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Micro-pollutant Degradation using Nanostructured Catalysts

Nano-yapılı Katalizör Kullanılarak Mikrokirleticilerin Giderilmesi

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Abstract

Today, organic anti-microbic substances have increased the concern due to their potential health effects on human and natural life. Triclosan (TCS) is the commonly known as anti-bacterial or anti-microbic and cleaning products. There is strong evidence that water plants and other aquatic species are more sensitive to triclosan. New products are resulting from the decomposition of triclosan, which easily founded at the effluent of wastewater treatment plants. TCS is a kind of an endocrine distractive chemical and gives damage to the aquatic eco-system and human health in the long term. The purpose of this study was to investigate the elimination of TCS from wastewater by using the photo-oxidation method. The removal of TCS studied using ultraviolet light and newly developed catalysts. The Poly(dimethylsiloxane) (PDMS) modified Nafion/Silica composite catalyst was successfully destroyed the TCS to the sucrose without any iron sludge production. In addition, it is possible to re-use the catalyst several times with negligible iron leaching amounts. Consequently, PDMS modified catalyst was successfully applied to destroyed TCS in 60 minutes of exposure time with using only 34 mg/L H_2O_2 and 0.1g of catalyst.

Anahtar kelimeler: Triclosan, Nafion/iron catalyst, Photo-oxidation, Box-Behnken UV-oxidation

Öz

Günümüzde, organik anti-mikrobik maddelerin kullanımı, insan sağlığı ve doğal yaşam üzerindeki potansiyel etkileri nedeniyle kaygıları arttırmaktadır. Triklosan (TCS), temizlik ürünlerinde yaygın olarak kullanılan ve anti bakteriyel veya anti-mikrobik olarak bilinen bir maddedir. Su bitkilerinin ve diğer su canlılarının triklosan'a daha duyarlı olduğuna dair güçlü kanıtlar vardır. Trikolosanın ayrışması sonucunda oluşabilecek yeni bileşiklere arıtma tesisleri çıkışında rastlanabilmektedir. TCS bir tür endokrin bozucu kimyasaldır ve sucul eko sisteme ve uzun vadede insan sağlığına zarar verir. Bu çalışmanın amacı, foto-oksidasyon yöntemini kullanarak TCS'in atıksudan uzaklaştırılmasını incelemektir. TCS'nin giderimi ultraviyole ışık ve yeni geliştirilen katalizörler kullanılarak incelenmiştir. Poli (dimetilsiloksan) (PDMS) modifiye edilmiş Nafion / Silica kompozit katalizörü, TCS'yi, herhangi bir demir çamuru üretimi olmadan sükroza başarıyla parçalamıştır. Ayrıca, katalizörü ihmal edilebilir demir liçi miktarları ile birkaç kez tekrar kullanmak mümkündür. Sonuç olarak, PDMS ile değiştirilmiş katalizör, sadece 34 mg/L H_2O_2 ve 0.1 g katalizör kullanılarak 60 dakika oksidasyon süresince TCS başarıyla parçalanmıştır.

Keywords: Triklosan, Nafion/demir katalizörü, Foto oksidasyon, Box-Behnken, UV-oksidasyonu.

1 Introduction

Triclosan (2, 4, 4-trichloro-2-hydroxy diphenyl ether) is a chlorinated aromatic, and a non-ionic compound (Figure 1). It is widely used for antimicrobial purposes, and it is a low soluble in water, and a white powdered solid (12 mg/L) [1]. Triclosan has been manufactured under the license of Swiss specialty chemical company Ciba since the 1960s, especially over the past 25 years all over the world.

Because of the antibacterial properties, triclosan has been used increasingly in recent years. On the other hand, unfortunately, triclosan has endocrine-disrupting properties. It is discharged from wastewater treatment plant effluents into the natural environment without any decay [1]. The behavioural changes at different TCS concentrations were determined for the different test organisms. Behavioural changes of *Poecilia reticulata* and *Danio rerio* were observed, such as fast-moving, uncontrolled swimming, trying to escape out of the water, vertical action to the water surface, loss of balance, respiratory difficulties, chills, and inversion [2].

