50/5/5. However, generated amounts of predicted by-products and their species are resulted difference on photo-Fenton treatment and photo-Fenton like treatment.

Keywords: Triclosan, photo-Fenton process, photo-Fenton like process, Box-Behnken method.

İLERİ OKSİDASYON YÖNTEMLERİ İLE TRİKLOSAN ARITIMI

ÖZ

Triklosan anti-bakteriyel kişisel bakım ürünlerinde en çok kullanılan aktif bileşenlerden biridir ve son yıllarda artan miktarlarda kullanılmaktadır. Atıksu arıtma tesisleri çıkış suyunda kolayca bulunabilmekte ve atıksu arıtma tesisi çıkış suyuyla alıcı ortama deşarj edilmektedir. Triklosanın parçalanması sonucu oluşan yan ürünler, endokrin bozucu özellikler göstermektedir.

Bu çalışmanın amacı, Box-Behnken istatiksel deney tasarımı kullanılarak, ileri oksidasyon yöntemi ile sulu çözeltiden triklosan gideriminin karşılaştırılmasıdır. Triklosan, hidrojen peroksit ve demir iyon konsantrasyonlarının triklosan giderimini etkisi, araştırılmıştır. Farklı zamanlarda reaktörden alınan numuneler, daha önce triklosan ve yan ürünleri tanımlanan HPLC cihazı ile analiz edilmiştir.

Triklosan giderim veriminin yanı sıra 2,4-Diklorofenol ve 2,4,6-Triklorofenol konsantrasyonları da oluşumu beklenen yan ürünler olarak analiz edilmiştir. Triklosanın gideriminin tamamı bir saat içinde gerçekleştirilmiştir, ayrıca tam mineralizasyon 2,4- Diklorofenol ve 2,4,6-Triklorofenol gibi bazı ara bileşiklerin oluşumunu gösteren altmış dakika içinde dahi gerçekleşmemiştir. Triklosan ve yan ürünlerin en yüksek giderim verimi veren optimum reaktif dozları Box-Behnken yöntemi kullanılarak belirlenmiştir bulundu.

Foto-Fenton arıtımında, en yüksek triklosan giderimi (yüzde doksan dokuz) elde edilmiş ve yan ürün olarak 2,4-Diklorofenol oluşumu gözlemlenirken foto-Fenton benzeri arıtımda, yüksek verimli triklosan giderimi (yüzde doksan yedi) ve yan ürün olarak 2,4-Diklorofenol ve 2,4,6-Triklorofenol oluşumu gözlemlenmiştir.

Foto-Fenton proses ve foto-Fenton benzeri proses, yüzde doksan beşten fazla triklosan giderim verimi ile sonuçlanmıştır. Foto-Fenton prosesinde, en yüksek

triklosan giderimi H_2O_2/Fe (II)/triklosan oranı 50/2/0,1 ile elde edilmiştir. Foto-Fenton benzeri proseste, yüksek triklosan verimi, H_2O_2/Fe (III)/triclosan oranı 50/5/5 ile elde edilmiştir. Ancak, oluşması beklenen yan ürünlerin oluşan miktarları ve özellikleri foto-Fenton proseste ve foto-Fenton benzeri proseste farklı sonuçlanmıştır.

Anahtar Kelimeler: Triklosan, foto-Fenton prosesi, foto-Fenton benzeri proses, Box-Behnken yöntemi.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER ONE
INTRODUCTION

1.1 The Problem Statement

Environmental pollution had been a fact of life especially for last centuries but it became a real problem since the start of the industrial revolution. The carrying capacity of earth is significantly smaller than the demands placed on it by large numbers of human populations. The treatment capacity of the natural environment does not enough for the decomposing of pollution source, anymore. Especially, synthetic materials that are produce by human activities does not treat appropriately. Industries began manufacturing and using synthetic materials such as plastics, polychlorinated biphenyls (PCBs), and inorganic pesticides. These materials are not only toxic, they also accumulate in the environment. Likewise, Triclosan is also a synthetic chemical that is synthesized in laboratory and it was first registered as a pesticide in 1969 by US. EPA.

Triclosan (2,4,4'–trichloro-2'-hydroxydiphenyl ether) is a chlorinated aromatic compound. It is produced by partially oxidizing benzene or benzoic acid. Its functional groups include both phenols and ethers. It is used as a synthetic broad-spectrum antimicrobial agent. Because of the triclosan's antimicrobial and antifungal properties, it is used an active ingredient in a variety of products where it acts to slow or stop the growth of bacteria, fungi, and mildew. According to EPA regulations, triclosan is used in commercial, institutional and industrial premises and equipment; residential and public access premises; and as a material preservative.

Commercial, institutional and industrial premises and equipment uses include conveyor belts, fire hoses, dye bath vats and ice making equipment. As a material preservative, triclosan is used in many products including adhesives, fabrics, vinyl, plastics, polyethylene, polyurethane, polypropylene, floor wax emulsions, textiles (footwear, clothing), caulking compounds, sealants, rubber, and latex paints. There

are multitudes of residential and public access premises uses including direction application to commercial HVAC coils, and use as a materials preservative in toys, paints, mattresses, clothing, brooms, mulch, floors, shower curtains, awnings, tents, toilet bowls, urinals, garbage cans, refuse container liners, insulation, concrete mixtures, grouts, and upholstery fabrics etc.

According to EU Biocide Directive 1998/8/EC, triclosan is used in product type's human hygiene, private and public health area, veterinary hygiene. According to the information provided by COLIPA (Cosmetics Europe), the quantity of triclosan used within the EU reached approximately 450 tons (as 100% active) in the year 2006. In the EU, about 85% of the total volume of triclosan is used in personal care products, compared to 5% for textiles and 10% for plastics and food contact materials. Triclosan was listed in 1986 in the European Economic Community (EEC) directive 76/768 (Annex VI and subsequent amendments) its use is permitted at a maximum concentration of 0.3% (w /w).

In humans, triclosan is rapidly and completely absorbed from the gastrointestinal tract, while a lower rate of absorption occurs dermally. It has been found in human blood, plasma and milk (Allmyr, Adolfsson-Erici, McLachlan & Sandborgh-Englund 2006; Allmyr et al., 2008; Adolfsson-Erici, Pettersson & Parkkonen 2002). In some studies show that triclosan is highly bioaccumulative and cause endocrine disruption, skin irritation, allergy susceptibility, and also other ecological toxicity to the aquatic and terrestrial environment (Lindström et al., 2002; Fernandes, Pascoal & Cassio, 2011; Coogan, Edziyie, La Point & Venables, 2007). Moreover, it can disrupt the nitrogen cycle in sensitive soils at certain concentrations (Kookana et al., 2011).

Like every other chemical ingredients, triclosan is also release into the environment. Triclosan is transported through the domestic or industrial waste stream to wastewater treatment plants. Because of widespread use of triclosan, it finds its way to wastewater treatment plants and it is discharged into the natural environment. Incomplete removal of triclosan from wastewater treatment plants as well as

spreading the triclosan laden sludge into soils, leads to triclosan being distributed in soils and surface waters (Bedoux, Roig, Thomas, Dupont & Le Bot 2012).

According to Reiss, Mackay, Habig & Griffin (2002), the great extent (96%) of triclosan containing products are eventually rinsed down the drain and discharged with wastewater effluent. In this respect, triclosan 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, Muller, Tixier & Pillonel, 2002; Halden & Paul, 2005). For example, high levels were found in South China in the Pearl River system, where the triclosan concentration levels reached a maximum of 1.023 μg/L (Peng et al, 2008) and 478 μg/L (Zhao et al., 2010).

In the USA, triclosan was found in the Hudson River Estuary (Wilson et al. 2009), Key Largo Harbor (Singh et al., 2010), Georgia (Kumar, Priya, Peck & Sajwan, 2010), and Mississippi River (Kolpin, Furlong & Meyer, 2002) at a maximum concentration varying from 10 to 35 μg/L. In japan, triclosan levels of water bodies are detected similar with USA (Nishi, Kawakami & Onodera, 2008) and in Canada (Hua, Bennett & Letcher, 2005). The highest concentrations of triclosan in river water were quite recently reported in the Kaveri, Vellar, and Tamiraparani rivers in India, with values of 3800 μg/L, 5160, and 944 μg/L, respectively (Ramaswamy, Shanmugam, Velu, Rengarajan & Larsson, 2011). Because of increased uses of triclosan containing products and their freely and uncontrolled release into waste stream, triclosan concentration in water bodies may vary in different years by consumption variation (Bedoux et al., 2012). For example, in Charleston Harbor (DeLorenzo et al., 2008), the average triclosan concentration in 2006 was 0.6 μg/L compared to concentration of 7.5 μg/L in 2008 (Fair et al., 2009).

In Europe, the presence of triclosan in surface water was investigated in some countries such as Germany, Italy, Switzerland, Greece, Spain, Romania etc. (Bedoux et al., 2012). In Germany, the triclosan concentration is vary from 3 to 10 μg/L in the Ruhr river catchments area. High values were also detected for water bodies

contaminated by wastewater treatment plant effluents. Triclosan was detected in Italian and Swiss lakes at concentrations up to 14 μg/L. In Switzerland, triclosan level was found in lakes and in a river with concentrations ranging from 1.4 to 74 μg/L (Lindström et al. 2002). In the UK, triclosan level in a river ranged from 19 to 80 μg/L. The highest values of triclosan were found in rivers in Spain, with levels up to 285 μg/L in the.

Effluent from wastewater treatment plants contains a complex mixture of anthropogenic and natural compounds. Due to its physical and chemical properties, triclosan is accumulated onto sludge at about 0.4–30 mg/kg (Bedoux et al., 2012). For example in a study, soil samples collected over two years, from different agricultural sites in Michigan previously amended with sludge, revealed triclosan concentration 0.16-1.02 μg/kg and 90 to 7060 μg/kg triclosan was found in sludge from Michigan wastewater treatment plants (Cha & Cupples, 2009). The Targeted National Sewage Sludge Survey (USEPA 2009) reported concentration value of 133 mg/kg triclosan in sludge.

1.2 Characteristics of Triclosan

Triclosan, (2, 4, 4-trichloro-2-hydroxydiphenyl ether) (Figure 1.1) is a nonionic, broad spectrum antimicrobial chemical. Triclosan is a white powdered solid with a slight aromatic/phenolic odor and with low soluble in water (12 mg/L; Reiss et al., 2002). Triclosan is a chlorinated aromatic compound, which has functional groups representative of both ethers and phenols. Phenols often show anti-bacterial properties.

According to International Union of Pure and Applied Chemistry (IUPAC), its name is 5-Chloro-2-(2,4-dichlorophenoxy) phenol. Some other common name of triclosan are2,4,4'-trichloro-2'-hydroxydiphenyl ether phenol, 5-chloro-2-(2,4-dichlorophenoxy)-5-Chloro-2-(2,4-dichlorophenoxy) phenol, Irgasan DP - 300R, Irgaguard B1000, VIV-20. Triclosan has been produced under the license of Swiss

specialty chemical company Ciba since the 1960s especially over the past 25 years in all over the world.
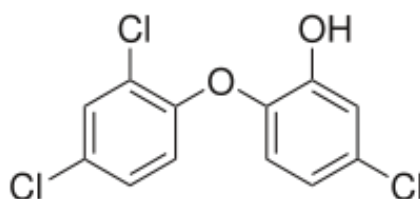
Figure 1.1 Molecular structure of triclosan

Also, some of physicochemical properties of triclosan are given in Table 1.1 (Reiss et al., 2002; National Industrial Chemicals Notification and Assessment Scheme (NICNAS), 2009; Scientific Committee on Consumer Products (SCCP), 2009)

Table 1.1 Physicochemical properties of triclosan

Physicochemical Properties of Triclosan	
Chemical formula	$C_{12}H_7C_{l3}O_2$
Molecular weight	289.54 g/mole
Appearance	White solid
Density	1.49 g/cm^3
Melting point	55–57 °C
Decomposition temperature	280-290 °C
Vapor pressure (at 25°C)	5.2×10^{-6} Pa
Water solubility (at 20°C)	12 mg/L
Boiling point	120 °C
Octanol-water partition coefficient(at 25°C)	4.8log K_{OW}
Adsorption to suspended solids	47,454 K_{OC}, ml/g
Dissociation constant	7.9 pKa
Henry's constant	1.5×10^{-7} atm-m^3/mole
Half-life in surface water	2-2000 d

Results of its chemical properties, triclosan are hydrolytically buffered over the pH 4-9 range. Because of hydrophobicity of triclosan, the presence of one aromatic [OH$^{..}$] group, were enables higher solubility under alkaline pH conditions. Thus, ionized triclosan (at pH~12) displayed a weaker affinity and lower solubility extents when compared to lower pH values (Delgado, Holguin & Martínez, 2012).

Photolytically, triclosan degrades rapidly under continuous irradiation from artificial light at 25°C in a pH 7 aqueous solution, with a calculated aqueous photolytic half-life of 41 minutes. There are some evidences in the literature that these by-products may be more stable and more toxic than the parent compound (Canosa et al., 2005).

From the waste streams to the different environmental compartments, triclosan can undergo various transformation processes. In the literature, high rates of chemical, photochemical, sonochemical, or biological transformation of triclosan have been described, but always leading to the formation of byproducts (Bedoux et al,. 2012)

Generally, the removal efficiency of the treatment of triclosan is depending on the initial concentrations, pH, matrix, and experimental conditions. Interesting are the always by-products generated. While chlorophenols are the main by-products of chemical treatments of triclosan as in this study and methyltriclosan is generated in biological treatments of triclosan (Bedoux et al., 2012). Considering triclosan concentrations in wastewater treatment plant influents, some of by-products are expected to be non-negligible, some of them presenting higher toxicity than triclosan.

Chlorinated triclosan derivative products figured below. Three chlorinated triclosan derivative products: 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) (Figure 1.2) (Canosa et al., 2005).
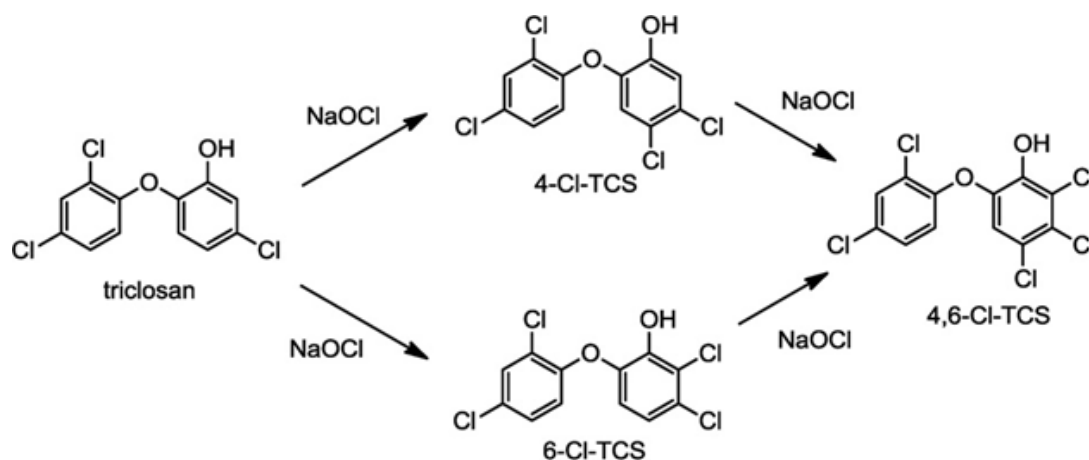
Figure 1.2 Pathways for degradation of triclosan.

