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Degradation of Triclosan by Photo-Fenton Oxidation

Ebru ÇOKAY*[1], Merve ÖZTAMER[1]

[1]Department of Environmental Engineering, Dokuz Eylul University, Buca, 35160, Izmir, Turkey

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Abstract: Triclosan is one of the most used active ingredients in antibacterial personal care products and its usage increased in recent years. Triclosan has recently attracted the attention researchers from the fields of water treatment due to its existence in water environments. This study has been executed to investigate the removal of triclosan with photo-Fenton process and to observe by-product formation after oxidation. Effects of operational parameters namely the concentrations of Triclosan, H_2O_2 and Fe(II) on oxidation of triclosan were investigated by using Box-Behnken statistical experiment design and the surface response analysis. It was found that the triclosan concentration has a more profound effect than H_2O_2 and Fe(II) concentrations for removal of triclosan in the aqueous solution. Complete removal of triclosan was accomplished within a hour, however, 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. Optimal H_2O_2/Fe(II)/TCS ratio resulting by maximum triclosan removal (98.5%) was found to be 50/2/0.1, respectively.

Triklosanın Foto-Fenton Oksidasyon Yöntemi ile Parçalanması

Anahtar Kelimeler
Box-Behnken yöntemi,
Foto-Fenton prosesi;
Triklosan

Özet: Triklosan, antibakteriyel kişisel bakım ürünlerinde en çok kullanılan aktif maddelerden biridir ve son yıllarda kullanımı artmıştır. Bu çalışmada, triklosanın foto-Fenton yöntemi ile arıtılması ve yan ürünlerinin oluşumu araştırılmıştır. Triklosan, H_2O_2 ve Fe(II) konsantrasyonlarının triklosan giderimine olan etkileri, Box-Behnken istatistiksel deney tasarımı ve yüzey cevabı analizi kullanılarak araştırılmıştır. Triklosan derişiminin triklosan gideriminde H_2O_2 ve Fe(II) derişimlerinden daha etkin olduğu gözlenmiştir. Triklosan'ın tamamen parçalanması bir saatte gerçekleşirken tamamen mineralizasyonu gerçekleşmemiştir. 2,4-Diklorofenol ve 2,4,6-Triklorofenol gibi bazı ara bileşiklerin oluştuğu gözlenmiştir. Foto-Fenton prosesinde, en yüksek triklosan giderimi (%98.5) için H_2O_2/Fe(II)/TCS oranının 50/2/0.1 olduğu saptanmıştır.

**Sorumlu yazar: Ebru ÇOKAY ebru.cokay@deu.edu.tr*

1.Introduction

Triclosan is one of the most used active ingredients in antibacterial personal care products and its usage increased in recent years. Also, triclosan have endocrine-disrupting properties. Because of its 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 as a material preservative. Like every other chemical ingredients, triclosan is also released into the environment.

Triclosan is transported by means of domestic or industrial waste stream to wastewater treatment plants. Both incomplete removal of triclosan from wastewater treatment plants and spill out of spreading the triclosan laden sludge into soils, lead to triclosan spoils in soil and surface waters [1]. Therefore, triclosan has recently attracted the attentions of the researchers from water treatment field due to its existence in water environments as a result of widely usage in the world.

Triclosan, (2, 4, 4-trichloro-2-hydroxydi phenyl ether) (Figure 1) is a nonionic, a chlorinated aromatic compound broad spectrum antimicrobial chemical. Additionaly, it is a white powdered solid with a slight aromatic/phenolic odor and with low soluble in water (12 mg/L) [2]. Some physicochemical properties of triclosan are listed in Table 1 [2,3,4]. As can be seen in Table 1, triclosan has a highly hydrophobic nature with high log KOW value as 4.76 that it is likely to be absorbed in sediment. However, high amount of its usage, triclosan concentration increase in surface water and wastewater. Moreover, its half-life varies between 2 to 2000 days depending on the latitude and time of the year [5].

