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Diclofenac Degradation by Ozone-Based Oxidation Processes: PROMETHEE Method, Kinetic and Cost-Effectiveness Study

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ABSTRACT

In this study, the treatment of diclofenac (DCF), which is a pain reliever belonging to non-steroid anti-inflammatory drug group, was investigated by ozone-based oxidation processes. In experiments; pH (6–7) and 10 min reaction times were kept constant and the effects of different initial concentrations (5 mg/L, 10 mg/L and 20 mg/L), ozone doses (5 and 8 ppm), power of UV lamps (16 W and 32 W) and catalysts (0.1 g ZnO, In_2O_3, CuO and Fe_2O_3) were studied. Initially, studies were performed for the photocatalytic ozone oxidation process to determine which catalyst was more effective in DCF treatment, and study results were evaluated according to the PROMETHEE decision-making method. As a result of the evaluation based on DCF removal, energy consumption and cost parameters, ZnO was chosen as the best catalyst. In the following catalytic and photocatalytic ozone oxidation processes, studies continued with ZnO catalyst. In the second step of the study, the effect of DCF initial concentration, ozone dose and UV light intensity was determined. According to the results of the study, max degradation was obtained 100% in O_3/UV/ZnO and O_3/UV oxidation processes, at 5 mg/L DCF concentration, 5 ppm ozone dose, 16 W UV lamp and at 4- and 5-min reaction time, respectively. The highest total organic carbon (TOC) removal was obtained 76% in O_3/UV/ZnO process. O_3, O_3/UV and O_3/ZnO oxidation processes for 5 mg/L DCF were found to be better suited to pseudo-first-order kinetics rate model.

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Cost Evaluation; Diclofenac; Kinetic; Ozone Oxidation; Photocatalytic Ozonation; PROMETHEE Method; Zinc Oxide

Introduction

Diclofenac (DCF) is one of the leading pollutants of endocrine-disrupting chemicals. DCF is a widely used class of non-steroidal anti-inflammatory drugs (NSAIDs) (Barbieri et al. 2012; Zhang, Geißen, and Gal 2008). DCF is a toxic pollutant (Buser, Poiger, and Müller 1998; Cooper and Song 2012; Lonappan et al. 2016; Schwaiger et al. 2004; Yu et al. 2013). DCF cannot be adequately treated in wastewater treatment plants and poses problems in the ecosystem (Zhang, Geißen, and Gal 2008). Thus, DCF pollutants are encountered in the effluent, surface water, drinking water and groundwater of treatment plants (Heberer 2002; Rabiet et al. 2006; Siemens et al. 2008; Wu et al. 2009). Due to the low removal efficiency of DCF in conventional wastewater treatment plants, new treatment methods need to be investigated. During the DCF degradation reaction, major decomposition products such as chloro derivatives and carbazole groups were produced (Chen et al. 2016; Hama Aziz et al. 2017; Yu et al. 2013; Zhang et al. 2017). Carbazole, which is a very stable colored intermediate product, was identified in the literature as the main by-product of DCF photolysis (Kanakaraju et al. 2014; Keen et al. 2013; Musa and Eriksson 2009; Yu et al. 2013). It had been determined by literature studies that Advanced Oxidation Processes were more suitable for removing toxic effects of DCF (Cooper and Song 2012; Hama Aziz et al. 2017; Yu et al. 2013). As a result of DCF degradation, no toxic by-products were detected in photocatalytic ozonation and photocatalytic oxidation systems (Aguinaco et al. 2012; Moreira et al. 2015).

There are several studies on the treatment of DCF. These are such as; fenton and photo-fenton (Manu 2012; Pérez-Estrada et al. 2005), fenton type photocatalyst (Arzate-Salgado et al. 2016), UV/H_2O_2 and ozone (Vogna et al. 2004), ozone and activated carbon (Beltrán et al. 2009a), activated carbon ozonation (Beltrán et al. 2009b), heterogeneous catalytic oxidation (Hofmann et al. 2007), sonolysis and ozonation (Naddeo et al. 2009), catalytic ozone (Chen et al. 2016), photocatalytic ozone (Aguinaco et al. 2012; Beltrán, Aguinaco, and García-Araya 2010) and photocatalytic oxidation (Cheng et al. 2015; Cordero-García et al. 2016; Zhang, Zhou, and Deng 2016; Zhang et al. 2017). TiO_2 (Aguinaco et al. 2012; Beltrán, Aguinaco,