Chlorinated triclosan derivative products are of environmental concern because they may retain or possess enhanced levels of antimicrobial and endocrine-disrupting properties, relative to triclosan. Additionally, these by-products are known to undergo photolysis in natural waters to form the respective dioxins, 2,3,7-trichlorodibenzo-p-dioxin, 1,2,8-trichlorodibenzo-p-dioxin, and 1,2,3,8-tetrachlorodibenzo-p-dioxin (Buth, Grandbois, Vikesland, McNeill & Arnold, 2009). The toxicity of the chlorinated triclosan derivative product, dioxin photoproducts has been estimated to be 10 times higher than the toxicity of 2,8-DCDD (Ontario Ministry of the Environment, 1984), the photoproduct of triclosan, for dioxin toxicity/receptor binding generally increases with chlorine substitution in the lateral positions.

While wastewater-derived chlorinated triclosan derivative products may play an important role in the environmental impact of triclosan. It has been reported that chlorination used during treatment produces chlorophenols, which are more persistent and highly toxic compounds. Because of these compounds, which are not currently analyzed, the total concentration of triclosan and related by-products in drinking water was underestimated.

1.3 Characteristics of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol

One major degradation product of treatment of triclosan is 2,4-Dichlorophenol (Figure 1.3), which was a maximum of 93.8-96.6% of the applied triclosan. In this study, 2,4-Dichlorophenol is recorded as a main by-product. 2,4-Dichlorophenol is a chlorinated derivative of phenol with the molecular formula $C_6H_4Cl_2O$. 2,4-Dichlorophenol is used primarily as an intermediate in the preparation of the herbicide. Otherwise, naturally it is a photo-degradation product of the common antibacterial and antifungal agent triclosan along with the dioxin 2,8-dichlorodibenzo-p-dioxin (Singer et al., 2002).
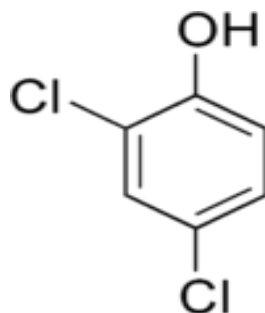
Figure 1.3 Molecular structure of 2,4-Dichlorophenol

Table 1.2 Physicochemical properties of 2,4-Dichlorophenol

Physicochemical Properties of 2,4-Dichlorophenol	
Chemical formula	$C_6H_4Cl_2O$
Molecular weight	163.0 g/mole
Appearance	Colorless Crystals, White/Pale yellow solid
Density	1.38 g/cm^3
Melting point	45 °C
Vapor pressure (at 25°C)	16 Pa
Water solubility (at 20°C)	4.5 g/L
Boiling point	210 °C
Octanol-water partition coefficient (at 25°C)	3.6 log P_{OW}

Table 1.2 consist of some main properties of 2,4-Dichlorophenol which are related to the subject (U.S. EPA Integrated Risk Information System 2,4-Dichlorophenol (CASRN 120-83-2), Hazardous Subjects Data Base, 2001).

One of the other by-product of triclosan is 2,4,6-Trichlorophenol (Figure 1.4) that is a synthetic, colorless crystalline solid that is slightly soluble in water and soluble in organic solvents. It has been used primarily in pesticide formulations and as a wood preservative, although most uses have been cancelled in the US. When heated to decomposition, 2,4,6-Trichlorophenol emits toxic and corrosive fumes of hydrochloric acid and other toxic gases. Exposure of humans to 2,4,6-Trichrophenol via inhalation has been reported to cause respiratory effects, altered pulmonary

function and pulmonary lesions. It is reasonably anticipated to be a human carcinogen (Agency for Toxic Substances and Disease Registry (ATSDR)).
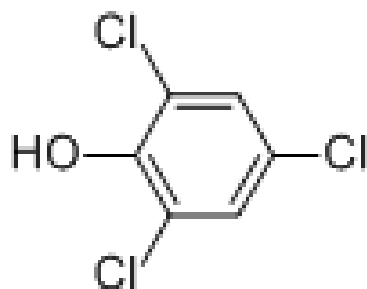
Figure 1.4 Molecular structure of 2,4,6-Trichlorophenol

Table 1.3 consist of some main properties of 2,4,6-Trichlorophenol which are related to the subject (U.S. EPA Integrated Risk Information System 2,4,6-Trichlorophenol (CASRN 88-06-2), Hazardous Subjects Data Base, 2000).

Table 1.3 Physicochemical properties of 2,4,6-Trichlorophenol

Physicochemical Properties of 2,4-Dichlorophenol	
Chemical formula	$C_6H_3Cl_3O$
Molecular weight	197.45 g/mole
Appearance	White to off-white crystalline solid
Density	1.675 g/cm^3
Melting point	69 °C
Boiling point	246 °C

1.4 Triclosan On Behavior of Environmental Conditions

1.4.1 Biodegradation of Triclosan

Under anaerobic conditions and in the dark, triclosan is quite stable. Triclosan is readily biodegradable under aerobic conditions, but not under anaerobic conditions (McAvoy, Schatowitz, Jacob, Hauk & Eckhoff, 2002). Because of the high hydrophobicity of triclosan, another pathway of removing triclosan from water in wastewater treatment plants is through the sorption of triclosan and its by-products to particles and sludge (10-15%) (Kanda, Griffin & James, 2003).

9

1.4.2   Adsorption of Triclosan

Triclosan was seriously adsorbed onto sediments, biosolids, sludge, and also plastic tubes that used into the experimental reactor on their study. Thus, plastic and glass tubes were used and it was found that triclosan adsorbed by unit area of plastic tubing was about 100 times greater than glass one. So that, in this study, we were use only glass tubes to minimize the adsorption of triclosan. Otherwise, obtained results might be incorrect.

1.4.3   Photodegradation of Triclosan

Photodegradation is the most documented degradation process for triclosan. Chemical treatment (chlorination and ozonolysis), photodegradation (including photocatalytic oxidation), and sonolysis conversions were described as pseudo first-order reaction kinetics of degradation of triclosan. Physical and chemical factors had a large influence on triclosan degradation such as the pH of the aqueous solution, salinity, the presence of metal ions, and some kind of acid (humic acid) in wastewater and irradiation conditions like UV wavelength or sunlight (Bedoux et al., 2012).

Triclosan is extremely resistant to high and low pH, despite its high chemical stability. Triclosan can be easily degraded in the environment via photodegradation. Eight by-products were identified after photodegradation of triclosan, including chlorinated phenols, chlorohydroxydiphenyl ethers, 2,7- and 2,8-dichlorodibenzo-p-dioxin, and a possible dichlorodibenzodioxin isomer or dichlorohydroxy-di-benzofuran (Tixier, Singer, Canonica & Stephan, 2002; Sanchez-Prado et al., 2006a; 2006b; Canosa et al., 2005).

Some of these products show higher toxicity compared to toxicity of triclosan but have been shown to be degraded in the environment by bacteria like Pseudomonas. The final products are CO_2 and chlorine with chlorocatechols.

In order to complete the treatment of wastewaters containing triclosan, several works in the literature have proposed chemical oxidation of this emerging pollutant. For example in ozonation process of triclosan results the potential generation of harmful by-products (Zhang, Yamada & Tsuno, 2008) and also performing of ozonation process have corrosion problem. On the other hand, exposure of triclosan to UV-irradiation in photocatalytic processes or sunlight can be result to the formation of highly toxic and persistent chlorinated by-products (Munoz, De Pedro, Casas & Rodriguez, 2012) Because of these reasons, UV–irradiation were chosen for applied Advanced Oxidation Process (AOP) of experiments. Also, because of the traditional treatment methods are allowed mainly transfer the contaminants from one phase to another, leaving a problem of disposal of the transferred material.

1.5 Treatment Methods Used for Triclosan Removal

The presence of toxic and refractory pollutants in the discharge of wastewaters and in some cases in water supplies is a topic of global concern. Triclosan is one of the most used active ingredient in antibacterial personal care products and usage of triclosan increases in recent years. It can easily detect in wastewater effluent water and it is discharged from wastewater treatment plant effluents into the natural environment.

Different methods were developed for the removal of triclosan from wastewater. Conventional techniques commonly applied for the removal of triclosan from wastewater include chemical, biological and physical methods.

More stringent discharge limits imposed by legislation to the treatment plants in the last years. Therefore, in recent years removal of harmful pollutants present in water supplies was investigated by means of a variety of chemical procedures instead of conventional wastewater treatment plants. Among them, AOPs, which are constituted by the combination of several oxidants such as UV radiation, ozone, hydrogen peroxide (Meunier Canonica & Von Gunten., 2006)

1.6 Advanced Oxidation Processes

1.6.1 Theory of Advanced Oxidation Processes

Advanced oxidation is used to convert pollutants to products such as CO_2 and H_2O or to intermediate products that are more readily biodegradable or removable by adsorption (Eckenfelder, 1989). In recent years, advanced oxidation processes (AOPs) have emerged as potentially powerful methods which are capable of transforming the pollutants into harmless substances (Esplugas, Yue & Pervez, 1994). These methods almost all rely on the generation of very reactive nonselective transient oxidizing species such as the hydroxyl radical, $OH^{\bullet}$, which has also been identified as the dominant oxidizing species (Masten & Davies, 1994).

When generated, these radicals react rapidly and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules (Buxton, Greenstock, Helman & Ross 1988). Although the hydroxyl radicals are short lived, they have a higher oxidation potential than ozone, chlorine, or hydrogen peroxide, and their unstable nature increases their reaction speed. Table 1.4 lists the redox potential of several oxidative species commonly used in water and wastewater treatment.

Table 1.4 Redox potential for commonly used oxidants in water

Oxidant	Oxidation Potential, V
Fluorine	3.0
Hydroxyl Radical	2.8
Ozone	2.1
Hydrogen Peroxide	1.8
Potassium Permanganate	1.7
Chlorine Dioxide	1.5
Chlorine	1.4

Generation of OH$^{\bullet}$ radicals is commonly accelerated by combining ozone, hydrogen peroxide (H_2O_2), UV radiation, ferrous and ferric salts (Fe (II) and Fe (III)). Because of these, UV plus H_2O_2, lighted photo-Fenton, darked photo-Fenton, O_3/H_2O_2 and O_3/UV hold the greatest promise to detoxify water and wastewater.

1.6.2   Fenton Treatment

The Fenton reaction is a widely used catalytic oxidation method based on electron transfer between H_2O_2 and metal ions (Fe (II)) serving as homogeneous catalyst. The efficiency of the Fenton's reagent is based on the hydroxyl radical generation by a mixture of H_2O_2 and Fe (II) ions as shown in the following reaction (1.1) (Ashraf, Muhammad & Alhadrami, 2006).

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + OH^- + OH^{\bullet}$$

(1.1)
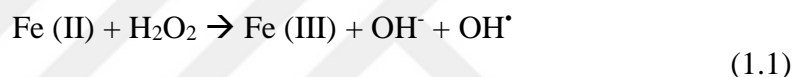
1.6.3   Photo-Fenton Treatment

The recently developed photo-Fenton treatment was shown to be an effective AOP for oxidation of recalcitrant organic compounds (Ruppert Bauer & Heisler, 1993). The mechanism of the photo-Fenton treatment is based on the hydroxyl radical generation by a mixture of H_2O_2 and Fe (II) ions (Fenton reaction) as shown in the following reaction (1.2) (Ashraf, Muhammad & Alhadrami, 2006).

$$Fe\ (II) + H_2O_2 \rightarrow Fe\ (III) + OH- + OH^{\bullet}$$

(1.2)
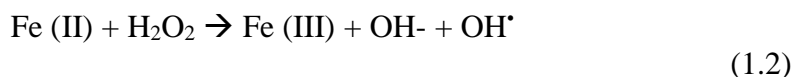
Another reaction also produces additional hydroxyl radicals and regenerates Fe (II) ions under illumination which is known as the photo-Fenton reaction (1.3) (Faust & Hoigne, 1990).

$$Fe\ (III) + H_2O + hv \rightarrow Fe\ (II) + H+ + OH^{\bullet}$$

(1.3)
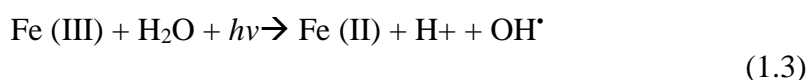
Consequently, higher concentrations of OH$^{\bullet}$ radicals and Fe (II) can be attained with the UV/H$_2$O$_2$/Fe (II) treatment as compared to the conventional Fenton's reagent treatment. The reaction time needed for the photo-Fenton process is extremely low and depends on the operating pH and the concentrations of H$_2$O$_2$ and Fe (II).

1.6.4 Photo-Fenton Like Treatment

In the photo-Fenton like process, H$_2$O$_2$ in a catalytic cycle reacts with iron ions as the catalyst. This process involves the production of reactive and non-selective hydroxyl radicals and can initiate the degradation reactions by reacting with the organic molecules.

In photo-Fenton like process, a powerful, non-selective source of oxidation ($\bullet$OH) is generated from H$_2$O$_2$ in the presence of Fe (III) ions according to the following simplified reactions (1.4), (1.5), (1.6) and (1.7).

$$\text{Fe (III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe (II)} + \text{H}^+ + \text{HO}_2^{\bullet}$$
(1.4)

$$\text{Fe (II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe (III)} + \text{OH}^- + \bullet\text{OH}$$
(1.5)

$$\text{Fe (III)} + \text{H}_2\text{O} \rightarrow \text{Fe (II)} + \text{H}^+ + \bullet\text{OH}$$
(1.6)

$$\text{H}_2\text{O}_2 + hv \rightarrow 2 \bullet\text{OH}$$
(1.7)
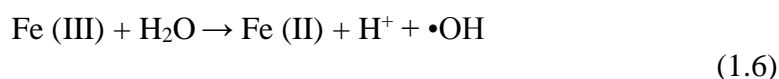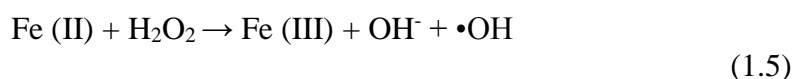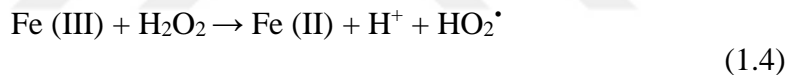
However, the optimal operating conditions and reagent concentrations need to be determined in order to reduce the cost of photo-Fenton like treatment also and to improve the extent of triclosan removal.

The photo-Fenton like process is a multifactor system that different factors such as the initial concentration of target compounds, the initial dosage of oxidants, pH and other operating conditions have effect on the process efficiency.

The optimization of the factors by classical methods needs extra time, materials, and large number of experiments. Also, classical methods fail to consider the combined effects of all the parameters involved. A statistical experimental design could overcome the limitations of conventional methods and consequently optimize the affecting factors.