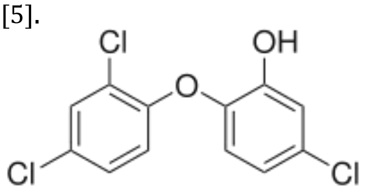

Figure 1. Molecular structure of triclosan

Table 1. Physicochemical properties of triclosan

Physicochemical Properties of Triclosan	
Chemical formula	$C_{12}H_7Cl_3O_2$
Molecular weight	289.54 g/mole
Appearance	White solid
Density	1.49 g/cm^3
Melting point	55–57°C
Vapor pressure (at 25°C)	5.2×10-6 Pa
Water solubility (at 20°C)	12 mg/L
Octanol-water partition coefficient(at 25°C)	4.8log KOW
Half-life in surface water	2-2000 d

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 [6,7]. 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 [8], and 478 µg/L [9].

In Europe, the presence of triclosan in surface water was investigated in some countries such as Italy, Switzerland, Greece, Spain, Romania etc. [10]. 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 In the UK, triclosan level in a river ranged from 19 to 80 µg/L. The highest values of triclosan were found as 285 µg/L in rivers in Spain [11]. The highest concentrations of triclosan in river 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 [12].

Triclosan has been added into the draft specific pollutants' list prepared in accordance with Water Framework Directive (WFD-2000/60/EC). Triclosan is a spesific substances and it has annual avarage-environmental quality standart (AA-EQS) and maximum avarege concentation-environmental quality standart (MAC-EQS). These values are 0.12 ppb and 1.1 ppb, respectively. According to this, monitoring studies should be done for the concentration of triclosan in surface waters consistently and necessary precautions and actions should also be taken. Some treatment technologies are recommended to for removal of triclosan in wastewater.

Generally, the removal efficiency of triclosan is depending on the initial triclosan concentration, pH, matrix, and experimental conditions. Considering triclosan concentrations in wastewater treatment plant influents, some of by-products are expected to be non-negligible. Some of them show higher toxicity than triclosan. Eight by-products were identified after photodegradation of triclosan, including chlorinated phenols (2,4-dichlorophenol, 2,4,6-trichlorophenol), 4-chlorocatechol and 4-choloro-2,4-dihyroxydiphenyl ether 2,7- and 2,8-dichlorodibenzo-p-dioxin, and a possible dichlorodibenzodioxin isomer or dichlorohydroxy-di-benzofuran [13,14,15,16,17].

Recently, advanced oxidation processes (AOPs) were used as potential powerful methods that are capable of transforming the pollutants into harmless substances [18]. Almost all AOP's rely on the generation of reactive free radicals, such as hydroxyl, OH• with a redox potential of 2.8 V [19]. The free radicals react rapidly with most of the organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules [20]. The resulting organic radicals then react with oxygen to initiate a series of oxidation reactions leading mineralization of the organics to produce CO_2 and H_2O [21]. Therefore, advanced oxidation is a promising alternative for mineralization and reducing recalcitrant organic compounds in water samples.

A limited number of studies were reported in the literature on photolysis of triclosan. However, the reported studies were mainly focused on the analysis and identification of the main products with proposals for the reaction mechanisms of photoreactions. Chlorinated by-products of triclosan may play an important role in the environmental impact of triclosan. As it has been reported that chlorination used during treatment produces chlorophenols which are more persistent and highly toxic compounds [22]. Due to these by-products that have not been analyzed and evaluated, the total concentration of triclosan and related by-products in surface water or wastewater was underestimated. Based on these shortcomings, triclosan was selected as recalcitrant organic compound in order to observe triclosan removal and to evaluate by-products of triclosan in this study.

Advanced oxidation of triclosan containing aqueous solution by the Photo-Fenton oxidation was investigated in terms of triclosan and its byproducts removal. The effects of initial triclosan, Fe(II) and H_2O_2 concentrations on oxidation of triclosan were investigated by using a Box-Behnken statistical experiment design method. The main objective of the study was to statistically determine the most favorable levels of the parameters for the treatment of triclosan containing water samples and also to observe and to evaluate by-products of triclosan.

