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Degradation of Triclosan by Photo-Fenton like Oxidation

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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 like process and to observe by-product formation after oxidation. Effects of operational parameters namely the concentrations of Triclosan, H_2O_2 and Fe(III) on oxidation of triclosan were investigated by using Box-Behnken statistical experiment design and the surface response analysis. 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(III)/TCS ratio resulting by maximum triclosan removal (97%) was found to be 50/5/5, respectively.

Triklosanın Foto-Fenton Benzeri Oksidasyon Yöntemi ile Parçalanması

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

Özet: Triklosan, antibakteriyel kişisel bakım ürünlerinde en çok kullanılan aktif maddelerden biridir ve son yıllarda kullanımı artmıştır. Triklosanın sucul ortamda ki varlığı nedeniyle son yıllarda bu konularda çalışan araştırmacıların dikkatini çekmiştir. Bu çalışmada, triklosanın ileri oksidasyon yöntemlerinden foto-Fenton yöntemi ile arıtılması ve yan ürünlerinin oluşumu araştırılmıştır. Triclosan, H_2O_2 ve Fe(III) derişimlerinin triklosan giderimine olan etkileri, Box-Behnken istatistiksel deney tasarımı ve yüzey cevabı analizi kullanılarak araştırılmıştır. 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 benzeri prosesinde, en yüksek triklosan giderimi (%97) için H_2O_2/Fe(III)/TCS oranının 50/5/5 olduğu saptanmıştır.

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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].

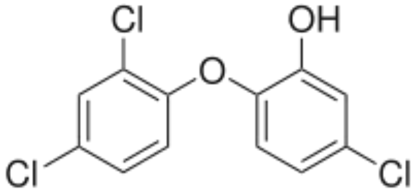

Figure 1. Molecular structure of triclosan

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 K_{OW} value as 4.76 that it is likely to be absorbed in sediment with high organic carbon content. Also having relatively low water solubility and quite high KOC value, it generally persists in soils and aquatic sediments [5]. Moreover, its half-life varies between 2 to 2000 days depending on the latitude and time of the year [6].

Triclosan has been added into the draft specific pollutants' list prepared in accordance with Water Framework Directive (WFD-2000/60/EC). 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.

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
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 KOW
Adsorption to suspended solids	47,454 KOC, ml/g
Dissociation constant	7.9 pKa
Henry's constant	1.5x10-7 atm-m^3/mole
Half-life in surface water	2-2000 d

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 [7,8,9,10,11].

Recently, advanced oxidation processes (AOPs) were used as potential powerful methods that are capable of transforming the pollutants into harmless substances [12]. Almost all AOP's rely on the generation of reactive free radicals, such as hydroxyl, OH• with a redox potential of 2.8 V [13]. 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 [14]. 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 [15]. 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 [16]. 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 this study.

Advanced oxidation of triclosan containing aqueous solution by the Photo-Fenton like oxidation was investigated in terms of triclosan and its byproducts removal. The effects of initial triclosan, Fe(III) 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.

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) [17-18]. Box- Behnken design [19] and D-optimal design [20].

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 [21]. 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 [22-23].

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 (III) sulfate hydrate used as source of Fe(III) in the Photo-Fenton like oxidation was analytical grade and purchased from Alfa Aesar Company. Concentrated stock solutions of Fe(III) (250 mg/L) were prepared for further dilution to obtain solutions of desired concentrations. Fe(III) stock solution was stored in dark to prevent oxidation of Fe(III). 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 like experiments were carried out at room temperature (23±2^{o}C) using different hydrogen peroxide and ferric ion concentrations at pH of 3 which is suitable for Photo-Fenton like process [24]. 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(III) (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 2.1 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 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.

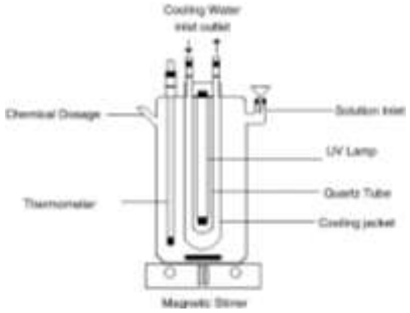

Figure 2. Schematic diagram of the lab-scale photochemical installation.