The response function for the triclosan degradation was related to the changes in initial concentrations of triclosan, H_2O_2 and Fe (II)/Fe (III) ions which used as a catalyst. Also molar ratio of H_2O_2 and Fe (II)/Fe (III) ions are effected the photodegradation of triclosan.

Advantages and disadvantages of AOPs

The advantages of advanced oxidation processes over biological and physical methods can be summarized as follows:

1. High treatment efficiencies enhanced by the fact that OH• radicals may be produced by different mechanisms which can be adapted to specific treatment requirements,

2. Fast reaction rates yielding relatively small reactor volumes,

3. High flexibility and the possibility of incorporation into water recycling processes,

4. Operation under mild conditions such as T = 20-30 ◦C and pH = 5-8,

5. Advanced oxidation technologies as a pre-treatment or post-treatment combined with a conventional biological treatment is an alternative for non-biodegradable or toxic wastewater treatment.

However, the destructive nature of AOPs have to be carefully compared with the high operation costs as well as the difficulties encountered in the control of accumulation of the oxidation products (Colonna, Caronna & Marcandalli, 1999).

One common problem for some of the AOPs is the high demand of electrical energy for UV lamps and ozone generator causing high operational costs. However, Fenton and solar-Fenton treatments are less costly. Minimization of the required irradiation time and the energy consumption by optimization of the other reaction conditions such as operational pH, chemicals used and concentrations, pollutant/oxidant ratio are very important.

1.7 Triclosan Removal by AOPs

Son, Ko & Zoh, (2009) demonstrated that TiO_2-photocatalytic degradation of triclosan is mainly achieved by radicals, and once they are produced in photocatalysis, they can further degrade dioxin-type intermediates. To achieve enhanced oxidation condition, the presence of H_2O_2 is important (Yu, Kwong, Luo & Cai, 2006).

First-order degradation rates of some complex chemical compounds with UV/H_2O_2 increased significantly than those with UV photolysis alone (Kim et al., 2008). Low pressure (LP) and medium pressure (MP) UV lamps with 254 nm wavelength emission were used in removal of these complex chemicals like pharmaceutical compounds in water (Pereira, Linden & Weinberg, 2007b ; Canonica, Meunier & Gunten., 2008).

Oxidation behaviors of an organic compound by UV and UV/H_2O_2 may not be the same as its oxidation behaviors in mixed solutions with several coexisting compounds due to wide variation in their physiochemical characteristics and some limiting conditions (available photon energy, other oxidizing species such as hydroxyl radical etc.) (Piccoli, Fiori, Andrisano & Orioli, 2002)

1.8 Box-Behnken Statistical Experiment Design

Design of experiments by using statistical methods can be used for optimization of the process variables in multivariable systems. The response surface methodology (RSM) is a useful tool used for analysis of complex systems involving many variables and objective functions. The RSM and statistical experiment design comprises a group of statistical techniques for model building and prediction of the system behavior (Sastry & Khan, 1998; Hamed & Sakr, 2001). The RSM has been used by many investigators as an efficient statistical technique for optimization of multi-variable systems with minimum number of experiments (Francis et al., 2000; Vohra & Satyanarayana, 2002).

Different types of statistical experiment designs include 3-level factorial; central composite (CCD) (Boza et al., 2000; Box & Wilson, 1951), Box- Behnken (Singh, Dodge, Durrani & Khan, 1995) and D-optimal designs (Sanchez-Lafuenteet, Furlanetto & Fernandez-Arevalo, 2002). A modified central composite experimental design known as the Box-Behnken design (BBD) is an independent, rotatable quadratic design containing no embedded factorial or fractional factorial design (Ragonese Macka, Hughes & Petocz, 2002). Among all the statistical experiment design methods, Box-Behnken design requires fewer runs than the other design methods, such as 15 runs for a 3-factor experiment design. Moreover, the method allows calculation of the response function at intermediate levels which are not experimentally studied (Sastry & Khan 1998; Hamed & Sakr, 2001). A comparison of BBD with the other response surface designs (central composite, Doehlert matrix and three-level full factorial design) has shown that the BBD and Doehlert matrix are slightly more efficient than the central composite design, but much more efficient than the three-level factorial designs (Ferreira et al., 2007). The Box-Behnken statistical experiment design and the RSM were reported to be useful in optimization of the three variable response functions (Hamed & Sakr, 2001). The optimization process involves studying the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response function,

predicting the response of the fitted model and checking the adequacy of the model by the ANOVA tests.

The independent variables were the concentration of triclosan (X_1), hydrogen peroxide (X_2), and ferrous ion (X_3). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively. Response functions describing variations of dependent variables (percent pesticide, occurrence of by-products or TOC) with the independent variables (X_i) can be written Equation (1.8) as follows:

$$Y = b_o + \Sigma\ b_i*X_i + \Sigma\ b_{ij}*X_i*X_j + \Sigma\ b_{ii}*X_i^2$$

(1.8)

where Y is the predicted response (percent pesticide, occurrence of by-products or TOC), b_0 is the offset term and b_i is the linear effect while b_{ii} and b_{ij} are the square and the interaction effects, respectively. The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial equation (1.9) as follows.

$$Y = b_0 + b_1 X_1 + b_2 X + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{23} X_2 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2$$

(1.9)

This approach was selected because relatively fewer combinations of the variables were used to estimate a potentially complex response function. Fifteen experiments are needed to calculate 9 coefficients of the second-order polynomial regression model. This model contains one block term, three linear, three quadratic and three interaction terms. The response function coefficients were determined by regression using the experimental data and the Stat-Ease Design Expert 9 computer program.

Coded points used in Box-Behnken statistical design are presented in Table 1.5. The results of analysis of variance (ANOVA) are also presented in tables indicating the fact that that the predictability of the model is at >95% confidence interval. Response function predictions are in good agreement with the experimental data with

a coefficient of determination (R^2) of larger than 0.99. Furthermore, the computed F value is much greater than that of the tabular F 0.01 (14.14) value of 3.70 suggesting that the treatment is highly significant. P values of less than 0.05 for any factor in analysis of variance (ANOVA) indicated a significant effect of the corresponding variable on the response.

Table 1.5 Coded levels of the experimental data points used in Box-Behnken statistical design

Run	X_3 Pesticide,	X_1 H_2O_2,	X_2 Fe(II) or pH,
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

1.9 Objectives and Scope of the Thesis

Objectives of the proposed study can be summarized as follows:

1. To investigate the effectiveness of different advanced oxidation processes for the treatment of Triclosan identified as priority pollutants by the European Water Framework Directive 2000/60/EC.

2. To determine optimum catalyst and oxidant dosages and reaction time by using the Box-Behnken statistical experiment design and the response surface methodology yielding maximum Triclosan removals and to evaluate formation of triclosan by-products.

3. To compare the oxidative performances of the selected advanced oxidation processes in terms of triclosan removals and formation of by-products.

CHAPTER TWO
MATERIALS AND METHODS

2.1 Triclosan Removal by the AOPs

2.1.1 Chemicals

High purity grade (99.5%) of Triclosan($C_{12}H_7C_{13}O_2$), (CAS No:3380-34-5),high purity grade (99.5%) of 2,4-Dichlorophenol ($C_6H_4Cl_2O$), (CAS No:120-83-2) and high purity grade (99.5%) of 2,4,6-Trichlorophenol ($C_6H_3Cl_3O$) (CAS No:88-06-2) were purchased from Dr. Ehrenstorfer GmbH. These chemicals were used for obtaining calibration curve in HPLC device. Acetonitrile gradient grade for liquid chromatography 99.9% (CH_3CN) was purchased from Merck and that was used to as HPLC solvents.

High purity grade (99%) of Triclosan (CAS No: 3380-34-5) used for preparing stock solution in experiments was purchased from Alfa Aesar. Physico-chemical characteristics of Triclosan are summarized in Table 1.1.Methanol, 99.5% (CH_3OH) purchased from Merck was used in order to dissolve Triclosan in stock solution.

Hydrogen peroxide solution (35% w/w) (CAS No: 7722-84-1) obtained from Merck were used as an oxidant. Iron (II) sulfate heptahydrate, 98% ($FeSO_4·7H_2O$) (CAS No: 7782-63-0) used as source of Fe (II) in the photo-Fenton treatment was analytical grade and purchased from Alfa Aesar Company. Iron (III) sulfate hydrate exsiccated, ($Fe_2(SO_4)3.xH_2O$) (CAS No.: 10028-22-5) used as source of Fe (III) in the photo-Fenton like treatment was analytical grade and purchased from Riedel-de Haën company (manufactured in Sigma-Aldrich Laborchemikalien GmbH). Concentrated stock solutions of Fe (II) and Fe (III) (250 mg/L) were prepared for further dilution to obtain solutions of desired concentrations. Stock solutions were stored in dark to prevent oxidation of Ferrous/Ferric ions.

pH adjustments were done by using either sodium hydroxide or sulfuric acid solutions. All other chemicals were of analytical grade and used without any further purification. Water used for chemical and stock solutions was purified using a Mili-Q system (milipore filtration).

2.1.2 Experimental Procedure

Photo-Fenton and photo-Fenton like experiments were carried out at room temperature (23 ± 2 ℃) using different hydrogen peroxide and ferrous ion concentrations at pH of 3 which is suitable for photo-Fenton treatment (Hsueh, Huang, Wang & Chen et al., 2005). For that reason, pH adjustment to obtain pH value of the solution as 3 was applied with sulfuric acid solution addition. Measurement of pH was done by using thermo scientific Orion pH meter 720a. The pH meter was calibrated by using the standard pH solutions before use. Required amounts of sulfuric acid solution were added to the sample in order to obtain the desired pH in the solution.

For a standard reaction run, 2 L of the synthetic wastewater sample was used. For preparing synthetic wastewater, distilled water and triclosan stock solution was mixed to obtain determined concentration of triclosan which are 0.1, 5.05 and 10 mg/L. After pH adjustment, synthetic solution with desired concentration of the triclosan was placed in the reactor and predetermined amounts of oxidant and the catalyst were injected to the reactor at the beginning of each experiment. In batch experiments, Fe (II) (catalyst) was mixed well with synthetic wastewater before the addition of hydrogen peroxide (oxidant). The experiments were started by addition of the H_2O_2 to the reactor. The UV lamp was immediately turned on. The time at which the ultraviolet lamp was turned on was considered as time zero or the beginning of the experiment. Samples withdrawn from the reactor at certain time intervals were analyzed immediately to avoid further reactions. Samples (30 ml) of raw and treated triclosan solutions were withdrawn for analysis.

pH and conductivity levels were measured. Samples taken from the reactor were centrifuged on Hettich Universal 320 R benchtop centrifuge before HPLC analyze in order to prevent clogging in column. Due to the fragility of the glass tubes, samples were centrifuged about 10 minutes at 3000 rpm. After the centrifuge application, samples were removed to HPLC samples tubes which were proper for using HPLC device.

2.1.3   Experimental Set-up

2.1.3.1   Configuration of UV Reactor

Figure 2.1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations. All batch photo-oxidation experiments were performed in the completely mixed, batch, cylindrical photochemical reactor with a total volume of 2.2 L. The reactor is made of glass and does not contain any metal parts. The outside of the reactor was covered with an aluminum sheet for protection of human eyes to excessive UV radiation and to keep in the UV-light. The upper part of the reactor has inlets for feeding reactants, sample removal and ports for measuring temperature and withdrawing samples. The reactor was open to air and a Teflon-coated magnetic stirring bar was placed at the bottom of the reactor to provide a proper mixing. The reactor was placed on a magnetic stirrer (WiseStir MSH-20A).

The UV irradiation source was a 16 W low-pressure mercury vapor lamp (maximum emission at 254 nm) placed in a quartz tube. The intensity of the UV radiation was measured using the ferrioxalate actinometry method and estimated to be $4.98*10^{-6}$einstein/s (mole of photons/second). Since the light source produces heat, the lamp was surrounded with a water-cooling jacket to conduct experiments at room or controlled temperatures; the lamp was axially centered and immersed in the reactor.
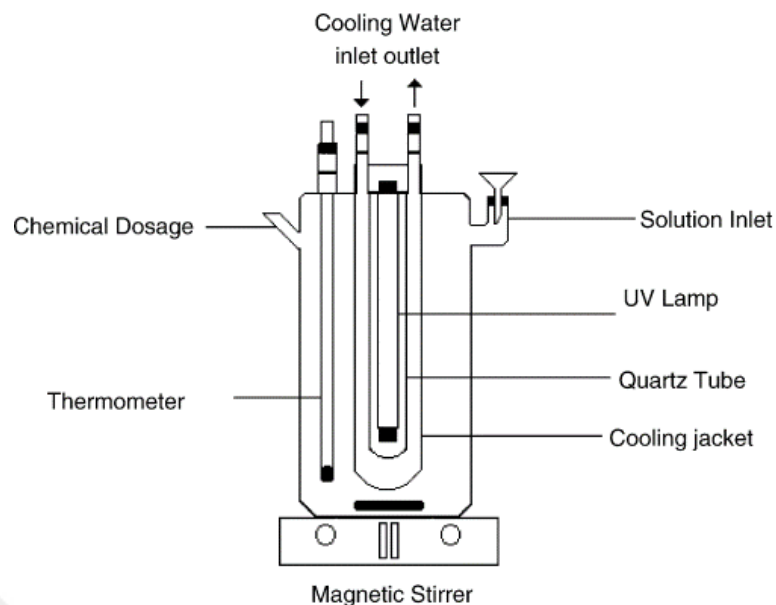
Figure 2.1 Schematic diagram of the lab - scale photochemical installation.

2.1.4 *Analytical Methods*

Samples removed from UV reactor at pre-determined time intervals were centrifuged and then analyze immediately for triclosan measurement. Triclosan, 2,4-Dichlorophenol and 2,4,6-Trichlorophenol (potential by-products of photo oxidation of triclosan) concentrations of the samples was analyzed using an HPLC (Agilent 1100 model, USA) equipped with a UV-detector and a C18 column. The mobile phase composition was H_2O/acetonitrile with a ratio 25/75. The UV-detection was operated at 280 nm. The flow rate was 1.5 mL min-1 and the injection volume was 20 μL. Under these conditions, the retention time for triclosan was 5 min. The calibration curve for triclosan was constructed using the peak areas of the standard samples and were analyzed under the same conditions as that of the experimental samples. Stock solution of triclosan was prepared in 1 liter water and was stored properly by protecting from the light. The calibration curve was prepared for concentrations between 10 mg/L and 0.001 mg/L triclosan with a linearity of $R^2 =$ 0.99997.

The reaction times for 2,4-Dichlorophenol and 2,4,6-Trichlorophenol were 1,680 min. and 2,120 min. respectively. The calibration curves were prepared for

concentrations between 5 mg/L and 0.001 mg/L for 2,4-Dichlorophenol and 2,4,6-Trichlorophenol with a linearity of R^2= 0.99996 and 0.99993.

Limit of detection (LOD) and Limit of Quantification (LOQ) of the fundamental components of analytical measurements. Both of two calculations especially substantial for evaluating obtained results.