1.1.Design of experiments

The classical approach of changing one variable at a time to study the effects of variables on the response is a complicated technique particularly for multivariable systems and also when more than one response is considered. Statistical design of experiments reduces the number of experiments to be performed, considers interactions among the variables and can be used for optimization of the operating parameters in multivariable systems. Response surface methodology (RSM) is used when only several significant factors are involved in optimization. Different types of RSM designs include 3-level factorial design, central composite design (CCD) [23]. Box- Behnken design [24] and D-optimal design [25].

A modified central composite experimental design known as the Box-Behnken design, is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points where the variable combinations are at the midpoints of the edges of the variable space and at the center [26]. Among all the RSM designs, Box-Behnken design requires fewer runs than the others, e.g, 15 runs for a 3-factor experimental design. By careful design and analysis of experiments, Box-Behnken design allows calculations of the response function at intermediate levels which were not experimentally studied and shows the direction if one wishes to change the input levels in order to decrease or increase the response [27].

2. Material and Method

2.1. Chemicals

High purity grade (99.5%) of Triclosan ($C_{12}H_7C_{l3}O_2$), high purity grade (99.5%) of 2,4-Dichlorophenol ($C_6H_4Cl_2O$) and high purity grade (99.5%) of 2,4,6-Trichlorophenol ($C_6H_3Cl_3O$) 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 used to as HPLC solvents.

High purity grade (99%) of Triclosan used for preparing stock solution in experiments was purchased from Alfa Aesar. Physico-chemical characteristics of Triclosan are summarized in Table 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) obtained from Merck were used as an oxidant. Iron (II) sulfate heptahydrate, 98% ($FeSO_4{\cdot}7H_2O$) used as source of Fe(II) in the photo-Fenton process, was analytical grade and purchased from Alfa Aesar Company. Concentrated stock solutions of Fe(II) (250 mg/L) were prepared for further dilution to obtain solutions of desired concentrations. Fe (II) stock solution was stored in dark to prevent oxidation of Fe(II). The pH of aqueous solutions was adjusted using either sodium hydroxide or sulfuric acid. All other chemicals were of analytical grade and used without any prior purification. Water for chemical solutions was purified using a Milli-Q system.

2.2. Experimental procedure

Photo-Fenton experiments were carried out at room temperature (23 ± 2^{o}C) using different hydrogen peroxide and ferrous ion concentrations at pH of 3 which is suitable for photo-Fenton process [28]. For that reason, pH adjustment as 3 was applied with sulfuric acid solution addition in order to obtain pH value of the solution. Measurement of pH was done by using thermo scientific Orion pH meter 720a.

For a standard reaction run, 2 L of the synthetic wastewater sample was used. By preparation of 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 triclosan was placed in the reactor and predetermined amounts of oxidant and 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 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 trasfered to HPLC samples tubes which were proper for using HPLC device.

2.3. Experimental set-up

2.3.1. Configuration of UV Reactor

Figure 2 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 removals 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.

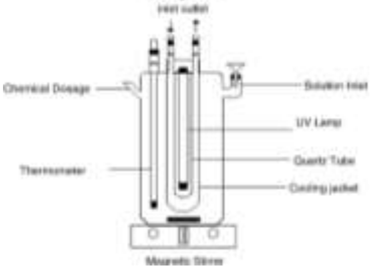

Figure 2. Schematic diagram of the lab-scale photochemical installation.

2.3.2. Analytical Methods

Samples removed from UV reactor at pre-determined time intervals were centrifuged and then analyzed immediately for triclosan measurement. Triclosan, 2,4-Dichlorophenol (2,4-DCP) and 2,4,6-Trichlorophenol (2,4,6-TCP) 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 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-DCP and 2,4,6-TCP 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-DCP and 2,4,6-TCP with a linearity of R^2= 0.99996 and 0.99993.

3.Results and Discussion

Box Behnken statistical experiment design and the response surface methodology [29] was used to investigate the effects of the three independent variables on the response function and to determine the optimal conditions maximizing the percent removal of triclosan and minimize formation of by-products. The optimization procedure 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. Box-Behnken statistical experiment design was used to evaluate the main effects, interaction effects, and quadratic effects of reaction conditions (H_2O_2, Fe (II) and initial triclosan dose) on the triclosan removal. The independent variables were the dose of hydrogen peroxide (X_1), ferrous ion (X_2) and 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. The dependent variables were the triclosan removal (Y_1), 2,4-DCP formation (Y_2), and 2,4,6-TCP formation (Y_3).

