

# Removal of Diclofenac Sodium from Aqueous Environments Using Heterogeneous Photocatalysis Treatment

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**Abstract:** The occurrence, fate and effects of Pharmaceuticals compounds (PhCs) in the environmental system have been attracted special attention in the world as a new emerging contaminants due to their potential impact on humans, animals and microorganisms even at low concentrations. Conventional wastewater treatment technologies, including biological, thermal and physical treatments, are demonstrated to be insufficient for removal of many pharmaceuticals residues from wastewater, due to their low biodegradability and high chemical stability. Advanced oxidation processes (AOPs), are one of the most promising treatment technologies for elimination of such relentless compounds. The current study was focused on the efficacy of various oxidation processes for degradation of diclofenac sodium (DCF) as a one of the most widespread pharmaceuticals present in sewage. The experimental phase was divided into two parts: Photolysis and heterogeneous photocatalysis. Concerning photocatalysis experiments, TiO<sub>2</sub> as a catalyst has been used in two forms: (i) as dispersed powder; (ii) immobilized on the surface of blue slabs. Kinetic studies of DCF were accomplished and its photoproducts were identified using liquid chromatography coupled with mass spectrometry system (LC-MS). Heterogeneous photocatalysis by using TiO<sub>2</sub> dispersed powder shows the fastest extent of degradation with 54.6 min of half-life ( $t_{1/2}$ ). Nevertheless, the recovery of the suspended catalyst from the treated solution still form a problem after the treatment process. Direct photolysis and photocatalysis using TiO<sub>2</sub> immobilized system showed approximately

comparable results ( 71 and 79 min respectively), in contrast, the degradation pathway for each process was different which yielded a diversity in the photoproducts in each process.

In conclusion, the overall results suggested that using both photolysis and heterogeneous photocatalysis are promising alternative techniques towards protecting the environment from this emerging contaminants.

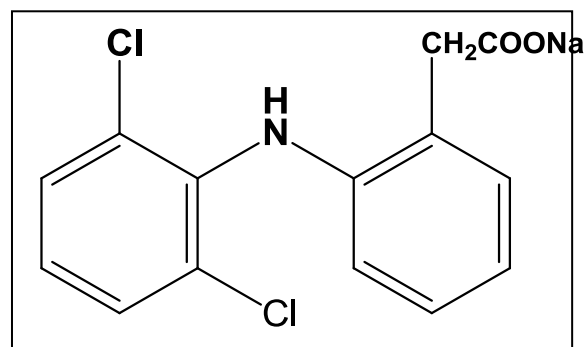
**Keywords:** Anti-inflammatory drugs, advanced oxidation process, wastewater, photocatalysis, TiO<sub>2</sub>, photo-degradation, DCF.

## 1. Introduction

The occurrence and persistence of pharmaceutical compounds (PhACs) in the aquatic environment have caused a rising concern about the presence of these new emerging contaminants, of their potential impacts on the aqueous ecosystems and human health even at low concentrations [1, 2]. There are different sources for PhACs in the environment but, probably, the main is the high consumption of pharmaceuticals by humans and animals which provides a continuous release of these substances or their metabolites to the environment [3, 4]. Also, the improper disposal of unused or expired medicines that have been pumped into the sinks or toilets from pharmaceutical manufacturing facilities, hospitals and houses [5].

These pharmaceuticals and their metabolites end up in the sewage system and reach to wastewater

treatment plants (WWTPs) [6]. The conventional wastewater treatment plants, which involve physical, biological and chemical stages, demonstrated to be insufficient to remove completely pharmaceuticals present in wastewater [7, 8]. Consequently, effluents finally released into receiving water bodies, and as a result they have been detected in a wide range of environmental samples including surface water, ground water and drinking water in the range between  $\text{ngL}^{-1}$  and  $\mu\text{gL}^{-1}$  [9, 10]. Among the various pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) gain a special relevance from being the most frequently mentioned environmental contaminants due to the high consumption rate of these drugs [11, 12]. Diclofenac (DCF) (2-[2-(2,6-dichloroanilino) phenyl] acetic acid) is a common non-steroidal anti-inflammatory drug (NSAID), mostly used as its sodium salt in medical care as an analgesic, antiarthritic and antirheumatic (Figure 1) [13]. Diclofenac is one of the most widely available drugs in the world, and approximately hundreds of tons are consumed annually worldwide [14]. This pharmaceutical is relatively stable in the environment because it is sensible to light and can undergo to photochemical decomposition in surface water under solar radiation [5]. However, diclofenac is one of the most frequently detected compounds in water at concentrations up to  $2 \mu\text{gL}^{-1}$  [15]. However, diclofenac is one of the most frequently detected compounds in water at concentrations up to  $2 \mu\text{gL}^{-1}$  [15]. Therefore, and due to insufficient ability of the conventional wastewater technologies as mentioned previously to eliminate such kinds of pollutants, employing advanced treatment technologies gained a vital importance in order to protect the aquatic environment from the adverse effects of these hazard pollutants. Advance oxidation processes (AOPs) are one of the most promising treatment technologies for successful degradation of pharmaceuticals in aqueous matrices [16], AOPs include several technologies such as photolysis, ozonation, photocatalysis, photo-Fenton and sonolysis [17]. The most popular and effective type of AOPs employed in water and wastewater treatment is the heterogeneous photo-catalysis with semiconductors [18,19]. In heterogeneous photocatalysis, dispersed solid particles of semiconductor efficiently absorb large fractions of the UV spectrum, and they generate chemical oxidants from dissolved oxygen or water in situ [18]. Among the various semiconductors employed,  $\text{TiO}_2$  is the most preferable material for the photo-catalytic process [19], due to its high photosensitivity, non-toxic nature, large band gap, chemical stability and lower cost [20].