LOD is the lowest quantity of the substance with a given confidence, that can be distinguished from the absence of it in sample but cannot be quantified; whereas, LOQ is the lowest quantity of the substance that can be quantified with a given level of confidence (Vial & Jardy, 1999). The formula for the LOD and LOQ are presented respectively Equations (2.1) and (2.2) as follows:

$$LOD = 3*\sigma$$

(2.1)

$$LOQ = 10* \sigma$$

(2.2)

Where σ is refers to standard deviation. LOD correspond 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 hand, LOQ correspond to amount of substance determined by 10 times of the standard deviation.

In this respect, LOD and LOQ were calculated for Triclosan, 2,4-Dichlorophenol and 2,4,6-Trichlorophenol in synthetic water individually and listed in Table 2.1.

Table 2.1 LOD and LOQ values of Triclosan and it's by products

Substance	LOD (mg/L)	LOQ (mg/L)
Triclosan	0.03	0.12
2,4-Dichlorophenol	0.02	0.08
2,4,6-Trichlorophenol	0.04	0.15

2.2 The Box–Behnken Experimental Design

Box–Behnken statistical experiment design and the response surface methodology (Abbasi, Ahmad & Wasim, 1987) were used to investigate the effects of the three independent operating variables on the response functions and to determine the optimal combination of variables resulting in maximum triclosan removal efficiency. Also, the production of selected possible by-products concentrations which were 2,4-Dichlorophenol and 2,4,6-Trichlorophenol was consider.

A modified central composite experimental design known as the Box–Behnken design is an independent, rotatable quadratic design method with no embedded or fractional factorial points. The variable combinations of these factorial points are at the midpoints of the edges of the variable space and at the center (Çatalkaya & Kargı, 2007).The optimization procedure involves studying the response of the statistically designed combinations, estimating the coefficients by fitting the experimental data to the response functions, predicting the response of the fitted model and checking the adequacy of the model to perform of treatment procedure. Also Box-Behnken design allows calculations of the response function at intermediate levels and enables estimation of the system performance at any experimental point within the range studied.

Photo oxidation experiments were carried out using different hydrogen peroxide and ferrous or ferric ion concentrations at the pH 3 which is reported to be a suitable pH for photo-Fenton and photo-Fenton like treatments (Hamed & Sakr, 2001). For that reason, pH was adjusted to 3 for all experiments.

For photo-Fenton process and photo-Fenton like process, the independent significant variables were the hydrogen peroxide (H_2O_2) concentration (X_1), ferrous (Fe (II)) or ferric ions (Fe (III)) concentration (X_2), initial concentration of triclosan (X_3). The low, center and high levels of each variable are designated as -1, 0 and +1, respectively, as shown in Table 2.2. The dependent variables or objective functions are related to each other. The dependent variables were the percent removal of

triclosan (Y_1), occurrence of 2,4-Dichlorophenol (2,4-DCP) (Y_2) and occurrence of 2,4,6-Trichlorophenol (2,4,6-TCP) (Y_3).

The H_2O_2 concentration (X_1) varied between 1 and 50 mM while, ferrous or ferric ions concentration (X_2) varied between 0.1 and 5 mM, because of the molar ratio of H_2O_2/Fe (II) or Fe (III) were selected as 10. H_2O_2/Fe (II) or Fe (III) molar ratios were determined to depending on calculation of theoretical H_2O_2 demand of oxidizing of triclosan. All of these selections were performed to applying an effective oxidation process. The initial concentration of triclosan (X_3) was ranged from 0.1 to 10 mg/L.

Table 2.2 Levels of variables in Box-Behnken design

Variable	Symbol	Coded Variable Level		
		Low	Center	High
		-1	0	+1
Hydrogen peroxide concentration (mM)	X_1	1	25.5	50
Ferrous or ferric ions concentration (mM)	X_2	0.1	2.55	5
Initial concentration of triclosan (mg/L)	X_3	0.1	5.05	10

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 Results and Discussion

Photo-Fenton and photo-Fenton like oxidations of triclosan containing water were investigated by using Box-Behnken experimental design. Triclosan, considered as a highly toxic, persistent priority substance by the EU (European Commission, 2001) is one of the most used active ingredient in antibacterial personal care products.

3.1.1   Photo-Fenton Oxidation

In the Box-Behnken design, the independent variables were the concentration of triclosan (X_3 = 0.1-10 mg/L), hydrogen peroxide (X_1 = 1-50 mM), and ferrous ion (X_2 = 0.1-5 mM). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 3.1. The dependent variables (or objective functions) were the percent triclosan removal (Y_1), 2,4-DCP (Y_2) and 2,4,6-TCP (Y_3) occurrences. The experimental conditions of the Box-Behnken experiment design are presented in Table 3.1. The center point (0, 0, 0) was repeated three times and almost the same results were obtained indicating the reproducibility of the data. Observed and predicted percent triclosan removals are compared in Table 3.2

Table 3.1 The experimental conditions of the Box-Behnken experiment design for photo-Fenton oxidation

Run #	Actual Coded and Levels					
	X_1, H_2O_2 (mM)		X_2, Fe (II) (mM)		X_3, TCS (mg/L)	
	Coded Levels	Actual Levels	Coded Levels	Actual Levels	Coded Levels	Actual Levels
1	+1	50	+1	5	0	5.05
2	+1	50	-1	0.1	0	5.05
3	-1	1	+1	5	0	5.05
4	-1	1	-1	0.1	0	5.05

Table 3.1 The experimental conditions of the Box-Behnken experiment design for photo-Fenton oxidation (continue)

5	0	25.5	+1	5	+1	10
6	0	25.5	+1	5	-1	0.1
7	0	25.5	-1	0.1	+1	10
8	0	25.5	-1	0.1	-1	0.1
9	+1	50	0	2.55	+1	10
10	+1	50	0	2.55	-1	0.1
11	-1	1	0	2.55	-1	0.1
12	-1	1	0	2.55	+1	10
13	0	25.5	0	2.55	0	5.05
14	0	25.5	0	2.55	0	5.05
15	0	25.5	0	2.55	0	5.05

Table 3.2 Observed and predicted percent removals for the response functions (Y_1) for photo-Fenton oxidation

Run No	Predicted percent removals	Observed percent removals
	Y_1, TCS removal (%)	Y_1, TCS removal (%)
1	87.45	86.58
2	99.70	97.55
3	65.85	68.00
4	79.93	80.80
5	2.05	7.00
6	81.22	75.00
7	69.66	75.88
8	39.95	35.00
9	83.88	79.80
10	92.51	99.60
11	87.92	92.00
12	47.09	40.00
13	82.04	82.06
14	82.04	82.00
15	82.04	82.06

The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the

response function (Y) and the independent variables (X) can be approximated by a quadratic polynomial Equation (3.1) as follows:

$$Y= b_0+b_1X_1+b_2X_2+b_3X_3+b_{1,2}X_1X_2+b_{1,3}X_1X_3+b_{2,3}X_2X_3+b_{1,1}X_1{}^2+b_{2,2}X_2{}^2+b_{3,3}X_3{}^2$$

(3.1)

The coefficients of the response functions for different dependent variables were determined correlating the experimental results with the response functions by using a Stat-Ease Design Expert 9.0 regression program.

The model F-value of 18.15 implies the model is significant for triclosan removal. P value of < 0.05 for any factor in the analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. X_1-H_2O_2, X_3-TCS, X_2-Fe (II) X_3-TCS, $(X_2$-Fe (II)$)^2$, $(X_1$-$H_2O_2)^2$, $(X_3$-TCS$)^2$ are significant model terms. These experiment parameters are affecting the results directly. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in appendices as tables, indicating the fact that that the predictability of the model is within the 95% confidence interval. In the photo-Fenton experiment, the response functions with the determined coefficients for the percent removal of triclosan (Y_1) occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3) are presented by Equations (3.2), (3.3) and (3.4).

$$Y_1= + 51.77202 - 1.24196X_1 + 20.53498X_2 + 9.61251X_3 + 7.62182 \times 10^{-3}X_1X_2 + 0.066378X_1X_3 - 2.24449X_2X_3 + 0.025675X_1{}^2 - 2.36880X_2{}^2 - 0.79997X_3{}^2$$

(R-Squared = 0.9703)

(3.2)

$$Y_2= + 0.66504 - 0.052059X_1 + 0.39233X_2 + 0.11901X_3 + 1.10561 \times 10^{-3}X_1X_2 - 3.70831 \times 10^{-5}X_1X_3 + 2.13523 \times 10^{-3}X_2X_3 + 8.87897 \times 10^{-4}X_1{}^2 - 0.076930X_2{}^2 - 0.011388X_3{}^2$$

(R-Squared = 0.9694)

(3.3)

$$Y_3 = + 0.23199 - 0.025393X_1 - 0.071478X_2 + 0.14479X_3 + 1.00857 \times 10^{-3}X_1X_2 - 2.65269 \times 10^{-3}X_1X_3 - 0.010885X_2X_3 + 4.34228 \times 10^{-4}X_1^2 + 0.012059X_2^2 + 5.84157 X_2^2 \text{ (R-Squared} = 0.9654)$$

(3.4)

On the basis of the coefficients in Equations (3.2), (3.3) and (3.4), it can be said that percent triclosan removal decreases with initial concentration of triclosan (X_3) while increasing with the H_2O_2 concentration (X_1) and Fe (II) concentrations (X_2). The H_2O_2 concentration has a more profound effect on percent removal of triclosan as compared to Fe (II) concentrations.

Occurrence of the selected by-products which are occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3) increases with the Fe (II) concentration (X_2), the H_2O_2 concentration (X_1). Otherwise, Fe (II) concentration (X_2) a more profound effect by the occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3).

3.1.2 Removal of Triclosan

Response functions with determined coefficients were used to estimate variations of response functions with the independent variables under different conditions. Figure 3.1 shows the effect of initial Fe (II) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when initial concentration of triclosan was 10 mg/L.

31
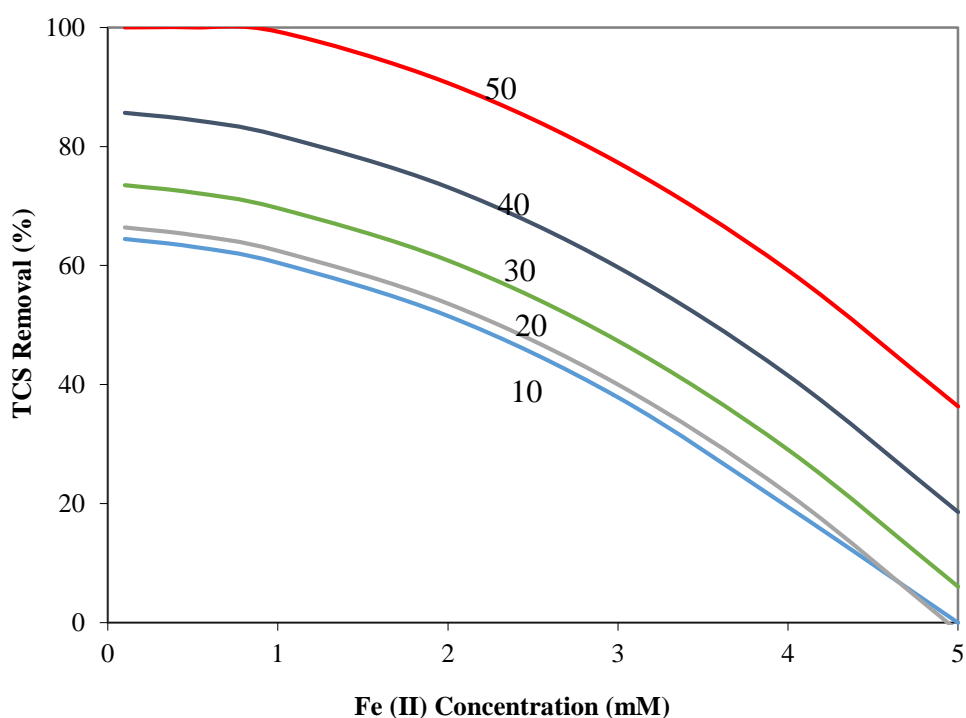
Figure 3.1 Variation of percent triclosan removals with Fe (II) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 10 mg/L. (Photo-Fenton process).

At high triclosan concentrations such as 10 mg/L, complete degradation was realized at H_2O_2 concentration of 50 mM and Fe (II) concentrations below 1 mM after 60 min reaction time while higher concentrations of Fe (II) did not result in complete triclosan degradation.

Percent triclosan removals were 40, 75.88 and 79.80% when H_2O_2 concentrations of 1, 25 and 50 mM, respectively at a Fe (II) concentration of 0.1 mM and at an initial triclosan concentration of 10 mg/L.

Figure 3.2 shows the effect of initial Fe (II) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when initial concentrations of triclosan was 5 mg/L.
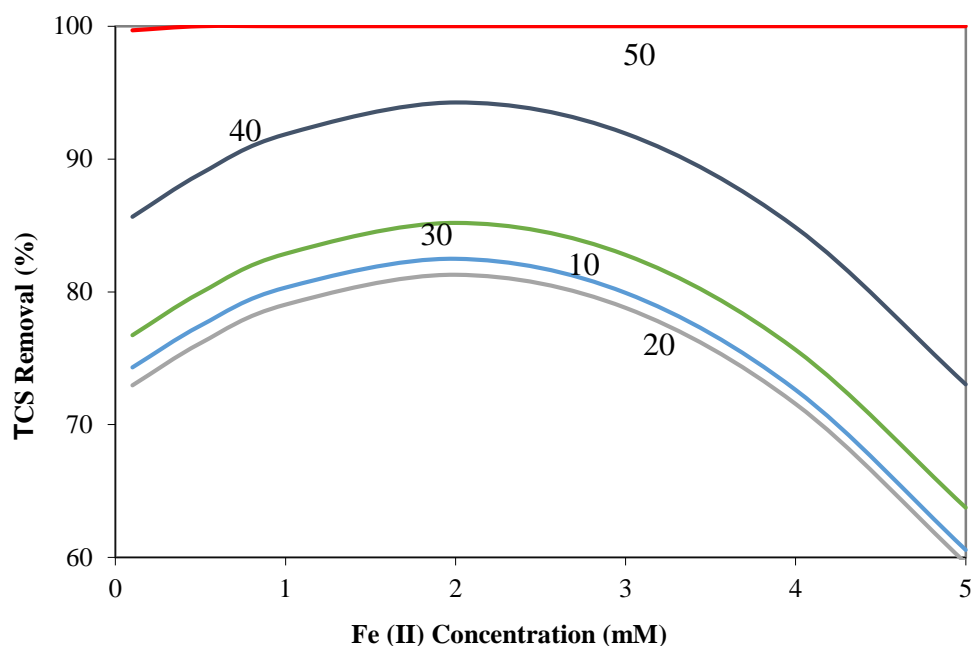
Figure 3.2 Variation of percent triclosan removals with Fe (II) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 5 mg/L. (Photo-Fenton process).

Percent triclosan removal increased with increasing initial hydrogen peroxide concentration at all initial triclosan concentrations. At triclosan concentrations at 5 mg/L, triclosan removal slightly decreased with increasing Fe (II) concentrations above 2.5 mM due to adverse effects of high Fe (II) concentrations such as inhibition effect on UV light.