Photo-degradation of triclosan is suggested the most suitable degradation process in the literature. Chemical oxidation, photooxidation (including photocatalytic oxidation), and sonolysis degradations were described of triclosan. Physical and chemical factors had a strong effect on triclosan elimination, such as the presence of metal ions, the pH of the aqueous solution, humic acid and salinity in wastewater and type of UV light, and intensity [3].

Triclosan is resistant to high and low pH, despite its high chemical stability. Triclosan can be easily removed from wastewater by oxidation. However, eight by-products recognized during photo-degradation of triclosan, such as; chlorinated phenols, 2,7- and 2,8-dichlorodibenzo-dioxin, chlorohydroxydiphenyl ethers and a dichlorohydroxy-dibenzofuran or dichlorodibenzodioxin isomer [3].

It is very important to degrade the triclosan until the end product because of the higher toxicity effects of these by-products compared to the toxicity of triclosan. The final products are CO_2 and chlorine with chlorocatechols. In the ozonation process of triclosan results the potential generation of harmful by-products [4] and also performing of ozonation process have a corrosion problem. Instead, applying the UV-oxidation to the triclosan may cause in the conversion of extremely toxic and recalcitrant chlorinated by-products [5].

Son, Ko, and Zoh [6] established that TiO_2-photocatalytic degradation of triclosan is mainly achieved by radicals, and once they are produced in photocatalysis, they can further

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degrade dioxin-type intermediates. To obtain enhanced oxidation conditions, the presence of H_2O_2 is important [7].

By-products produced by UV and UV / H_2O_2 oxidation of organic compounds may vary. In particular, other substances present in the matrix significantly affect the oxidation process. (available photon energy, other oxidizing species such as hydroxyl radical etc.) [8].

In this work, the photo-Fenton reaction applied using a high surface area catalyst which is produced PDMS modified Nafion/silica composite by applying sol-gel technology. One of the aims of this study is to develop an iron-containing catalyst that can prevent the formation of sludge in AOP processes and can be reused. For this reason, the catalysts are applied to degrade triclosan. Because of these reasons, UV–irradiation was chosen for the applied Advanced Oxidation Process (AOP) of experiments. Also, because of the traditional treatment methods are allowed mainly to transfer the contaminants from one phase to another, leaving a problem of disposal of the transferred material.
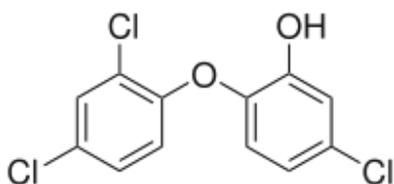

Figure 1: Molecular structure of triclosan

2 Materials and Methods

2.1 Materials

Tetraethoxysilane (TEOS) used a precursor of silica, and purchased from Fisher Scientific. PDMS (hydroxy-terminated poly(dimethylsiloxane)) and Nafion oligomer used as a structure modifier and keeps the iron inside for Photo-Fenton reaction, respectively, and obtained from Sigma-Aldrich. $FeCl_2x4H_2O$ used as a source of Fe(II) and purchased from Merck. TEOS, PDMS and Nafion polymers dissolved by using THF (tetrahydrofuran) and IPA (Isopropanol) as solvents. NaOH (sodium hydroxide) and HCl (hydrochloric acid) used for condensation and catalyzing hydrolysis, respectively.

Triclosan ($C_{12}H_7Cl_3O_2$, CAS No: 3380-34-5) purchased from Alfa Aesar (high purity grade (99%)) and used for a pollutant. Because of the low solubility of triclosan, 99.5% of Methanol (CH_3OH) used to dissolve triclosan in the stock solution and Methanol purchased from Merck. For the HPLC analyses acetonitrile was obtained by Riedel-de Haën. In all experimental studies ultra-high purity water used and produced by a NANOpure Diamond UV water purification system. 35% w/w H_2O_2 (Hydrogen peroxide) (CAS No: 7722-84-1) solution used as an oxidant and obtained from Merck.