**Figure 1:** Chemical structures of diclofenac sodium.

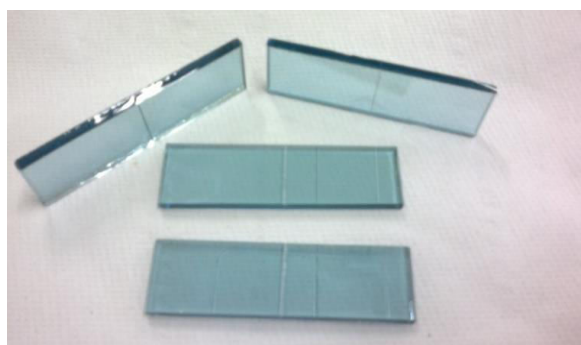
In this work, the efficacy of two oxidation processes (Photolysis and heterogeneous photocatalysis using a solar simulator light) towards removal of DCF from aqueous phase were studied. To the best of our knowledge, the vast majority of the investigations and applications on heterogeneous photocatalysis ( $\text{TiO}_2$ ) have employed the traditional suspension form in water treatment processes. Therefore, this study aims to evaluate the fixation or immobilization of semiconductor ( $\text{TiO}_2$ ) over a stationary glass slabs as an alternative to the traditional form. This approach would circumvent the need for filtration to recover the catalyst from the reaction mixture, and as a result save a post treatment stage and decrease the operational costs. The work also concentrated on the identification of the photoproducts and intermediates during the degradation process by using liquid chromatography coupled with mass spectrometry (LC-MS). As well as all kinetics studies have been, conducted.

## 2. Experimental

### 2.1 Materials and Equipments

**Materials:** All chemicals and reagents were of analytical grade, and they were purchased from Sigma-Aldrich Corporation (USA). Commercial  $\text{TiO}_2$  P-25 from Degussa (80% anatase, 20% rutile, surface area  $50 \pm 15 \text{ m}^2/\text{g}$ , non porous) and  $\text{TiO}_2$  Merck (BET specific surface area (pure anatase,  $10 \text{ m}^2/\text{g}$ ) were used as the photo catalysts. Grafted  $\text{TiO}_2$  thin blue glasses were obtained from Pilkington (UK) (Figure 2). PTFE (Polytetrafluoroethylene) filters,  $0.2 \mu\text{m}$  pore size, filter-Ø: 25mm were purchased from Macherey-Nagel GmbH & Co. KG (Duren-Germany). All the solutions were daily prepared in ultra-pure water from a bidistilled purification system.

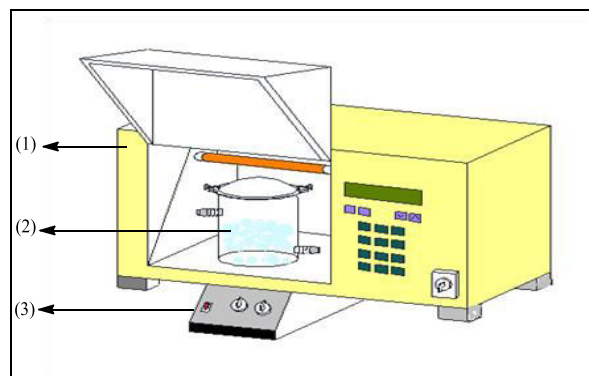
Anti-Inflammatory drug Diclofenac sodium pure standard was obtained from Birzeit Pharmaceutical company (Palestine) with 99 % purity.