The initial concentration of triclosan (X_3) was ranged from 0.1 to 10 mg/L. The highest concentrations of triclosan in river were reported as 5160µg/L in India [12]. For that reason, range of triclosan doses in this study is acceptable for real conditions and surface waters. Although, triclosan is highly hydrophobic nature, high amount of its usage, triclosan concentrations increase in surface water and wastewater.

Table 2. Levels of variables in Box-Behnken Design

Variable	Symbol	Low (-1)	Center (0)	High (+1)
H_2O_2 (mM)	X_1	1	25.5	50
Fe (II) (mM)	X_2	0.1	2.55	5
Triclosan (mg/L)	X_3	0.1	5.05	10

The experimental conditions of the Box-Behnken experiment design for photo-Fenton oxidation are presented in Table 3. Observed and predicted results using Box-Behnken design are also presented in Table 4.

Table 3. The experimental conditions of the Box-Behnken experiment design in photo-Fenton oxidation

Run	X_1, H_2O_2 (mM)		X_2, Fe (II) (mM)		X_3, TCS (mg/L)	
No	Coded	Actual	Coded	Actual	Coded	Actual
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 4. Observed and predicted results for the response functions for photo-Fenton Oxidation

	Predicted Results			Observed Results		
Run No	Y_1,TCS removal (%)	Y_2, 2,4-DCP formation (mg/L)	Y_3, 2,4,6-TCP formation (mg/L)	Y_1, TCS removal (%)	Y_2, 2,4-DCP formation (mg/L)	Y_3, 2,4,6-TCP formation (mg/L)
1	87.45	0.95	0.05	86.58	0.96	0.06
2	99.70	0.63	0.12	97.55	0.49	0.06
3	65.85	1.02	0.61	68.00	1.16	0.67
4	79.93	0.96	0.93	80.80	0.96	0.91
5	2.05	0.24	0.23	7.00	0.15	0.10
6	81.22	0.11	0.00	75.00	0.05	0.00
7	69.66	0.00	0.68	75.88	0.05	0.62
8	39.95	0.00	0.00	35.00	0.06	0.00
9	83.88	1.01	0.00	79.80	1.09	0.09
10	92.51	0.94	0.07	99.60	0.98	0.00
11	87.92	1.13	0.12	92.00	1.05	0.00
12	47.09	1.22	1.31	40.00	1.18	1.38
13	82.04	0.82	0.09	82.06	0.82	0.09
14	82.04	0.82	0.09	82.00	0.83	0.09
15	82.04	0.82	0.09	82.06	0.82	0.09

3.1. The regression model

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 (second-order) polynomial equation as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3+b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (1)$$

This approach was selected as relatively fewer combinations of the variables were chosen to estimate a potential complex response function. A total of 15 experiments are needed to calculate 9 coefficients of the second-order polynomial regression model. This model contains one block term, three linear terms, three quadratic terms, and three interaction terms. The coefficients of the response functions for different dependent variables were determined correlating the experimental results with the relevant functions used in a Stat-Ease regression program. Different response functions with the determined coefficients are presented by Eqs. (2) to (4).

The results of analysis of variance (ANOVA) are also presented in Tables 5-7 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.

On the basis of the coefficients in Equations (2), (3) and (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.

$$Y_1 = 51.77202 - 1.24196X_1 + 20.53498X_2 + 9.61251X_3 + 7.62182 \times 10^{-3}X_1X_2 + 0.066378X_1X_3 - 2.24449X_2X_3 + 0.025675X_1^2 - 2.36880X_2^2 - 0.79997X_3^2 \ (R^2=0.9703) \tag{2}$$

$$Y_2 = 0.66504 - 0.052059X_1 + 0.39233X_2 + 0.11901X_3 + 1.10561 \times 10^{-3}X_1X_2 - 3.70831 \times 10^{-5}X_1X_3 + 2.13523 \times 10^{-3}X_2X_3 + 8.87897 \times 10^{-4}X_1^2 - 0.076930X_2^2 - 0.011388X_3^2 (R^2=0.9694) \tag{3}$$