2.2 Experimental procedures

The procedure of the synthesis of the catalyst was given in our previous study [9]. After catalyst production, the catalyst morphology analyzed by using the Scanning Electron Microscope (SEM), and also elemental analysis of the catalyst was done using Energy-Dispersive X-ray Spectroscopy (EDX).

Due to the low solubility of the TCS in water, 100 mg/L TCS stock solution prepared using Methanol. Then, for each experiment TCS diluted using ultrapure water to the chosen concentration. The quantity of the catalyst and hydrogen peroxide were varied in all experiments according to the applied model. After the addition of the hydrogen peroxide, the time was chosen as the beginning of the experiments.

The photocatalytic reactions set up are given below, as shown in Figure 2. 100 mL of TCS solution used for experimental studies and mixed with a stirrer during experiments. For the oxidation reaction, the light source obtained from five Phillips UVC lamps (each 8 W/m^2).

2.3 The Box–Behnken Experimental Design

Box–Behnken experimental design method [10] was applied to optimize the reaction conditions during TCS removal experiments.

Figure 2: Experimental set-up

The Box–Behnken experimental design is an adapted central composite design known as 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 the centre [11]. It is also possible estimation of the system performance at any experimental point within the range studied with the design method. Three independent variables, which were hydrogen peroxide, catalyst, and TCS concentrations, chosen.

For the photo-Fenton process, the independent variables were the hydrogen peroxide (H_2O_2) concentration X1, catalyst concentration X2, initial concentration of TCS X3. The minimum, centre, and maximum points of each variable are nominated as -1, 0, and +1, respectively, as shown in Table 1. The objective functions or dependent variables are related to each other. The dependent variable was the percent removal of triclosan (Y_{TCS}) (Eq.1).

$$YTCS = b0 + b1X1 + b2X2 + b3X3 + b12X1X2 + b13X1X3 + b23X2X3 + b11X1^2 + b22X2^2 + b33X3^2 \qquad (1)$$

The H_2O_2 concentration X1 chosen between 34 mg/L and 1700 mg/L while, catalyst concentration X2 varied between 0.1 and 0.2 g. The beginning amount of TCS X3 changing from 0.1 to 10 mg/L. All these ranges selected according to literature data to obtained effective degradation of TCS.

Table 1: The experimental points according to the Box-Behnken design method

| Run | Actual Coded and Levels | | | | | |
| | X1, H_2O_2 (mg/L) | | X2, Catalyst (g) | | X3, TCS (mg/L) | |
	Coded Levels	Actual Levels	Coded Levels	Actual Levels	Coded Levels	Actual Levels
1	(+1)	1700	(+1)	0.2	0	5.05
2	(+1)	1700	(−1)	0.1	0	5.05
3	(−1)	34	(+1)	0.2	0	5.05
4	(−1)	34	(−1)	0.1	0	5.05
5	0	867	(+1)	0.2	(+1)	10
6	0	867	(+1)	0.2	(−1)	0.1
7	0	867	(−1)	0.1	(+1)	10
8	0	867	(−1)	0.1	(−1)	0.1
9	(+1)	1700	0	0.15	(+1)	10
10	(+1)	1700	0	0.15	(−1)	0.1
11	(−1)	34	0	0.15	(−1)	0.1
12	(−1)	34	0	0.15	(+1)	10
13	0	867	0	0.15	0	5.05
14	0	867	0	0.15	0	5.05
15	0	867	0	0.15	0	5.05

2.4 Analytical Techniques

TCS measurements were done using Agilent 1260 model HPLC contained with an Eclipse XDB-C18 column, and a MWD UV-detector. The H_2O/acetonitrile composition used for the mobile phase with a ratio of 25/75. Samples centrifuged before analysing and measured at 280 nm. The injection volume of samples was 20 µL, and the flow rate was 1.0 mL/min. The TCS retention time was 2.5-3 minutes under these conditions. The calculation of the TCS concentration was done according to peak areas, both preparing the calibration curve and analysing the samples. The calibration curve for TCS prepared with linearity of 0.9986 (R^2), and concentrations ranges of TCS were between 0.001 mg/L and 10 mg/L.

