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DEGRADATION OF ETHYLPARABEN USING PHOTO-FENTON-LIKE OXIDATION OVER $BiFeO_3$

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ABSTRACT

The degradation of ethylparaben using photo-Fenton-like oxidation was investigated in the presence of a $BiFeO_3$ catalyst. Firstly, the catalyst was synthesized using the sol-gel method and characterized via BET and FT-IR analyzes and then, a parametric study was carried out in order to determine the optimum reaction conditions for the degradation of ethylparaben. In this context, the effects of catalyst loading, $[H_2O_2]_o$, pH, and temperature on the degradation were investigated. According to the results, the optimum reaction conditions were determined for a 5 ppm ethylparaben solution as 0.25 g/L catalyst loading, a pH of 3, and 2 mM $[H_2O_2]_o$ and a 97.7% degradation of ethylparaben was accomplished. Iron leaching at the optimum conditions was evaluated as 1.53 ppm and it is lower than the E.U. iron concentration limitation (2 ppm) in the water. The kinetic study was carried out at the optimum reaction conditions at three different temperatures (25, 35, and 45 °C). The degradation of ethylparaben using photo-Fenton-like oxidation fitted the first order reaction kinetic model. The reaction rate constants were determined as 0.041, 0.050, and 0.069 min^{-1} for 25, 35, and 45 °C, respectively. The activation energy was found as 20.4 kJ/mol.

Keywords: Ethylparaben, Perovskite, Photo-Fenton oxidation

1. INTRODUCTION

Micropollutants are defined as organic substances occurring in water at low concentrations. They consist of many synthetic substances such as active pharmaceutical ingredients, compounds with biocidal properties, food additives, cosmetics ingredients or detergents, and also naturally occurring substances such as hormones [1]. However, they may affect the biochemical processes in nature even at such low concentrations.

Parabens are one of the groups of micropollutants based on personal care products. Hence, micropollutants in the aquatic environment have recently become an environmental concern all over the world [2]. Parabens have been used for nearly 100 years for their anti-microbial and anti-fungal properties [3]. Although they have been widely used in the pharmaceutical, food, and cosmetic industries, their hazardous have only started to appear recently [3]. Ethylparaben is one of the most common paraben derivatives and it is widely used as an antioxidant and preservative, which is used in a wide variety of industries including: food production, personal care products, pharmaceutical, and cosmetics [4]. Due to the wide spread consumption, they were detected in the environment, so, they are threat to aquatic life, the environment, and human health [4]. Therefore, there is a need for them to be removed from wastewater.

Several methods have been developed and have been applied in water treatment technology. There are two main wastewater treatment methods, the Conventional Treatment Processes and the Advanced Oxidation Processes (AOPs). The conventional wastewater treatment processes consist of coagulation/flocculation followed by settling, filtration, and/or flotation and have been used since the early 20th century [5]. However, they are not efficient in the removal of toxic and bio-recalcitrant organic pollutants from wastewater [6]. On the other hand, AOPs have been widely used in the last 15

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years because of their versatility and large range of applicability. AOPs are one of the powerful clean technologies in reducing complex organic matter and can eliminate odor, color, and contaminants in organic complex wastewater [7]. The final products of AOPs are CO_2 and H_2O and it can be concluded that the final products are not hazardous for the environment and human health. Fenton oxidation is one of the most common AOPs. Fenton's reagent is a mixture of H_2O_2 and ferrous iron, which generates hydroxyl radicals. The main advantages of this procedure are technological simplicity, excellent results in pollutant removal, inexpensiveness, and safety [8]. The photo-Fenton oxidation is performed in the presence of an iron content catalyst, hydrogen peroxide, and UV-visible light. Photo-Fenton process could be applied in treating many industrial wastewaters, landfill leachate, dye house industry, quinoline (aromatic compound), organic compounds and phenolic wastes, trichloroethylene, and wastewater from the paper industry [9].

Perovskite type catalysts can be used as photocatalyst and have a general formula: ABO_3, where A is usually a rare earth cation and B a transition metal cation [10]. Perovskite type catalysts are preferred due to their effectiveness in catalytic oxidation and also, they provide high thermal stability, exchangeability of cations, and considerable activity [11]. In literature, bismuth ferrite nanoparticles show a high catalytic activity degradation of Reactive Black 5 [12] and $BiFeO_3$ is effective on the degradation of phenol and methyl tert-butyl ether (MTBE) [13].

In literature, there are many AOPs such as photocatalysis [6,14,15], Sonochemical oxidation [16] photo-sonochemical oxidation [17], ozonation [18], used in the treatment of parabens. In most of the studies, TiO_2 has attracted considerable attention as photocatalyst due to its wide band gap energy and good photocatalytic activity. According to the literature survey, the degradation of parabens has not been studied in the presence of perovskite type of catalysts, instead the parabens have been degraded in the presence of several catalysts including TiO_2 and Fe(III)-citrate complexes. For instance, Velegraki et al. (2014) and Lin et al. (2009) studied photocatalysis of methylparaben in the presence of TiO_2 catalyst under solar and UV light irradiation, respectively [14, 15]. Feng et al. (2014) studied on the catalytic degradation of parabens using Fe(III)-citrate complexes [6]. Consequently, the main contribution of this study to the literature is the usage of perovskite type catalysts for the degradation of ethylparaben. Performing the parametric and the kinetic studies in the presence of $BiFeO_3$ catalyst is the innovative object of this study.

