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# Degradation of diclofenac in aqueous solution by homogeneous and heterogeneous photolysis

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## Abstract

**Background:** Pharmaceuticals have arisen as emerging environmental pollutants due to their potential impact on humans, animals and microorganisms even at low concentrations. Conventional wastewater treatment plants are known to be ineffective for removal of many pharmaceuticals present in wastewater. Advanced oxidation processes are one of the most promising treatment technologies for degradation of such persistent compounds. The current study was focused on the efficacies of various oxidation processes for degradation of diclofenac (DCF) as one of the most widespread pharmaceuticals.

**Methods:** The efficacy of UV photolysis, hydrogen peroxide photolysis, homogeneous and heterogeneous Fenton/photo-Fenton treatment for removal of DCF from aqueous solution was examined. The impact of pH, hydrogen peroxide concentration, and catalyst type on DCF removal was assessed. The identification of DCF photo-degradation products with GC-MS (EI) technique was carried out.

**Results:** According to results of the present study direct photolysis proved main contributing reaction pathway in all studied systems with UV irradiation. Fast decrease in pH value observed during all studied processes started at pH 5, 7, and 9 led to the system controlled by DCF precipitation-degradation-re-dissolution conditions. The enhanced efficacy of promoted photolysis proved dependent on the rate of pH decrease to value below $pK_a$ at the beginning of the process. After reaching acidic pH values of the surrounding solution the DCF degradation was controlled by the solubility independently of treatment method applied. The highest DCF degradation efficacy was attained by the heterogeneous photo-Fenton treatment at initial pH 11. Thus, DCF 90% conversion time decreased from 48 to 23.5 min for UV photolysis and heterogeneous photo-Fenton process (3.8 mM $H_2O_2$), respectively.

**Conclusions:** DCF was quite resistant to all tested processes. The application of the Fenton-based treatment and UV/$H_2O_2$ did not show vital advantages compared to UV photolysis when the initial pH was 7 or 9. Direct photolysis proved main process contributing to DCF degradation in all studied systems combined with UV irradiation. The present study was the first to evaluate the efficacy of photo-Fenton catalysed by goethite for DCF degradation in aqueous solution. The latter proved the most efficient one among the Fenton-based processes.

**Keywords**: Advanced oxidation processes, photolysis, photo-Fenton process, pharmaceutical, UVC radiation, goethite

## Background

The presence of pharmaceutical residues in municipal, surface, ground- and even drinking water is an emerging environmental problem due to the potential impact on human health and the environment even at low concentrations. Pharmaceuticals used by human or animal are only partially consumed in the organism and excreted through urine or faeces in unchanged or/and metabolized form. Drugs are released into the wastewater not only after medical application, but also during manufacturing and improper disposal of unused or expired medicines. Unit operations used in wastewater treatment plants (WWTP) are known to be ineffective for removal of many pharmaceuticals present in wastewater. Consequently, effluents finally released into the receiving water bodies contain from ng L$^{-1}$ to µg L$^{-1}$ of these pollutants [1-2].

Among the various pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) are of the greatest environmental interest due to their widespread availability. Diclofenac (2-(2,6-dichlorophenylamino)phenylacetic acid, DCF) is one of the most consumed NSAIDs (annual DCF consumption estimated as 940 tons [3]) commonly used in medical care as an analgesic, antiarthritic and antirheumatic agent. Being resistant to biodegradation, it is ubiquitously present in the aquatic environment and detected in effluents of WWTP [3]. This pharmaceutical is relatively stable in the environment, but similar to others NSAIDs is sensitive to photolysis. DCF is known to undergo solar radiation induced photochemical decomposition in surface waters. However, it is still one of the most frequently

detected compounds in water at concentrations up to 2 µg L$^{-1}$ [4]. Although the ecotoxicity of DCF is relatively low, in combination with other drugs present in water, the toxic effects increase considerably [5]. Conventional WWTP, typically based on biological processes, are capable of removing some substances, but non-biodegradable compounds (*e.g.* DCF) may escape the treatment.