**Figure 2:** Grafted TiO<sub>2</sub> thin blue glasses.

Photolysis / Photocatalysis equipments: Photolysis, photocatalysis with TiO<sub>2</sub> powder and photocatalysis with immobilized TiO<sub>2</sub> on thin blue glass experiments were accomplished using batch reactor system, this system consist of:

- (1) Suntest CPS<sup>+</sup> Solar Simulator (Heraeus Instruments, Germany) equipped with a xenon lamp, temperature sensor and water-cooling circuit. The xenon lamp was filtered by an optically stable borosilicate UV filter (Atlas Material Testing, France) delivering a light emission spectrum similar to that of the sun with a UV cut-off at 290 nm. The pyrex reactor that contains the solution placed inside the chamber of the suntest device.
- (1) Pyrex batch reactor, the capacity of the reactor is 300 ml, it's outer perimeter reactor is covered by aluminum foils and only the upper surface is exposed to radiation.
- (2) Magnetic stirrer device (Falc F20 Mini Magnetic stirrer. Progen Scientific, Merton. London) is employed to maintain a continuous stirring for the solution inside the pyrex reactor during the experiments. A schematic drawing of the batch reactor system is shown in (Figure 3).



**Figure 3:** A schematic drawing of the batch reactor system: (1) Suntest CPS<sup>+</sup> Solar Simulator, (2) Pyrex batch reactor and (3) Magnetic stirrer device.

#### Analytical instrumentation:

- (1) High Performance Liquid Chromatography system (HPLC) (Agilent technologies 1200 series) (Avondale, PA,USA) equipped with an Eclipse XDB-C18 (3 μm particle size, 4.6 mm × 150 mm) column (Phenomenex-USA) using a diode array detector.
- (2) LC/MS system: LC system coupled to a hybrid quadrupole ion trap (LTQ) - fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Thermo fisher scientific Bremen, Germany). In this system the chromatographic separations were performed at ambient temperature using a Gemini C18 HPLC column (150 × 2.0 mm, 5 μm; Phenomenex, UK).
- (3) Scanning electron microscope (SEM): scanning electron microscope (SEM) (LEO model EVO50XVP, Carl Zeiss AG - EVO® 50 Series, Germany).

#### 2.2 Analytical methods

In batch reactor system, samples of 2 mL were taken at determined time intervals. Samples of photocatalysis/TiO<sub>2</sub> powder experiments were filtered through a 0.2 μm filters to remove TiO<sub>2</sub> particles. Changes in the concentration of each drug was observed from its characteristic absorption at selected nm, using HPLC system through the following method:

- Column: Eclipse XDB-C18 (3 μm particle size, 4.6 mm × 150 mm).
- Mobile phase: 1% CH<sub>2</sub>O<sub>2</sub> (V/V):ACN (65:35).
- Wavelength: 254 nm.
- Flow rate: 1.0 mL/min.

Several aqueous solutions (from 0.5 to 50.0 mg L<sup>-1</sup>) of DCF were filtered and 20 µL of the filtrated solutions were injected into the HPLC and analyzed, peak areas vs. concentration of DCF were plotted and the calibration curve was obtained with a determination coefficient (R<sup>2</sup>) of 0.9999. The limit of detection (LOD) of DCF for this method was 0.15 mg L<sup>-1</sup>, and the limit of quantitation (LOQ) was 0.45 mg L<sup>-1</sup>.

### 2.3 Characterization of the Pilkington Active<sup>TM</sup> Blue glass

The elemental analysis for the grafted TiO<sub>2</sub> thin Pilkington blue glasses was performed by using scanning electron microscope. Some cross sections obtained from the Pilkington Active<sup>TM</sup> Blue glass were analyzed. The thin sections were coated with a 30 nm-thick carbon films. Semi quantitative analyses of the elemental composition of the different layers were obtained using a Ge ED Oxford-Link detector equipped with a Super Atmosphere Thin Window. Operating conditions of the SEM were: 15 kV accelerating potential, 500 pA probe current and about 10 mm of working distance (WD).

Thin sections of glass were prepared by the Department of Health and Environmental Science, Bari University. Samples were embedded in resin epoxy plugs and then polished.

### 2.4 Photolysis and photocatalysis procedures

#### 2.4.1 Photolysis

Photochemical experiments were conducted by using solar irradiation system. Working solutions of diclofenac sodium (25 mg L<sup>-1</sup>) were prepared when used by dilution from stock solution (100 mg L<sup>-1</sup>). To investigate the effect of hydrolysis, the same experiment in the dark was performed. The tests were carried out with extreme care to ensure uniform experimental conditions during the degradation kinetics. At determined time intervals, samples of 2.0 mL were taken and immediately analyzed by HPLC system according to the analysis method mentioned above. The photolysis treatment was carried out in a glass Pyrex batch reactor (Part 2, figure 3). 250 mL from the prepared solution were placed into well closed reactor, then placed in a radiation field inside the Suntest (solar simulator) device (Part 1, Figure 3), which reproduces the spectral distribution of solar irradiation, the aqueous solution containing drug was mixed continuously with magnetic stirrer during the experiment (Part 3, Figure 3).

#### 2.4.2 Photocatalysis

Photocatalysis processes includes photocatalysis with commercial TiO<sub>2</sub> powder and photocatalysis with immobilized TiO<sub>2</sub> on thin Pilkington Active<sup>TM</sup> Blue glass.