In this study, ethylparaben was chosen as the target pollutant because of its hazardous effects on human and environmental health and photo-Fenton-like oxidation was selected to treat the ethylparaben because it is known as an effective process for the degradation of organic substances. Therefore, $BiFeO_3$ was chosen for removal of ethylparaben using photo-Fenton-like oxidation because many studies in literature have revealed that bismuth based perovskite type catalysts show an effectiveness for the degradation of organic substances. In this context, firstly, the catalyst was synthesized using the sol-gel method and then, the effect of the reaction parameters, pH, catalyst loading, initial hydrogen peroxide concentration, and temperature were investigated. The optimum conditions for the degradation of ethylparaben using photo-Fenton-like oxidation were determined. In order to investigate the amount of iron leaching into the treated solution at the optimum conditions was tested using Atomic Absorption Spectroscopy (AAS).

2. EXPERIMENTAL

2.1. Chemicals

High purity ($\geq$ 99) ethylparaben was purchased from Sigma-Aldrich and ethylparaben solution was prepared with ultrapure water obtained using a Millipore Waters Milli-Q water purification system. The perovskite-type catalyst ($BiFeO_3$) was synthesized using iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$

(Merck), bismuth (III) nitrate pentahydrate, $Bi(NO_3)_3.5H_2O$ (Sigma-Aldrich), and citric acid (Atabay) and ethylene glycol (Merck). The hydrogen peroxide was purchased from Merck (30% purity).

2.2. Catalyst Preparation and Characterization

The perovskite type catalyst ($BiFeO_3$), as powder, was prepared according to the procedure that was reported by Lee et al. [19]. The $BiFeO_3$ powder catalyst was synthesized using $Bi(NO_3)_3.5H_2O$ and $Fe(NO_3)_3.9H_2O$ using a stoichiometric ratio. The citric acid and also the ethylene glycol were added to the solution which included bismuth (III) nitrate pentahydrate and iron (III) nitrate nonahydrate in an excess amount. Then, the solution was heated until a gel formed. After that, the gel was dried at 150 °C for 6 hours and then was calcinated at 900 °C for 4 hours.

The synthesized catalyst is characterized via BET (Autosorb-6B) and specific surface area of the catalyst was measured after degassed at 350 °C for 3 hours. FT-IR analysis of the synthesized catalyst was carried out for 400-4000 cm^{-1} scanning range with a Perkin Elmer Spectrometer using KBr pellet technique. In this context, 1 mg of the sample with 100 mg of KBr are mixed and so, a typical pellet which is containing 1 wt% of sample was prepared.

2.3. Experimental Set-up and Procedure

All experiments were carried out in a glass reactor with a 250 ml volume and solar lamps (500 W x2) were located on the left and right side of the reactor.

A 25 ppm ethylparaben stock solution was prepared using ultrapure water (Millipore Milli-Q) and kept in the dark. The parametric study experiments were carried out with 5 ppm ethylparaben solutions diluted from the stock solution. The synthesized perovskite type catalysts was placed in the glass reactor and the two solar lamps were located to the left and right side of the reactor. During the experiments a magnetic stirrer was used for mixing the solution.

2.4. Experiments

Most of the researches on the degradation of parabens in the presence of several catalysts by AOPs are investigated at different initial concentrations in the range of 300 µg/L and 10 ppm. Hence, in this study, the initial concentration of ethylparaben is selected as 5 ppm and all experiments were performed using a 5 ppm ethylparaben solution. The parametric study for the photo-Fenton-like oxidation was carried out in the presence of the $BiFeO_3$ catalyst. In this context, the effect of the pH (3, 5, and 7), catalyst loading (none, 0.1, 0.25, and 0.5 g/L), initial H_2O_2 concentration (none, 1, 2, and 4 mM), and temperature (25, 35, and 45 °C) were investigated for the parametric study of the photo-Fenton-like oxidation. According to the results, the optimum reaction conditions were determined. Then, a kinetic study for the degradation of ethylparaben using the photo-Fenton-like oxidation was investigated at three different temperature values (25, 35, and 45 °C) under the optimum conditions. According to the results, the reaction rate constants and activation energy were determined.

2.5. Analysis

The ethylparaben concentration during the degradation experiments was determined using high performance liquid chromatography (HPLC) (Shimadzu Co.) and the instrument model: LC-20A (UV detector, C-18 column). The column temperature was 40 °C, the wavelength of the detector was 254 nm, a mobile phase consisting of acetonitrile and water (40:60 v/v) was used, and the mobile phase was 1 mL/min.

An iron leaching test was performed by atomic absorption spectroscopy (AAS) for all of the catalyst screening and parametric study experiments.