After photo-degradation experiments, iron leakage and the H_2O_2 concentration in the wastewater were measured according to 1,10-Phenanthroline methods [12], [13] and

Quantofix peroxide test papers (sourced from Sigma Aldrich) (for 0.5 – 25 mg/l H_2O_2), correspondingly.

3 Results and Discussions

3.1 Catalyst Characterization Results

The catalyst was prepared according to the procedure that is given by Baycan and Li Puma, 2018 [9]. The catalyst characterized by using SEM and EDX, and the results show in Figure 3-4 and Table 2. The BET surface area (95 m^2/g) (ASAP 2020 analyser) and zeta potential (-52 at pH 7) (oxford instruments) were also measured.
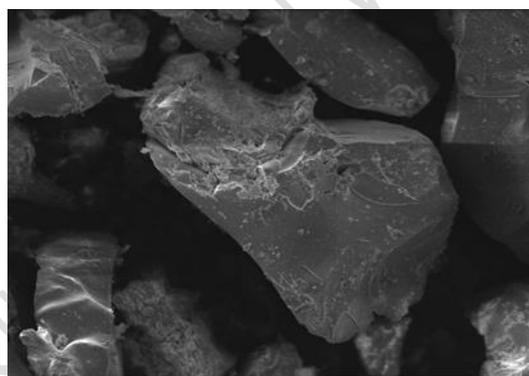

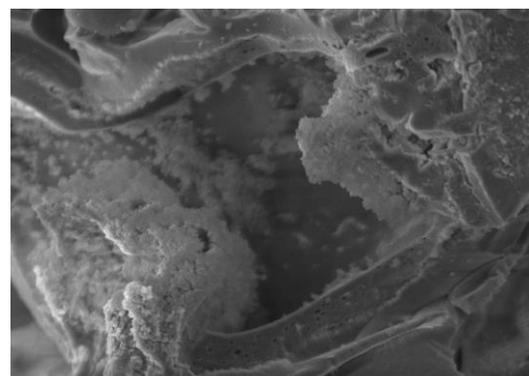Figure 3: Higher resolution Scanning Electron Microscope image of the catalyst

Figure 4: Higher resolution Scanning Electron Microscope image of the damaged area

The surface morphology and the catalyst's characteristics determined with SEM technology. The catalyst did not have a uniform morphology, whereas it was found to be very porous, and there were damaged areas (Figure 4).

The iron content of the catalyst determined by the EDX elemental analysis, shown in Table 2. The amount of iron added to the mixture for catalyst formation is theoretically only 0.15%, and EDX results supported this amount. The weight

percentages of components were kept very low, and the composite fixed at 4 wt % of Nafion.

Table 2: Energy-dispersive X-ray spectroscopy (EDX) results

	Spectrum 1	Spectrum 2	Spectrum 3
Element	Wt%	Wt%	Wt%
O	45.9	51.0	50.0
Si	28.0	25.1	24.9
C	15.0	12.0	14.9
F	6.0	2.6	5.2
Na	3.9	8.0	2.9
Cl	1.1	1.1	1.9
Fe	0.1	0.1	0.2

3.2 Triclosan Degradation Experiments

At the beginning of the study, to see the adsorption effects of the catalyst, both the presence and absence of UV light adsorption experiments carried out, and only a 5% adsorption effect seen. Another evaluation was to examine the presence of the H_2O_2/UV effect on the oxidation with and without catalyst addition. Consequently, the photo-Fenton reaction was effectively degraded TCS. Because of the study, it observed that in the presence of the iron-containing catalyst, the hydroxyl radical production yield better than only UV and H_2O_2 containing process as given by the literature [14].