2.3.2. Analytical Methods

Samples removed from UV reactor at pre-determined time intervals were centrifuged and then 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 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.

3.Results and Discussion

Box Behnken statistical experiment design and the response surface methodology [25,26] 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 (III) and initial triclosan dose) on the triclosan removal. The independent variables were the dose of hydrogen peroxide (X_1), ferric 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 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(III)was selected as 10. H_2O_2/Fe(III) molar ratio was determined based on calculation of theoretical H_2O_2 demand of triclosan oxidation. All these selections were performed for applying an effective oxidation process. The initial concentration of triclosan (X_3) was ranged from 0.1 to 10 mg/L.

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(III)(mM)	X_2	0.1	2.55	5
Triclosan (mg/L)	X_3	0.1	5.05	10

The dependent variables (or objective functions) were the triclosan removal (Y_1), 2,4-DCP formation (Y_2), and 2,4,6-TCP formation (Y_3). The experimental conditions of the Box-Behnken experiment design for Photo-Fenton like oxidation are presented in Table 3. Observed and predicted results as removal percentages using Box-Behnken design are also presented in Table 4.

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

Run	X_1, H_2O_2 (mM)		X_2, Fe(III)(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 percent removals for the response functions (Y) in Photo-Fenton like Oxidation

Run No	X_1, H_2O_2 (mM)	X_2, Fe(III) (mM)	X_3, TCS (mg/L)	Predicted TCS removal (%) Y_1,	Observed TCS removal (%) Y_1,
1	50	5	5.05	97.27	97.00
2	50	0.1	5.05	75.53	76.60
3	1	5	5.05	46.47	45.40
4	1	0.1	5.05	93.88	94.15
5	25.5	5	10	56.41	58.70
6	25.5	5	0.1	80.95	80.00
7	25.5	0.1	10	87.05	88.00
8	25.5	0.1	0.1	75.99	73.70
9	50	2.55	10	80.02	78.00
10	50	2.55	0.1	72.78	74.00
11	1	2.55	0.1	70.53	72.55
12	1	2.55	10	49.80	48.58
13	25.5	2.55	5.05	60.57	60.05
14	25.5	2.55	5.05	60.57	60.50
15	25.5	2.55	5.05	60.57	61.17

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.

The response functions for percentual triclosan removal (Y_1), 2,4-DCP formation (Y_2) and 2,4,6-TCP formation (Y_3) have the following forms:

$$Y_1 = 100.49210 - 1.15728X_1 - 16.67960X_2 - 1.21190X_3 + 0.28800X_1X_2 + 0.057658X_1X_3 - 0.73387X_2X_3 + 9.07677\times10^{-3}X_1^2 + 2.04345X_2^2 + 0.092269X_3^2 \quad (\text{R-Squared} = 0.9920) \qquad (2)$$

$$Y_2 = 0.24987 - 0.013367X_1 - 0.057470X_2 + 5.57251X_3 + 8.19074\times10^{-3}X_1X_2 + 2.58213\times10^{-3}X_1X_3 - 7.44816\times10^{-3}X_2X_3 \quad (\text{R-Squared} = 0.9635) \qquad (3)$$

$$Y_3 = 0.098496 - 5.29978\times10^{-3}X_1 - 39.721\times10^{-3}X_2 + 0.062342X_3 + 1.99650\times10^{-3}X_1X_2 - 2.13785\times10^{-4}X_1X_3 - 0.010360X_2X_3 \quad (\text{R-Squared} = 0.9610) \qquad (4)$$

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(III)concentrations (X_2). The H_2O_2 concentration has a more profound effect on percent removal of triclosan as compared to Fe(III)concentrations.

