



# Comparative study on photooxidative treatment of diclofenac: Response surface and mechanistic modeling



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## ABSTRACT

The study evaluates the applicability of photooxidative processes for the degradation of diclofenac (DCF), frequently encountered pharmaceutical compound in water bodies. Response surface modeling (RSM) and mechanistic modeling (MM) were used to describe UV-C/H<sub>2</sub>O<sub>2</sub> and UV-C/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> processes. The influence of initial pH, oxidant concentration and type on the process effectiveness was assessed in terms of mineralization kinetics. The evaluation of process parameters significance, and their optimization within investigated range, was successfully performed by RSM. The predicted values deviated from the experimental results by 2.6%. It was found out that oxidant concentration and type are highly influential parameters. The both studied processes can be applied in relatively wide pH range due to its minor influence on mineralization kinetics. The simultaneous prediction of several process responses: DCF conversion, mineralization, oxidant consumption and pH changes were successfully achieved by MM. Predicted values deviated from the experimental data ≤1.5%. At determined optimal conditions for both processes, the treatment time required for complete DCF conversion and 90% mineralization by UV-C/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was 8 times lower in comparison to UV-C/H<sub>2</sub>O<sub>2</sub> process.

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## 1. Introduction

The pharmaceuticals are of particular concern due to their ubiquity in the aquatic environment and their health effects [1]. They have an important role in both humans and animals health care, but may have the potential to negatively affect non-target living organisms as they are designed to be biologically active. Primary and secondary wastewater treatment (WWT) technologies are not specifically designed to remove some of contaminants of emerging concern (CEC) and their metabolites. Consequently, various pharmaceuticals are detected in different environmental matrices worldwide, including WWT plant effluents, surface, ground and drinking waters [1,2]. None of pharmaceuticals is currently listed among priority substances by EU. During the recent prioritization process two endocrine disruptors, 17 $\alpha$ -ethinylestradiol and 17 $\beta$ -estradiol, and non-steroidal anti-inflammatory drug, diclofenac (DCF), are proposed to be included in the first watch list [3]. DCF is one of the most widely available drugs in the world. Approximately 100 tons of this prescription drug are sold annually worldwide and is often found as a persistent toxic waste. The average concentrations detected in influents and effluents of municipal sewage treatment plants and surface waters are in the low  $\mu\text{g L}^{-1}$ .

However, even at very low concentrations there are adverse effects in different organisms [4].

Since conventional WWT systems do not efficiently remove DCF, advanced treatment technologies capable of its complete removal or destruction of its biological activity, need to be evaluated and eventually employed. The application of advanced oxidation technologies (AOTs) seems as a reasonable solution [5,6]. AOTs are based on the generation of highly reactive radical species, primarily hydroxyl radicals (HO $\cdot$ ), and are capable to provide complete degradation/mineralization of the majority of organics in water. The complete abatement of high organic loads might be costly, but in the case of recalcitrant micropollutants AOTs offer viable solution [7]. Photochemical AOTs, which consider the application of UV irradiation source(s) and addition of strong oxidants, are shown to be highly effective in the treatment of various organics [8–16]. Although the most typical oxidant applied is hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), recent researches are directed toward persulfates (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>). Persulfates ( $E^\circ = 2.05 \text{ V}$ ) are characterized by high solubility and stability at ambient temperature, while the sulfate ions, which are the major products of persulfate reduction, are relatively harmless and considered to be environmentally friendly [17].

Generally, the effectiveness of photochemical AOTs depends on process parameters related to the reactor design and characteristics of reaction mixtures. According to the Beer–Lambert law [18], radiant power, irradiation wavelength, and effective length path are in direct relationship with the quantity of radical species gener-

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ated, determining the kinetics of photolysis, while the flow regime determines the mass transfer within the applied treatment. These parameters should be optimized through the reactor geometry and design. Characteristics of reaction mixture are determined by wastewater composition, as well as values of operating parameters: pH, oxidant type and concentration, which should be optimized for each particular case [12,13,15–17]. Operating pH determines the quantity and type of radicals generated under the photolysis of oxidant applied [15,16,18]. It also determines the ionic forms of parent pollutants and their by-products, thus influencing the overall process kinetics [9]. The concentration of oxidant determines the quantity of radicals generated, taking into account the scavenging effect when present in excess [15–17]. The oxidant type determines the type and quantity of radicals generated due to inherent optical properties of oxidant [15,16].

The simulation of system behavior and prediction of process effectiveness in dependence on process parameters is of crucial importance when evaluating appropriate technologies for (waste) water treatment for practical application. The common modeling actions consider the application of statistical/empirical approach such as response surface modeling (RSM) or artificial neural networking (ANN), and phenomenological approach based on mechanistic modeling (MM). The first approach enables the simple and fast detection of influential process parameters and provides their straightforward correlation with process effectiveness in the term of chosen response. Besides, it may provide system optimization within the tested range of process parameters. Latter approach, describing process chemistry and occurring phenomena with the set of differential equations, enables the prediction of system behavior outside of tested boundaries through several responses representing either targeted organics elimination and/or process parameters [9,12,15,19].

