





# Removal of Diclofenac and Metformin from Water in Laboratory Photo Reactor <sup>+</sup>

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Abstract: Diclofenac (DCF) and metformin (MET) are pharmaceuticals often detected in influents and effluents of municipal sewage treatment plants and surface waters which may cause adverse effects to human health and the environment. In recent years, advanced oxidation processes (AOPs) have been demonstrated to be effective technology for the removal of many organic pollutants. The objective of this study was to evaluate the removal and toxicity of investigated pharmaceuticals by UV and UV/H2O2 processes. UV irradiation was provided by a Pen Ray lamp emission at 254 nm which was covered with a quartz tube and placed in the middle of the reactor. Experimental conditions of the process were: [DIC, MET] = 10 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 2.5 mM, reaction time 3 h. Results obtained by only UV exposition of solution showed that diclofenac and metformin were degradated 30% and 50% during 3 h test. Addition of 2.5 mM H<sub>2</sub>O<sub>2</sub> to photo reactor contributed to 90% and 100% removal of DCF and MET, respectively. Inhibition toxicity test of MET increased in the following range: 13% (C0) < 38% (UV) < 77% (UV/ H<sub>2</sub>O<sub>2</sub>), while toxicity measured for DCF solutions followed the range: 33% (UV) < 75% (C0) < 78% (UV/H<sub>2</sub>O<sub>2</sub>). The results confirmed that addition of hydrogen-peroxide accelerated the removal of investigated pharmaceuticals, but at the same time, lead to formation of the more toxic intermediates. The possible reason for better removal efficiency of metformin can be related to its simpler aliphatic structure in comparison to more aromatic diclofenac.

Keywords: diclofenac; metformin; advanced oxidation processes; wastewater treatment

## 1. Introduction

Pharmaceuticals' increasing consumption and adverse effects on environment or human bodies have been attained extensive attention. Based on their uptake mechanism and route administration they are expelled as a mixture of metabolites, neutral substances, or conjugated complex with an inactivating compound attached to the molecule [1]. The emission of these emerging contaminants has emerged as an environmental problem and rather poor wastewater management could not effectively eliminate these compounds [2]. Diclofenac (DCF) is one of the most widely available nonsteroidal anti-inflammatory pharmaceuticals, which is included in the first "watch" list in order to gather monitoring data of priority substances in water [3]. Metformin (MET) is an oral antidiabetic pharmaceutical to treat type 2 diabetes and a potential anticancer agent. Metformin is not metabolized by the human body and is 100% excreted and as much as 70% through urine and the rest in feces [4]. Despite a large conversion in waste water treatment plants before discharge, metformin was still one of the most abundant pharmaceuticals found in WWTP effluents and surface waters [2].

In recent years, advanced oxidation processes (AOPs) have been demonstrated to be effective technology for the removal of many organic pollutants [5]. Among AOPs, Fenton-type reactions have been identified as effective methods which produce hydroxyl-radicals by the reaction between iron salts and hydrogen-peroxide. The advantages of these processes are the safe and environmentally-benign nature of reagents and relatively simple operating principles as well as short reaction time and the absence of mass transfer limitations. The photo-Fenton process is similar to the Fenton process but it offers higher removal efficiencies by employing irradiation. In this process, the generation of hydroxyl radicals accelerates in comparison with the "simple" Fenton process [6].

Studies involving the removal of MET and DIC from aqueous solutions and detailed information regarding the overall degradation process are scarce. Therefore, the present study aims to investigate MET and DIC degradation in aqueous medium induced by UV and UV/H<sub>2</sub>O<sub>2</sub> processes in laboratory photo reactor. The solutions toxicity was evaluated with a *Vibrio fischeri* assay.

#### 2. Materials and Methods

#### 2.1. Chemicals

Metformin hydrochloride and diclofenac sodium salt (initial concentration, C0 = 10 mg/L) with a purity of over 99% were used. Their main physico-chemical characteristics are presented in Table 1. Hydrogen-peroxide (30% *w/w*) was also used as received. Solvents for analytical determination were methanol and dichlormethane (J.T. Baker). Stock solutions of pharmaceuticals and other solutions were prepared in deionized water (DI) and diluted as required.