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

Source	Sum of squares	d.f.	Mean square	F Value	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^{+3}	329.60	1	329.60	62.18	0.0005
X_3-TCS	90.92	1	90.92	17.15	0.0090
$X_1 X_2$	1195.43	1	1195.43	225.51	< 0.0001
$X_1 X_3$	195.58	1	195.58	36.90	0.0017
$X_2 X_3$	316.84	1	316.84	59.77	0.0006
X_{12}	109.60	1	109.60	20.68	0.0061
X_{22}	555.51	1	555.51	104.79	0.0002
X_{32}	18.87	1	18.87	3.56	0.1178
Residual	26.50	5	5.30		
Lack of Fit	25.87	3	8.62	27.15	0.0357
Pure Error	0.64	2	0.32		
Total (Corr)	3316.29	14			

R-squared= 0.9920, R-squared (adjusted for df) = 0.9776, standard error of estimate = 2,3

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	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^{+3}	0.62	1	0.62	28.63	0.0007
X_3-TCS	0.54	1	0.54	24.81	0.0011
X_1 X_2	0.97	1	0.97	44.53	0.0002
X_1 X_3	0.39	1	0.39	18.07	0.0028
X_2 X_3	0.033	1	0.033	1.50	0.2551
Residual	0.17	8	0.022		
Lack of Fit	0.17	6	0.029	44.96	0.0219
Pure Error	1.278E-003	2	6.392E-004		
Total (Corr)	4.76	14			

R-squared = 0.9635, R-squared (adjusted for df) = 0.9361, standard error of estimate = 0,15

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	0.39	6	0.066	32.87	< 0.0001
X_1-H_2O_2	7.970E-003	1	7.970E-003	3.98	0.0810
X_2-Fe^{+3}	0.081	1	0.081	40.61	0.0002
X_3-TCS	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	2.689E-003	1	2.689E-003	1.34	0.2797
X_2 X_3	0.063	1	0.063	31.57	0.0005
Residual	0.016	8	2.000E-003		
Lack of Fit	0.016	6	2.642E-003	35.98	0.0273
Pure Error	1.469E-004	2	7.343E-005		
Total (Corr)	0.41	14			

R-squared = 0.9610, R-squared (adjusted for df) = 0.9318, standard error of estimate = 0,045

Observed and predicted percent occurrences for the response functions (Y) are presented in Table 8.

Table 8. Observed and predicted percent occurrences for the response functions (Y) for Photo-Fenton like Oxidation

Run No	Predicted Results			Observed Results		
	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	97.27	1.83	0.13	97.00	1.98	0.17
2	75.53	0.29	0.10	76.60	0.30	0.08
3	46.47	0.00	0.00	45.40	0.02	0.00
4	93.88	0.27	0.40	94.15	0.29	0.39
5	56.41	1.01	0.07	58.70	0.84	0.09
6	80.95	0.67	0.02	80.00	0.60	0.00
7	87.05	0.63	0.52	88.00	0.61	0.59
8	75.99	0.00	0.00	73.70	0.01	0.00
9	80.02	1.64	0.24	78.00	1.76	0.21
10	72.78	0.49	0.00	74.00	0.51	0.00
11	70.53	0.11	0.00	72.55	0.11	0.00
12	49.80	0.00	0.35	48.58	0.10	0.31
13	60.57	0.56	0.15	60.05	0.41	0.11
14	60.57	0.56	0.15	60.50	0.45	0.13
15	60.57	0.56	0.15	61.17	0.41	0.11

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(III) 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.