3. RESULTS AND DISCUSSION

3.1. Characterization

The synthesized catalyst is characterized via BET and FT-IR analyzes. According to the BET analysis result, the BJH method cumulative adsorption surface area is determined as 4.37 m^2/g. Rusevova et al. synthesized $BiFeO_3$ catalyst and its surface area is determined as 3.2 m^2/g [13]. Hence, synthesized catalyst in this study has higher surface area with respect to the mentioned study. So that, it can be concluded that this synthesis method gives an advantage in order to obtain large surface areas.

FT-IR spectrum in the range of 400-4000 cm^{-1} for the synthesized catalyst is given in Figure 1. Perovskite type structures must have Fe-O stretching bond characteristically [20, 21] and this bond gives a sharp peak around 550 nm. The synthesized catalyst has the metal-oxygen bonds as expected; so that it can be proved that the synthesized catalyst has perovskite structure.

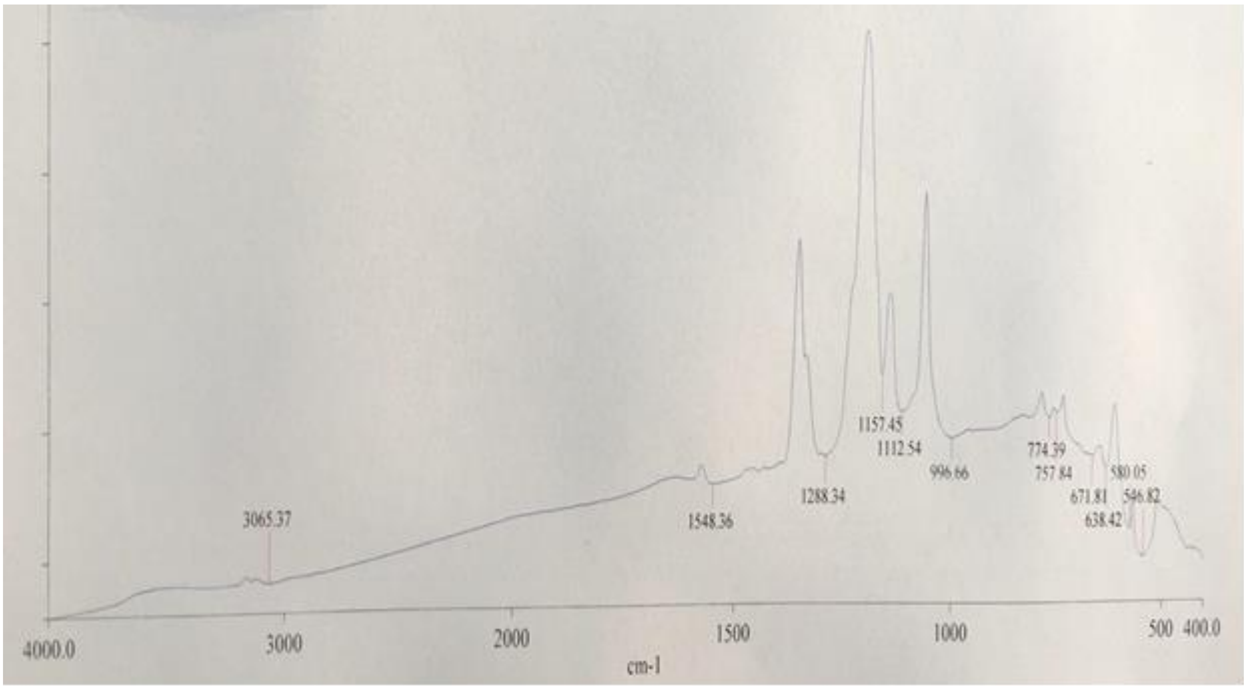

Figure 1. FTIR spectrum of $BiFeO_3$ catalyst

3.2. Experimental Results

The parametric study for the degradation of ethylparaben was performed in the presence of a $BiFeO_3$ catalyst. In the context of the parametric study, the effect of pH (3, 5, and 7), catalyst loading (none, 0.1, 0.25, and 0.5 g/L), $[H_2O_2]_o$ (none, 1, 2, and 4 mM), and also temperature (25, 35, and 45 °C) were investigated. Firstly, the pH effect was investigated and the results are illustrated in Figure 2.

Almost the same and rather low degradation efficiency is observed at a pH 5 and pH 7 during the whole reaction time because hydroxide, ($Fe(OH_3)$), forms by precipitation of iron at high pH values and hydrogen peroxide degrades into water and oxygen due to this form of iron [22]. Due to this decomposition, less hydroxyl radicals form and weak degradation efficiency is achieved. On the other hand, the higher degradation efficiency was observed at a pH 3. According to the results of the pH effect experiments, it can be concluded that weak acidic and neutral pH values do not show considerable effect on the degradation of ethylparaben. The pH value effects the formation of hydroxyl radicals and degradation efficiency and in the photo-Fenton-like processes, the maximum degradation efficiency is obtained around a pH 3 [23]. For example, Petala A. et al. carried out a study on the degradation of ethylparaben over an N-TiO_2 catalyst in the presence of solar light and this study showed that the highest degradation efficiency was performed at the acidic medium and there was no considerable degradation at the neutral and alkaline medium [24]. Hence, it can be concluded that the results obtained by this study are in consistent with the literature. So, due to the results of the pH effect experiments, the optimum pH value was decided as pH 3. Then, the catalyst loading effect is investigated at a pH 3 and the results are given in Figure 3.