Substance	Structure	Molecular weight (g/mol), M <sub>w</sub>	Log Kow	Solubility in Water (mg/L), Sw
Diclofenac	CI H CI CI	318	0.7	2430
Metformin	H <sub>2</sub> N NH NH H <sub>2</sub> N CH <sub>3</sub> HCl	165	-2.64	$1.06 \times 10^{6}$

Table 1. Physico-chemical characteristics of diclofenac and metformin [7].

#### 2.2. Preparation of the Synthetic Solution and Experimental Procedure

Diclofenac and metformin stock solutions (1000 mg/L) were prepared weekly using DI water and stored in the dark at 4 °C. UV irradiation was provided by a Pen Ray lamp emission at 254 nm which was covered with a quartz tube and placed in the middle of the reactor. During photolytic experiments, temperature was maintained at 25 °C by using external water cooling around the reactor. Experimental conditions of the process were: [DIC, MET] = 10 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 2.5 mM, reaction time 3 h.

### 2.3. Analytical Procedure

The efficiency removals were monitored using UV/VIS spectrophotometer (Shimadzu UV-1800, Japan). DCF and MET concentration were measured at  $\lambda$  = 276 and 232 nm, respectively. The toxicity test for bacteria *Vibrio fischeri* was done according to ISO 11348-1: 2008 Water quality – Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminiscent bacteria test) [8].

## 3. Results and Discussion

Results obtained by only UV exposition of solution showed that diclofenac and metformin were degradated 30% and 50% during 3 h test. Addition of 2.5 mM H<sub>2</sub>O<sub>2</sub> to photo reactor contributed to 90% and 100% removal of DCF and MET, respectively (Table 2).

Trachmont	Removals (%)		
Treatment	Diclofenac	Metformin	
UV	30	50	
UV/H2O2	90	100	

Table 2. Results of efficiency removals of DIC and MET after UV treatments.

The full spectra of both pharmaceuticals during the treatments were presented in Figure 1. As it can be seen from the spectra, 3 h of treatment is proved to be enough for degradation of diclofenac, especially after UV/H<sub>2</sub>O<sub>2</sub> process. Although, similar conclusion could be retrieved for metformin, after both, UV and UV/H<sub>2</sub>O<sub>2</sub> treatments, higher peaks appeared in the lower UV region, indicating transformation of metformin to other organic compounds.



Figure 1. Absorption UV/VIS spectra of investigated pharmaceuticals.

Inhibition toxicity test of MET increased in the following range: 13% (C0) < 38% (UV) < 77% (UV/H<sub>2</sub>O<sub>2</sub>), while toxicity measured for DCF solutions followed the range: 33% (UV) < 75% (C0) < 78% (UV/H<sub>2</sub>O<sub>2</sub>) (Table 3). One can conclude that degradation products of metformin are more toxic than the parent compound. Similar conclusions were confirmed by other authors in the case of different organic compounds [6]. In the case of diclofenac, its initial concentration and UV/H<sub>2</sub>O<sub>2</sub> by-product had similar toxicity (75–78%), while UV irradiation decreased its initial toxicity from 75% to 33%.

Treatment	Toxicity inhibition (%)		
Ireatment	Diclofenac	Metformin	
Initial concentration, (C0)	75	13	
UV	33	38	
UV/H2O2	78	77	

**Table 3.** Results of toxicity inhibition tests of DIC and MET after UV treatments.

## 4. Conclusions

In this paper, the degradation of metformin and diclofenac in aqueous solution under UV irradiation was investigated in a lab-scale photo reactor. The results confirmed that addition of hydrogen-peroxide accelerated the removal of investigated pharmaceuticals, but at the same time, lead to formation of the more toxic intermediates. The possible reason for better removal efficiency of metformin can be related to its simpler aliphatic structure in comparison to more aromatic diclofenac.

**Author Contributions:** A.L.M. and M.B.-T. designed the experiment. D.K. and D.T.P. helped with the data analysis. J.J. performed the experiments. A.K. performed toxicity tests and data analysis. B.D. contributed reagents and materials.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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