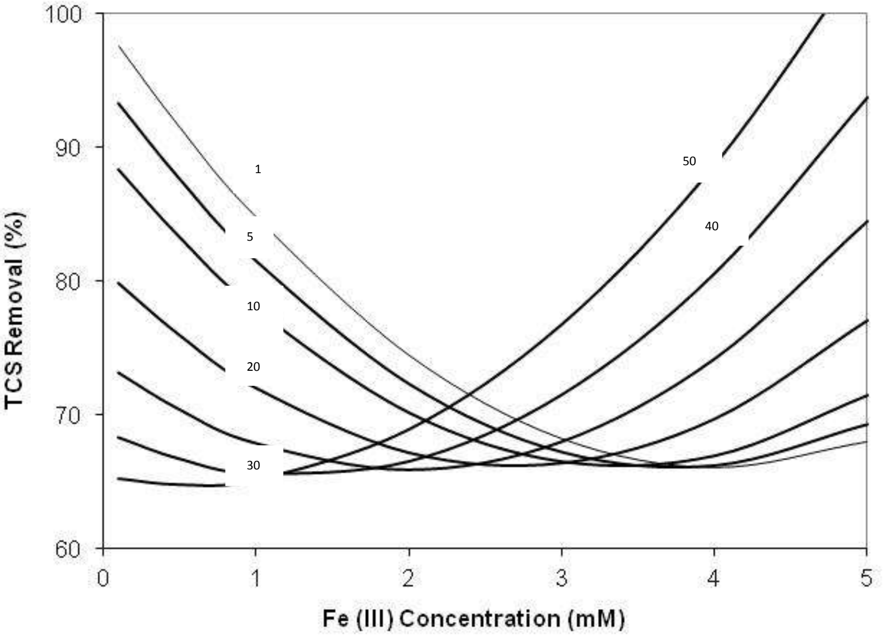

Figure 3. Variation of percent triclosan removals with Fe(III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 0.1mg/L.

As shown in Figure 3, Percent triclosan removals were 97.6, 73.2 and 65.3% when H_2O_2 concentrations of 1, 30 and 50 mM, respectively at a Fe(III) concentration of 0.1 mM. It can be said that requirement of hydrogen peroxide concentration to remove triclosan was small at low ferric ion concentration. At this situation, high oxidant usage resulted in low triclosan removal efficiency due to excess H_2O_2/Fe (III) molar ratio. At high H_2O_2 concentrations, probably H_2O_2 served as a free-radical scavenger for itself reducing the [$OH^\bullet$].

$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$ (3.8)
$OH^\bullet + HO_2^\bullet \rightarrow H_2O + O_2$ (3.9)

In agreement with Glaze *et al.,* (1995) a reduction in pesticide removal was observed at high H_2O_2 concentrations indicating the adverse effects of excess H_2O_2.

In addition to this, complete degradation was realized at H_2O_2 concentration of 50 mM and Fe(III) concentrations above 5 mM after 60 min reaction time. Percent triclosan removals were 100 and 65% when Fe(III) concentrations of 5 and 1 mM, respectively, at a H_2O_2 concentrations of 50 mM and initial triclosan concentration of 0.1 mg/L. These conditions were sufficient to optimize molar ratio and to remove triclosan.

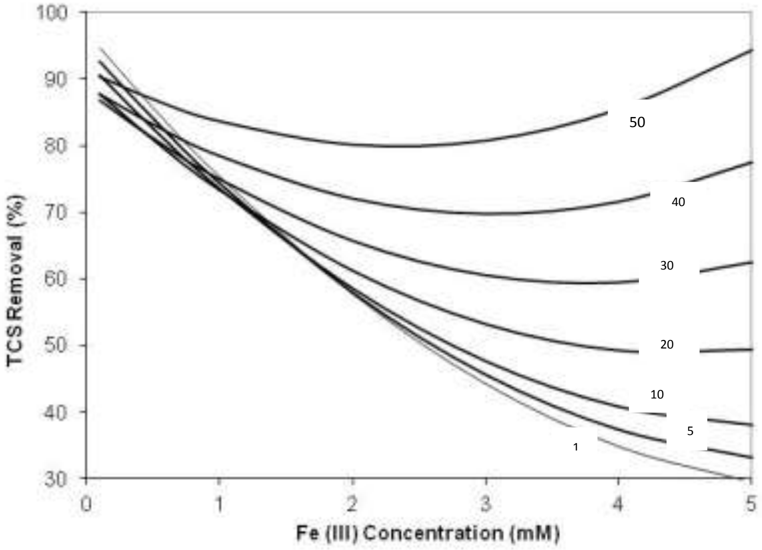

Figure 4. Variation of percent triclosan removals with Fe(III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 10 mg/L.