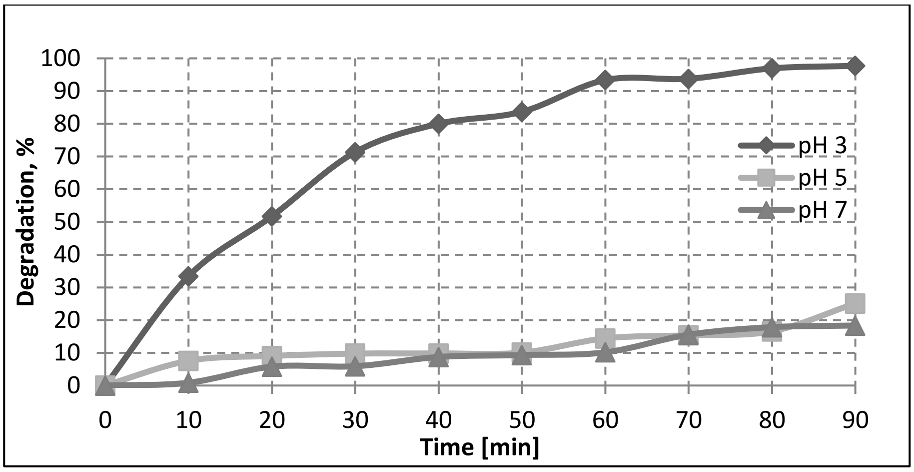

Figure 1. pH effect on the photo-Fenton-like oxidation

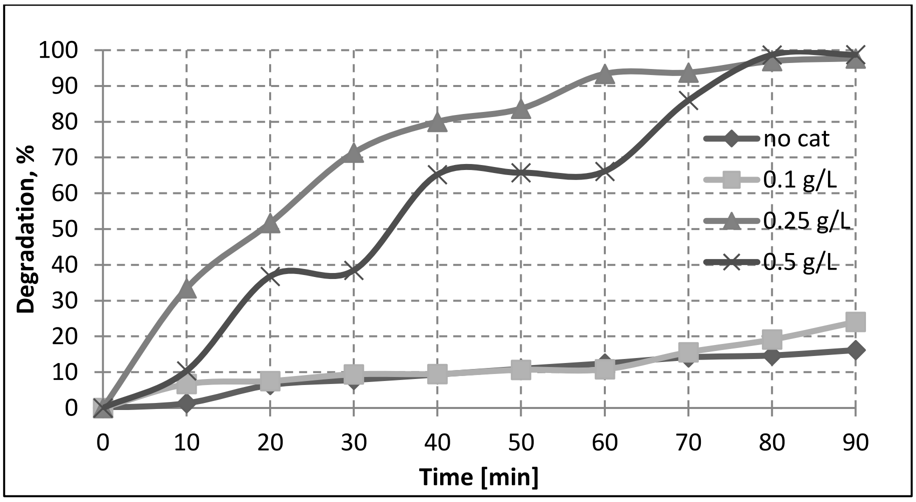

Figure 2. Catalyst loading effect on photo-Fenton-like oxidation

When the catalyst loading increases, the Fe^{2+} concentration increases and thus, the formation of $Fe(OH)^{2+}$ increases [22]. Due to this, the degradation efficiency increases. However, the catalyst loading should be optimized, because, if the catalyst is used excessively, the scavenging effect may be observed and it may cause a decrease in the degradation efficiency. In this context, firstly, the absence of the catalyst was tested and the lowest and slowest degradation (almost 16%) was observed. Then, 0.1 g/L catalyst loading was tested and almost the same degradation efficiency as the absence of the catalyst was observed with this catalyst loading during the whole reaction time. After that, 0.25 g/L and 0.5 g/L catalyst loadings were tested. According to the results, the degradation rate increases continuously using 0.25 g/L and 0.5 g/L catalyst loading but the degradation rate with 0.5 g/L catalyst loading was observed as being slower than the 0.25 g/L catalyst loading. So, it can be deduced that the scavenging effect was observed using 0.5 g/L catalyst loading and hence, the optimum catalyst loading was be chosen as 0.25 g/L. After that, the effect of $[H_2O_2]_o$ was investigated using 0.25 g/L catalyst loading at pH 3. During the reaction, the H_2O_2 degraded into hydroxyl radicals in the presence of the catalyst and due to the formation of hydroxyl radicals, the degradation efficiency enhanced. However, an excess amount of it can lead to a scavenging effect so that the needed amount has to be optimized. In this context, the experiments were carried out with 1, 2, and 4 mM $[H_2O_2]_o$ and also the absence of H_2O_2 was tested and the results are illustrated in Figure 4.