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

Table 5. ANOVA test for response function Y_1 (% TCS removal)

Source	Sum of squares	d.f.	Mean square	F Value	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^{+2}	346.5	1	346.5	6.39	0.0526
X_3-TCS	1223.15	1	1223.15	22.57	0.0051
$X_1\ X_2$	0.84	1	0.84	0.015	0.9059
$X_1\ X_3$	259.21	1	259.21	4.78	0.0804
$X_2\ X_3$	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
Residual	271.01	5	54.2		
Lack of Fit	271.01	3	90.34	75281.23	< 0.0001
Pure Error	2.40×10^{-3}	2	1.20×10^{-3}		
Total (Corr)	9125.14	14			

R-squared= 0.9703, R-squared (adjusted for df) = 0.9168, standard error of estimate = 7,36

Table 6. ANOVA test for the response function Y_2 (% 2,4-DCP Formation)

Source	Sum of squares	d.f.	Mean square	F Value	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^{+2}	0.073	1	0.073	4.66	0.0834
X_3-TCS	0.014	1	0.014	0.90	0.3856
$X_1\ X_2$	0.018	1	0.018	1.13	0.3374
$X_1\ X_3$	8.090×10^{-5}	1	8.090×10^{-5}	5.166×10^{-3}	0.9455
$X_2\ X_3$	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
Residual	0.078	5	0.016		
Lack of Fit	0.078	3	0.026	1298.20	0.0008
Pure Error	4.019×10^{-5}	2	2.009×10^{-5}		
Total (Corr)	2.56	14			

R-squared = 0.9694, R-squared (adjusted for df) = 0.9143, standard error of estimate = 0,13

Table 7. ANOVA test for the response function Y_3 (2,4,6-TCP Formation)

Source	Sum of squares	d.f.	Mean square	F Value	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^{+2}	0.074	1	0.074	4.32	0.0921
X_3-TCS	0.60	1	0.60	35.06	0.0020
$X_1 X_2$	0.015	1	0.015	0.86	0.3969
$X_1 X_3$	0.41	1	0.41	24.22	0.0044
$X_2 X_3$	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
Residual	0.085	5	0.017		
Lack of Fit	0.085	3	0.028	$1.598 \times 10^{+6}$	< 0.0001
Pure Error	3.564×10^{-8}	2	1.782×10^{-8}		
Total (Corr)	2.47	14			

R-squared = 0.9654, R-squared (adjusted for df) = 0.9031, standard error of estimate = 0,13

3.2 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 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 0.1 mg/L. As expected, percent triclosan removal increased with increasing initial hydrogen peroxide at low triclosan concentrations such as 0.1 mg/L.

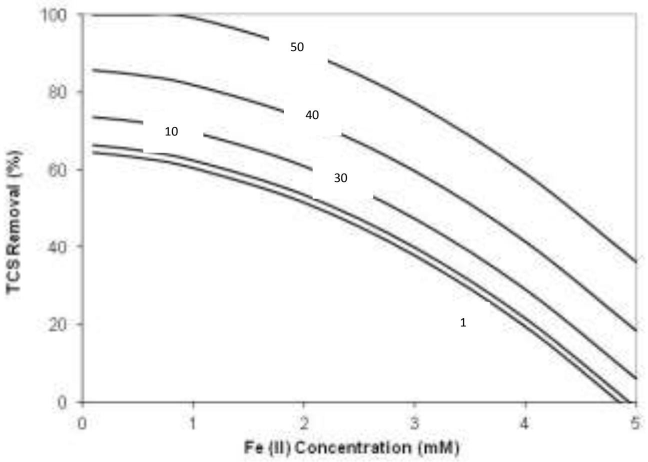

Figure 3. Variation of percent triclosan removals with Fe (II) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 0.1 mg/L.

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. In addition to this, complete degradation was realized at H_2O_2 concentration of 50 mM and Fe (II) concentrations above 5 mM after 60 min reaction time. 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.