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.

As can be seen in Figure 4, percent triclosan removals were 75, 75 and 84% when H_2O_2 concentrations of 1, 30 and 50 mM, respectively at a Fe(III) concentration of 0.1 mM and at an initial triclosan concentration of 10 mg/L. When ferrous ion concentration increased to 5 mM, percent triclosan removals were 27.5, 62.5 and 94% when H_2O_2 concentrations of 1, 30 and 50 mM, respectively. It can be said that complete degradation was realized at H_2O_2 concentration of 50 mM and Fe(III) concentrations nearly 0.1 mM after 60 min reaction time while higher concentrations of Fe(III) did not result in complete triclosan degradation expecially low hydrogen peroxide concentration. Because, high iron concentrations can also scavenge $OH^•$ yielding lower levels of oxidation. 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(III) 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(III)/triclosan concentration yielding the highest triclosan removal (97.6%) was 1/0.1/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 50/5/10 yielding 94.3% 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_1 X_2, X_2X_3, X_1^2, X_2^2) were significant and played important roles in degradation of triclosan by the photo-Fenton like treatment as summarized in Table 5. Photo-Fenton like treatment more effective at high oxidant and catalyst doses 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-Dichlorophenol (Y_2) increases with the Fe(III) concentration (X_2), the H_2O_2 concentration (X_1). This situation is not good for oxidation processes. In addition to this, Fe(III) concentration (X_2) a more profound negative effect by the formation of 2,4-Dichlorophenol (Y_2). So, it can be said that high concentration of oxidant and catalyst is not suitable for optimum reaction conditions to mineralize triclosan.

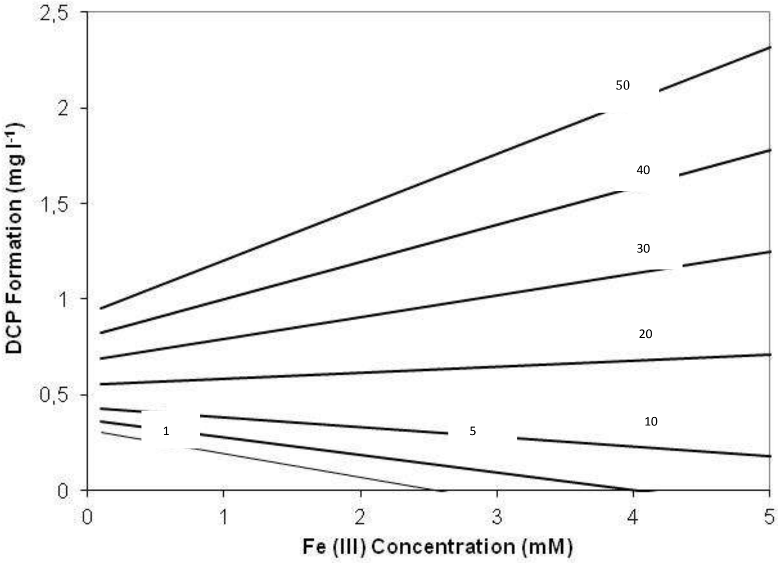

Figure 5. Variation of 2,4-DCP Formation with Fe(III) concentrations at different initial H_2O_2 concentration at initial concentration of triclosan was 5 mg/L.

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 (4 µg l^{-1}) was 20/3/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 20/3/10 yielding 262 µg l^{-1}DCP formation.

The ANOVA analysis also indicated that all three variables triclosan, H_2O_2 and Fe (III) concentrations (X_1^2, X_2^2 and X_3^2) were significant and played important roles in formation of byproducts by the photo-Fenton like oxidation as summarized in Table 6.

According to TCP formation (Figure 6), it can be said that formation of the byproduct named as 2,4,6-TCP decreases with H_2O_2 concentration and Fe(III) concentration. However above 50mg/L hydrogen peroxide concentration, when ferric ion increased TKF formation was increased.

