Micro-Pollutant degradation using nanostructured catalysts

N nano-Yapılı katalizör kullanılarak mikrokarıleticilerin giderilmesi

Neval BAYCAN

1Department of Environmental Engineering, Engineering Faculty, Dokuz Eyal University, Izmir, Turkey.

Corresponding author/Yazılan Yazar

Received/Geliş Tarihi: 12.12.2019
Accepted/Alan Tarihi: 27.05.2020

Abstract

Today, organic anti-microbial 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-microbial and cleaning products. There is strong evidence that water plants and other aquatic species are more sensitive to triclosan. New products are results 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 ecosystem 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 min. of exposure time with using only 34 mg/L H₂O₂ and 0.1g of catalyst.

Keywords: Triclosan, Nafion/Demir katalizör, Photo 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.

Figure 1. Molecular structure of triclosan.

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 dichlorodibenzo-dioxin 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 CO₂ 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 degrade dioxin-type intermediates. To obtain enhanced oxidation conditions, the presence of H$_2$O$_2$ is important [7]. By-products produced by UV and UV/H$_2$O$_2$-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 Nafton/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.

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 Nafton oligomer used as a structure modifier and keeps the iron inside for Photo-Fenton reaction, respectively, and obtained from Sigma-Aldrich. FeCl$_2$·4H$_2$O used as a source of Fe(II) and purchased from Merck. TEOS, PDMS and Nafton 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$_{7}$ClO$_{2}$, 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$_3$OH) used to dissolve triclosan in the stock solution and Methanol purchased from Merck. For the HPLC analyses acetonitrile was obtained by Riedel-de Haen. In all experimental studies ultra-high purity water used and produced by a NANOpure Diamond UV water purification system. 35% w/w H$_2$O$_2$ (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.

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$_2$O$_2$) 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).

\[
Y_{TCS} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2
\]

The H$_2$O$_2$ 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.

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$_2$O/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 min. 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 (R²), and concentrations ranges of TCS were between 0.001 mg/L and 10 mg/L.

| Table 1. The experimental points according to the box-behnken design method. |
|-----------------|-----------------|-----------------|-----------------|
| Run             | Actual Coded and Levels | X1, H₂O₂ (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 |

After photo-degradation experiments, iron leakage and the H₂O₂ 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 H₂O₂), 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 m²/g) (ASAP 2020 analyser) and zeta potential (-52 at pH 7) (oxford instruments) were also measured.

| Table 2. Energy-dispersive X-ray spectroscopy (EDX) results. |
|-----------------|-----------------|-----------------|-----------------|
| Element         | Spectrum 1      | Spectrum 2      | Spectrum 3      |
| Wt%             | Wt%             | Wt%             |
| O                | 45.9            | 51.0            | 50.0            |
| Si               | 28.0            | 25.1            | 24.9            |
| Fe               | 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             |

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 Nafton. After the photo-degradation experiments, iron leakage and the H₂O₂ 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 H₂O₂), correspondingly.

#### 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 H₂O₂/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 H₂O₂ 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 H₂O₂ 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 2. Finally, the model was 0.0271. X1 2

\[ \text{YTCS} = + 78.3195 - 4.19864X1 + 1.10934X2 \\
+ 3.96669X3 - 1.0561 \times 10^{-16}X2X3 \\
- 2.07076X1X3 - 2.21867X2X3 \\
+ 4.1071X1X2 - 5.73413X2X3 \\
- 5.44048X1X3 (R2 = 0.9204) \]  

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. X1-H2O2, X3-TCS, (X2-Catalyst)2, (X3·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 (YTCS) 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).

| 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 H2O2 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 H2O2. 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 H2O2 amount [16].

\[ H2O2 + OH \rightarrow H2O + H2O2 \]  

The H2O2 radicals generated during oxidation (Eq. 3) probably scavenging the active •OH radicals by further reactions (Eq.4):

\[ HO2• + OH \rightarrow H2O + O2 \]

H2O2. 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 H2O2 amount [16].

\[ H2O2 + OH \rightarrow H2O + H2O2 \]  

The HO2• radicals generated during oxidation (Eq. 3) probably scavenging the active •OH radicals by further reactions (Eq.4):

\[ HO2• + OH \rightarrow H2O + O2 \]
To see the effect of TCS concentration on removal efficiency, 
H$_2$O$_2$ addition, and the TCS addition changed between 34 mg/L
and 1700 mg/L, 0.1 mg/L and 10 mg/L in this set of analysis, 
correspondingly, whereas the catalyst was constant at 0.15 g. 
Variations of percent TCS removals with H$_2$O$_2$ 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 conc. 
at different H$_2$O$_2$ 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 | k$_1$ (min$^{-1}$) | R$^2$ |
|-----|------------------|------|
| H$_2$O$_2$ | 0.92 | 0.05 |

When using UV/H$_2$O$_2$ (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$_2$O$_2$. During Fenton process treatment efficiency was only 
31% (5 mg/L Fe$^{2+}$, 50 mg/L H$_2$O$_2$). For the photo-Fenton 
process, both extending the reaction time or addition of H$_2$O$_2$
do dosage caused to have a positive impact on degradation 
efficiency. In this work, H$_2$O$_2$ 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 bond 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$_2$O$_2$ 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$_2$O$_2$ 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 34 mg/L H$_2$O$_2$ concentration which was 
the minimum addition of H$_2$O$_2$. Therefore, no excess H$_2$O$_2$ 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$_2$O$_2$ 
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$_2$O$_2$ and minimum catalyst concentration. After 
Photo-oxidation of TCS could be destroyed to sucrose.