Advanced oxidation processes (AOPs) are one of the most promising treatment technologies for successful degradation of pharmaceuticals in aqueous matrices [6]. Several AOPs have been tested for DCF removal from water/wastewater including photolysis and UV/H$_2$O$_2$ process [6-7], homogeneous Fenton/photo-Fenton oxidation [2,5], heterogeneous catalytic oxidation with H$_2$O$_2$ [9], *etc*. However, among the various advanced oxidation technologies proposed for the degradation of DCF the heterogeneous Fenton-based process with goethite catalyst has not yet been investigated.

The main drawbacks associated with homogeneous catalysts in the Fenton process are the narrow pH range of operation to avoid the formation and subsequent precipitation of iron oxyhydroxide and the need to recover dissolved iron ions from the treated solution by supplementary treatment process. The application of heterogeneous catalyst (*e.g.* naturally occurring minerals) in the Fenton treatment overcomes the above-mentioned problems and results in extended periods of catalyst life without requiring regeneration or replacement, in easy removal of the catalyst from the treated water by sedimentation or filtration, and in Fenton-like reactions over a wide range of pH value [10]. The heterogeneous Fenton-based processes involving naturally occurring minerals (hematite a-Fe$_2$O$_3$, goethite a-FeOOH, magnetite Fe$_3$O$_4$, *etc.*) proved feasible alternative for water/wastewater treatment [11]. Goethite has been recognized as the preferred mineral oxide catalyst since it appears to have the fastest reaction with H$_2$O$_2$ [12].

In the present study the degradation of DCF using UV photolysis, H$_2$O$_2$ photolysis, homogeneous and heterogeneous Fenton/photo-Fenton processes was investigated. The efficacies of various oxidation processes on DCF removal from aqueous solution were compared. The identification of main by-products of DCF degradation by AOPs applied was carried out.
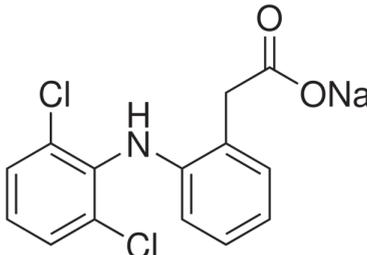
## Methods
### Chemicals and materials
Diclofenac sodium salt and goethite (α-FeOOH, 30-50 mesh) were purchased from Sigma-Aldrich; acetonitrile (99.8%, isocratic grade for HPLC) was obtained from Baker. The structure and the basic data concerning DCF are presented in **Table 1**. The specific surface area of goethite was measured by multipoint N$_2$-BET analysis using a sorptometer KELVIN 1042 (COSTECH Instruments) as 112.5 m$^2$ g$^{-1}$. All other chemicals were of analytical grade and used without further purification.

Stock solutions with initial DCF concentration of 100 mg L$^{-1}$ were prepared in twice-distilled water. The solution was mixed for several hours to achieve complete DCF dissolution. As the solubility of DCF is low below the pK$_a$ value (4.15), all experiments were conducted at initial pH ≥5. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

### Experimental procedure
A mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside the reactor was used as an UV source. The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry [13] was 3.59 ± 0.12 µ Einstein s$^{-1}$. The constant temperature (22±1°C) in the reactor was maintained using a cooling jacket. All Fenton-based process trials were carried out in batch mode and in non-buffered solutions. DCF solutions were treated in 1 L cylindrical glass reactor with permanent

**Table 1. The structure and main properties of studied pharmaceutical**

| Pharmaceutical | Diclofenac sodium salt |
| --- | --- |
| Empirical formula | C$_{14}$H$_{10}$Cl$_2$NNaO$_2$ |
| Molecular formula | |



| | |
| --- | --- |
| CAS Nr. | 15307-79-6 |
| Molecular weight, g mol$^{-1}$ | 318.13 |
| pK$_a$ | 4.15 [3] |

agitation at a speed to provide complete mixing for uniform distribution and full suspension of iron catalyst particles for a period of 120 min; samples were withdrawn at selected time intervals and filtered through a Millipore filter (0.45 µm). The reaction was stopped by adding 2 drops of 1 M aqueous solution of NaOH.

The homogeneous Fenton reaction ($H_2O_2/Fe^{2+}$) was initiated by adding $H_2O_2$ (0.94-2.5 mM) to DCF solution (pH 5 or pH 7) containing a known amount of $Fe^{2+}$ ion. The molar ratio of $H_2O_2/Fe^{2+}$ was kept invariable at 10:1. Heterogeneous Fenton-based treatment trials ($H_2O_2/\alpha$-FeOOH) were carried out with 1 g $L^{-1}$ of goethite at pH values of 7. The suspensions were continuously stirred for 30 min prior to $H_2O_2$ addition to establish the adsorption/desorption equilibrium between the DCF and the catalyst particles.

