Remediation of Aquatic Environments Contaminated with Hydrophilic and Lipophilic Pharmaceuticals by TiO₂-photoassisted Ozonation

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Abstract

Degradation and mineralization of the hydrophilic pharmaceuticals diclofenac and clofibric acid in aqueous media were investigated under indoor UV illumination (super high-pressure Hg lamp) and under outdoor solar exposure. Indoor experiments were carried out using three different protocols: (i) UV ozonation of TiO₂ dispersions (UV/TiO₂/O₃), (ii) UV-irradiated TiO₂ oxygenated dispersions (UV/TiO₂/O₂), and (iii) UV ozonation of the solutions (UV/O₃). Results from these protocols were established by total organic carbon (TOC) assays, HPLC chromatography (IC-HPLC) and by the evolution of Cl⁻, NO₃⁻ and NH₄⁺ ions (where appropriate). Indoor remediation of aquatic ecosystems contaminated with these two pharmaceuticals occurred in the order (photodegradation/mineralization): for diclofenac after 120 min, UV/TiO₂/O₃ (100%/92%) > UV/O₃ (97%/47%) > UV/TiO₂/O₂ (43%/35%); for clofibric acid after 30 min, UV/TiO₂/O₃ (99%/92%) > UV/O₃ (94%/33%) > UV/TiO₂/O₂

(68%/41%). Complete dechlorination of diclofenac followed the same sequence (time): UV/TiO₂/O₃ (30 min) > UV/O₃ (60 min) > UV/TiO₂/O₂ (>>120 min), whereas for clofibric acid the times needed for complete dechlorination were 10 min (UV/O₃) > 30 min (UV/TiO₂/O₃) > 60 min (UV/TiO₂/O₂). Under outdoor solar exposure, the 300-L dispersions containing tens of ppm of diclofenac and clofibric acid pharmaceuticals (0.10 mM) were completely remediated by the UV/TiO₂/O₃ protocol after only 4 hrs of sunlight exposure. Remediation of aqueous dispersions of the lipophilic orally bioactive estrogen ethynylestradiol (EE) and the non-steroidal anti-inflammatory drug (NSAID) indomethacin was also examined under indoor conditions; the EE by all three protocols, while the NSAID by the UV/TiO₂/O₃ protocol alone. The EE displayed unusual behavior during the photodegradation and mineralization events because of solubility issues, while the NSAID photodegraded nearly quantitatively (96%) within 6 hrs and was totally dechlorinated in less than 2 hrs.

Keywords: Diclofenac; Clofibric acid; Ethynylestradiol; Indomethacin; Advanced oxidation processes (AOPs)

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1. Introduction

Recent years have witnessed the emerging presence of pharmaceuticals that were designed to be bioactive in aquatic environments. Residues of such pharmaceuticals as anti-inflammatories, analgesics, beta blockers, lipid regulators, antibiotics, anti-epileptics, estrogens, anti-cancers, and contraceptives, among others, have recently been detected in

49 effluents of several sewage treatment plants, and in many surface, ground and drinking waters
50 worldwide [1–4]. Sewage treatment plants cannot completely eliminate these pharmaceuticals
51 and consequently they are too often discharged into surface and ground waters. Accordingly,
52 these recalcitrant non-biodegradable substances tend to accumulate in aquatic environments.
53 Thus, an effective treatment technology to decompose such hazardous organics is desirable.

54 Advanced oxidation processes (AOPs) provide some of the most attractive protocols for
55 the degradation and/or mineralization of non-biodegradable compounds. Among these,
56 photocatalyzed reactions that involve the highly reactive hydroxyl radicals ($\bullet\text{OH}$) have proven as
57 most appropriate [5–9]. A commonly used photocatalyst in these AOPs is the n-type
58 semiconductor TiO_2 , a photoactive, inexpensive, non-toxic and stable material when exposed to
59 chemical and photo-corrosive treatments. The objective of this AOP in photocatalytic
60 applications to treatment of wastewaters is the detoxification of these waters by degradation and
61 ultimate mineralization of environmentally persistent organic pollutants. Disadvantages of the
62 photocatalytic protocol, however, are the slow oxidation dynamics and the expensive cost of
63 photons. The combination of the now rather common TiO_2 -photoassisted methodology with
64 ozonation should enhance process efficiency in the remediation of contaminated aquatic sites
65 through synergistic effects of various factors that lead to faster dynamic processes. For instance,
66 photocatalytic ozonation processes involving UV irradiation previously examined by us [10, 11]
67 and others [12–18] have displayed a remarkable enhancement of mineralization processes.