Percent triclosan removals were 86.58 and 97.55 % when Fe (II) concentrations of 5 and 0.1 mM, respectively, at a H_2O_2 concentration of 50 mM and at an initial triclosan concentration of 5 mg/L, indicating Fe (II) limitations at high Fe (II) concentrations.

Percent triclosan removals were 80.80 and 97.60% when H_2O_2 concentrations of 1 and 50 mM, respectively at a Fe (II) concentration of 0.1 mM and an initial triclosan concentration of 5 mg/L.

Figure 3.3 shows the effect of initial Fe (II) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when initial concentrations of triclosan was 0.1 mg/L.
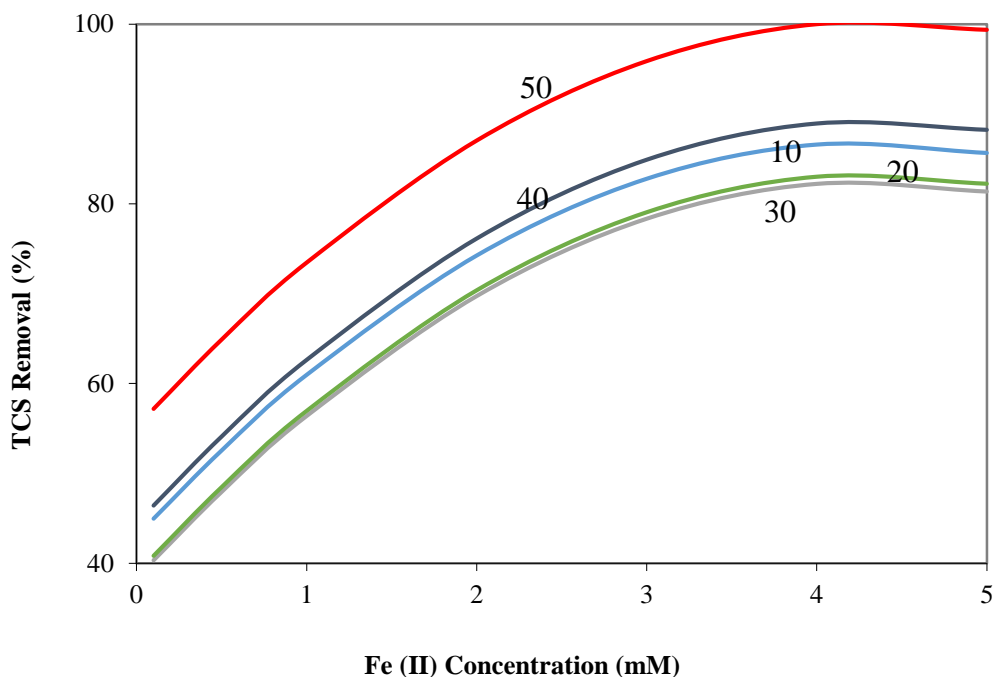
Figure 3.3 Variation of percent triclosan removals with Fe (II) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 0.1 mg/L. (Photo-Fenton process).

Percent triclosan removals were 75 and 35 % when a Fe (II) concentrations of 5 and 0.1 mM, respectively, at a H_2O_2 concentrations of 25 mM and initial triclosan concentration of 0.1 mg/L, indicating Fe (II) limitations at low Fe (II) concentrations.

Percent triclosan removals were 92 and 99.6% when H_2O_2 concentrations of 1 and 50 mM, respectively, at an initial triclosan concentration of 0.1 mg/L and at a Fe (II) concentration of 2 mM.

These results are in agreement with the literature reports, where a beneficial effect of increasing Fe (II) was observed in photo-degradation of pesticides (Krutzler et al., 1999). However, high iron concentrations can also scavenge OH$^•$ yielding lower levels of oxidation. Apparently the use of high catalyst concentrations inhibited the removal of color due to formation of radical scavengers. Moreover, there is a need for strict pH control to avoid precipitation of iron hydroxides which can prevent

penetration of light due to high turbidity or optical density of the solution slowing down the generation of Fe (II) and consequently the degradation reaction.

At low triclosan concentration of 0.1 mg/L, the optimal H_2O_2/Fe (II)/triclosan concentration yielding the highest triclosan removal (99.60%) was 50/2/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 50/2/10 yielding 79.80% triclosan removal.

The ANOVA analysis indicated that all three variables triclosan, H_2O_2 and Fe (II) concentrations and the interactions (X_1, X_3, X_1 X_3, X_2X_3, and X_3^2) were significant and played important roles in degradation by the photo-Fenton treatment as summarized in Appendices A.1, A.2 and A.3 as tables.

3.1.3 Occurrences of By- products

Table 3.3 Observed and predicted occurrences for the response functions (Y_2) and (Y_3) for photo-Fenton oxidation

Run No	Predicted percent occurrences		Observed percent occurrences	
	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)
1	0.95	0.05	0.96	0.06
2	0.63	0.12	0.49	0.06
3	1.02	0.61	1.16	0.67
4	0.96	0.93	0.96	0.91
5	0.24	0.23	0.15	0.10
6	0.11	0.00	0.05	0.00
7	0.00	0.68	0.05	0.62
8	0.00	0.00	0.06	0.00
9	1.01	0.00	1.09	0.09
10	0.94	0.07	0.98	0.00
11	1.13	0.12	1.05	0.00
12	1.22	1.31	1.18	1.38
13	0.82	0.09	0.82	0.09
14	0.82	0.09	0.83	0.09
15	0.82	0.09	0.82	0.09

3.2 Photo-Fenton Like Oxidation

In the Box-Behnken design, the independent variables were the concentration of triclosan ($X_1 = 0.1$-10 mg/L), hydrogen peroxide ($X_2 = 1$-50 mM), and ferric ion ($X_3 = 0.1$-5 mM). The low, center and high levels of each variable are designated as -1, 0, and +1, respectively as shown in Table 3.4 The dependent variables (or objective functions) were the percent triclosan removal (Y_1), 2,4-DCP (Y_2) and 2,4,6-TCP (Y_3) occurrences. The experimental conditions of the Box-Behnken experiment design are presented in Table 3.4. The center point (0, 0, 0) was repeated three times and almost the same results were obtained indicating the reproducibility of the data. Observed and predicted percent triclosan removals are compared in Table 3.5.

Table 3.4 The experimental conditions of the Box-Behnken experiment design for photo-Fenton like oxidation

Run No	Actual Coded and Levels					
	X_1, H_2O_2 (mM)		X_2, Fe (III) (mM)		X_3, TCS (mg/L)	
	Coded Levels	Actual Levels	Coded Levels	Actual Levels	Coded Levels	Actual Levels
1	+1	50	+1	5	0	5.05
2	+1	50	-1	0.1	0	5.05
3	-1	1	+1	5	0	5.05
4	-1	1	-1	0.1	0	5.05
5	0	25.5	+1	5	+1	10
6	0	25.5	+1	5	-1	0.1
7	0	25.5	-1	0.1	+1	10
8	0	25.5	-1	0.1	-1	0.1
9	+1	50	0	2.55	+1	10
10	+1	50	0	2.55	-1	0.1
11	-1	1	0	2.55	-1	0.1
12	-1	1	0	2.55	+1	10
13	0	25.5	0	2.55	0	5.05
14	0	25.5	0	2.55	0	5.05
15	0	25.5	0	2.55	0	5.05

Table 3.5 Observed and predicted percent removals for the response functions (Y_1) for photo-Fenton like oxidation

Run No	Predicted percent removals	Observed percent removals
	Y_1, TCS removal (%)	Y_1, TCS removal (%)
1	97.27	97.00
2	75.53	76.60
3	46.47	45.40
4	93.88	94.15
5	56.41	58.70
6	80.95	80.00
7	87.05	88.00
8	75.99	73.70
9	80.02	78.00
10	72.78	74.00
11	70.53	72.55
12	49.80	48.58
13	60.57	60.05
14	60.57	60.50
15	60.57	61.17

The coefficients of the response functions for different dependent variables were determined correlating the experimental data with the response functions by using a Stat-Ease regression program. Different response functions with the determined coefficients are presented by Equations (4.5), (4.6) and (4.7). The model F-value of 68.96 implies the model is significant for triclosan removal. P value of < 0.05 for any factor in analysis of variance (ANOVA) indicates a significant effect of the corresponding variable on the response. In this case X_1-H_2O_2, X_2-Fe^{+2}, X_3-TCS, (X_1-H_2O_2 X_2-Fe^{+2}), (X_1-H_2O_2 X_3-TCS), (X_2-Fe (II) X_3-TCS), (X_1-H_2O_2)^2, (X_2-Fe^{+2})^2 are significant model terms. The ANOVA tests for the other response functions gave similar results. The results of analysis of variance (ANOVA) are also presented in Appendices as tables indicating the fact that that the predictability of the model is at 95% confidence interval. In the photo-Fenton like experiment, the response functions with the determined coefficients for percent removal of triclosan (Y_1) occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3) are presented by Equations (3.5), (3.6) and (3.7).

$$Y_1 = + 100.49210 - 1.15728X_1 - 16.67960X_2 - 1.21190X_3 + 0.28800X_1X_2 + 0.057658X_1X_3 - 0.73387X_2X_3 + 9.07677 \times 10^{-3}X_1^2 + 2.04345X_2^2 + 0.092269X_3^2$$

(R-Squared = 0.9920)

(3.5)

$$Y_2 = + 0.24987 - 0.013367X_1 - 0.057470X_2 + 5.57251X_3 + 8.19074 \times 10^{-3}X_1X_2 - + 2.58213 \times 10^{-3}X_1 X_3 - 7.44816E \times 10^{-3}X_2 X_3$$

(R-Squared = 0.9635)

(3.6)

$$Y_3 = + 0.098496 - 5.29978 \times 10^{-3}X_1 - 39.721 \times 10^{-3}X_2 + 0.062342X_3 + 1.99650 \times 10^{-3}X_1X_2 - 2.13785 \times 10^{-4}X_1X_3 - 0.010360X_2X$$

(R-Squared = 0.9610)

(3.7)

On the basis of the coefficients in Equations (3.5), (3.6) and (3.7), it can be said that percent triclosan removal (Y_1) increase with the H_2O_2 concentration (X_1) while increasing with Fe (III) concentration (X_2). The H_2O_2 concentration has a more profound effect on oxidizing as compared to Fe (III) concentrations.

The percent removal of triclosan (Y_1) decreased with Fe (III) concentration (X_2) and occurrence of 2,4-Dichlorophenol (Y_2) increase and occurrence of 2,4,6-Trichlorophenol (Y_3) increase with Fe (III) concentration (X_2) decrease when the H_2O_2 concentration (X_1) is constant. According to these evaluations, removal efficiency of triclosan is decreased and occurrence of highly toxic by-products is increased using of excessive Fe (III) concentrations (X_2).

Occurrence of the selected by-products which are occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3) increases with the Fe (III) concentration (X_2), the H_2O_2 concentration (X_1). Otherwise, Fe (III)

concentration (X_2) a more profound effect by the occurrence of 2,4-Dichlorophenol (Y_2) and occurrence of 2,4,6-Trichlorophenol (Y_3).

3.2.1 Disappearance of Triclosan.

Response functions with determined coefficients were used to estimate variations of response functions with the independent variables under different conditions. Figure 3.4 shows the effect of initial Fe (III) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when an initial concentration of triclosan was 10 mg/L (Photo-Fenton like Process).

As expected, percent triclosan degradation increased with increasing initial H_2O_2 concentration at high Fe (III) concentrations.
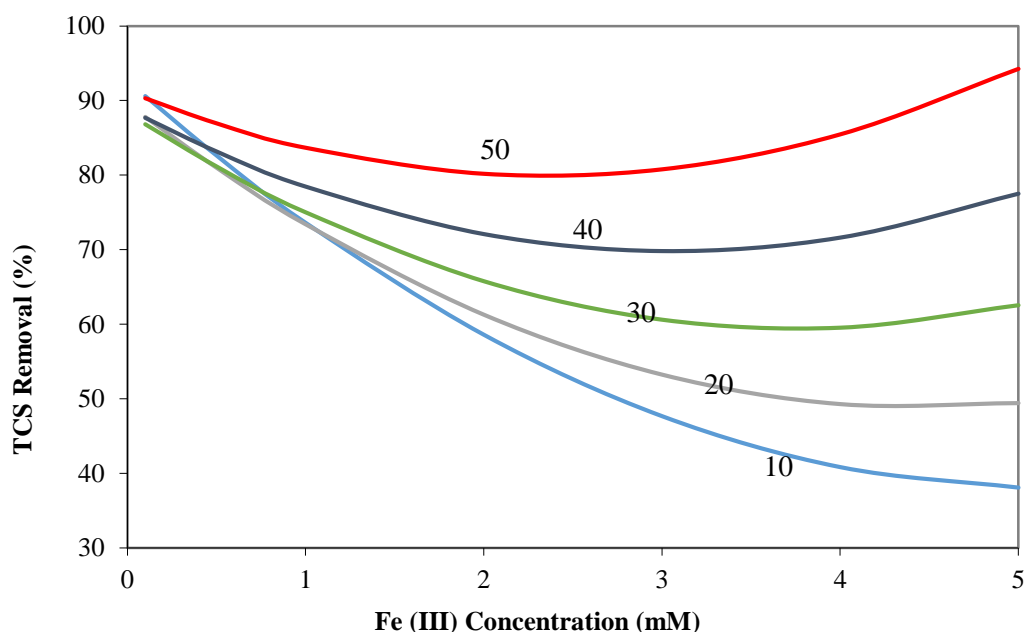
Figure 3.4 Variation of percent triclosan removals with Fe (III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 10 mg/L. (Photo-Fenton like process).

At high triclosan concentrations such as 10 mg/L, complete degradation was required at higher H_2O_2 concentration and for providing to molar ratio, also required higher Fe (III) concentrations. Otherwise, inadequate amount of H_2O_2 or iron ions are used, triclosan degradation did not completed after 60 min reaction time.

Figure 3.5 shows the effect of initial Fe (III) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when an initial concentration of triclosan was 5 mg/L (Photo-Fenton like Process).
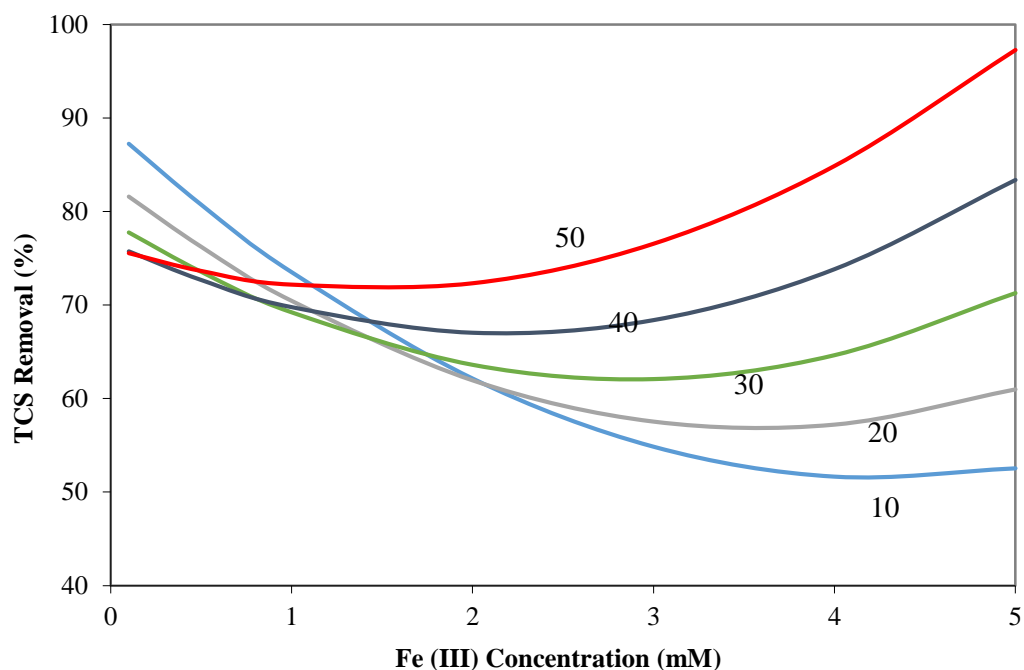
Figure 3.5 Variation of percent triclosan removals with Fe (III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 5 mg/L. (Photo-Fenton like process).