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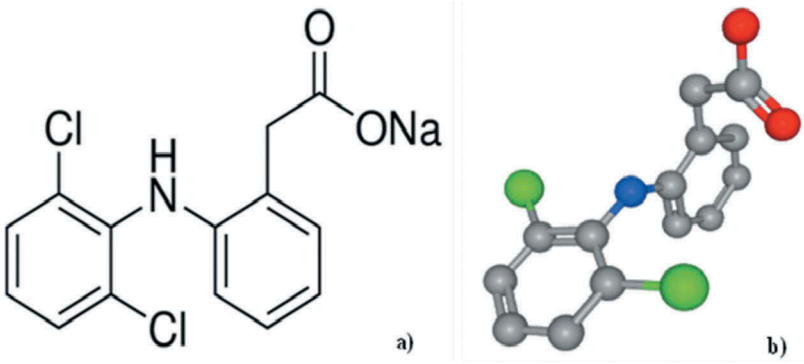

Figure 1. (a) Molecular structure of DCF sodium salt, (b) chemical structure of the parent model (https://pubchem.ncbi.nlm.nih.gov).

and García-Araya 2010; Calza et al. 2006), TiO_2- based zeolite catalyst (Salaeh et al. 2016), WO_3/TiO_2 oxide (Cordero-García et al. 2016), Ag-doped composites (Zhang, Zhou, and Deng 2016) and AgI/g-C_3N_4 composites (Zhang et al. 2017) were used as catalysts in the studies.

Advanced oxidation processes (AOPs) are chemical, photochemical and hydrothermal purification processes based on the formation of hydroxyl radicals ($OH^{\bullet}$) with high oxidation potential. These processes can convert without discrimination of toxic pollutants and recalcitrant organic substances into the final products such as CO_2 and H_2O (Buxton et al. 1988 ; Esplugas, Yue, and Pervez 1994; Legrini, Oliveros, and Braun 1993; Masten and Davies 1994). O_3, O_3/UV, O_3/ZnO and O_3/UV/ZnO processes are one of the AOPs based on ozonation. Hydrogen radicals are formed by the degradation of ozone and these processes are highly effective methods for the oxidation of toxic and refractory compounds.

In this study, the degradation of diclofenac with ozone-based Advanced Oxidation Processes and the effectiveness of catalysts (ZnO, In_2O_3, CuO and Fe_2O_3) were proposed and evaluated by using PROMETHEE decision-making method. DCF concentrations were determined by High-Performance Liquid Chromatography (HPLC) analysis and kinetic and cost-effectiveness were determined using these results and mineralization of DCF was examined by TOC analysis.

Material and methods

Materials

Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$) (2-[(2,6-dichlorophenyl)amino]-benzeneacetic acid sodium salt) was purchased from Sigma Aldrich. DCF aqueous solutions were prepared with pure water in the laboratory. DCF molecular structure is given in Figure 1 (https://pubchem.ncbi.nlm.nih.gov). ZnO, In_2O_3, CuO and Fe_2O_3 nanopowders (Sigma Aldrich) were used as catalysts.

Experimental system and degradation procedure

The experimental system consisted of an ozone generator, reaction tank and UV lamps. The ozone gas was produced by an ozone generator by using oxygen in the air and the gas was fed into the reactor with a diffuser. For the UV light source, low-pressure mercury lamps (4 × 8 W UVC type) were fitted in the reaction tank. The reaction tank was made of a 2 L volume quartz batch reactor. The effluent ozone gas from the reactor was bubbled in KI solution. The outline of the reactor used was indicated in our previous study (Arslan et al. 2018).

The experiments were performed with different initial concentrations of 1 L synthetic DCF solutions (5–10–20 mg/L). ZnO, In_2O_3, CuO and Fe_2O_3 used as catalysts and 0.1 g amount of catalyst was added into the reactor. Ozone dose was adjusted to be 5 ppm to 8 ppm from the generator and UV lamps turned on. The experimental results were evaluated by HPLC analyses for a reaction time of 10 min determined by preliminary studies. Mineralization was followed up to the 90th min by TOC analysis.

Analytical methods

Diclofenac concentrations were measured by using High-Performance Liquid Chromatography (HPLC) (Shimadzu LC-20AD) equipped with a UV detector at a wavelength of 280 nm. The column selected was a reversed-phase RP-18 endcapped (5 µm) Hibar ® RT 150-4.6 type. Mobile phase was a mixture of 50% acetonitrile and 50% ultrapure water which was composed of 0.05% acetic acid and used as isocratic flow mode. The injection flow rate and injection volume were 1.0 mL/min and 50 µL, respectively. The HPLC method was validated based on the International