##### 2.4.2.1 Photocatalysis with TiO<sub>2</sub> powder

In this experiment, the same steps in section (2.3.1) were followed, working solutions of diclofenac sodium (25 mg L<sup>-1</sup>) with 200 mg L<sup>-1</sup> TiO<sub>2</sub> were prepared, 250 mL of the solution was placed into well closed reactor, then placed in a radiation field inside the Suntest (solar simulator) device. At specific time intervals, samples of 2.0 mL were taken and immediately filtered through a 0.2 µm filter, and analyzed by HPLC system according to the analysis method mentioned above. The aqueous solution containing drug was mixed continuously with magnetic stirrer during the experiment.

##### 2.4.1.2 Photocatalysis with immobilized TiO<sub>2</sub> on thin blue glass

As in the previous sections, solution of 25.0 mg L<sup>-1</sup> was prepared, and then 250 ml transferred to the glass pyrex reactor, before that the blue glass had been placed vertically on the perimeter of the inner wall of the glass pyrex batch reactor, then transferred to the suntest CPS (solar simulator) device, and exposed to the solar irradiation with continues mixing using magnetic stirring, samples were taken (2 mL for each sample) at determined intervals then filtered and injected in HPLC system according to the analysis method mentioned above.

### 2.5 Kinetics study

The knowledge of reaction order is essential for finding the accurate integrated rate equation. By trying to fit data of various integrated rate equations, it is possible to verify the reaction order. Kinetic parameters were calculated using integrated equations describing zero-, first- and second- (Langmuir-Hinshelwood) order equations. The determination coefficient (R<sup>2</sup>) was used to check the best fit.

Kinetic parameters (reaction order (n), determination coefficient (R<sup>2</sup>), half-life (t<sub>1/2</sub>), kinetic constant (k) were obtained by linear regression of logarithmic concentration values determined as a function of time according to the following equations:

Zero-order:  $C_t = C_0 - kt$  (1)

First-order:  $\ln C_t = \ln C_0 - kt$  (2)

Second-order:  $C_0/C_t = 1 + (1/t_{1/2})t$  (3)

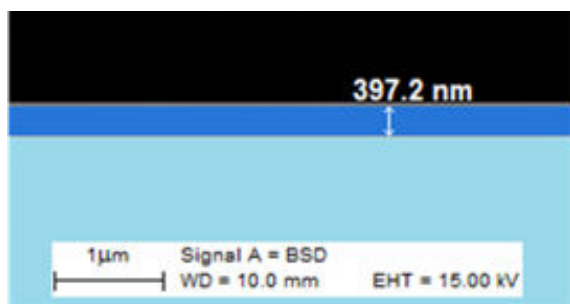
### 2.6 Identification of photoproducts

The Identification of DCF photoproducts in all experiments were carried out using LC/MS system in the same separation conditions. Negative ion ESI-MS was used for the detection of compounds of interest. Mass spectrometric conditions were optimized by direct infusion of standard solutions. The instrument was tuned to facilitate the ionization process and to achieve the highest sensitivity. The MS detector was tuned whenever the solvent flow rate conditions were changed, and the electro-spray voltage, heated capillary temperature and voltage, tube lens voltage, sheath gas flow rate and auxiliary gas flow rate were optimized until the ion transmission was maximized. Full-scan experiments were performed in the ICR trapping cell in the range  $m/z$  50–1000. Mass-to-charge ratio signals ( $m/z$ ) were acquired as profile data at a resolution of 100,000 (FWHM) at  $m/z$  400.

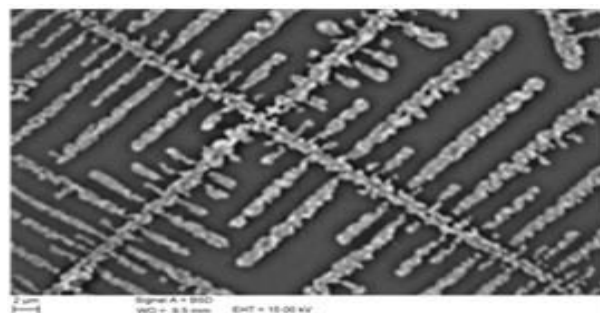
## 3. Results and discussion

### 3.1 Characterization of Pilkington Active™ TiO<sub>2</sub> coated Blue glass

(Figure 4) shows the SEM image of the cross section sample of the Blue glass, where the thickness of TiO<sub>2</sub> film was found to be 397.2 nm. (Figure 5) displays the fine-tooth comb geometry of TiO<sub>2</sub> coating on the Blues glass surface.



**Figure 4:** SEM colored micrograph of the Blue glass cross section showing the TiO<sub>2</sub> layer immobilized on the glass surface.