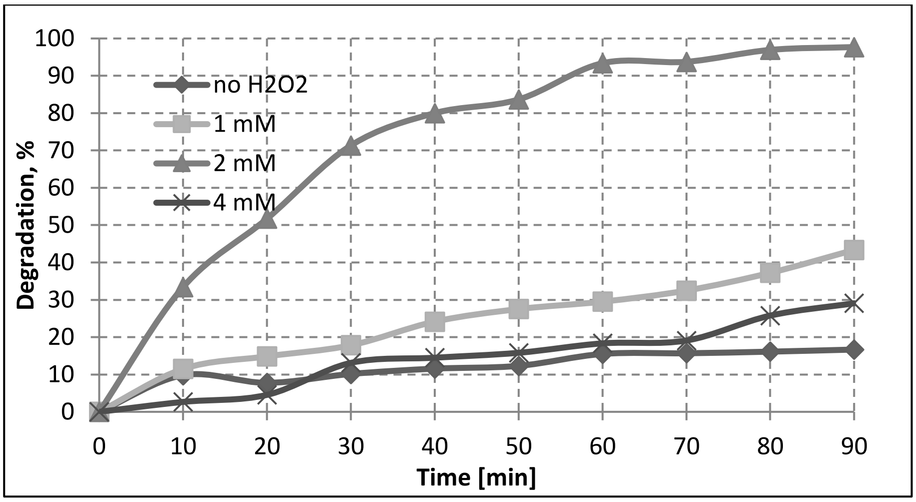

Figure 3. $[H_2O_2]_o$ effect on photo-Fenton-like oxidation

According to the results, the slowest and lowest degradation efficiency was observed in the absence of hydrogen peroxide and almost the same degradation efficiency was obtained in the presence of 4 mM $[H_2O_2]_o$. While the degradation rate was evaluated as almost 44% in the presence of 1 mM $[H_2O_2]_o$, it was evaluated as approximately 98% using 2 mM $[H_2O_2]_o$. Consequently, the highest and fastest degradation efficiency was observed with 2 mM $[H_2O_2]_o$. So, the low degradation efficiency for 4 mM $[H_2O_2]_o$ implies that the scavenging effect was observed. In light of the results, the optimum $[H_2O_2]_o$ was chosen as 2 mM. Consequently, according to the results of the parametric study for photo-Fenton-like oxidation, the optimum reaction conditions for 5 ppm were determined as pH 3, 0.25 g/L catalyst loading, and 2 mM $[H_2O_2]_o$ and the degradation efficiency was evaluated as almost 98% at 25 °C.

3.3. Kinetic Study

The kinetic study was carried out at three different temperature values, 25, 35, and 45 °C using the solar light for 90 minutes at the optimum reaction conditions (pH 3, 0.25 g/L catalyst loading, and 2 mM $[H_2O_2]_o$) as determined by the parametric study and the results are illustrated in Figure 5.

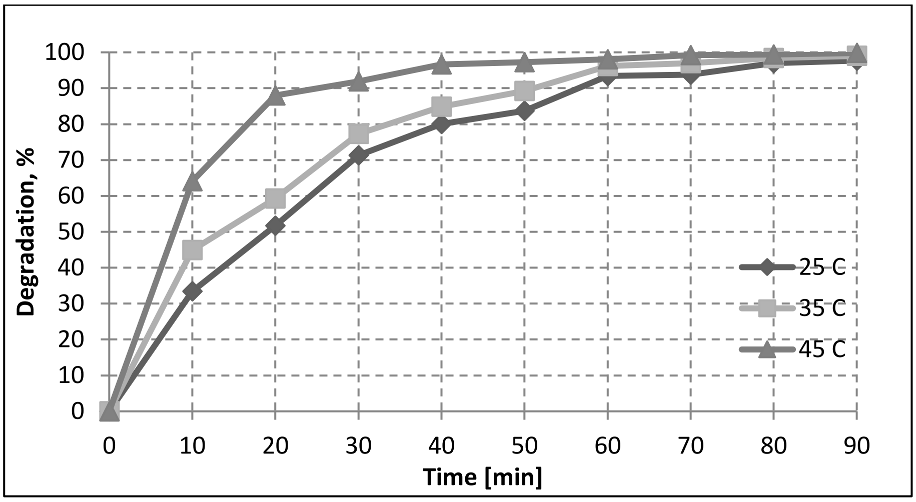

Figure 4. Temperature effect on photo-Fenton-like oxidation

In this context, the appropriate reaction kinetic model for the degradation of ethylparaben using photo-Fenton-like oxidation was described and the reaction rate constants and the activation energy for this process were determined. Two assumptions were made in order to determine the reaction order. The first one is that the heterogeneous reactions follow power law mechanism, and the second is that the surface reaction is dependent on just the ethylparaben concentration.

The first order kinetic expression was employed:

$$-r_A = -\frac{dC_A}{dt} = kC_A^m \qquad \text{Eq. (1)}$$

where, m=1

The power law model was tested for m=1 with the data collected from the experiments, using the integrated form of the equation.

$$ln\frac{C_{A_o}}{C_A} = k_1 t \qquad \text{Eq. (2)}$$

where; C_A is the concentration of ethylparaben, k_1 represents the apparent kinetic rate constants of the first-order reaction kinetics, and t is the reaction time.