Conference on Harmonization (ICH) requirements with validation parameters of accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ). The accuracy of the developed method, successive analysis for six different concentrations (1–2.5–5–10–20–30 mg/L) of standard DCF solution was determined using the developed method. The recovery was found within 90–110% and the results were within an acceptable range. Precision of the method was stated as the relative standard deviation (% RSD). It was determined by six replicate analyses at a concentration of 10 µg/mL of standard DCF solution using the developed method. The precision of the % RSD was smaller than 2% and the results were acceptable. The LOD and LOQ values were calculated based on standard deviation. The LOD and LOQ were found to be 0.7 µg/mL and 5.5 µg/mL, respectively. All results were within an acceptable range and this confirmed that the method was as accurate as for experimental evaluation. In the literature, similar results were obtained in the method validation studies for DCF (Ahmed et al. 2020; Alquadeib 2019; Goyal and Jain 2007; Heda et al. 2010).

Mineralization of DCF was determined by TOC analyses. TOC measurements were performed using Shimadzu brand TOC-L model analyzer.

Ozone-based oxidation reaction mechanisms

In an ozone process; organic pollutants are oxidized by direct reaction with molecular ozone or by indirect reactions with OH produced by the decomposition of ozone under alkaline conditions (Broséus et al. 2009). Ozone dissolves in water and forms a series of free radical chain reactions. Ozone takes place in chain reactions involving the steps of initiation, decomposition, propagation-proliferation and termination as follows (Umar et al. 2013):

$$\mathbf{O_3 + OH^- \rightarrow HO_2^- + O_2^{\cdot -}} \quad (2.1)$$

$$\mathbf{HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot -}} \quad (2.2)$$

$$\mathbf{O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2} \quad (2.3)$$

$$\mathbf{O_3^{\cdot -} + H^+ \rightarrow HO_3^{\cdot}} \quad (2.4)$$

$$\mathbf{HO_3^{\cdot} \rightarrow O_3^{\cdot -} + H^+} \quad (2.5)$$

$$\mathbf{HO_3^{\cdot} \rightarrow OH^{\cdot} + O_2} \quad (2.6)$$

$$\mathbf{O_3 + OH^{\cdot} \rightarrow HO_4^{\cdot}} \quad (2.7)$$

$$\mathbf{HO_4^{\cdot} \rightarrow HO_2^{\cdot} + O_2} \quad (2.8)$$

The O_3/UV (photolytic ozone) process is the use of UVphotons to activate ozone molecules. At the end of this process, hydroxyl radicals ($OH^{\cdot}$) generate (Zhou and Smith 2002). The realized process using ozone and UV starts with photolysis of ozone. Photolysis of ozone in water causes the formation of hydrogen peroxide (H_2O_2).

The reactions that occur during this process are given below;

$$\mathbf{O_3 + H_2O} + h\nu \rightarrow \mathbf{H_2O_2 + O_2} \quad (2.9)$$

$$\mathbf{H_2O_2} + h\nu \rightarrow \mathbf{2OH^{\cdot}} \quad (2.10)$$

$$\mathbf{2O_3 + H_2O_2 \rightarrow 2OH^{\cdot} + 3O_2} \quad (2.11)$$

In the catalytic ozonation process; catalysts are provided to accelerate the reaction. The reactions that occur during this process are as follows (Bashiri and Rafiee 2016);

$$\mathbf{O_{3(aq)} + ZnO \leftrightarrow O_{3(ad)}} \quad (2.12)$$

$$\mathbf{O_{3(ad)} \leftrightarrow O^{\cdot}_{(ad)} + O_{2(aq)}} \quad (2.13)$$

$$\mathbf{O^{\cdot}_{(ad)} + H_2O_{(s)} \rightarrow H_2O_{2(ad)}} \quad (2.14)$$

$$\mathbf{H_2O_{2(ad)} \rightarrow 2OH^{\cdot}_{(ad)} + ZnO} \quad (2.15)$$

In photocatalytic ozone processes, it is aimed to determine the effect of catalyst on treatment efficiency combined with UV light effect.

In this study, nanopowder ZnO was used as a catalyst. Therefore, the reaction equations for the O_3/UV/ZnO processes are given below (Malakootian et al. 2019);

$$\mathbf{ZnO} + h\nu \rightarrow \mathbf{e^- + h^+} \quad (2.16)$$

$$\mathbf{O_3 + e^- \rightarrow O_3^{\cdot -}} \quad (2.17)$$

$$\mathbf{O_3^{\cdot -} + H^+ \rightarrow O_2 + HO_3^{\cdot}} \quad (2.18)$$

$$\mathbf{HO_3^{\cdot} \rightarrow O_2 + OH^{\cdot}} \quad (2.19)$$

$$\mathbf{OH^{\cdot} + DCF \rightarrow H_2O + DCF \rightarrow CO_2 + H_2O} \quad (2.20)$$

PROMETHEE method

The PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations) method is a multiple decision-making method developed in 1982. PROMETHEE method is known as the most effective and easiest method in the field of solving multiple criteria problems. The method determines the order of decision points in the main stages of PROMETHEE I (partial order) and PROMETHEE II (full order). The PROMETHEE method is based on binary comparisons of alternatives (decision points) according to criteria (evaluation factors) (Belton and Stewart 2001; Brans, Vincke, and Mareschal 1986).