These results are in agreement with the literature reports, where a beneficial effect of increasing Fe (II) was observed in photo-degradation of pesticides [30]. Percent triclosan removal increased with increasing initial hydrogen peroxide concentration at all initial triclosan concentrations. However, this phenomenon is not viable for using high ferrous ion levels at all initial triclosan concentrations. As can be seen in Figure 4, 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.

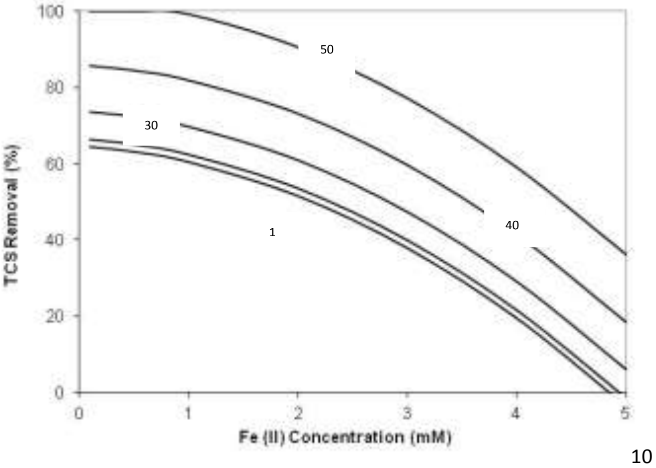

Figure 4. Variation of percent triclosan removals with Fe (II) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 10 mg/L.

When ferrous ion increased to 5 mM, percent triclosan removals were 0, 10 and 45% when H_2O_2 concentrations of 1, 25 and 50 mM, respectively. It can be said that 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. Because, high iron concentrations can also scavenge $OH^{\bullet}$ 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. As a result of these evaluations, 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 was also indicated that all three variables triclosan, H_2O_2 and Fe(II) concentrations and the interactions (X_1, X_3, X_2X_3, X_1^2, $X_2^2$and X_3^2) were significant and played important roles in degradation of triclosan by the photo-Fenton oxidation as summarized in Table 5.

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 formation as shown in Figure 5. Higher initial triclosan concentrations required higher amounts of the H_2O_2 concentrations for complete degradation. At this situation, formation of the highly toxic by-products was the critic limitation factor of the degradation. Formation of the by-products which are named as 2,4-DCP (Y_2) increases with the Fe(II) concentration (X_2), the H_2O_2 concentration (X_1). This situation is not good for oxidation processes. In addition to this, Fe(II) concentration (X_2) has a more profound negative effect by the formation of 2,4-DCP (Y_2). So, it can be said that high concentration of oxidant and catalyst are not suitable for optimum reaction conditions to mineralize triclosan.

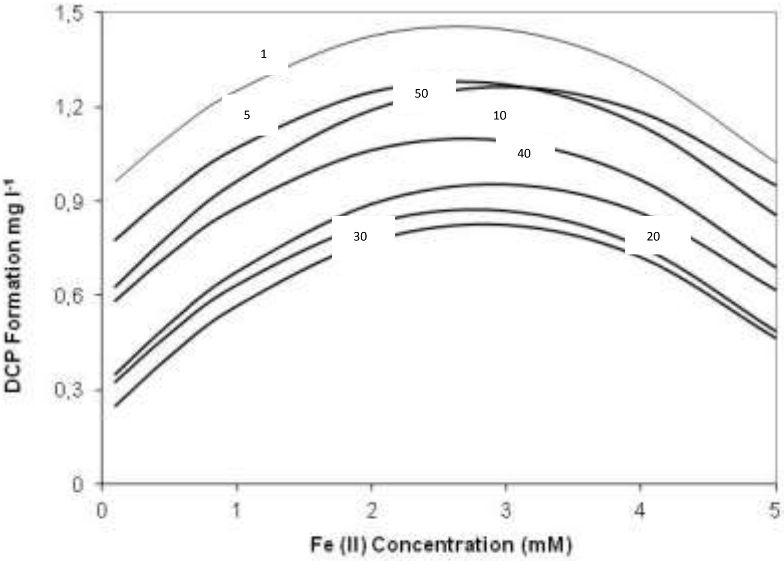

Figure 5. Variation of 2,4-DCP Formation with Fe (II) concentrations with different initial H_2O_2 concentrations at initial concentration of 5 mg/L triclosan.