The linearized first order kinetic is shown in Figure 6. A regression analysis based on the first order reaction kinetics for the degradation of ethylparaben was conducted. It was concluded that the regression coefficients (R^2) based on the first order reaction kinetics was a satisfied fit at the optimum reaction conditions for the different temperatures. The reaction rate constants were determined using the ln(C_A/C_{Ao}) vs. time graph.

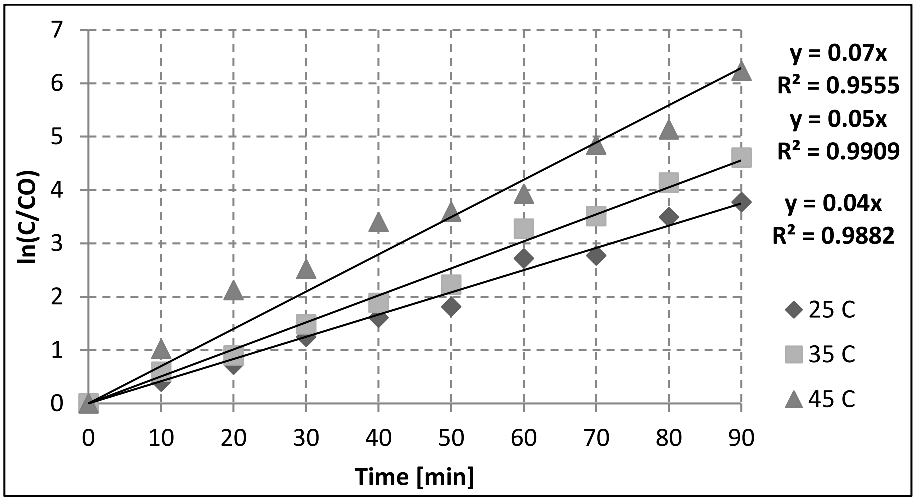

Figure 5. Linearized first order kinetic plots

The first order reaction rate constants were determined as 0.04, 0.05, and 0.07 min^{-1} for 25, 35, and 45 °C, respectively. According to the first order kinetic rate constants at the different temperatures, the activation energy E, for the degradation of ethylparaben using the photo-Fenton-like oxidation process was computed using the Arrhenius equation given in Eq. (3).

$$k = Ae^{\frac{-E}{RT}} \qquad \text{Eq. (3)}$$

where A is the pre-exponential (or frequency) factor, E is the activation energy (J mol^{-1}), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), and T is the reaction absolute temperature (K).

The Arrhenius plot of lnk versus 1/T is shown in Figure 7 and the activation energy was determined as approximately 20 kJ/mol.

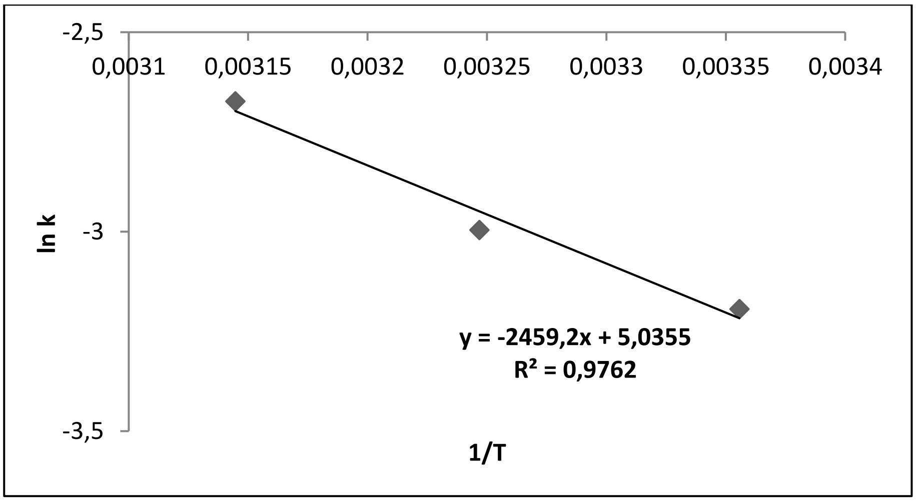

Figure 6. lnk vs 1/T

3.4. Comparison with Literature

Some researches on the degradation of different types of parabens by advanced oxidation processes in the presence of different catalysts are listed in Table 1 in order to compare the results of this study.

Different kinds of parabens such as benzylparaben and methylparaben are degraded using TiO_2 catalyst in various studies. For instance, Lin Y. (2009) and Velegraki T. (2014) studied on the degradation methylparaben of methylparaben in the presence of TiO_2 [14, 15]. According to the results, 80 % and 42 % mineralization were observed in the studies, respectively [14, 15]. Additionally, Lin Y (2011) studied on the degradation of benzylparaben and 90 % of TOC was obtained after 6 hours [25]. Feng X. et al. (2014) studied on the degradation of ethylparaben, methylparaben, butylparaben and propylparaben and according to the results, almost complete degradation was observed in the presence of Fe(III)-citrate complexes [6]. Petala et al. carried out a study on the degradation of ethylparaben by photocatalytic degradation in the presence of N-TiO_2 and according to the results, 98 % of ethylparaben (300 μg/L initial concentration) is degraded using 750 mg/L N-TiO_2 catalyst [24]. In this study, almost complete degradation was observed for 5 ppm ethylparaben solution using lower amount of $BiFeO_3$ than the amount of N-TiO_2 catalyst used in literature. It can be implied that even using low amount of perovskite type catalysts are more effective on the degradation of ethylparaben.