After each experimental study, iron-leaching analyses applied, the iron leakage was negligible quantity, and it was only 0.3 mg/L. To see the possibility of the catalyst reuse, after experiments, the catalyst was filtered, dried, and reused. This process applied tree times, and after at the end of third experiments, the removal efficiency reduced by approximately 15%. As a result of these experiments, it is possible to say that even if very small amounts of iron exists in the presence of H_2O_2 can produce hydroxyl radicals [15]. The important effect of the catalyst was the faster degradation rate of the TCS.

For TCS removal, the optimization of the experimental conditions studied using an oxidation process with using UV light, hydrogen peroxide, and iron-containing catalyst. The removal efficiencies obtained from experimental studies evaluated using multiple regression analysis based on the least-squares method. Correlation of the experimental results with the response functions for different dependent variables were determined by using the Design Expert 11 regression program. Calculated coefficients replaced in the result function in equation 1 and the expected TCS removal efficiency determined. The use of Response Surface Methodology ensures an empirical relationship between the independent variables X and the response function (Y_{TCS}). As a results of the RSM analysis the model can be approximated by a quadratic polynomial Equation (2) as below:

$$Y_{TCS} = +78.3195 - 4.19864X_1 + 1.10934X_2 + 3.96669X_3 - 1.8561 \times 10 - 16X_1X_2 - 2.07076X_1X_3 - 2.21867X_2X_3 + 4.10711X_1^2 - 5.73413X_2^2 - 5.44048X_3^2 \ (R^2 = 0.9204) \ (2)$$

The model can be interpreted according to F-value and P-value. These values obtained from ANOVA (analysis of variance) solutions. As a result of the ANOVA evaluation F-value of 6.43 and a P-value of < 0.05 indicate a significant effect of the corresponding variable on the response. The p-value in the model was 0.0271. X_1-H_2O_2, X_3-TCS, (X_2-Catalyst)^2, (X_3-TCS)^2 are significant model terms. These experimental parameters are affecting the results directly. In the photo-Fenton experiment, the response functions with the determined coefficients for the percent removal of TCS (Y_{TCS}) occurrence presented by Equations (2). The predicted values calculated using the constants that obtained from equation 2. Finally, the difference between the predicted and observed values of TCS removal efficiencies was smaller than 5% and it means that there is a meaningful correlation between predicted and observed results (Table 3).

Table 3: Observed and predicted values

Run Order	Observed Value (%Removal)	Predicted Value (%Removal)
1	82	85
2	82	83
3	95	94
4	95	91
5	88	86
6	74	74
7	79	79
8	74	76
9	76	75
10	74	71
11	74	75
12	84	87
13	77	78
14	80	78
15	79	78

To see the effects of the independent variables on the removal efficiency of TCS one variable kept constant and the other two changes between the minimum and maximum values. Figure 5 shows the effect of initial H_2O_2 concentration on percent TCS removal at different catalyst concentrations after 60 min of reaction time when the initial concentration of TCS was 5.05 mg/L. The maximum TCS removal efficiency was 95% and

obtained by the addition of 0.2 g or 0.1 g of catalyst and 34 mg/L H_2O_2. It has been observed that the removal efficiency decreases to 60% at increasing hydrogen peroxide concentrations. In general, an increase in the concentration of hydrogen peroxide at concentrations of 5.05 mg/L of TCS reduced the yield. This may be explained by the inhibition of the hydroxyl radicals by the existing excess H_2O_2 amount [16].

$$H2O2 + \bullet OH \rightarrow H2O + HO2 \bullet \qquad (3)$$
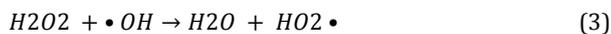
The $HO_2\bullet$ radicals generated during oxidation (Eq. 3) probably scavenging the active •OH radicals by further reactions (Eq.4):