The photo-Fenton experiments were carried out in the same reactor and treatment conditions as the Fenton experiments with the UV lamp located inside the reactor. In the homogeneous photo-Fenton trials the concentration of hydrogen peroxide was in the range of 0.63-1.9 mM; the pH value of the stock solution was adjusted to 7. The heterogeneous photo-Fenton experiments were carried at pH values of 7, 9 and 11 with $H_2O_2$ concentration from 0.63 to 3.8 mM.

The direct UV photolysis and $H_2O_2/UV$ experiments were carried out in the same reactor (1 L of stock DCF solution in a glass reactor with a permanent agitation speed for a period of 120 min). The pH value of the stock solution was in the range of 5 to 11. The $H_2O_2$ concentration varied from 0.63 to 1.9 mM.

Additionally, the experiments on adsorption effect of goethite and DCF oxidation with non-catalyzed hydrogen peroxide were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials. All experiments were duplicated and the data on DCF concentration was verified with at least three replicates. The results of the analysis of initial and treated samples are presented as the mean, with the standard deviation below 4% in all cases.

### Analytical methods
DCF concentrations were quantified by means of a CLAS MPm (Labio Ltd.) high performance liquid chromatograph equipped with a MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 µm) microcolumn and UV/VIS detector SAPHIRE. The isocratic method with a solvent mixture of 50% acetonitrile and 0.1% of acetic acid in water was applied. Samples were analyzed at a flow rate of 70 µL $min^{-1}$ and absorbance wavelength of 254 nm. The concentration of DCF was determined by using the standard chemical to fit the retention time.

The total iron concentration was quantified with phenanthroline method [14]. The initial hydrogen peroxide concentration in stock solutions was determined spectrophotometrically by measurement of the absorption of hydrogen peroxide at λ=254 nm. The residual hydrogen peroxide concentration was measured by the spectrophotometric method with $Ti^{4+}$ [15]. The chemical oxygen demand (COD) was determined by the closed reflux titrimetric method according to [14]. The correction of hydrogen peroxide interference on COD test was done by the correlation equation according to [16].

### Identification of DCF degradation by-products
The samples from selected trials were concentrated to dryness by water evaporation at room temperature and re-dissolved in methanol to a final volume of 2 mL.

GC-MS measurements were performed with a gas chromatograph GC-2010 (Shimadzu, Kyoto, Japan) equipped with a GCMS-QP2010 Plus mass selective detector. The column flow was maintained at 1.66 mL $min^{-1}$. The analytes were separated in a ZB-5MS column (30 m × 0.32 mm × 0.25 µm). The oven temperature program was 1.0 min at 105°C, 25°C $min^{-1}$ to 180°C, 5°C $min^{-1}$ to 250°C, 20°C $min^{-1}$ to 270 (holding time 3 min). The interface temperature was set at 280°C. The injector and the ion source temperature were 270 and 250°C, respectively. The MS detector was operated in the EI mode, scanning in the range of 50-400 m/z.

## Results and Discussion
### UV photolysis and UV/$H_2O_2$ process
DCF effectively absorbs UV light in the range between 200 and 300 nm with the absorption maximum at 273 nm, which tails well over 300 nm when the spectrum is measured up to 400 nm. In general, DCF is known to undergo both long wave and short wave UV photolysis. The former may occur even in natural surface water systems.

The experiments of UV photolysis and UV/$H_2O_2$ treatment of DCF were performed as preliminary trials for subsequent assessment of homogeneous and heterogeneous photo-Fenton treatment efficacy. In direct photolysis trials a spontaneous pH drop to 3.5 due to formation of hydrochloric and carboxylic acids was observed leading to precipitation of DCF (**Figure 1**). DCF is very water soluble in neutral-alkaline medium (50 g $L^{-1}$), but has low solubility (23.7 mg $L^{-1}$) at pH below $pK_a$ value [17]. Thus, under such acidic conditions, DCF precipitates from the solution.