PROMETHEE method consists of seven steps. Each of these steps is implemented in the Visual PROMETHEE software.

Step 1: The weights $w = (w_1, w_2, \ldots, w_k)$ and a set of alternatives evaluated by the criterion $C = (f_1, f_2, .., f_k)$ are formed.

Step 2: Define preference functions for criteria. Six different preference functions to be used in the application of the method; the first type (usual), the second type (U-type), the third type (V-type), fourth Type (Level), fifth Type (Linear), sixth Type (Gaussian).

Step 3: Common preference functions are determined for alternative pairs based on preference functions. The common preference function is determined for alternatives *a* and *b*.

Step 4: Preference indexes are determined for each alternative pair based on common preference functions. w_i (i = 1,2, …, k) is calculated by the preference index of alternatives *a* and *b*, which is evaluated by the criterion *k*.

Step 5: Positive (φ^+) and negative (φ^-) superiorities are determined for the alternatives. For alternative *a*, positive and negative superiorities are calculated.

Step 6: With PROMETHEE I, partial priorities are set. Partial priorities provide the identification of alternatives to each other, alternatives that are indistinguishable from each other, and alternatives that cannot be compared with each other.

Step 7: With PROMETHEE II, full priorities are calculated for alternatives. With the calculated full priority values, all alternatives are evaluated in the same plane and the exact order is determined.

For two alternatives such as a and b, depending on the calculated full priority value decisions are made given below:

If $\phi(a) > \phi(b)$, alternative *a* is superior to alternative *b*,

If $\phi(a) = \phi(b)$, alternatives *a* and *b* are indistinguishable (Dağdeviren 2008).

Results and discussion

The effect of catalyst type

ZnO, In_2O_3, CuO and Fe_2O_3 nanopowders were used as catalysts in this study. Visual PROMETHEE method was used to choose a suitable catalyst for DCF removal under the experimental conditions of 5 mg/L DCF, 5 ppm ozone dose and 2x8 W lamps. The model was developed to determine the weights of criteria (DCF removal, energy consumption and cost) based on the pairwise comparison. The positive flow (φ^+), negative flow (φ^-) and net flow (φ) values obtained from the Visual PROMETHEE method are shown in Table 1.

Based on the net flow results of this model, ZnO catalyst was found more admissible than CuO, Fe_2O_3 and In_2O_3 catalysts because of less treatment cost as well as lower energy consumption. According to this result, ZnO catalyst was used as a catalyst in the next studies.

Table 1. Results of visual PROMETHEE method.

Processes	φ	φ^+	φ^-
O_3/UV/ZnO	0.3316	0.3333	0.0017
O_3/UV/CuO	0.1111	0.2222	0.1111
O_3/UV/Fe_2O_3	−0.1100	0.1122	0.2222
O_3/UV/In_2O_3	−0.3328	0.0006	0.3333

Removal of DCF by ozone-based processes

Ozone, photo ozone, catalytic ozone and photocatalytic ozone oxidation methods were used as ozone-based advanced oxidation processes in this study. Firstly, the effect of the initial concentration of diclofenac was investigated in ozone oxidation process. The results of the experiments are shown in Figure 2 under the conditions of 5 ppm ozone dose and 5, 10, 20 mg/L of DCF concentration.

In Figure 2, the highest removal efficiencies were obtained at 5 and 10 mg/L DCF concentrations as 92% and 96%, respectively. In the literature, DCF concentrations above 10 mg/L require more than 10 min duration time for DCF degradation (Aguinaco et al. 2012; Beltrán et al. 2009a; Calza et al. 2006; Chen et al. 2016; Hama Aziz et al. 2017). It was observed that the time should be increased for rising removal efficiency of 20 mg/L initial concentration. In the 30 min of reaction, 99% removal efficiency was achieved.

DCF can be found in wastewater outlet and surface waters in concentration ranges of ng/L and mg/L (Lonappan et al. 2016). Therefore, this study was continued with the lowest DCF (5 mg/L) concentration.