The goal of the study was to evaluate and compare the effectiveness of photooxidative AOTs, UV-C/H<sub>2</sub>O<sub>2</sub> and UV-C/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, for the degradation of DCF in water. RSM served as a tool for screening the influence of key process parameters: pH, oxidant type and concentration, on the process effectiveness, and determining the optimal conditions within a rather wide range. MM was employed in order to simultaneously predict the behavior of several process responses providing a solid base for future scale-up.

## 2. Experimental

### 2.1. Chemicals

Diclofenac (DCF) in a form of sodium salt (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid sodium salt, C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>NNaO<sub>2</sub>, CAS: 15307-79-6, Sigma–Aldrich, USA) was used. Methanol (CH<sub>3</sub>OH, HPLC grade) and *ortho*-phosphoric acid (*o*-H<sub>3</sub>PO<sub>4</sub>, >85%), used in mobile phase for HPLC analyses, were also purchased from Sigma–Aldrich, USA. The inorganic chemicals: hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, w=30%), sodium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, p.a.), sodium hydroxide (NaOH, p.a.), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, >96%) were purchased from Kemika, Croatia. All experiments were performed with deionized water with conductivity less than 1 μS cm<sup>-1</sup>.

### 2.2. Procedure

The experiments were performed with DCF water solutions (c<sub>0</sub>=0.1 mM) in a glass water-jacketed batch photoreactor (total volume, V<sub>T</sub>=0.1 L, solution volume, V<sub>S</sub>=0.08 L, and T=25.0 ± 0.2 °C). The photoreactor was equipped with UV-C lamp (P<sub>0</sub>=1.04 × 10<sup>-6</sup> Einstein s<sup>-1</sup>), which was placed in the middle (irradiation path L = 1 cm), and magnetic stirrer in order to provide

effective mixing of reaction solution (mixing speed was 550 rpm). Initial pH values and oxidant (H<sub>2</sub>O<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) concentrations ranged from 3 to 11 and 1 mM to 20 mM, respectively (Table 1). DCF conversion and mineralization of total organic content were monitored throughout treatment period. Due to the slower elimination rate, mineralization data were used to estimate the kinetic order and observed degradation rates. The changes in pH and consumption of oxidants were monitored in experiments used for the calibration of mechanistic model. Due to the different elimination rates regarding the type of oxidant, the duration of the experiments varied from 30 to 100 min.

All experiments were performed in quintuplicates and averages were reported. The reproducibility of the experiments was >97.2%.

### 2.3. Analyses

The conversion of DCF was monitored by HPLC, Series 10, Shimadzu, Japan, equipped with UV-DAD, SPD-M10A<sub>VP</sub>, Shimadzu, Japan, using EC 250/4,6 120–5C18 column, Macherey-Nagel Nucleosil, Germany, and mobile phase CH<sub>3</sub>OH/buffer (65:35; buffer was consistent of 0.15% H<sub>3</sub>PO<sub>4</sub>, 5% CH<sub>3</sub>OH and 94.85% H<sub>2</sub>O) operating at 1.0 mL min<sup>-1</sup> flow. The mineralization of organic content of DCF water solutions was monitored by total organic carbon analyzer, TOC-V<sub>CPN</sub>, Shimadzu, Japan. Handylab pH/LF portable pH-meter, Schott Instruments GmbH, Mainz, Germany, was used for pH measurements. UV–vis spectrophotometer, Lambda EZ 201, Perkin Elmer, USA, was used for spectrometric determination of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> consumption during the treatment using modified metavanadate [20] and ferrous ammonium sulfate (FAS) [21] methods, respectively.

## 3. Calculations

### 3.1. Response surface modeling

The modified miscellaneous full factorial design (MMFFD) and RSM were employed in order to estimate the influence of pH, oxidant concentration and type on the photooxidative treatment efficiency based on the observed mineralization rates. Hence, these process parameters are represented by independent variables: X<sub>1</sub> (pH), X<sub>2</sub> (oxidant concentration) and X<sub>3</sub> (oxidant type). Their combined influence on mineralization kinetics (i.e., dependent variable; Y) was described by polynomial equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_{11} X_1^2 + \beta_2 X_2 + \beta_{22} X_2^2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (1)$$

where β<sub>0</sub> is intercept; β<sub>1</sub>, β<sub>2</sub>, β<sub>3</sub> are linear; β<sub>11</sub>, β<sub>22</sub> quadratic; and β<sub>12</sub>, β<sub>13</sub>, β<sub>23</sub> interaction coefficients. It is worth noting that categorical parameter (X<sub>3</sub>) can not be represented by quadratic term in (1); it has only mathematical, but not physical meaning. The values of independent variables were transformed in dimensionless coded values; three levels for X<sub>1</sub> and X<sub>2</sub> and two levels for X<sub>3</sub>. Table 1 summarizes the full experimental matrix and the obtained results and values of responses. The fitting of models was evaluated using the coefficient of determination (R<sup>2</sup>) and the analysis of variance (ANOVA). Calculations and analyses were performed using STATISTICA 10.0, StatSoft, USA, Design-Expert 7.1, StatEase, USA, and Mathematica 9.0, Wolfram Research, USA.

### 3.2. Mechanistic modeling

The mechanistic model (MM) applied in this study is originally developed, verified and validated in our previous studies focused on degradation of textile dyes by both applied photooxidation AOPs (UV-C/H<sub>2</sub>O<sub>2</sub> and UV-C/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) [22–24]. The part of MM related

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