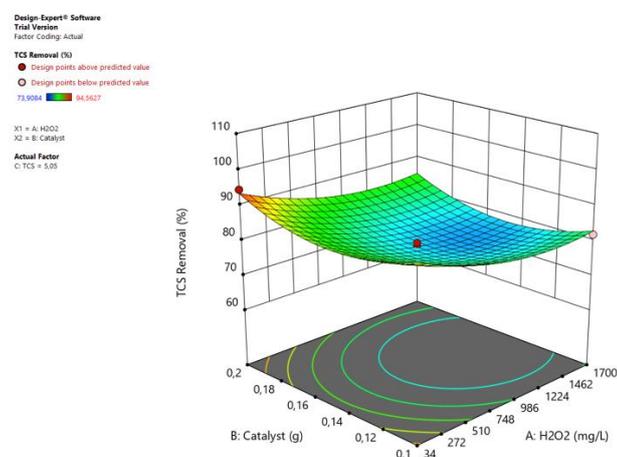$$HO2 \bullet + \bullet OH \rightarrow H2O + O2 \qquad (4)$$

Figure 5: The TCS removal efficiency as a function of catalyst concentrations at different H_2O_2 concentrations

(TCS = 5.05 mg/L).

To determine the effect of catalyst concentration on TCS removal efficiency at a constant H_2O_2 concentration (867 mg/L), by using response equation with calculated coefficients, some results predicted. Figure 6 depicts variations of percent TCS removals with the different catalyst concentrations and different TCS concentrations for the reaction time of 60 min and at a constant initial H_2O_2 of 867 mg/L. The maximum removal efficiency was obtained as 88% in 60 min. at a catalyst concentration of 0.2g. When the catalyst concentration was 0.1 g we obtained 74% removal efficiency.
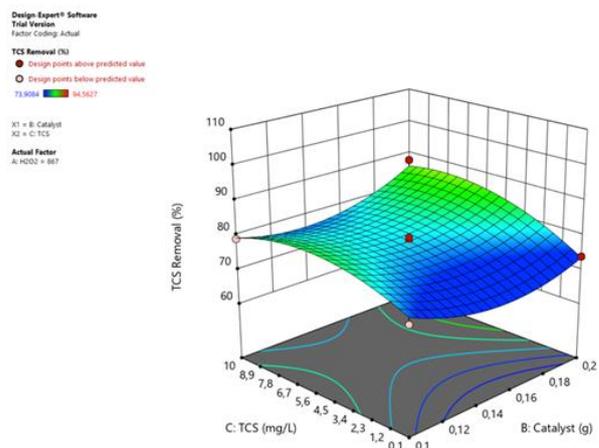
Figure 6: The TCS removal efficiency as a function of catalyst concentrations at changed TCS concentrations

(H_2O_2 = 867 mg/L).

To see the effect of TCS concentration on removal efficiency, H_2O_2 addition, and the TCS addition changed between 34mg/L and 1700mg/L, 0.1mg/L and 10mg/L in this set of analysis, correspondingly, whereas the catalyst was constant at 0.15g. Variations of percent TCS removals with H_2O_2 concentrations are depicted in Figure 7. The maximum elimination efficiency (95%) was achieved with the 5.05 mg/L TCS concentration. 79% removal efficiency was obtained when the initial concentration of TCS was 10 mg/L.
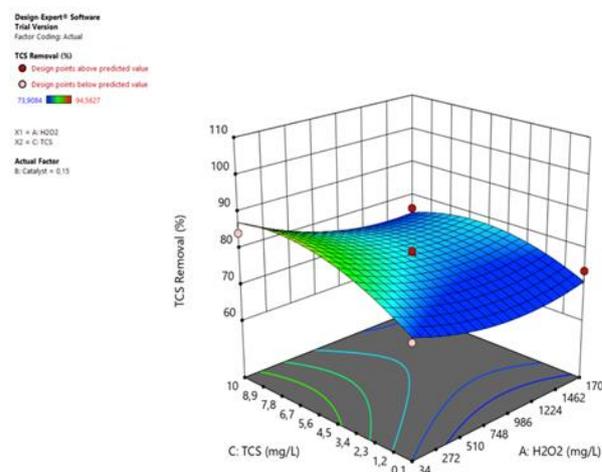
Figure 7: The TCS removal efficiency as a function of TCS concentrations at different H_2O_2 concentrations

(Catalyst = 0.15 g).