Consequently, the main difference of this study with the literature is that the perovskite type catalysts have not been used for the degradation of ethylparaben. And thus, usage of perovskite type catalyst provides some advantages such as less catalyst amount requirement and less reaction time for high degradation efficiencies.

Table 1. Literature review

No.	*Reference*	*Target Pollutant*	*Catalyst*	*Method*	*Optimum Conditions*	*Kinetic Model and Kinetic Rate Constants*	*% TOC Removal, % Degradation*
1	Petala A. et al., 2015	Ethylparaben	N- TiO_2	Photocatalytic oxidation	Catalyst calcination temperature, 600 °C catalyst loading, 750 mg/L $[C_{EP}]_0$=300 μg/L pH 6.5 $[H_2O_2]_0$=50 mg/L photon flux (solar), $1.3x10^{-4}$ E/(m^2s)	Pseudo-first order k_{app}~0.09 min^{-1}	98 % degradation in the first usage of N-TiO_2 (81 % degradation in the fifth usage of N-TiO_2)
2	Feng X. et al., 2014	Methylparaben (MP), Ethylparaben, Butylparaben and Propylparaben	Fe (III)-citrate complexes	Photocatalytic oxidation	$[C_{MP}]_0$=20 μM $[Fe(III)]_0/[citrate]_0$= 10/150 (μM) pH 6 simulated sunlight 1000 μM oxalate	Pseudo-first order MP - Fe(III)-citrate at pH 6 k_{obs}~0.03 min^{-1}	Almost completely degradation
3	Lin Y. et al., 2011	Benzylparaben (BP)	TiO_2	Photocatalytic oxidation	$[C_{BP}]_0$=10 ppm 2.5 g/L catalyst loading $[DO]_0$= 9 mg/L pH 7 light flux, $5.8x10^{15}$ photo-photonss^{-1}cm^{-2}	Pseudo-first order k_{app}=0.017 min^{-1}	approximately 90 % TOC after 6 hours
4	Lin Y. et al., 2009	Methylparaben (MP)	TiO_2	Photocatalytic oxidation	$[C_{MP}]_0$=10 ppm 2.5 g/L catalyst loading $[DO]_0$=18 mg/L pH 9 light flux, $5.8x10^{15}$ photo-photonss^{-1}cm^{-2}	Pseudo-first order k_{app}=0.01809 min^{-1}	80 % mineralization after 6 hours
5	Velegraki T. et al., 2014	Methylparaben (MP)	TiO_2	Photocatalytic oxidation	$[C_{MP}]_0$=0.001 ppm 0.5 g/L catalyst loading pH 5.2 150 W xenon ozone-free lamp	Pseudo-first order k_{app}=0.0595min^{-1}	42 % mineralization
6	This study	Ethylparaben (EP)	$BiFeO_3$	Heterogeneous photo-Fenton-like oxidation	$[C_{EP}]_0$=5 ppm 0.25 g/L catalyst loading pH 3 $[H_2O_2]_o$=2 mM	First order k=0.04 min^{-1} at 25 °C k=0.05 min^{-1} at 35 °C k=0.07 min^{-1} at 45 °C	~98 % degradation after 1.5 hours

4. CONCLUSION

In this study, the degradation of ethylparaben using the photo-Fenton-like oxidation was investigated in the presence of a $BiFeO_3$ perovskite type catalyst. Firstly, the catalyst was synthesized using the sol-gel method and characterized via BET and FT-IR analyzes. The parameters affecting the AOPs such as pH, catalyst loading, initial concentration of the hydrogen peroxide, and temperature were investigated in order to optimize the reaction conditions during the parametric study. According to the results, the optimum reaction conditions were determined as 0.25 g/L catalyst ($BiFeO_3$) loading, a pH 3 and 2 mM $[H_2O_2]_o$ resulting in an 98 % degradation of ethylparaben being achieved. Consequently, the kinetic study was carried out at the optimum reaction conditions for the three different temperatures (25, 35, and 45 °C). The degradation of ethylparaben using photo-Fenton-like oxidation was described using the first order reaction kinetic model. According to the results, the reaction rate constants were evaluated as 0.04, 0.05, and 0.07 min^{-1} for 25, 35, and 45 °C, respectively and the activation energy was found as approximately 20 kJ/mol. Iron leaching at the optimum reaction conditions was evaluated as 1.534 ppm and which is below the E.U. iron concentration limitation of 2 ppm in water.

REFERENCES

[1] Federal Office for the Environment FOEN, Micropollutants in municipal wastewater, Bern, 2012.

[2] Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, 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. Sci Total Environ 2014; 473–474:619–641.

[3] Błędzka D, Gromadzińska J, Wąsowicz W. Parabens. From environmental studies to human health. Environ Int 2014; 67: 27-42.