At triclosan concentrations below 5 mg/L since H_2O_2 requirement was low, triclosan removals decreased with increasing H_2O_2 concentrations above 1 mM H_2O_2 concentration at low Fe (III) concentrations due to excess H_2O_2/Fe (III) molar ratio and inhibition caused by high concentrations of H_2O_2. At high H_2O_2 concentrations, probably H_2O_2 served as a free-radical scavenger for itself reducing the [OH$^\bullet$] that are presented by reactions (3.8) and (3.9) as follow.

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$$

(3.8)

$$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$$

(3.9)
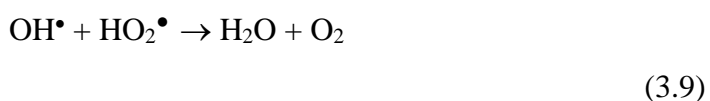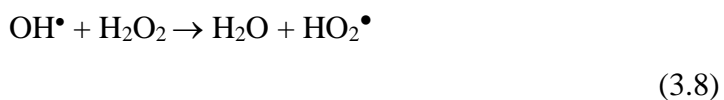
In agreement with Glaze, Kang & Lay, (1995) and Beltran, Ovejero & Rivas, (1996) a reduction in pesticide removal was observed at high H_2O_2 concentrations indicating the adverse effects of excess H_2O_2. Percent triclosan removals were 72.55 and 74% when H_2O_2 concentrations of 1 and 50 mM, respectively, at an initial triclosan concentration of 0.1 mg/L and at a Fe (II) concentration of 1 mM.
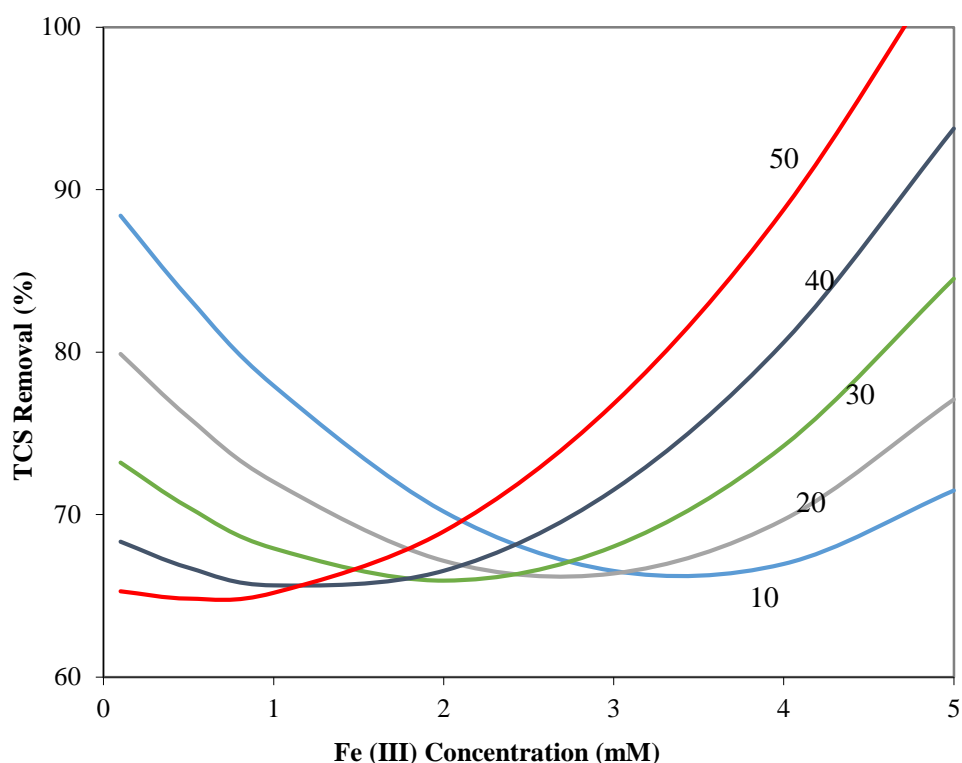
Figure 3.6 Variation of percent triclosan removals with Fe (III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 0.1 mg/L. (Photo-Fenton like process).

Figure 3.6 shows the effect of initial Fe (III) concentration on percent triclosan removal at different H_2O_2 concentrations after 60 min of reaction time when an initial concentration of triclosan was 0.1 mg/L (Photo-Fenton like Process).

Percent triclosan removals were 72.55 and 74 % when H_2O_2 concentrations of 1 and 25 mM, at respectively, an initial triclosan concentration of 0.1 mg/L and a Fe (III) concentration of 2 mM, indicating H_2O_2 limitations at low Fe (III) concentrations as shown in Figure 3.6. Percent triclosan removals were 80, 97 and

88% when H_2O_2 concentrations of 1, 25 and 50 mM, at respectively an initial triclosan concentration of 0.1 mg/L and at a Fe (II) concentration of 5 mM.

At low triclosan concentration of 0.1 mg/L, the optimal H_2O_2/Fe (III)/triclosan concentration yielding the highest triclosan removal (87.7%) was 50/5/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 50/5/0.1 yielding 80% triclosan removal.

The ANOVA analysis indicated that all three variables triclosan, H_2O_2 and Fe (III) concentrations and the interactions (X_1, X_2, X_3, $X_1 X_3$, X_2X_3, X_1^2, X_2^2) were significant and played important roles in degradation by the photo-Fenton Like treatment as summarized in Appendices A.1, A.2 and A.3 as tables.

3.2.2 Occurrence of By-products

Table 3.6 Observed and predicted occurrence for the response functions (Y_2) and (Y_3) for photo-Fenton like oxidation

Run No	Predicted percent occurrence		Observed percent occurrence	
	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)
1	1.83	0.13	1.98	0.17
2	0.29	0.10	0.30	0.08
3	0.00	0.00	0.02	0.00
4	0.27	0.40	0.29	0.39
5	1.01	0.07	0.84	0.09
6	0.67	0.02	0.60	0.00
7	0.63	0.52	0.61	0.59
8	0.00	0.00	0.01	0.00
9	1.64	0.24	1.76	0.21
10	0.49	0.00	0.51	0.00
11	0.11	0.00	0.11	0.00
12	0.00	0.35	0.10	0.31
13	0.56	0.15	0.41	0.11
14	0.56	0.15	0.45	0.13
15	0.56	0.15	0.41	0.11

At high triclosan concentrations such as 10 mg/L, complete degradation was realized at H_2O_2 concentration of 50 mM and Fe (II) concentrations below 1 mM after 60 min reaction time while higher concentrations of Fe (II) did not result in complete triclosan degradation.

3.3 Comparison of Advanced Oxidation Processes (AOPs)

Table 3.7 summarizes the conditions and the performances of the AOPs used for treatment of triclosan synthetic wastewater according to maximum percent treatment of triclosan via photo-Fenton process and Table 3.8 also summarizes the conditions and the performances of the AOPs used for treatment of triclosan synthetic wastewater according to maximum percent treatment of triclosan via photo-Fenton like process.

To compering of catalyst, Fe (III) is more effective than the Fe (II) on removal of triclosan at the lower H_2O_2 concentrations cause of that using Fe (III) as a catalyst is more cost effective and using Fe (III) results to increase of reaction rate of degradation of triclosan. Fenton like treatment prevents the Fe (II) inhibitions of the hydroxyl radicals.

Photo-Fenton treatment and photo-Fenton like treatment are resulted > 95% removal efficiency of triclosan. However, generated amounts of predicted by-products and their species are resulted difference on photo-Fenton treatment and photo-Fenton like treatment.

The one of the aim of this study is compare to used catalysts efficiency on degradation of triclosan but experiments shows that catalyst efficiency are mainly related to applied oxidant amounts. For example, if the applied H_2O_2 concentrations were high, then required catalyst amount is increase. Both of two catalysts which are Fe (II)/Fe (III) ions are shows these conditions.

Table 3.7 Comparison of triclosan synthetic wastewater treatment performances of different advanced oxidation processes at the end of 60 minutes of treatment according to maximum percent treatment of triclosan via photo-Fenton process

AOPs	Run no	X_1, H_2O_2 (mM)	X_2, Fe ion (mM)	X_3, TCS (mg/L)	Y_1, TCS removal (%)	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)
$UV/H_2O_2/Fe(II)$	10	50	2	0.1	99.60	0.98	0.00
$UV/H_2O_2/Fe(II)$	2	50	0.1	5	97.55	0.49	0.06
$UV/H_2O_2/Fe(II)$	9	50	2	10	79.80	1.09	0.09
$UV/H_2O_2/Fe(III)$	10	50	2	0.1	74.00	0.51	0.00
$UV/H_2O_2/Fe(III)$	2	50	0.1	5	76.60	0.30	0.08
$UV/H_2O_2/Fe(III)$	9	50	2	10	78.00	1.76	0.21

In photo-Fenton treatment, the highest triclosan removal (99.60%) was obtained with a H_2O_2/Fe (II)/triclosan ratio of 50/2/0.1 likewise in photo-Fenton like treatment the recorded triclosan removal is 74% at a H_2O_2/Fe (II)/triclosan ratio of 50/2/0.1.

Table 3.8 Comparison of triclosan synthetic wastewater treatment performances of different advanced oxidation processes at the end of 60 minutes of treatment according to maximum percent treatment of triclosan via photo-Fenton like process

AOPs	Run no	X_1, H_2O_2 (mM)	X_2, Fe ion (mM)	X_3, TCS (mg/L)	Y_1, TCS removal (%)	Y_2, 2,4-DCP occurrence (mg/L)	Y_3, 2,4,6-TCP occurrence (mg/L)
$UV/H_2O_2/Fe(III)$	1	50	5	5	97.00	1.98	0.17
$UV/H_2O_2/Fe(III)$	4	1	0.1	5	94.15	0.29	0.39
$UV/H_2O_2/Fe(III)$	7	25.5	0.1	10	88.00	0.61	0.59
$UV/H_2O_2/Fe(II)$	1	50	5	5	86.58	0.96	0.06
$UV/H_2O_2/Fe(II)$	4	1	0.1	5	80.80	0.96	0.91
$UV/H_2O_2/Fe(II)$	7	25.5	0.1	10	75.88	0.05	0.62

In photo-Fenton like treatment, the highest triclosan removal (97.00%) was obtained with a H_2O_2/Fe (III)/triclosan ratio of 50/5/5 likewise in photo-Fenton treatment, the recorded triclosan removal is 86.58% at a H_2O_2/Fe (II)/triclosan ratio of 50/2/0.1. At high H_2O_2 concentration, triclosan removals decreased due to scavenging effects of H_2O_2 concentrations and Fe (II)/Fe (III) concentrations on hydroxyl radicals.

However, generated amounts of predicted by-products and their species are resulted difference on photo-Fenton treatment and photo-Fenton like treatment. For example, at experiment no 10, generated amounts of 2,4-DCP is 0.98 mg/L at Photo-Fenton treatment and generated amounts of 2,4-DCP is 0.51 mg/L at Photo-Fenton like treatment. Also, generation of 2,4,6-TCP was not observed at both process. At experiment no 4, generated amounts of 2,4,6-TCP is 0.96 mg/L and 2,4-DCP is 0.91 at photo-Fenton treatment and generated amounts of 2,4,6-TCP is 0.29 mg/L and 2,4-DCP is 0.39 at Photo-Fenton like treatment.

To compering of catalyst, Fe (III) is more effective than the Fe (II) on generated amounts of predicted by-products and their species at the lower H_2O_2 concentrations cause of that using Fe (III) as a catalyst generate less amount of by-products and relatively less harmful by-products species.

Photo-Fenton treatment more effective at high H_2O_2 concentration but high initial H_2O_2 concentration also results high amount of by-products occurrence. Photo-Fenton like process does not need high amount of H_2O_2 concentration to achieve high removal rate of triclosan cause of that does not generate high amount of byproducts.

CHAPTER FOUR
CONCLUSIONS

Triclosan degradation by advanced oxidation processes (photo-Fenton and photo-Fenton like oxidation) was investigated over a large range of reactant concentrations. Box-Behnken statistical experiment design and the response surface methodology (RSM) were used for this purpose. Triclosan, peroxide and ferrous ion concentrations were considered as independent variables while percent triclosan removal and 2,4-DCP and 2,4,6-TCP occurrence were the objective functions. Experimental data was used to determine the coefficients of the response functions. Predictions obtained from the response functions were in good agreement with the experimental results indicating the reliability of the method used.

The RSM also provided a better understanding for the roles of Fe (II)/Fe (III) concentrations as a catalysts and H_2O_2 concentrations as an oxidizer on degradation of the triclosan for a large range of concentrations also provided to able to make H_2O_2 concentrations were found to be more effective than Fe (II)/Fe (III) concentrations for degradation when the molar ratio between concentration of H_2O_2 and concentrations of Fe (II)/Fe (III) is determined adequate significantly.

At a constant triclosan concentration percent triclosan removal increased with increasing H_2O_2 concentrations and Fe (II) concentrations up to a certain level above which triclosan removals decreased due to scavenging effects of H_2O_2 concentrations and Fe (II)/Fe (III) concentrations on hydroxyl radicals.

The optimal reagent concentrations varied with the initial triclosan concentrations. Lower initial triclosan concentrations required lower amounts of the H_2O_2 concentrations and Fe (II)/Fe (III) concentrations for complete degradation. Higher initial triclosan concentrations required higher amounts of the H_2O_2 concentrations and Fe (II)/Fe (III) concentrations for complete degradation. At this situation,

occurrence of the highly toxic by-products was the critic limitation factor of the degradation.

Because of applying the higher molar ratio of H_2O_2 concentrations and Fe (II)/Fe (III) concentrations is result increasing of the production of 2,4-Dichlorophenol and 2,4,6-Trichlorophenol amounts. As a result of these conditions, also necessarily increase required amount of the H_2O_2 concentrations and Fe (II)/Fe (III) concentrations thus economically disadvantage will occur at the performing or applied both of photo-Fenton and photo-Fenton like process on the water/wastewater treatment plants.