In UV photolysis at pH 5, DCF was completely precipitated at the beginning and the process kinetics was entirely governed by the continuous re-dissolution of DCF. 90% conversion was not achieved during 2 h of oxidation and the highest DCF removal was 85%. Therefore, DCF degradation was still occurring at pH around 3.5, even though it had undergone slight precipitation during the treatment, due to simultaneous precipitation-degradation-re-dissolution process. Similar observation was reported by [5]. In the case of direct photolysis experiment started at pH 7 and 9, fast decrease in pH also led to the system controlled by DCF re-dissolution process (**Figure 1**). However, in both cases 90% conversion was achieved in 115 and 80 min for

**Figure 1**. Change in pH during DCF degradation by UV photolysis at different initial pH values.
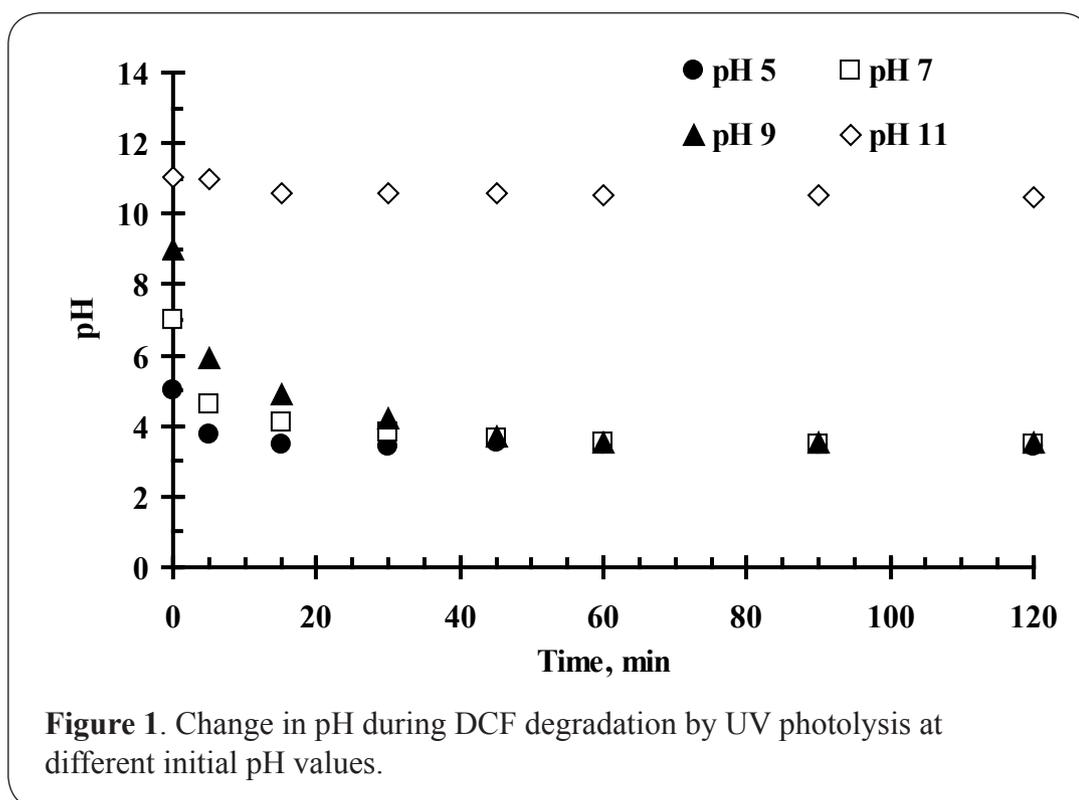
pH 7 and 9, respectively (**Figure 2**). Faster DCF removal compared to the trial at pH 5 was mainly due to effective drug degradation at the beginning of the treatment, i.e. pending pH decrease from initial to below $pK_a$ value.

Rivas *et al.,* [**18**] suggested that addition of free radical promoters does not enhance the efficiency of UV photolysis when irradiated substances have relatively high values of quantum yield ($\varphi$) and molar absorption coefficient ($\varepsilon$); moreover, a negative effect can be experienced. Reported $\varepsilon$ and $\varphi$ for DCF UV photolysis at 254 nm are 4260±130 $M^{-1}$ $cm^{-1}$ and 0.272±0.046 mol $Einstein^{-1}$, respectively [**19**]. On the other hand, Vogna *et al.,* [**20**] found that addition of hydrogen peroxide to UV system effectively induced DCF degradation. In the present study, different concentrations of hydrogen peroxide were tested to increase UV photolysis efficacy.