**Figure 5:** SEM micrograph of the Blue glass surface showing the fine-tooth comb of TiO<sub>2</sub> coating.

As shown in (Table 1), TiO<sub>2</sub> is a component present only on the glass surface along with other metal oxides such as iron oxide, while in the core glass it is absent and other metal oxides are countable. As reported in the Pilkington patent [21], cobalt oxide is present in low amounts (less than 75 μg/g) but it was not detectable by surface analysis used. Cobalt oxide may confer the blue color to the glass.

**Table 1:** EDX analysis of the glass surface coated with TiO<sub>2</sub>, compared to the glass core composition.

Elemental composition of the grafted surface	
Energy: 6.686 KeV, Counts: 250	
Elements	Wt. % ± SD
O	44.4 ± 0.1
Si	38.6 ± 0.1
Na	6.0 ± 0.0
Ca	5.5 ± 0.0
Mg	2.4 ± 0.0
Ti	1.5 ± 0.0
K	0.3 ± 0.0
Al	0.3 ± 0.0
Fe	0.3 ± 0.0
Elemental composition of the core glass	
Energy: 6.686 KeV, Counts: 250	
Elements	Wt. % ± SD
O	47.2 ± 0.1
Si	36.2 ± 0.1
Na	4.3 ± 0.0
Ca	6.0 ± 0.1
Mg	2.4 ± 0.0
Sn	2.1 ± 0.1
K	0.3 ± 0.0
Al	1.0 ± 0.0
Fe	0.4 ± 0.1
Cl	0.1 ± 0.0

### 3.2 Photolysis and photocatalysis processes

In the laboratory experiments, DCF dissolved in distilled water was found to be susceptible to both direct and indirect photolysis. The irradiation was performed by using a Solar Simulator equipped with a Xenon source. At environmentally relevant concentrations (i.e., optically dilute solutions;  $25 \text{ mg L}^{-1}$ ) and temperatures ( $25 \pm 3^\circ\text{C}$ ), DCF, approximately, degraded to about half of the initial concentrations within 71 min under solar light during direct photolysis experiment, and less than 55 min under photo-catalysis using  $\text{TiO}_2$ . While in photo-catalysis using  $\text{TiO}_2$  immobilized system, the degradation rate was approximately similar to that in direct photolysis, since DCF degraded to about half of the initial concentrations within 79 min. No significant loss of DCF was observed in the dark controls (both photolysis and photocatalysis), eliminating the possibility of thermal or hydrolytic degradation and showing that the adsorption of  $\text{TiO}_2$  does not have any vital role on DCF removal process.

The photo-degradation for DCF plotted as the natural logarithm of the ratios of the observed over the initial concentrations, exhibited approximately linear behavior ( $R^2$  ranging from 0.983 to 0.994). From the overall results, we can conclude that the decrease in DCF concentrations during direct simple photolysis and photocatalysis using  $\text{TiO}_2$  powder was convergent, since half-life ( $t_{1/2}$ ) for direct photolysis and photocatalysis using  $\text{TiO}_2$  was 71 and 54.6 min respectively.

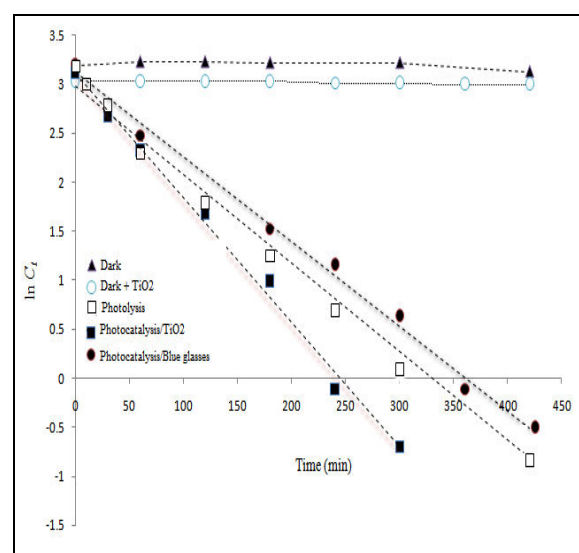
As well as, photocatalysis using  $\text{TiO}_2$  immobilized system achieved  $t_{1/2}$  79 min which is approximately similar to direct photocatalysis. Then a complete disappearance of DCF in photolysis was achieved within 480 min, in photocatalysis using  $\text{TiO}_2$  powder within 300 min and in photocatalysis using  $\text{TiO}_2$  immobilized system achieved in 420 min (Table 2). Photolysis and Photo-catalysis results are shown in (Figure 6).

Nevertheless, the comparison to be comprehensive, we must take in consideration the photoproducts that resulted from each process and their mineralization in conjunction with DCF decline.