Also, at the higher H_2O_2 concentrations using photo-Fenton like process more effective than the using photo-Fenton Process on the degradation of triclosan. To achieve to complete degradation of triclosan and limitation of produced by-products amounts should be required to optimize and to minimized reagent concentrations and also should be determined of optimum molar ratio of oxidant and catalyst, significantly.

Both of photo-Fenton treatment and photo-Fenton like treatment are resulted > 95% removal efficiency of triclosan. In photo-Fenton treatment, the highest triclosan removal (99.6%) was obtained with a H_2O_2/Fe (II)/triclosan ratio of 50/2/0.1. In photo-Fenton like treatment, the highest triclosan removal (97%) was obtained with a H_2O_2/Fe (III)/triclosan ratio of 50/5/5. However, generated amounts of predicted by-products and their species are resulted difference on photo -Fenton treatment and photo -Fenton like treatment.

To compering of catalyst, Fe (III) is more effective than the Fe (II) on generated amounts of predicted by-products and their species at the lower H_2O_2 concentrations cause of that using Fe (III) as a catalyst generate less amount of by-products and relatively less harmful by-products species.

Photo-Fenton treatment more effective at high H_2O_2 concentration but high initial H_2O_2 concentration also results high amount of by-products occurrence. Photo-Fenton like process does not need high amount of H_2O_2 concentration to achieve high removal rate of triclosan cause of that does not generate high amount of byproducts.

Recommendations for Future Research

- Performances of different advanced oxidation process were compared in this study in terms of the oxidant and catalyst requirements and removal efficiencies using triclosan containing water. The optimum conditions determined in this study can be used for treatment of real groundwater, surface water or wastewater containing triclosan.

- Different statistical experimental design methods may be used to determine the effects of large number of variables on treatment performances and to determine the optimum reaction conditions.

- Oxidation and degradation products of triclosan were determined and toxicity of these intermediates should be assessed using other toxicological and analytical methods.

- For a standard reaction run, synthetic wastewater sample was used in this study because of the negligible to any other intermediates chemicals those are already contained in wastewater sample. For the more realistic study, real wastewater samples and/or samples that taken from any wastewater treatment plant effluent can be used.

  .

REFERENCES

Abbasi, A. F., Ahmad, M. & Wasim, M. (1987). Optimization of concrete mix proportioning using reduced factorial experimental technique. *American Concrete Institute materials journal*, 84, 55–63.

Adolfsson-Erici, M., Pettersson, M. & Parkkonen, J. (2002). Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden. *Chemosphere*, 1485–1489.

Allmyr, M., Adolfsson-Erici. M., McLachlan M. S. & Sandborgh-Englund G. (2006). Triclosan in plasma and milk from Swedish nursing mothers and their exposure via personal care products. *Science of the Total Environment,* 372, 87-93.

Allmyr, M., Harden, F., Toms, L. M., Mueller, J. F., McLachlan, M. S., Adolfsson-Erici, M., Sandborgh-Englund, G., et al. (2008). The influence of age and gender on triclosan concentrations in Australian human blood serum. *Science of the Total Environment,* 393, 162-167.

Ashraf, S. S., Muhammad, A. R. & Alhadrami S. (2006). Degradation of Methyl Red using Fenton's reagent and the effect of various salts. *Dyes Pigments*, 69 (1-2), 74–78.

Agency for Toxic Substances and Disease Registry (ATSDR) (1990). Toxicological Profile for 2,4,6-Trichlorophenol, U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Bedoux, G., Roig, B., Thomas, O., Dupont, V. & Le Bot, B. (2012). Occurrence and toxicity of antimicrobial triclosan and by-products in the environment. *Environmental Science Pollution Research,* 19, 1044–1065.

Beltran, F.J., Ovejero, G. & Rivas, J. (1996). Oxidation of polynuclear aromatic hydrocarbon in water by UV radiation in combination with hydrogen peroxide. *Industrial Engineering Chemistry Research*, 35 (3), 883-889.

Box, G. E. P. & Wilson, K. B. (1951). On the experimental attainment of optimum multifactorial conditions. *Royal Statistics Society*, 13, 1-12.

Boza, A., De La Cruz, Y., Jordan, G., Jauregui-Haza, U., Aleman, A. & Caraballo, I., et al. (2000). Statistical optimization of a sustained-release matrix tablet of lobenzarit disodium. *Drug Development and Industrial Pharmacy*, 26 (12), 1303-1307.

Buth, J. M., Grandbois, M., Vikesland, P. J., McNeill, K. & Arnold, W. A. (2009). Aquatic photochemistry of chlorinated triclosan derivatives: Potential source of polychlorodibenzo-p-dioxins. *Environmental Toxicology Chemistry,* 28, 2555-2563

Buxton G. V., Greenstock C. L., Helman W. P. & Ross A. B. (1988). Critical review of data constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solutions. *Journal of Physical and Chemical Reference Data,* 17 (2), 513-586.

Canonica, S., Meunier, L. & Gunten, U. V. (2008). Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Research,* 42, 121-128

Canosa, P., Morales, S., Rodríguez, I., Rubí, E., Cela, R., Gómez, M., et al. (2005). Aquatic degradation of triclosan and formation of toxic chlorophenols in presence of low concentrations of free chlorine. *Analytical and Bioanalytical Chemistry,* 383, 1119-1126

Çatalkaya, E.Ç. & Kargı, F. (2007). Effects of operating parameters on advanced oxidation of diuron by the Fenton's reagent: A statistical design approach. *Chemosphere,* 69, 485-492.

Cha, J. & Cupples, A. M. (2009). Detection of the antimicrobials triclocarban and triclosan in agricultural soils following land application of municipal biosolids. *Water Research,* 43, 2522-2530.

Colonna, G. M., Caronna, T. & Marcandalli, B. (1999). Oxidative degradation of dyes by ultraviolet radiation in the presence of hydrogen peroxide. *Dyes and Pigments*, 41 (3), 211-220.

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

Delgado, D. R., Holguin, A. R. & Martínez, F. (2012). Solution thermodynamics of triclosan and triclocarban in some volatile organic solvents. *Revista De La Facultad De Química Farmacéutica,* (19) 1, 79-92

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

Eckenfelder, W., W. (1989). *Industrial water pollution control.* (2nd ed.). (300-310). New York, USA: McGraw-Hill, Inc.

Esplugas, S., Yue, P. L. & Pervez, M. I. (1994). Degradation of 4-chlorophenol by photolytic oxidation. *Water Research*, 28 (6), 1323-1328.

Fair, P. A., Lee, H. B., Adams, J., Darling, C., Pacepavicius, G., Alaee, M., Bossart, G. D., Henry, N., Muir, D., et al. (2009). Occurrence of triclosan in plasma of wild atlantic bottlenose dolphins (Tursiopstruncates) and in their environment. *Environmental Pollution,* 157, 2248-2254.

Faust, B. C. & Hoigne, J. (1990). Photolysis of Fe (III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment*, 24, 79-89.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brando, G. C., Da Silva, E. G. P., Portugal, L. A., Dos Reis, P. S., Souza, A. S. & Dos Santos, W. N. L., et al. (2007). Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta*, 597 (2), 179-186.

Fernandes, I., Pascoal, C. & Cassio, F., (2011). Intraspecific traits change biodiversity effects on ecosystem functioning under metal stress. *Oecologia,* 166, 1019-1028

Francis, F., Sabu, A., Nampoothiri, K. M., Ramachandran, S., Ghosh, S., Szakacs, G. & Pandey, A. (2000). Use of response surface methodology for optimizing process parameters for the production of α-amylase by Aspergillusoryzae. *Biochemical Engineering Journal*, 15 (2), 107 -115.

Glaze, W. H., Kang, J. & Lay, Y. (1995). Advanced oxidation processes. A kinetic model for the oxidation of 1,2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation. *Industrial Engineering Chemistry Research*, 34 (7), 2314-2323.

Halden, R. U. & Paul, D. H. (2005). Co-occurrence of triclocarban and triclosan in U.S. water resources. *Environmental Science and Technology*, 39, 1420-1426.

Hamed, E. & Sakr, A., (2001). Application of multiple response optimization technique to extended release formulations design. *Journal of Controlled Release,* 73, 329-338.

Hua, W., Bennett, E. R. & Letcher, R. J. (2005). Triclosan in waste and surface waters from the upper Detroit River by liquid chromatography-electrospray-tandem quadrupole mass spectrometry. *Environment International*, 31, 621-30.

Hsueh, C. L., Huang, Y. H., Wang, C. C. & Chen, C. Y., (2005). Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere*, 58 (10), 1409-1414.

Kanda, R., Griffin, P. & James, H. A., (2003). Pharmaceutical and Personal Care Products in Sewage Treatment Works. *Journal of Environmental Monitoring*. 5 (5), 823-30.

Kolpin, D. W., Furlong, E. T. & Meyer, M .T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environmental Science and Technology*, 36 (6), 1202-11.

Kim, I. H., Tanaka, H., Iwasaki, T., Takubo, T., Morioka, T., Kato, Y., et al. (2008). Classification of the degradability of 30 pharmaceuticals in water with ozone, UV and H_2O_2. *Water Science and Technology*, 57 (2), 195-200

Kumar, K. S., Priya, S. M., Peck, A. M. & Sajwan, K. S. (2010). Mass loadings of triclosan and triclocarban from four wastewater treatment plants to three rivers and landfill in Savannah, Georgia, USA. *Architecture Environmental Contamination and Toxicology,* 58, 275-285

Kookana, R. S., Sarmah, A. K., Van Zwieten, L., Krull, E., Van Zwieten, L., Singh, B., et al. (2011). Biochar application to soil: Agronomic and environmental benefits and unintended consequences. *Advances in Agronomy*, 112, 103-143.

Krutzler, T., Fallmann, H., Maletzky, P., Bauer, R., Malato, S. & Blanco, J. (1999). Solar driven degradation of 4-chlorophenol. *Catalysis Today*, 54 (2-3), 321–327.

Lindström, A., Buerge, I. J., Poiger, T., Bergqvist, P. A., Müller, M. D., Buser, H. R., et al. (2002). Occurrence and environmental behavior of the bactericide triclosan and its methyl derivative in surface waters and in wastewater. *Environmental Science and Technology,* 36, 2322-2329

Masten, S. J. & Davies, S. H. R. (1994). The use of ozonation to degrade organic contaminants in wastewaters. *Environmental Science and Technology,* 28 (1), 180A–185A.

McAvoy, D., Schatowitz, B., Jacob, M., Hauk, A. & Eckhoff, W. (2002). Measurement of triclosan in wastewater treatment systems. *Environmental Toxicology Chemistry,* 21, 1323–1329

Meunier, L., Canonica, S. & Von Gunten, U. (2006). Implications of sequential use of UV and ozone for drinking water quality. *Water Research*, 40 (9), 1864–1876.

Munoz, M., De Pedro, Z. M., Casas, J. A. & Rodriguez, J. J. (2012). Triclosan breakdown by Fenton-like oxidation. *Chemical Engineering Journal,* 198–199, 275–281

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

Nishi, I., Kawakami, T. & Onodera, S. (2008). Monitoring of triclosan in the surface water of the Tone Canal, Japan. *Bulletin of Environmental Contamination and Toxicology*, 80, 163-166

Piccoli, A., Fiori, J., Andrisano, V. & Orioli, M. (2002). Determination of triclosan in personal health care products by liquid chromatography (HPLC), *Il Farmaco* 57, 369-372

Peng, X., Yu, Y., Tang, C., Tan, J., Huang, Q., Wang, Z., et al. (2008). Occurrence of steroid estrogens, endocrine-disrupting phenols and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China. *Science of Total Environment,* 397, 158–166

Pereira, V. J., Linden, K. G. & Weinberg, H. S., (2007b). Evaluation of UV irradiation for photolytic and oxidative degradation of pharmaceutical compounds in water. *Water Research,* 41 (19), 4413-4423

Ragonese, R., Macka, M., Hughes, J. & Petocz, P. (2002). The use of the Box-Behnken experimental design in the optimisation and robustness testing of a capillary electrophoresis method for the analysis of ethambutol hydrochloride in a pharmaceutical formulation. *Journal of Pharmaceutical and Biomedical Analysis*, 27 (6), 995-1007.

Ramaswamy, B. R., Shanmugam, G., Velu, G., Rengarajan, B. & Larsson, D. G. J. (2011). GC–MS analysis and ecotoxicological risk assessment of triclosan, carbamazepine and parabens in Indian rivers. *Journal of Hazardous Materials*, 186, 1586-1593

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, 2483–2492

Ruppert, G., Bauer, R. & Heisler, G. J. (1993). The photo-fenton reaction, an effective photochemical wastewater treatment process. *Journal of Photochemistry and Photobiology A-Chemistry*, 73 (1), 75-78.

Sanchez-Lafuente, C., Furlanetto, S. & Fernandez-Arevalo, M. (2002). Didanosine extended-release matrix tablets: Optimization of formulation variables using statistical experimental design. *International Journal of Pharmaceutics*, 237 (1-2), 107-118.

Sanchez-Prado, L., Llompart, M., Lores, M., García-Jares, C., Bayona, J. M., Cela, R., et al. (2006a). Monitoring the photochemical degradation of triclosan in wastewater by UV light and sunlight using solid-phase microextraction. *Chemosphere* 65, 1338-1347.

Sanchez-Prado, L., Llompart, M., Lores, M., Fernández-Alvarez, M., García-Jares, C., Cela, R., et al. (2006b). Further research on photo-SPME of triclosan. *Analytical and Bioanalytical Chemistry*, 384, 1548- 1457.

Sastry, S. V. & Khan, M. A. (1998). Aqueous based polymeric dispersion: Plackett- Burman design for screening of formulation variables of atenolol gastrointestinal therapeutic system. *Pharmaceutica Acta Helvetiae*, 73 (2), 105- 112.

Scientific Committee on Consumer Products (SCCP), (2009). O*pinion on: Triclosan* Retrieved on October, 02 2015, from http://ec.europa.eu/health/ph_risk/committees/04_sccp/docs/sccp_o_166.pdf

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 and Technology,* 36, 4998–5004.

Singh, S. K., Dodge, J., Durrani, M. J. & Khan, M. A. (1995). Optimization and characterization of controlled release pellets coated with an experimental latex: I. Anionic drug. *International Journal of Pharmaceutics*, 125 (2), 243-255.

Singh, S. P., Azua, A., Chaudhary, A., Khan, S., Willett, K. L., Gardinali, P. R., et al. (2010). Occurrence and distribution of steroids, hormones and selected pharmaceuticals in South Florida coastal environments. *Ecotoxicology,* 19, 338-350

Son, H. S., Ko, G. & Zoh, K.D. (2009). Kinetics and mechanism of photolysis and TiO_2 photocatalysis of triclosan. *Journal of Hazardous Materials,* 166, 954–960.

Tixier, C., Singer, H. P., Canonica, S. & Stephan, R. (2002). Phototransformation of triclosan in surface waters: A relevant elimination process for this widely used biocide laboratory studies, field measurements, and modeling. *Environmental Science and Technology,* 36, 3482-3489

United States Environmental Protection Agency (USEPA) (2009). *Targeted national sewage sludge survey and analysis technical report*, USA: Environmental Protection Agency

Vial, J. & Jardy, A. (1999). Study of the Linear Range in HPLC Analyses with UV Detection: Methodology and Experimental Application to the Influence of the Analyte UV Spectrum. *Journal of High Resolution Chromatography*, 22 (4), 217-221.