Similar to UV photolysis the efficacy of UV/$H_2O_2$ process proved dependent on the solubility equilibrium of DCF controlled by the pH of the surrounding solution. The results indicated that DCF transformation in the UV/$H_2O_2$ process was influenced by direct photolysis; *i.e.* UV photolysis was responsible for 85-100% of DCF degradation by UV/$H_2O_2$ system (**Figure 2**). The addition of 0.63 and 0.94 mM $H_2O_2$ resulted in negligible efficacy enhancement or even in worse DCF reduction compared to UV photolysis independently of the initial pH value. Further increase in $H_2O_2$ concentration to 1.9 mM led to improvement in DCF degradation with

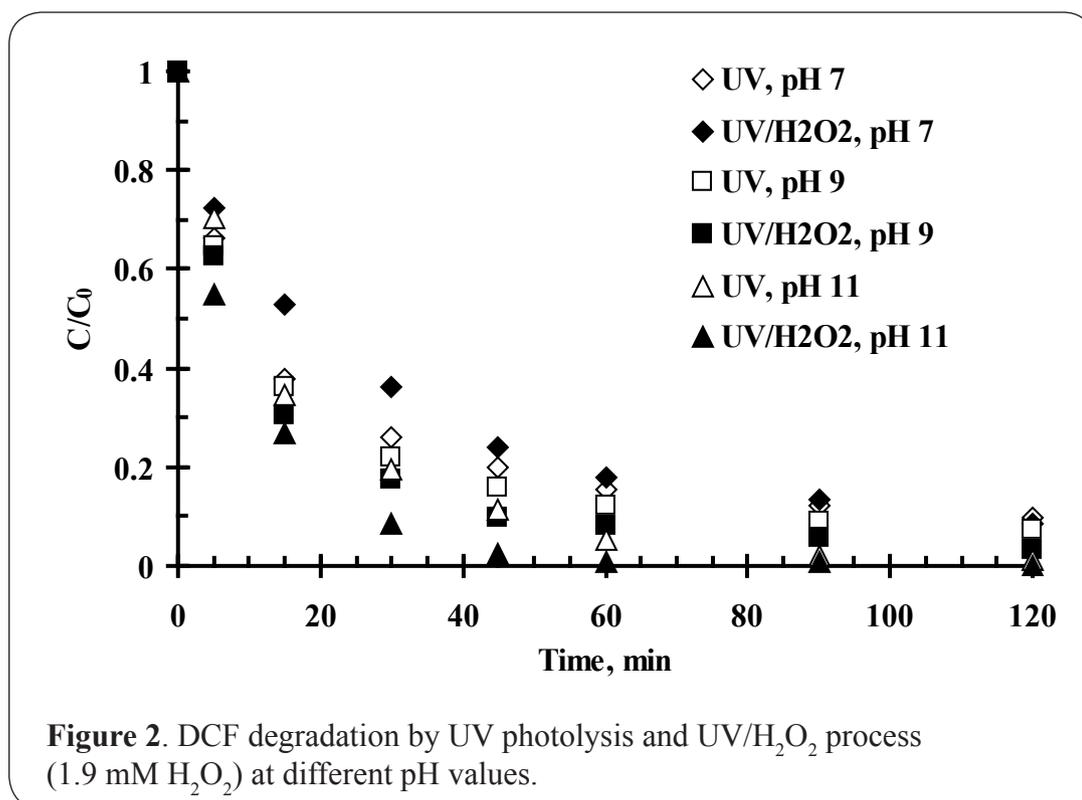pH increase from 7 to 11 (**Figure 2**). Thus, 90% conversion time ($T_{90\%}$) decreased from 48 to 28.5 min for UV photolysis and UV/$H_2O_2$ process at pH 11, respectively.

Blank trials with non-catalyzed hydrogen peroxide were performed at the same initial concentrations as the photo-catalytic experiments. No degradation of DCF was detected during 2 h of $H_2O_2$ oxidation.

Overall UV and hydrogen peroxide photolysis treatment efficacy was assessed by measuring COD. Low mineralization (not exceeding 15% after 2 h of oxidation) was observed in any case according to measured COD values. This fact indicated the formation of intermediates, which are more resistant to the photo-degradation than DCF itself.