In order to investigate the effect of ozone dose on DCF removal, 5 mg/L DCF initial concentration experiments were performed for 5 and 8 ppm ozone doses (Figure 3).

In Figure 3, under 10 min reaction conditions, 91% and 100% DCF removal efficiencies were obtained at 5 ppm and 8 ppm ozone doses, respectively. Approximately the same results were obtained for both ozone doses. Since 100% removal efficiency was achieved for 8 ppm, there was no need to work at a higher O_3 concentration. The removal efficiency of 5 ppm ozone in the first 5 min was expected to increase using UV and catalyst effect. Aguinaco et al. (2012) stated that there was no significant effect of increasing ozone concentration for DCF degradation (Aguinaco et al. 2012).

2 × 8 W and 4 × 8 W lamps were used for investigation of UV light effect at the determined initial DCF

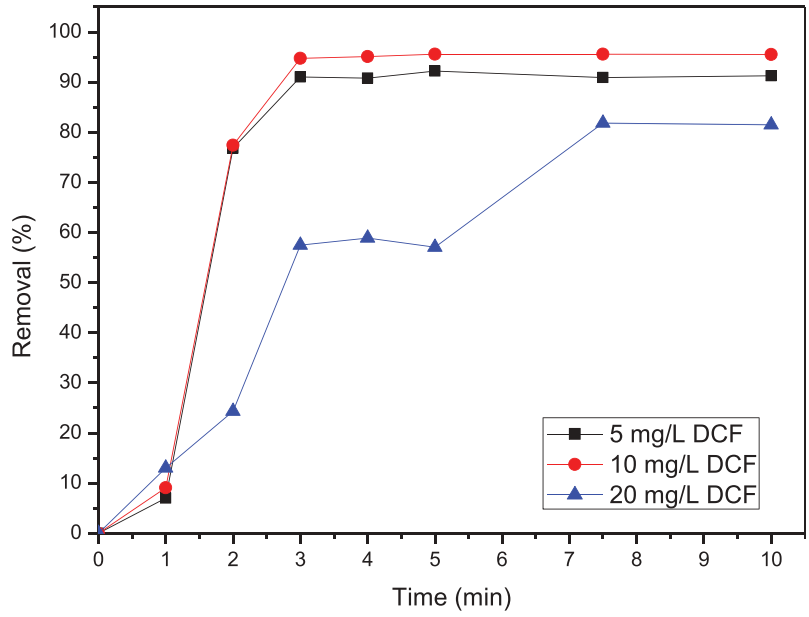

Figure 2. The effect of the initial concentration (Co = 5, 10, 20 mg/L DCF, O_3 = 5 ppm, reaction time = 10 min).

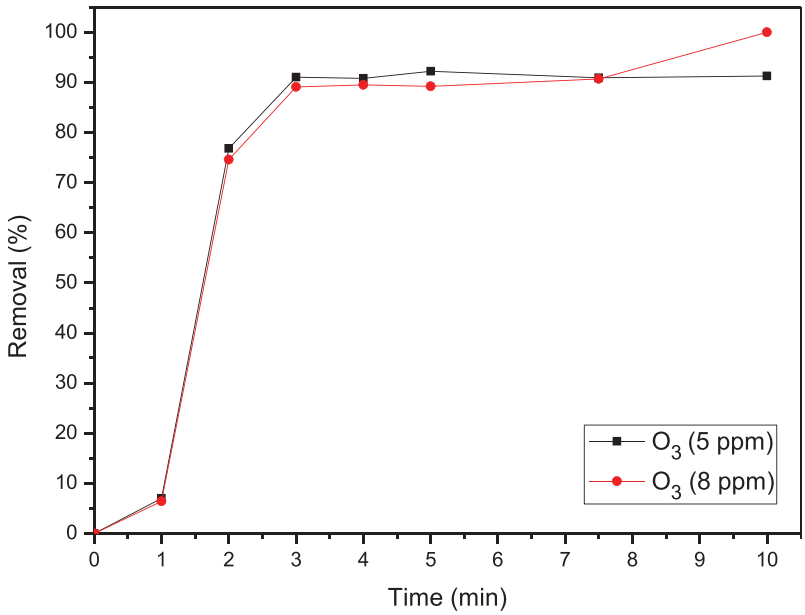

Figure 3. The effect of ozone dose (Co = 5 mg/L DCF, O_3 = 5 and 8 ppm, reaction time = 10 min).

concentration and ozone dose. The results of O_3/UV oxidation processes are evaluated in Figure 4.