From this point of view, the results show that the complete mineralization of photoproducts during photocatalysis using  $\text{TiO}_2$  powder was achieved approximately after 8 hours, and after 11 hours by using immobilized  $\text{TiO}_2$ , while during photolysis process photoproducts were mineralized after 24 hours. On the other hand, the diversity in degradation pathways between the processes

resulted in formation of some different photoproducts. The degradation pathways and identification of photoproducts will be explained in details in the next section.

Accordingly, we can conclude that interaction of DCF with sunlight directly (photolysis) can lead to DCF complete degradation, but need a long time to mineralize the photoproducts while in presence of  $\text{TiO}_2$  which acts as an active semi-conducting agent and efficiently absorb large fraction of light and generate electron-hole pairs which subsequently generate oxidative species ( $\cdot\text{OH}$  radicals), from dissolved oxygen or water in situ [18], which react with DCF in solution and mineralize it and its photoproducts within short period.



**Figure 6:** Time course mineralization of DCF at  $25 \text{ mg/L}$  initial concentration in batch reactor (photolysis, photocatalysis) solar (lamp Heraeus TNN 15/32). Experimental conditions: DCF concentration =  $25 \text{ mg/L}$ ,  $[\text{TiO}_2] = 200 \text{ mg/L}$ , solar intensity (sunny day) =  $500 \text{ Wm}^{-2}$ .

An increase catalyst concentration could show an increase of DCF degradation for the first few minutes due to the fact that number of DCF molecules adsorbed and photon absorbed increases with increase in catalyst loading. The increase degradation during the photo-catalysis process was probably due to an increase in availability of catalytic sites and adsorption sites. However, the increase of catalyst loading beyond the optimum may result in the agglomeration of catalyst particles, hence the part of the catalyst surface become unavailable for photon absorption and degradation rate decrease.

We can notice that photocatalysis with TiO<sub>2</sub> powder achieved the desired goal (mineralization of DCF and its photoproducts in short time), but the problem is the need for a post treatment stages to recover the catalyst from the reaction mixture. Thus, using TiO<sub>2</sub> immobilized system over blue glass slabs would circumvent the need for filtration to recover the catalyst from the reaction mixture, and also achieve the desired efficacy in mineralization of both DCF and its photoproducts in approximately short time.

**Table 2:** Kinetic parameters of the photolysis, photocatalysis using TiO<sub>2</sub> and photocatalysis using TiO<sub>2</sub> immobilized system. k: rate constant, R<sup>2</sup>: correlation coefficient, t<sub>1/2</sub>: half-life

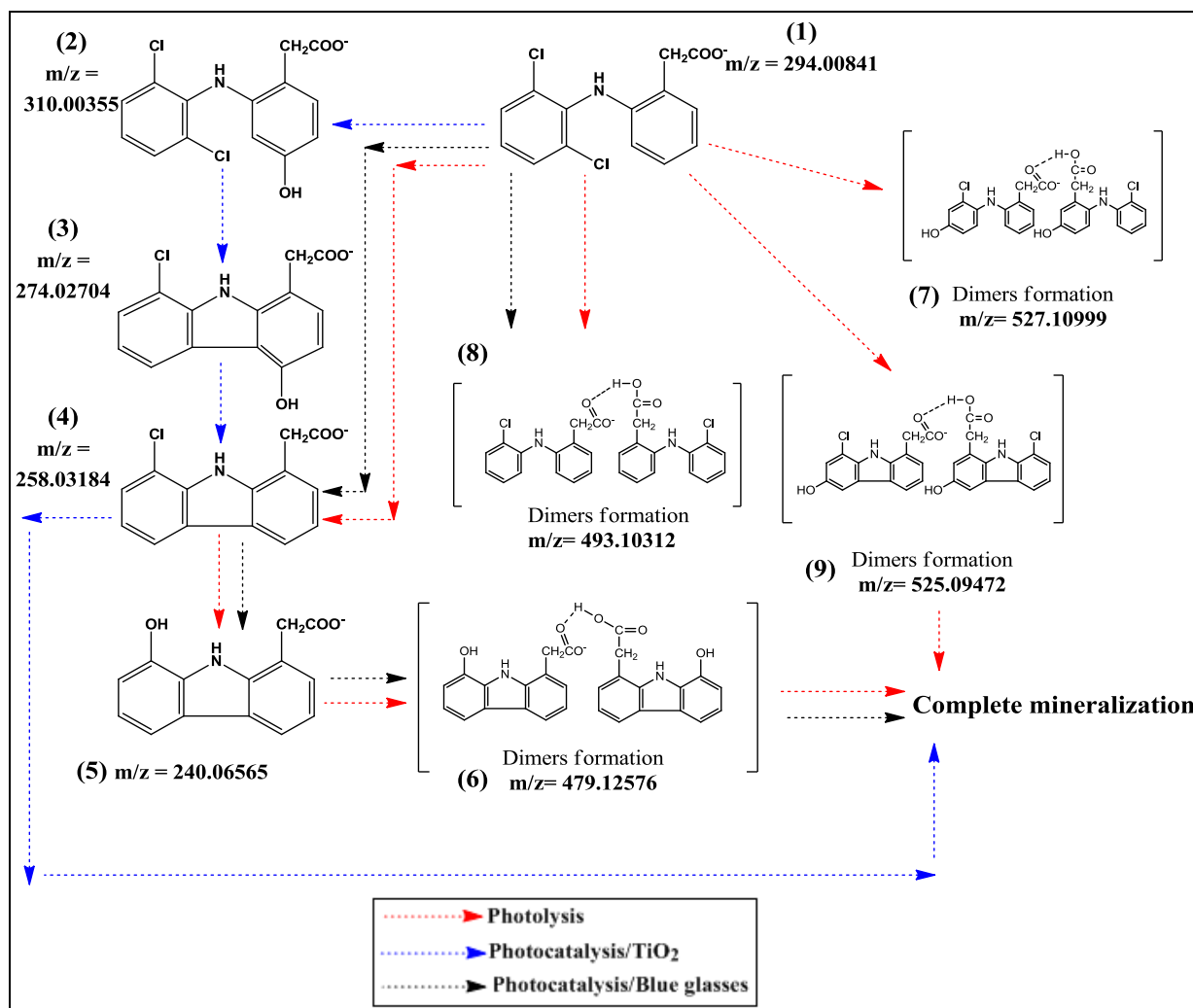
Conditions	Order	k (min <sup>-1</sup> )	R <sup>2</sup>	t <sub>1/2</sub> (min)
Photolysis	1	0.009	0.9	70.7
Photocatalysis/TiO <sub>2</sub> powder	1	0.012	0.9	54.6
Photocatalysis/TiO <sub>2</sub> immobilized	1	0.008	0.9	79.7