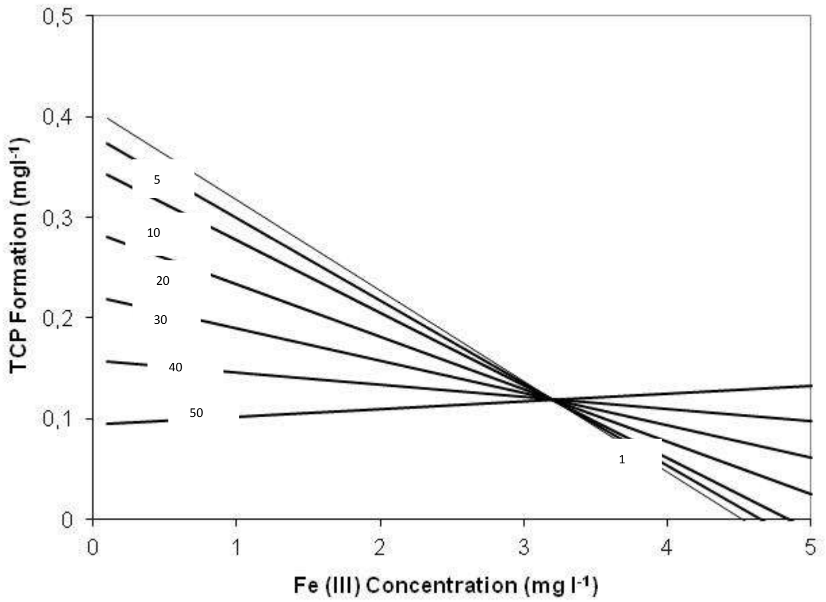

Figure 6. Variation of 2,4,6-TCP Formation with H_2O_2 concentrations at different Fe (III) concentration at initial concentration of triclosan was 5 mg/L.

As a result of these evaluations, at low triclosan concentration of 0.1 mg/L, the optimal H_2O_2/Fe(III)/triclosan concentration yielding the lowest TCP formation (0 μg l^{-1}) was 1/3/0.1, while at a high triclosan concentration of 10 mg/L this ratio was 1/3/10 yielding (290μg l^{-1}) the lowest TCP formation. The ANOVA analysis also indicated that all three variables H_2O_2 and triclosan concentrations and the interactions (X_1, X_3,) were significant and played important roles in formation of byproducts by the photo-Fenton like oxidation as summarized in Table 7.

4.Discussion and Conclusion

Triclosan degradation by advanced oxidation processes (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 ferric 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. Percent triclosan removal decreases with initial concentration of triclosan (X_3) while increasing with the H_2O_2 concentration (X_1) and Fe(III) concentrations (X_2). The H_2O_2 concentration has a more profound effect on percent removal of triclosan as compared to Fe(III) concentrations. Photo-Fenton like treatment is resulted >95% removal efficiency of triclosan. 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. 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(III) concentrations for complete degradation. Higher initial triclosan concentrations required higher amounts of the H_2O_2 concentrations and Fe(III) concentrations for complete degradation. Formation of the by-products which are named as 2,4-Dichlorophenol (Y_2) and 2,4,6-Trichlorophenol (Y_3) increases with the Fe(III) concentration (X_2), the H_2O_2 concentration (X_1). This situation is not good for oxidation processes. In addition to this, Fe(III) concentration (X_2) a more profound negative effect by the formation of 2,4-Dichlorophenol (Y_2) and 2,4,6-Trichlorophenol (Y_3). So, formation of the highly toxic by-products was the critic limitation factor of the degradation. In addition to this, high concentration of oxidant and catalyst is not suitable for optimum reaction conditions. In photo-Fenton treatment, the highest triclosan removal (97%) was obtained with a H_2O_2/Fe(III)/triclosan ratio of 50/5/10. At these reaction conditions, 2,4-Dichlorophenol and 2,4,6-Trichlorophenol were observed as 2.31 mg l^{-1} and 0.132 mg l^{-1}, respectively.

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