In Figure 4, it could be indicated that UV lights positively affected the reaction. In the first 5 min reaction, 100% removal efficiency was obtained using 2x8 W energy. It was then preferred to work with 2 × 8 W lamp in the O_3 /UV process as more energy would be consumed with 4 × 8 W, which would eventually increase the treatment cost. Shu et al. (2013) investigated the UV doses required for 90% removal efficiency with direct UV and UV/H_2O_2 processes for the treatment of DCF (Shu et al. 2013). They determined that only the UV dose in the direct UV process was high and the addition of H_2O_2 significantly reduced the UV dose.

By using ZnO catalyst which was determined by the PROMETHEE method, the effects of catalytic ozone (O_3/ZnO) and photocatalytic ozone (O_3/UV/ZnO) oxidation processes on DCF removal were also investigated. The results obtained are evaluated in Figure 5 against the other processes outcomes.

In Figure 5, at the end of the 10-min reaction, 100% DCF removal efficiency was achieved in other oxidation

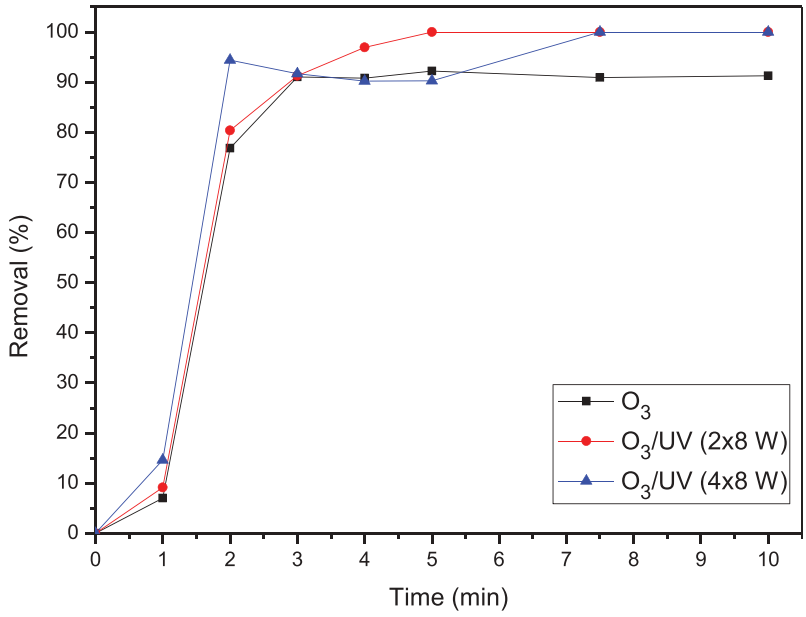

Figure 4. The UV light effect (Co = 5 mg/L DCF, O_3 = 5 ppm, UV lamps = 2 × 8 W and 4 × 8 W, reaction time = 10 min).

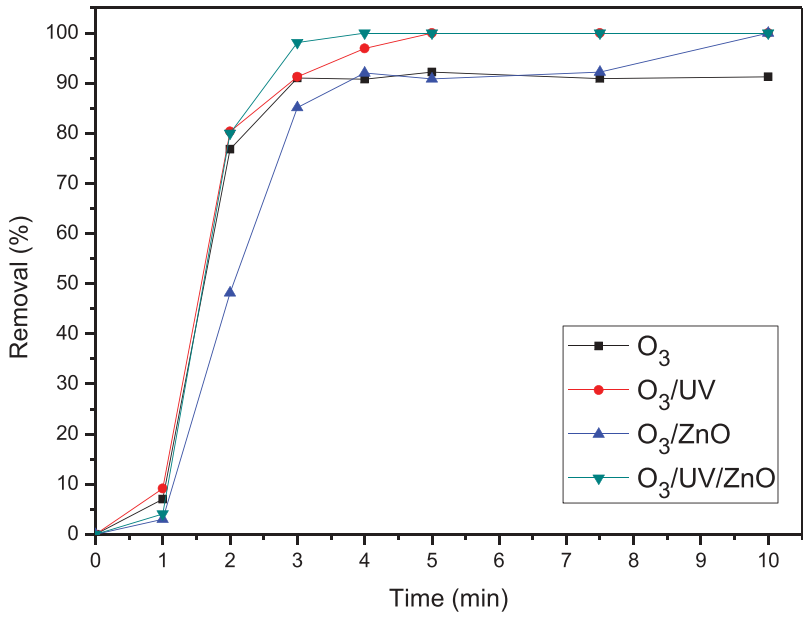

Figure 5. Catalytic and photocatalytic ozone oxidation processes effects (Co = 5 mg/L DCF, O_3 = 5 ppm, UV lamps = 2 × 8 W, Catalyst amount = 0.1 g ZnO, reaction time = 10 min).