As a result of these evaluations, at low triclosan concentration of 0.1 mg/L, the optimal H_2O_2/Fe(II)/triclosan concentration yielding the lowest DCP formation (0.002 mgl^{-1}) was 27.5/0.2/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 27.8/0.15/10 yielding 0.045 mg l^{-1} DCP formation. The ANOVA analysis has shown that all three variables triclosan, H_2O_2 and Fe(II) concentrations (X_1^2, X_2^2 and X_3^2) were significant and played important roles in formation of by-products by the photo-Fenton oxidation as summarized in Table 6.

According to TCP formation, it can be said that formation of the byproduct named as 2,4,6-TCP decreases with H_2O_2 concentration but increases with Fe(II) concentration.

As a result of these evaluations, at low triclosan concentration of 0.1 mg/L, the optimal H_2O_2/Fe(II)/triclosan concentration yielding the lowest TCP formation (0.00 mg l^{-1}) was 25/0.1/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 50/5/10 yielding (0.00 mg l^{-1}) the lowest TCP formation. The ANOVA analysis has demonstrated that all three variables H_2O_2 and triclosan concentrations and the interactions (X_1, X_3, X_1X_3 and X_1^2) were significant and played important roles in formation of by-products by the photo-Fenton oxidation as summarized in Table 7.

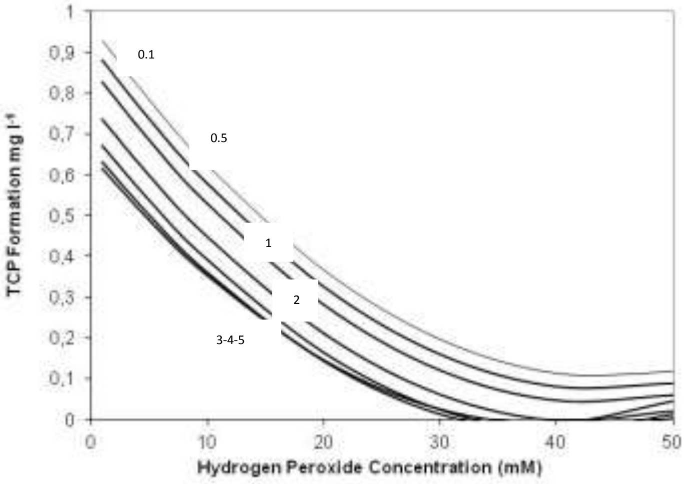

Figure 6. Variation of 2,4,6-TCP Formation with H_2O_2 concentrations with different Fe (II) concentration at initial concentration of 5 mg/L triclosan.

4. Discussion and Conclusion

Triclosan degradation by photo-Fenton 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. 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. In photo-Fenton treatment, the optimum conditions were based on initial triclosan concentrations. Lower initial triclosan concentrations required lower amounts of the H_2O_2 concentrations and Fe(II) concentrations while higher initial triclosan concentrations required higher amounts of oxidant and catalyst for complete degradation. The H_2O_2 concentration has a more profound effect on percent removal of triclosan as compared to Fe(II) concentrations in photo-Fenton process. In this context, high initial H_2O_2 concentration results high formation of by-products such as 2,4-DCP and 2,4,6-TCP. This situation is not good for oxidation processes. Based on this, it can be concluded that high concentration of oxidant and catalyst is not suitable for optimum reaction conditions. After these evaluations, the highest triclosan removal (99.5%) was obtained with a H_2O_2/Fe(II)/triclosan ratio of 50/0.1/10. At these reaction conditions, 2,4-DCP and 2,4,6-TCP were observed as 0.297 mgl^{-1} and 0.232 mg l^{-1}, respectively, in photo-Fenton treatment. As a conlusion, photo-Fenton process can be used for the removal of triclosan and by-products, at real conditions.

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