Vohra, A. & Satyanarayana, T. (2002). Statistical optimization of the medium components by response surface methodology to enhance phytase production by Pichia anomala. *Process Biochemistry*, 37 (9), 999-1004.

Wilson, B., Chen, R. F., Cantwell, M., Gontz, A., Zhu, J., Olsen, C. R., et al. (2009). The partitioning of triclosan between aqueous and particulate bound phases in the Hudson River estuary. *Marine Pollution Bulletin,* 59, 207-212

Yu, J. C., Kwong, T. Y., Luo, Q. & Cai, Z. (2006). Photocatalytic oxidation of triclosan. *Chemosphere,* 65, 390-399

Zhang, H., Yamada, H. & Tsuno, H. (2008). Removal of endocrine-disrupting chemicals during ozonation of municipal sewage with brominated byproducts control. *Environmental Science and Technology,* 42, 3375-3380.

Zhao, J. L., Ying, G. G., Liu, Y. S., Chen, F., Yang, J. F., Wang, L., et al. (2010). Occurrence and risks of triclosan and triclocarban in the Pearl River system, South China: From source to the receiving environment. *Journal of Hazardous Material,* 179, 215-222

APPENDICES

RAW EXPERIMENTAL DATA

A. 1. ANOVA Tests for Triclosan Removal Using Photo-Fenton Treatment

Table A. 1. 1 ANOVA test for the response function Y_1 (% Triclosan removal)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	8854.13	9	983.79	18.15	0.0026
$X_1(H_2O_2)$	855.53	1	855.53	15.78	0.0106
X_2 (Fe (II))	346.5	1	346.5	6.39	0.0526
X_3 (Triclosan)	1223.15	1	1223.15	22.57	0.0051
X_1X_2	0.84	1	0.84	0.015	0.9059
X_1X_3	259.21	1	259.21	4.78	0.0804
X_2X_3	2963.71	1	2963.71	54.68	0.0007
X_1^2	876.95	1	876.95	16.18	0.0101
X_2^2	746.48	1	746.48	13.77	0.0138
X_3^2	1418.62	1	1418.62	26.17	0.0037
Total error	271.01	5	54.2		
Total (corr)	271.01	3	90.34	75281.23	< 0.0001
	2.40×10^{-3}	2	1.20×10^{-3}		
	9125.14	14			

Table A. 1. 2 ANOVA test for the response function Y_2 (DCP Occurrence)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	2.48	9	0.28	17.59	0.0028
$X_1(H_2O_2)$	0.082	1	0.082	5.27	0.0702
X_2 (Fe (II))	0.073	1	0.073	4.66	0.0834
X_3 (Triclosan)	0.014	1	0.014	0.90	0.3856
X_1X_2	0.018	1	0.018	1.13	0.3374
X_1X_3	8.090×10^{-5}	1	8.090×10^{-5}	5.166×10^{-3}	0.9455
X_2X_3	2.682×10^{-3}	1	2.682×10^{-3}	0.17	0.6961
X_1^2	1.05	1	1.05	66.98	0.0004
X_2^2	0.79	1	0.79	50.28	0.0009
X_3^2	0.29	1	0.29	18.36	0.0078
Total error	0.078	5	0.016		
Total (corr)	0.078	3	0.026	1298.20	0.0008
	4.019×10^{-5}	2	2.009×10^{-5}		
	2.56	14			

Table A. 1. 3 ANOVA test for the response function Y_3 (TCP Occurrence)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	2.38	9	0.26	15.50	0.0038
$X_1 (H_2O_2)$	0.95	1	0.95	55.64	0.0007
X_2 (Fe (II))	0.074	1	0.074	4.32	0.0921
X_3 (Triclosan)	0.60	1	0.60	35.06	0.0020
X_1X_2	0.015	1	0.015	0.86	0.3969
X_1X_3	0.41	1	0.41	24.22	0.0044
X_2X_3	0.070	1	0.070	4.08	0.0994
X_1^2	0.25	1	0.25	14.68	0.0122
X_2^2	0.019	1	0.019	1.13	0.3360
X_3^2	7.564×10^{-4}	1	7.564×10^{-4}	0.044	0.8417
Total error	0.085	5	0.017		
Total (corr)	0.085	3	0.028	$1.598 \times 10^{+6}$	< 0.0001
	3.564×10^{-8}	2	1.782×10^{-8}		
	2.47	14			

A. 2. ANOVA Tests for Triclosan Removal Using Photo-Fenton Like Treatment

Table A. 2. 2 ANOVA test for the response function Y_1 (% Triclosan removal)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	3289.79	9	365.53	68.96	0.0001
$X_1(H_2O_2)$	526.83	1	526.83	99.38	0.0002
X_2 (Fe (III))	329.60	1	329.60	62.18	0.0005
X_3 (Triclosan)	90.92	1	90.92	17.15	0.0090
X_1X_2	1195.43	1	1195.43	225.51	< 0.0001
X_1X_3	195.58	1	195.58	36.90	0.0017
X_2X_3	316.84	1	316.84	59.77	0.0006
X_1^2	109.60	1	109.60	20.68	0.0061
X_2^2	555.51	1	555.51	104.79	0.0002
X_3^2	18.87	1	18.87	3.56	0.1178
Total error	26.50	5	5.30		
Total (corr)	25.87	3	8.62	27.15	0.0357
	0.64	2	0.32		
	3316.29	14			

Table A. 2. 2 ANOVA test for the response function Y_2 (DCP Occurrence)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	4.58	6	0.76	35.17	< 0.0001
$X_1 (H_2O_2)$	2.03	1	2.03	93.48	< 0.0001
X_2 (Fe (III))	0.62	1	0.62	28.63	0.0007
X_3 (Triclosan)	0.54	1	0.54	24.81	0.0011
X_1X_2	0.97	1	0.97	44.53	0.0002
X_1X_3	0.39	1	0.39	18.07	0.0028
X_2X_3	0.033	1	0.033	1.50	0.2551
X_1^2	0.17	8	0.022		
X_2^2	0.17	6	0.029	44.96	0.0219
X_3^2	1.278×10^{-3}	2	6.392×10^{-4}		
Total error	4.76	14			
Total (corr)	0.078	3	0.026	1298.20	0.0008
	4.019×10^{-5}	2	2.009×10^{-5}		
	2.56	14			

Table A. 2. 3 ANOVA test for the response function Y_3 (TCP Occurrence)

Source	Sum of squares	Df	Mean Square	F ratio	P value
Model	0.39	6	0.066	32.87	< 0.0001
$X_1 (H_2O_2)$	7.970×10^{-3}	1	7.970×10^{-3}	3.98	0.0810
X_2 (Fe (III))	0.081	1	0.081	40.61	0.0002
X_3 (Triclosan)	0.18	1	0.18	91.00	< 0.0001
$X_1 X_2$	0.057	1	0.057	28.72	0.0007
$X_1 X_3$	2.689×10^{-3}	1	2.689×10^{-3}	1.34	0.2797
$X_2 X_3$	0.063	1	0.063	31.57	0.0005
X_1^2	0.016	8	2.000×10^{-3}		
X_2^2	0.016	6	2.642×10^{-3}	35.98	0.0273
X_3^2	1.469×10^{-4}	2	7.343×10^{-5}		
Total error	0.41	14			
Total (corr)	0.085	3	0.028	$1.598 \times 10^{+6}$	< 0.0001
	3.564×10^{-8}	2	1.782×10^{-8}		
	2.47	14			

A. .3 Raw Data for Kinetic Studies on Pesticide Degradation and By-products Occurrences

Table A. 3. 1 Raw data for triclosan degradation using photo-Fenton treatment at different experimental conditions

Time (min)	Run no														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	5.00	5.00	5.00	5.00	10.00	0.10	10.00	0.10	10.00	0.10	0.10	10.00	5.00	5.00	5.00
2.5	0.82	4.09	3.27	3.52	4.05	0.09	7.87	0.13	3.02	0.05	0.09	6.64	1.10	1.25	1.37
5	0.89	4.04	3.26	3.47	3.69	0.00	8.47	0.09	2.49	0.05	0.06	6.66	1.11	1.05	1.32
10	0.78	3.06	3.20	2.75	3.56	0.05	8.12	0.07	2.79	-	0.04	6.66	1.11	1.08	1.01
15	0.82	2.43	2.73	2.52	4.41	0.03	7.55	0.10	2.43	-	0.05	6.67	1.09	1.15	1.10
30	0.83	0.96	2.71	1.23	4.02	0.04	6.01	0.07	2.44	0.04	0.06	5.70	1.01	1.14	1.10
45	0.82	0.43	2.09	0.97	3.94	0.05	3.70	0.06	2.13	0.07	-	5.24	0.96	0.92	1.06
60	0.68	0.12	1.62	0.46	4.03	0.08	2.41	0.08	2.02	0.03	0.05	4.51	0.91	0.91	1.07

Table A. 3. 2 Raw data for triclosan degradation using photo-Fenton like treatment at different experimental conditions

Time (min)	Run no														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	5.00	5.00	5.00	5.00	10.00	0.10	10.00	0.10	10.00	0.10	0.10	10.00	5.00	5.00	5.00
2.5	3.27	3.06	3.37	2.88	4.69	0.03	4.67	0.04	4.10	0.04	0.07	6.77	2.70	3.43	3.21
5	3.26	2.73	3.36	2.66	4.61	0.02	4.07	0.03	3.39	0.02	0.06	6.84	2.47	3.23	3.21
10	3.04	2.54	3.17	2.31	4.59	0.03	3.24	0.03	3.34	0.03	0.04	6.21	2.63	2.53	3.40
15	0.16	2.27	3.27	1.91	4.58	0.03	3.79	-	3.31	0.03	0.04	5.98	2.97	2.75	2.63
30	0.14	2.19	2.96	1.21	3.99	0.03	2.36	-	3.43	-	0.02	5.53	2.45	2.55	2.72
45	0.17	1.67	2.01	0.52	4.27	0.00	1.11	0.03	2.67	0.03	0.02	5.43	1.95	2.51	2.38
60	0.13	1.18	2.76	0.30	4.13	0.00	0.85	-	2.60	-	0.03	5.14	2.02	1.44	1.96

Table A. 3. 3 Raw data for DCP Occurrence using photo-Fenton treatment at different experimental conditions

Time (min)	Run no														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.71	0.06	0.82	0.02	0.27	0.01	0.09	0.02	1.49	0.00	0.95	0.07	0.00	0.58	0.45
2.5	0.68	0.03	0.07	0.20	0.26	0.01	0.09	0.05	0.82	0.04	0.01	0.06	0.46	0.83	0.41
5	0.68	0.08	0.07	0.21	0.27	0.06	0.00	0.07	0.77	0.07	0.03	0.07	0.59	0.06	0.43
10	0.71	0.30	0.01	0.17	0.17	0.00	-	0.10	0.85	0.06	0.04	0.28	0.73	0.38	0.83
15	0.74	0.48	0.09	0.26	0.18	0.00	-	0.02	0.82	0.98	0.03	0.11	0.75	0.43	0.76
30	0.76	0.49	0.08	0.28	0.18	0.00	-	0.12	0.79	0.06	0.03	0.15	0.51	0.35	0.76
45	0.64	0.12	0.09	0.66	0.19	0.02	-	0.03	0.75	0.05	0.03	0.17	0.39	0.35	0.82
60	0.65	0.11	0.06	0.21	0.17	0.01	-	0.01	0.73	0.12	0.07	0.21	0.44	0.57	0.50

Table A. 3. 4 Raw data for DCP Occurrence using photo-Fenton like treatment at different experimental conditions

Time (min)	Run no														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.38	0.12	0.04	0.03	0.35	0.17	0.19	0.16	0.84	0.51	0.10	0.12	0.14	0.14	0.14
2.5	0.39	0.11	0.05	0.11	0.31	0.14	0.16	0.16	0.98	0.39	0.31	0.04	0.20	0.28	0.06
5	0.28	0.15	0.06	0.11	0.30	0.10	0.20	0.12	0.83	0.35	0.02	0.04	0.21	0.14	0.08
10	0.15	0.16	0.06	0.14	0.34	0.09	0.20	0.10	0.80	0.46	0.07	0.08	0.16	0.13	0.10
15	0.25	0.16	0.06	0.14	0.36	0.09	0.25	0.09	0.85	0.49	0.05	0.08	0.24	0.17	0.11
30	0.35	0.24	0.08	0.32	0.32	0.10	0.61	0.03	1.02	0.43	0.07	0.12	0.33	0.18	0.11
45	0.44	0.30	0.09	0.29	0.38	0.09	0.50	0.11	0.88	0.41	0.08	0.14	0.35	0.21	0.20
60	0.47	0.29	0.12	0.27	0.44	0.09	0.57	0.16	1.13	0.44	0.05	0.20	0.41	0.23	0.21

Table A. 3. 5 Raw data for TCP Occurrence using photo-Fenton treatment at different experimental conditions

Time (min)	Run no														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
0	0.01	-	0.06	-	-	-	-	-	0.10	-	-	0.00	0.00	-	0.00
2.5	0.00	-	0.26	-	-	-	0.00	0.00	-	-	-	0.11	0.03	-	0.00
5	0.00	-	0.38	-	-	-	0.01	0.01	0.00	-	-	0.12	0.02	0.02	0.00
10	0.01	-	0.49	0.14	0.00	-	0.05	0.05	-	-	-	0.52	0.02	0.00	0.05
15	0.03	0.00	0.74	0.51	0.00	-	0.10	0.10	-	-	-	0.61	0.00	0.01	0.05
30	0.02	0.00	0.72	0.50	0.02	-	0.32	0.32	-	-	-	0.92	0.06	0.00	0.05
45	0.08	0.03	0.77	0.10	0.06	-	0.52	0.52	0.05	-	-	1.26	0.04	-	0.09
60	0.07	0.02	0.73	0.22	0.10	-	0.52	0.52	0.02	-	-	1.38	0.06	-	0.00

Table A. 3. 6 Raw data for TCP Occurrence using photo-Fenton like treatment at different experimental conditions

Time (min)	Run no														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0.17	0.00	-	0.00	0.09	-	0.13	-	0.04	-	-		0.11	0.07	-
2.5	0.00	0.01	-	0.07	-	-	0.05	-	0.04	-	-	0.00	0.00	0.00	0.00
5	0.00	0.02	-	0.12	0.10	-	0.09	-	0.05	-	-	-	0.00	0.01	0.00
10	0.00	0.05	-	0.15	0.10	-	0.15	-	0.01	-	-	0.04	0.04	0.01	0.02
15	0.15	0.03	-	0.17	0.09	-	0.21	-	0.06	-	-	0.05	0.01	0.02	0.01
30	0.01	0.08	-	0.39	0.07	-	0.32	-	0.06	-	-	0.10	0.01	0.03	0.03
45	0.04	0.07	-	0.27	0.07	-	0.69	-	0.06	-	-	0.16	0.02	0.06	0.08
60	0.04	0.05	-	0.15	0.08	-	0.47	-	-	-	-	0.21	0.02	0.10	0.07