processes except O_3 process. In O_3/UV/ZnO process, 98% removal efficiency was reached in 3 min. The activity of ZnO catalyst was found to be better under UV light. Moreira et al. (2015) reported DCF degradation in photocatalytic ozonation and application studies using direct UV/Vis (Moreira et al. 2015). Aguinaco et al. (2012) studied O_3/UV/TiO_2 photocatalytic ozonation process for DCF removal and found complete elimination of DCF at 6 min of reaction. Studies on the complete degradation of diclofenac are available in the literature by using ozone and TiO_2 photocatalysis processes (García-Araya, Beltrán, and Aguinaco 2010), photocatalytic ozonation and application (Moreira et al. 2015), and ozone and activated carbon (Beltrán et al. 2009a).

The best DCF removal efficiencies along the 10 min reaction were determined under O_3

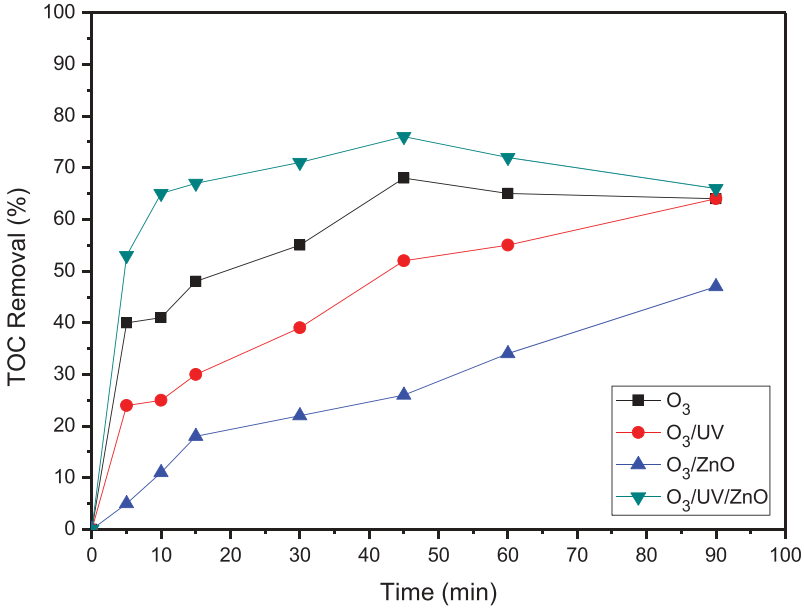

Figure 6. The TOC removal efficiencies for DCF treatment (C_0 = 5 mg/L DCF, O_3 = 5 ppm, UV lamps = 2 × 8 W, Catalyst amount = 0.1 g ZnO, reaction time = 90 min, pH = 6–7).

/UV/ZnO > O_3/UV > O_3/ZnO > O_3 oxidation processes, respectively.

Mineralization efficiency of DCF

Determining the mineralization efficiency of the DCF pollutant is important for environmental aspect. DCF mineralization efficiency is also investigated in Figure 6, by using ozone-based advanced oxidation processes.

In Figure 6, the highest TOC removal efficiency was obtained as 76% in the O_3/UV/ZnO photocatalytic ozone process for 45 min reaction time. When DCF was completely degraded at the 10th min, TOC removal was determined as 65%. This TOC removal efficiency was related to incomplete mineralization. Process effectiveness on TOC removal efficiencies at the end of the 60 min reaction was followed as O_3/UV/ZnO > O_3 > O_3 /UV > O_3/ZnO respectively. Pocostales, Álvarez, and Beltrán (2011) obtained 50% TOC removal efficiency in their catalytic ozonation studies using Co_3O_4/Al_2O_3 catalyst at 30 mg/L DCF, 20 mg/L ozone dose and 60 min reaction time (Pocostales, Álvarez, and Beltrán 2011). Aguinaco et al. (2012) obtained 60% to 75% of TOC removal efficiency in photocatalytic ozonation studies using TiO_2 catalyst at 60 min reaction time. Hama Aziz et al. (2017) determined the highest TOC removal obtained by photocatalytic ozonation process for DCF degradation (Hama Aziz et al. 2017).

Determination of reaction kinetics

HPLC results of experimental studies performed at different ozone-based oxidation processes for DCF degradation were evaluated according to pseudo-first-order kinetics rate model. The following Equations [3.1 and 3.2] are used to determine the rate constant (k) values for this model (Fathinia et al. 2016; Konstantinou and Albanis 2004; Mecha et al. 2016; Mehrjouei, Müller, and Möller 2014).

$$-\frac{\mathbf{dC}}{dt} = k\mathbf{C} \tag{3.1}$$

$$\mathbf{ln}\frac{\mathbf{C_0}}{\mathbf{C_t}} = kt \tag{3.2}$$

C_0 and C_t (mg/L) are the initial and final concentrations of DCF solutions, t is the current time (min) and k is the kinetic constant (min^{-1}). The results of the calculations are given in Table 2.