In general, we believe that more modifications in grafted TiO<sub>2</sub> thin blue glasses such as increasing the concentration of TiO<sub>2</sub> on the sheets surfaces or changing the amount of metal oxides in the blue glasses, will improve the effectiveness of this substrates. The preliminary results indicate that this method could be promising for use in wastewater treatment field, since it's totally clean and it doesn't require additional post treatment stage to recover TiO<sub>2</sub> as we mentioned previously.

### 3.3 Identification of transient photoproducts

In order to identify DCF degradation products, samples were collected at various time intervals and analyzed. DFC by-products generated by photolysis and photocatalytic processes were identified by LC (FT-ICR) MS system, into the m/z range of 50-1000 in negative ionization mode. Results indicate the formation a number of some identical products with similar pathways; and a number of different products with different pathways (Table 3).

The analysis of samples at zero time in photolysis and photocatalytic experiments resulted in formation a product at m/z 296 (1) (Figure 7).



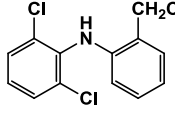
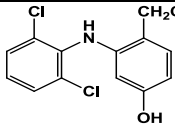
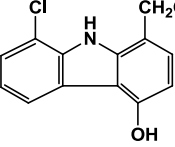
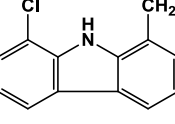
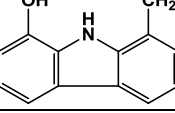
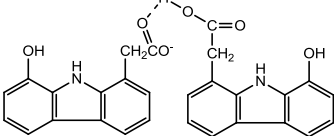
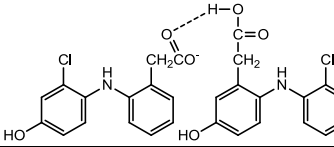
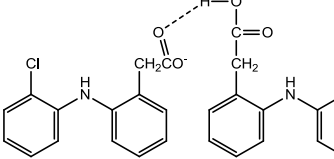
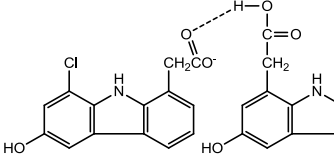
**Figure 7:** Photodegradation mechanism for diclofenac sodium.

which represent diclofenac compound after loss of sodium from diclofenac sodium. In photocatalysis (TiO<sub>2</sub> powder) experiment, it was observed that the first step in the degradation pathway was the formation of a product at  $m/z$  310 (2) (Figure 7), corresponding to the addition of 16 mass units to the parent product (1). This is consistent with hydroxylation of the aromatic ring, the addition of the electrophilic hydroxyl radical to the aromatic ring with subsequent elimination of hydrogen radical yielding the phenolic products [22, 23]. Subsequently, a product at  $m/z$  274 (3) (Figure 7) was observed, corresponding to the loss of HCl from the primary phenolic product ( $m/z$  310). This suggests that phenolic substitute chlorine group subsequently underwent cyclization to form a five-membered ring. The last product identified in

photocatalysis (TiO<sub>2</sub> powder) experiment was observed at  $m/z$  258 (4) (Figure 7), corresponding to the loss of OH group from product (3). Then the degradation progressed and a complete mineralization has been achieved after 8 hours. In photolysis and photocatalysis using TiO<sub>2</sub> immobilized over blue glasses sheets the degradation was going with similar pathways and generating approximately the same products. In this degradation pathway the product with  $m/z$  294 (1) was transformed to product (4) with  $m/z$  258 directly. The second step was the formation of a product with  $m/z$  240 (5) (Figure 7). This is consistent with hydroxylation of the aromatic ring and substitution with chlorine group.