### 5 Author contribution statements

In the study, Neval Baycan contributed to the creating the idea, 
designing, obtaining resources and materials, collecting data, 
performing analyzes, literature review, writing and critical 
review.

### 6 Ethics committee approval and conflict of 
interest statement

There is no need to obtain permission from the ethics 
committee for the article prepared.

There is no conflict of interest with any person / institution in 
the article prepared.
7 References

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

[2] Çelebi H, Gök O. "Effect of triclosan exposure on mortality and behavioral changes of Poecilia reticulata and Danio rerio". Human and Ecological Risk Assessment: An International Journal, 24(5), 1327-1341, 2018.

[3] Bedoux G, Roig B, Thomas O, Dupont V, Le Bot B. "Occurrence and toxicity of antimicrobial triclosan and by-products in the environment". Environmental Science and Pollution Research, 19(4), 1044-1065, 2012.

[4] Zhang H, Yamada H, Tsuno H. "Removal of endocrine-disrupting chemicals during ozonation of municipal sewage with brominated byproducts control". Environmental Science and Technology, 42(9), 3375-3380, 2008.

[5] Munoz M, De Pedro ZM, Casas JA, Rodriguez JI. "Triclosan breakdown by Fenton-like oxidation". Chemical Engineering Journal, 198-199, 275-281, 2012.

[6] Son HS, Ko G, Zoh KD. "Kinetics and mechanism of photolysis and TiO2 photocatalysis of triclosan". Journal of Hazardous Materials, 166(2-3), 954-960, 2009.

[7] Yu JC, Kwong TY, Luo Q, Cai Z. "Photocatalytic oxidation of triclosan". Chemicals, 65(3), 390-399, 2006.

[8] Piccoli A, Fiori J, Andrisano V, Orioli M. "Determination of triclosan in personal health care products by liquid chromatography (HPLC)". Il Farmaco, 57(5), 369-372, 2002.

[9] Baycan N, Li Puma G. "Nanostructured catalysts for photo-oxidation of endocrine disrupting chemicals". Journal of Photochemistry and Photobiology A: Chemistry, 364, 274-281, 2018.

[10] Abbasi AF, Ahmad M, Wasm M. "Optimization of concrete mix proportioning using reduced factorial experimental technique". American Concrete Institute Materials Journal, 84(1), 55-63, 1987.

[11] Çatalkaya EÇ, Karg F. "Effects of operating parameters on advanced oxidation of diuron by the Fenton’s reagent: A statistical design approach". Chemosphere, 69(3), 485-492, 2007.

[12] Sandell EB. "Colorimetric Determination of Traces of Metals". 3rd ed. New York, USA, Interscience Publishers, 1959.

[13] Harris D. "Quantitative Chemical Analysis: Determination of iron with 1,10-Phenanthroline". 6th ed. New Jersey, USA, Prentice Hall, 2003.

[14] Gmurek M, Olak-Kucharzyk M, Ledakowicz S. "Photochemical decomposition of endocrine disrupting compounds-a review". Chemical Engineering Journal, 310(2), 437-456, 2017.

[15] Otriz de la Plata G, Alfano O, Cassano A. “The heterogeneous photo-Fenton reaction using goethite as catalyst”. Water Science & Technology, 61(12), 3109-3116, 2010.

[16] Asaithambi P, Sajjadi B, Abdul Aziz AR. “Ozone (O3) and sono (US) based advanced oxidation processes for the removal of color, COD, and determination of electrical energy from landfill leachate”. Separation and Purification Techniques, 172, 442-451, 2017.

[17] Luo Y, Guo W, Ngo HH, Nghiem LD, Hai F, Zhang J, Liang S, Wang XC. “A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment”. Science of the Total Environment, 473-474, 619-641, 2014.

[18] Latch DE, Packer JL, Arnold WA, McNeill K. “Photochemical conversion of triclosan to 2,8-dichlorodibenzo-p-dioxin in aqueous solution”. Journal of Photochemistry and Photobiology A: Chemistry, 158(1), 63-66, 2003.

[19] Son HS, Ko G, Zoh KD. "Kinetics and mechanism of photolysis and TiO2 photocatalysis of triclosan". Journal of Hazardous Materials, 166(2-3), 954- 960, 2009.

[20] Constantin LA, Nitoi I, Cristea NI, Constantin MA. “Possible degradation pathways of triclosan from aqueous systems via TiO2 assisted photocatalysis”. Journal of Industrial and Engineering Chemistry, 58, 155-162, 2018.