### The Fenton and photo-Fenton treatment

The Fenton process trials ($H_2O_2/Fe^{2+}$) were conducted at pH 5 and 7. The experiments with initial pH 5 indicated rapid pH decrease below $pK_a$ value, resulting in the system completely controlled by precipitation-degradation-re-dissolution process. DCF removal during 2 h was very moderate, *e.g.* 25% in trial with 0.94 mM $H_2O_2$. The increase in initial pH to 7 resulted in improved DCF removal (40 and 70% of DCF were degraded during the Fenton treatment at 0.94 and 2.5 mM $H_2O_2$ concentration, respectively). However, fast pH decrease was still observed in systems with pH 7 indicating effective degradation of DCF at the beginning of the Fenton reaction and subsequent slow removal

**Figure 2**. DCF degradation by UV photolysis and UV/$H_2O_2$ process
(1.9 mM $H_2O_2$) at different pH values.

influenced by drug's re-dissolution.

As to the heterogeneous Fenton process, the goethite catalysed Fenton-based reaction is a surface controlled process that depends on $H_2O_2$ concentration, on the iron mineral surface area and on other system parameters (pH, *etc.*). The overall heterogeneous reaction will include various steps such as diffusion of chemicals to the surface, surface complex formation, actual electron transfer, desorption of products, and regeneration of the reactive sites [**10**].

The results showed no removal of DCF during 2 hours of the heterogeneous Fenton reaction independent of $H_2O_2$ concentration in the range of 0.63-3.8 mM. The amount of the total dissolved iron in the bulk solution for $H_2O_2$/α-FeOOH system was less than 0.03 mg $L^{-1}$ after 120 min of oxidation, indicating solely heterogeneous pathway of reaction. Some decrease in $H_2O_2$ concentration observed during the goethite catalyzed Fenton-based oxidation is most likely due to partial $H_2O_2$ decomposes to oxygen and water at the surface of the heterogeneous catalysts without producing dissolved radicals [**10**]. Prolonged experiments with overall duration of 24 h resulted in negligible degradation of DCF with less than 5% removal. The sorption experiments demonstrated no DCF removal due to adsorption on the catalyst surface.

Since solely $H_2O_2$ did not led to complete mineralization of DCF by UV/$H_2O_2$ process the photo-Fenton treatment proved promising alternative to enhance DCF degradation

in aqueous solution. Similar to direct and hydrogen peroxide photolysis the photo-Fenton process (both homogeneous and heterogeneous) kinetics were governed by the continuous re-dissolution of DCF. Thus, trials with initial pH 7 and 9, demonstrated pH decrease to 3.5 during the experiment.

The homogeneous photo-Fenton treatment was conducted at initial pH 7. Iron precipitated at this pH value producing highly light-absorbing iron hydroxide colloids. In general, photo-reductive decomposition of ferric-complexes can release ferrous iron to the solution, which will produce additional hydroxyl radicals in the presence of hydrogen peroxide. The results of DCF removal revealed similarity among the homogeneous photo-Fenton process and UV/$H_2O_2$ system (pH 7). Thus, DCF degradation was slower during UV/$H_2O_2$/$Fe^{2+}$ process compared to direct photolysis at neutral pH value. This fact can be explained by faster decrease in pH below $pK_a$ value leading to the treatment process controlled by continuous DCF re-dissolution.