**Table 3:** Fragmentation obtained from MS/MS spectra of diclofenac  $m/z$  294 ( $C_{14}H_{11}NO_2Cl_2$ ).

Compound No.	Molecular formula [M-H] <sup>-</sup>	Accurate m/z [M-H] <sup>-</sup>	Structural formula	Oxidation Process	RT (min.)	Error (ppm)
(1)	$C_{14}H_{11}NO_2Cl_2$ 2 <sup>-</sup>	294.0084 1		Photolysis Photocatalysis/TiO <sub>2</sub> Photocatalysis/B.G.*	17.51	-0.93
(2)	$C_{14}H_{10}NO_3Cl_2$ 2 <sup>-</sup>	310.0035 5		Photocatalysis/TiO <sub>2</sub>	9.06	1.04
(3)	$C_{14}H_9NO_3Cl$	274.0270 4		Photocatalysis/TiO <sub>2</sub>	5.56	1.79
(4)	$C_{14}H_9NO_2Cl_2$	258.0318 4		Photolysis Photocatalysis/TiO <sub>2</sub> Photocatalysis/B.G.*	16.96	1.59
(5)	$C_{14}H_{10}NO_3$	240.0656 5		Photolysis Photocatalysis/B.G.*	14.18	-1.99
(6)	Dimers $C_{28}H_{19}N_2O_6$	479.1257 6		Photolysis Photocatalysis/B.G.*	15.17	-1.98
(7)	Dimers $C_{28}H_{19}N_2O_9$	527.1099 9		Photolysis	10.05	1.79
(8)	Dimers $C_{28}H_{17}N_2O_7$	493.1031 2		Photolysis Photocatalysis/B.G.*	14.45	1.83
(9)	Dimers $C_{28}H_{17}N_2O_9$	525.0947 2		Photolysis	12.84	1.46

\* grafted TiO<sub>2</sub> thin Pilkington blue glasses

During photolysis and photocatalysis/blue glasses in addition to the photoproducts mentioned, the presence of dimer products have been detected,

some of these dimer products formed with ( $m/z$  493, 479, 525 and 527) are responsible for the color developed during the photo-transformation

process. The ion at accurate mass  $m/z$  479.12576, which gives the best fit formula of  $C_{28}H_{19}N_2O_6$  (neutral molecule). This formula is exactly twice that of product (6), which suggests dimer formation. The ion at  $m/z$  493.10312 is also closely related to product (6), differing by only 1 oxygen and 3 hydrogen atom. Thus, it appears that losses from chlorine form the carbazole structure followed by hydroxyl substitution of chlorine to form product (6). This structure is activated by the phenol structure and is easily dimerised [24]. This pathway leads to all chlorine-free dimers. This is a major pathway turning the solution brown.

#### 4. Conclusions

Interaction of DCF with sunlight during photolysis can lead to complete disappearance in appropriate time, while mineralization of photoproducts has been achieved after 24 hours. Photo-catalysis processes ( $TiO_2$  powder and immobilized system) are able to remove both DCF and photoproducts within short time ranging from 8 to 11 hours. All photo-degradation processes have followed a 1<sup>st</sup> order kinetic with  $t_{1/2}$  54.6 min for photocatalysis ( $TiO_2$  powder), 79.7 min for photocatalysis ( $TiO_2$  immobilized) and 70.7 min for photolysis.

In this study, we have shown that (LC-ESI-MS) is a powerful technique for the chemical elucidation of DCF photo-transformation products and has proved to be one of the most powerful approaches currently existing to investigate suspected or unknown and to determine the destruction pathways and the reaction by-products proposed. Product identification was consistent with known hydroxylation mechanism involving attack on the aromatic rings. The number of by-products in photo-catalysis ( $TiO_2$  powder) experiment was less than those in photolysis and photocatalysis with  $TiO_2$  immobilized system, as well as the presence of dimer products have been detected in both those in photolysis and photocatalysis with  $TiO_2$  immobilized system.

Finally, we can conclude that Photocatalysis with ( $TiO_2$  powder) is an effective way for removal of DCF and its by-products, but we believe that photocatalysis with  $TiO_2$  immobilized system with more modifications could be promising for use in wastewater treatment field, since it's totally clean and it doesn't require additional post treatment stage to recover  $TiO_2$ .

#### 5. References

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