According to results; ozone-based oxidation processes (O_3, O_3/UV, O_3/ZnO and O_3/UV/ZnO) were found suitable to the first-order kinetics rate model. Pérez-Estrada et al. (2005), found that DCF degradation followed first-order kinetics in the decomposition of diclofenac by solar-driven photocatalysis studies (Pérez-Estrada et al. 2005). In this study, the half-life ($t_{1/2}$) of the reactions was calculated from the obtained rate constants. The lowest half-life ($t_{1/2}$ = 0.7 min) was achieved in O_3/UV/ZnO process. The low half-life for 5 mg/L DCF indicated that the stability of DCF was low.

Table 2. The calculated reaction rate kinetics according to concentrations of DCF.

Processes	DCF concentration (mg/L)	O_3 doze (ppm)	UV (W)	Pseudo-first-order kinetic		
				k (min^{-1})	R^2	$t_{1/2}$ (min)
O_3	5	5	-	0.591	0.945	1.2
O_3	5	8	-	0.538	0.936	1.3
O_3/UV	5	5	2x8	0.819	0.966	0.8
O_3/UV	5	5	4x8	0.624	0.814	1.1
O_3/ZnO	5	5	-	0.530	0.945	1.3
O_3/UV/ZnO	5	5	2 × 8	0.997	0.879	0.7
O_3	10	5	-	0.445	0.831	1.6
O_3	20	5	-	0.193	0.965	3.6

Table 3. Cost assessment based on the treatability of DCF.

Processes	DCF concen. (mg/L)	O_3 dose (ppm)	Time (min)	Ozone generator operating time (s)	Ozone generator energy consumption (kWh)	UV lamp energy consump. (kWh)	O_3 gen. Energy consump. (€)	UV lamp energy consump. (€)	0.1 g Catalyst consump. (€)	Total cost (€)
O_3	5	5	10	441	0.096	0	0.004	0	0	0.004
O_3	5	8	10	170	0.037	0	0.001	0	0	0.001
O_3/UV (2 × 8 W)	5	5	5	163	0.035	0.0013	0.001	0.00005	0	0.001
O_3/UV (4 × 8 W)	5	5	7.5	486	0.105	0.0040	0.004	0.00015	0	0.004
O_3/ZnO	5	5	10	580	0.126	0	0.005	0	0.204	0.209
O_3/UV/ZnO (2 ×8 W)	5	5	4	230	0.050	0.0011	0.002	0.00004	0.204	0.206
O_3	10	5	10	305	0.066	0	0.002	0	0	0.002
O_3	20	5	10	768	0.166	0	0.006	0	0	0.006

Cost assessment of treatability of diclofenac

The cost evaluation was conducted according to the results of the highest removal efficiencies obtained from DCF concentrations (Table 3).

In Table 3, the lowest treatment costs were obtained in O_3 and O_3/UV oxidation processes at different DCF concentrations and different UV lamp energy. In the shortest reaction time (4 min) and the best DCF removal efficiency (100%) was obtained at O_3/UV/ZnO oxidation process and the treatment cost of this process was calculated to be 0.206 €.

Conclusion

In the present study, UV light and catalyst effect together with O_3 process were found to have a positive effect on DCF removal efficiencies. By O_3/UV/ZnO process, DCF was completely degraded in a short reaction time, but 65% mineralization occurred during the 10 min reaction time. The data of the O_3, O_3/UV, O_3/ZnO and O_3/UV/ZnO oxidation processes were found to be appropriate to the first-order reaction kinetics. The least treatment cost was obtained as 0.001 € in the O_3 and O_3/UV oxidation processes at 100% DCF removal efficiencies, with a 5 mg/L DCF concentration, 5 and 8 ppm ozone dose, 2 × 8 W UV lamp and 10 min reaction time.

By using PROMETHEE decision-making method which is a multi-criteria priority-setting method; ZnO catalyst was found to be more acceptable than other catalysts in DCF treatment. Thus, it can be said that the PROMETHEE method can be used to select the best catalyst for DCF treatment at catalytic and photocatalytic ozone oxidation processes.

Ozone, catalytic ozone, photolytic ozone and photocatalytic ozone oxidation process usage can be recommended as an alternative treatment method for DCF removal and especially when ZnO catalyst can be used as a catalyst.

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