3.3 Degradation Kinetics of Triclosan

When TCS removal was examined, it was found that it conforms to first-order kinetics. (Table 4). The faster degradation of the TCS could be illuminated with stronger absorption of photons in the UVC area of the electromagnetic spectrum.

Table 4: The TCS reaction rate constant (with catalyst)

	TCS
R^2	0.92
k_1 (min^{-1})	0.05

When using UV/H_2O_2 (50 mg/L) together, the micro pollutants transformed and eliminated better instead of UV treatment alone (a total degradation of 81%) [17]. Additionally, the transformation increased further up to 97% after 30 min of UV/H_2O_2. During Fenton process treatment efficiency was only 31% (5 mg/L $Fe^{2+,3+}$/50 mg/L H_2O_2). For the photo-Fenton process, both extending the reaction time or addition of H_2O_2 dosage caused to have a positive impact on degradation efficiency. In this work, H_2O_2 and catalyst concentration used less than from the literature.

3.4 LC/QTOF/MS Results

Agilent 6550 QTOF/LC/MS used to determine the metabolites of TCS. For this reason, treatment experiments were repeated at optimum points. And after this experimental study sample was analysed with LC/QTOF/MS. On the word of this analysis, the breakdown of the double bound and hydroxylation of the aromatic ring would lead to the formation of sucrose after 60 min. And also, it could not be determined any chlorinated compounds. Probably, chloride ions could be converted to chloride gas during oxidation. Chloride gas was not measured during oxidation, further studies will be needed [18]. Another TCS degradation pathway was through the hydroxyl radicals attack on carbon atoms substituted with Cl atoms of the non-phenolic fraction [19], other possible TCS degradation pathway [20] was represented by hydroxyl radicals' addition to a phenolic fraction. In our work all these by-products could be eliminated, it means that enough reaction time and catalyst and oxidants could be destroyed all rings and could be converted TCS to sucrose (Figure 8).
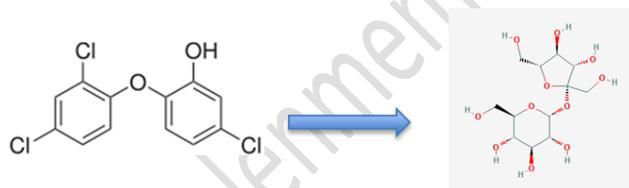

Figure 8: Possible triclosan degradation pathway

4 Conclusions

First objective of the study was to produce a reproducible nano-catalyst for advanced oxidation of wastewaters and the most important specification of the catalyst is not produce a waste iron sludge after oxidation. The second aim was to see if the catalyst could be degraded TCS to the end product by using photo-Fenton processes.

The Poly(dimethylsiloxane) modified Nafion/Silica composite catalyst was successfully destroyed the TCS to the sucrose without any iron sludge production. And also, it is possible to re-use the catalyst several times with negligible leaching of iron.

In this study, TCS oxidation was carried out under UVC radiation by using H_2O_2 and iron-containing catalyst. This advanced treatment method leads to the removal of TCS in wastewater treatment. The analysis results are designed according to Box Behnken statistical program. As a result of the experiments, it could be seen that initial TCS concentration and H_2O_2 amounts are significant factors for TCS removal. When the catalyst added in the system the hydroxyl radical production was accelerated. The maximum TCS removal efficiency was obtained by using of 34mg/L H_2O_2 concentration which was the minimum addition of H_2O_2. Therefore, no excess H_2O_2 is required for the removal of TCS. It has been observed that removal efficiency decreases with increasing hydrogen peroxide concentrations. This may be explained by the inhibition of the hydroxyl radicals by excess H_2O_2 concentration. At a high concentration of hydrogen peroxide known as a hydroxyl radical scavenger. The optimal conditions over 95% TCS removal was determined with the addition of minimum H_2O_2 and minimum catalyst concentration. After Photo-oxidation of TCS could be destroyed to sucrose.

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