The heterogeneous photo-Fenton trials were conducted at pH in the range from 7 to 11. Generally, minerals containing ferric oxides (*e.g.* goethite) need ultraviolet radiation to accelerate the reduction of $Fe^{3+}$ to $Fe^{2+}$. The results of goethite catalysed photo-Fenton system indicated similarity to UV/$H_2O_2$ process as the increase in $H_2O_2$ concentration and pH led to additional DCF removal if compared to direct photolysis (**Figures 3** & **4**). Thus, $T_{90\%}$ was decreased from 115
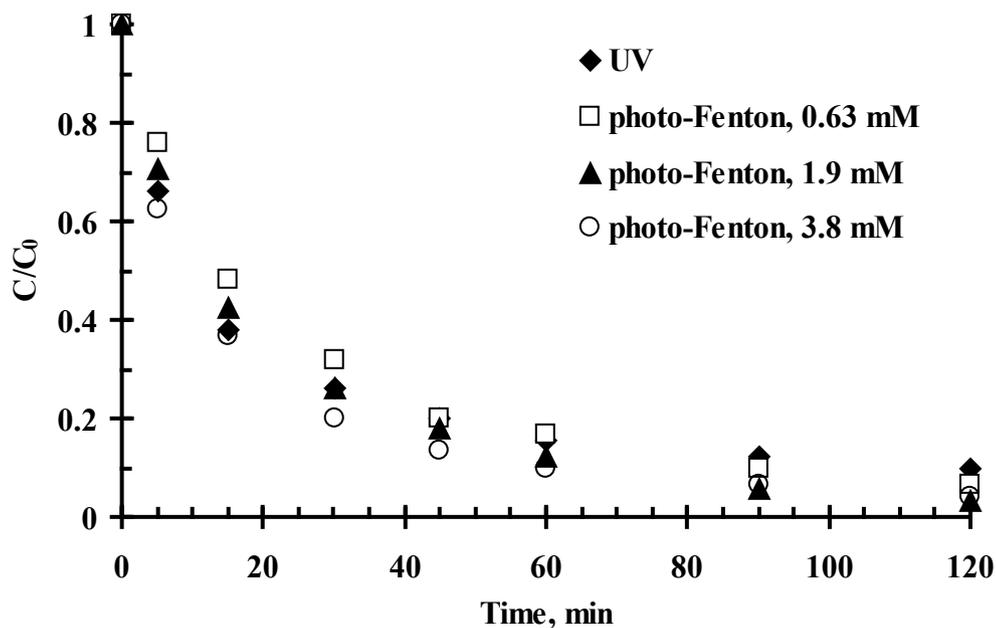
**Figure 3**. DCF degradation by heterogeneous photo-Fenton treatment (pH 7) at different $H_2O_2$ concentrations.
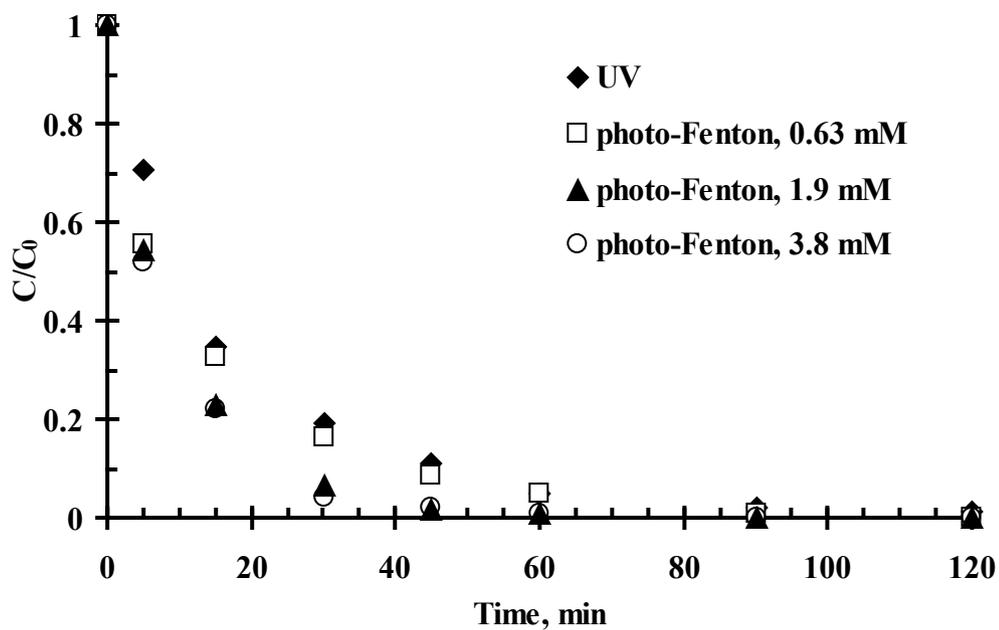


**Figure 4**. DCF degradation by heterogeneous photo-Fenton treatment (pH 11) at different $H_2O_2$ concentrations.

to 69 min and from 80 to 42 min for photo-Fenton treatment (1.9 mM $H_2O_2$) at pH 7 and 9, respectively, if compared to direct photolysis. The $H_2O_2$ utilization in the heterogeneous photo-Fenton and UV/$H_2O_2$ processes was comparable as well and resulted in 25-30% at pH 7 and 9. At pH 11 residual $H_2O_2$ concentrations was less than 5% in all cases, probably due to $H_2O_2$ auto-decomposition at elevated pH values.