[4] Frontistis Z, Antonopouou M, Venieri D, Dailianis S, Konstantinou I, Mantzavinos D. Solar photocatalytic decomposition of ethyl paraben in zinc oxide suspensions. Cat Today 2016; (in press)

[5] Zemmouri H, Drouichea M, Sayeh A, Lounici H, Mameri N. Coagulation Flocculation Test of Keddara's Water Dam Using Chitosan and Sulfate Aluminium. Procedia Eng 2012; 33:254-260.

[6] Feng X, Chen Y, Fang Y, Wang X, Wang Z, Tao T, Zuo Y. Photodegradation of parabens by Fe(III)-citrate complexes at circumneutral pH: Matrix effect and reaction mechanism. Sci Total Environ 2014; 472: 130–136.

[7] Enjarlis E. Application of Coagulation-advanced Oxidation Process by O_3/GAC in the Fan Belt. Wastewater Treatment APCBEE Procedia 2014; 9:145-150.

[8] Domínguez JR, Mušoz MJ, Palo P, González T, Peres JA, Cuerda-Correa EM. Fenton advanced oxidation of emerging pollutants: parabens. Int J Energ Environ Eng 2014; 5:89.

[9] Sevimli MF, Deliktaş E, Şahinkaya S, Güçlü B. A comparative study for treatment of white liquor by different applications of Fenton process. Arab J Chem 2014; 7, 6:1116-1123.

[10] Orge CA, Órfão JJM, Pereira MFR, Barbero BP, Cadús LE. Lanthanum-based perovskites as catalysts for the ozonation of selected organic compounds. Appl Catal B-Environ 2013; 140–141:426– 432.

[11] Grabowska E. Selected perovskite oxides: Characterization, preparation and photocatalytic properties-A review. Appl Catal B-Environ 2016; 186:97–126.

[12] Soltani T, Entezari MH. Solar photocatalytic degradation of RB5 by ferrite bismuth nanoparticles synthesized via ultrasound. Ultrason Sonochem 2013; 20:1245–1253.

[13] Rusevova K, Köferstein R, Rosell M, Richnow MM, Kopinke F, Georgi A. $LaFeO_3$ and $BiFeO_3$ perovskites as nanocatalysts for contaminant degradation in heterogeneous Fenton-like reactions. Chem Eng J 2014; 239:322–331.

[14] Lin Y, Ferronato C, Deng N, Wu F, Chovelon J. Photocatalytic degradation of methylparaben by TiO_2 : Multivariable experimental design and mechanism. Appl Catal B-Environ 2009; 88:32–41.

[15] Velegraki T, Hapeshi E, Fatta-Kassinos D, Poulios I. Solar induced heterogeneous photocatalytical degradation of methylparaben. Appl Catal B-Environ 2015; 178:2-11.

[16] Sasi S, Rayaroth MP, Devadasan D, Aravind UK, Aravindakumar CT. Influence of inorganic ions and selected emerging contaminants onthe degradation of Methylparaben: A sonochemical approach. J Hazard Mater 2015; 300:202–209.

[17] Daghrir R, Dimboukou-Mpira A, Seyhi, Drogui P. Photosonochemical degradation of butyl-paraben: Optimization, toxicity and kinetic studies, Sci Total Environ 2014; 490:223–234.

[18] Tay KS, Rahman NA, Abas MRB. Ozonation of parabens in aqueous solution: Kinetics and mechanism of degradation. Chemosphere 2010; 81:1446–1453.

[19] Lee MJ, Jun JH, Jung JS, Kim YR, Lee SH. Catalytic Activities of Perovskite-type $LaBO_3$ (B=Fe, Co, Ni) Oxides for Partial Oxidation of Methane. B Kor Chem Soc 2005; 26, 10:1591–1596.

[20] Jiang J, Zou J, Anjum MN, Yan J, Huang L, Zhang Y, Chen J. Synthesis and characterization of wafer-like $BiFeO_3$ with efficient catalytic activity. Solid State Sci 2011; 13:1779-1785.

[21] Wang J, Wei Y, Zhang J, Ji L, Huang Y, Chen Z. Synthesis of pure-phase $BiFeO_3$ nanopowder by nitric acid-assisted gel. Mater Lett 2014; 124:242–244.

[22] Sreeja PH, Sosamony KJ. A Comparative Study of Homogeneous and Heterogeneous Photo-fenton Process for Textile Wastewater Treatment. Procedia Technol 2016; 24:217 – 223.

[23] Ebrahiem EE, Al-Maghrabi MN, Mobarki AR. Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology. Arab J Sci Eng 2013; http://dx.doi.org/10.1016/j.arabjc.2013.06.012

[24] Petala A, Frontistis Z, Antonopoulou M, Konstantinou I, Kondarides DI, Mantzavinos D. Kinetics of ethyl paraben degradation by simulated solar radiation in the presence of N-doped TiO_2 catalysts. Water Res 2015; 81:157-166.

[25] Lin Y, Ferronato C, Deng N, Chovelon J. Study of benzylparaben photocatalytic degradation by TiO_2. Appl Catal B-Environ 2011; 104(3-4):353–360.