The efficacy of promoted photolysis proved dependent on the rate of pH decrease (from initial to value below $pK_a$) at the beginning of the process. After reaching acidic pH of the surrounding solution the DCF degradation was stable and controlled by the solubility independently of treatment method applied. The highest efficacy improvement was attained in UV/$H_2O_2$/α-FeOOH system at pH 11, where pH decreased only to 10, and the process was not determined by the solubility equilibrium of DCF. The $T_{90\%}$ for UV photolysis and heterogeneous photo-Fenton process (3.8 mM $H_2O_2$) was 48 and 23.5 min, respectively (**Figure 4**).

Similar to UV and UV/$H_2O_2$ systems, no substantial mineralization of DCF was observed in any studied Fenton-based process with initial pH 7 and 9. COD removal was ca 15% after 2 h of oxidation. In the case of pH 11 and elevated $H_2O_2$ concentration (1.9 mM), COD was essentially reduced (up to 60%) indicating overall efficacy of the process under strongly alkaline conditions.

### Identification of intermediates

In the present study, no derivatization procedures were undertaken prior to injection of the samples into GC-MS (EI) system, and highly polar or non-volatile by-products could escape the scope of the technique. Identification of by-products was done by comparison of full-scan mass spectra of the peaks with mass spectral library (NIST/EPA/NIH (NIST 08)) or by identification of the fragmentation patterns.

The results of the present study indicated similar GC-MS chromatogram patterns for UV photolysis, UV/$H_2O_2$ and UV/$H_2O_2$/α-FeOOH systems. Two photo-transformation products were detected; other by-products were in trace concentrations (below the method detection limits) even during the first few minutes of DCF degradation. The main detected photo-transformation product with formula $C_{14}H_9Cl_2NO$ (MW 277) was identified as 1-(2,6-dichlorophenyl)indolin-2-one. This compound was also reported [4] as one of the major photo-decomposition products of DCF in pure water. However, the application of GC-MS for sample analysis could be the reason for such observation, since 1-(2,6-dichlorophenyl)indolin-2-one can be formed due to a high temperature used in this method. The other observed photo-transformation product with formula $C_{14}H_{10}ClNO$ (MW 243) was apparently described as C-2 (8-chloro-9H-carbazole-1-acetic aldehyde) [21]. The analysis of mass spectrum of the latter by-product indicated mass differences of Δ=28 and Δ=35 pointing to the existence of one chlorine atom and an aldehyde function. In order to prove this assumption further detailed analysis is required.

## Conclusions

DCF was quite resistant to all tested AOPs. The application of the Fenton-based treatment and UV/$H_2O_2$ did not show vital advantages compared to UV photolysis when the initial pH was 7 or 9. Direct photolysis proved main process contributing to DCF degradation in all studied systems combined with UV irradiation. The fast pH decrease of the surrounding solution to 3.5 observed during all studied processes started at pH 5, 7 and 9 led to system controlled by DCF precipitation-degradation-re-dissolution. The efficacy of UV/$H_2O_2$, homogeneous and heterogeneous photo-Fenton systems proved dependent on time of pH decrease at the beginning of the process. After reaching pH values below DCF $pK_a$ the degradation was controlled by the solubility independently of treatment method applied. The present study was the first to evaluate the efficacy of photo-Fenton catalysed by goethite for DCF degradation in aqueous solution. The latter proved the most efficient one among the Fenton-based processes. The identification of DCF degradation by-products by GC-MS (EI) technique was done indicating 1-(2,6-dichlorophenyl)indolin-2-one and 8-chloro-9H-carbazole-1-acetic aldehyde as two detectable photo-transformation products.

### Competing interests
The authors declare that they have no competing interests.

### Authors´ contributions
IE contributed to research design, fulfilled the experiments and analyses, contributed to data interpretation and drafted the manuscript. ND contributed in conception, research design, data interpretation and manuscript draft. MT contributed in conception, research design and manuscript draft. All authors approved the manuscript.

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