68 In the present study, we examined the photocatalytic oxidation, degradation and ultimate
69 mineralization of selected pharmaceuticals such as the hydrophilic and water-soluble
70 non-steroidal anti-inflammatory drug (NSAID) diclofenac, and clofibric acid (a metabolite of the
71 cholesterol-lowering pharmaceutical drug Clofibrate), together with the lipophilic
72 ethynylestradiol (an orally bio-active estrogen used in almost all modern formulations of

combined oral contraceptive pills) and indomethacin (a non-steroidal anti-inflammatory drug commonly used as a prescribed medication to reduce fever, pain, stiffness, and swelling) in aqueous solutions under indoor experimental conditions using a super high-pressure mercury lamp as the UV light source and three different protocols. Diclofenac and clofibric acid were also examined in an outdoor pilot-scale detoxification setup with variable sunlight as the only irradiation and energy source. The purpose of the outdoor pilot-scale tests were to reduce the otherwise expensive costs of light energy (UV photons) [19–23].

2. Experimental section

2.1 Materials

The photocatalyst was P-25 TiO₂ (Degussa; surface area, *ca.* 53 m² g⁻¹; mean diameter, *ca.* 30 nm; composition; 87% anatase and 13% rutile). Reagent grade sodium diclofenac and clofibric acid were purchased from Tokyo Kasei Industries Co. Ltd., whereas ethynylestradiol and indomethacin were supplied by Wako Pure Chemical Industries Co. Ltd. Ozone was produced from pure oxygen gas using an ozone generator (EcoDesign ED-OG-S1). All other chemicals were used as received.

(Structures of substrates examined here)

2.2 Photodegradation procedures

To examine the differences in reaction dynamics between the various protocols used, the solutions were subjected to the following protocols: namely, (i) **UV/TiO₂/O₃ protocol** – titanium dioxide was suspended in an aqueous solution of the substrates and purged with ozone gas during UV light irradiation (or varying sunlight); (ii) **UV/TiO₂/O₂ protocol** – oxygen gas was bubbled

in the aqueous TiO_2 suspension to saturation prior to subjecting it to constant UV light irradiation; (iii) **UV/ O_3 protocol** – ozone gas was bubbled through the TiO_2 -free solution during the entire UV light irradiation period.

The dispersions were initially mixed for about 10 min in a sonication bath to ensure a uniform dispersion, following which they were subjected to magnetic agitation with a stirrer to maintain a uniform reacting mixture during the photooxidative processes.

Total organic carbon assays were performed on a Shimadzu TOC-5000A analyzer. Chromatographic analyses for Cl^- , NO_3^- and NH_4^+ ions were carried out on a JASCO Ion Chromatograph equipped with a Shodex IC column. In laboratory experiments, the substrate solutions (500 mL) were placed in a Pyrex glass vessel containing TiO_2 and were subsequently irradiated with a 75-W Toshiba SHL-100UVQ2 super high-pressure Hg lamp (light irradiance, 3 mW cm^{-2} ; wavelength, 360 nm; UV radiometer model UVR-36 from Topcon Co.). In solar experiments, the electric power for the reactor system, the pumps, the stirrer, the ozone generator, the radiometer and the computer was entirely supplied by a Sharp NE70H solar cell battery.

In all experiments, various aliquots of the degraded suspensions were collected at fixed time intervals during the degradation/mineralization. The degradation yield of the aromatic ring opening was determined by measuring the UV absorption of the aromatic moiety with a JASCO V-570 UV-visible spectrometer. Mineralization was followed by monitoring the time profiles of TOC loss in the solutions or dispersions. These assays were performed after removal of the TiO_2 particles by centrifugation and filtration through a 0.2 μm PTFE filter. The concentration of ozone in the water was determined by iodometric analyses: 15 ppm in laboratory experiments and 6 ppm in the solar experiments; O_3 flow was kept constant throughout.

3. Results and Discussion

3.1 Laboratory experiments – Hydrophilic pharmaceuticals

The Diclofenac case: Oxidative degradation of diclofenac in aqueous solution was performed by the three different (i–iii) protocols mentioned above. The decrease of the concentration of diclofenac occurred via a first-order process; about 43% of the substrate was photodegraded within 2 hrs of irradiation (UV/TiO₂/O₂ protocol), whereas in the presence of ozone the photodegradation carried out with protocols (i) and (iii) was significantly faster as evident in **Figure 1a**: $k = 0.24 \pm 0.01 \text{ min}^{-1}$ (UV/TiO₂/O₃), $0.069 \pm 0.005 \text{ min}^{-1}$ (UV/O₃), and $0.0047 \pm 0.0002 \text{ min}^{-1}$ (UV/TiO₂/O₂). Clearly, the lowest reaction rate appeared with the use of the TiO₂-photoassisted reaction under oxygenated conditions (protocol ii). The presence of ozone in TiO₂ dispersions significantly enhanced the reaction dynamics nearly 50-fold. Time profiles in the change of TOC levels are reported in **Figure 1b**, the corresponding kinetics being $k = 0.024 \text{ min}^{-1}$ (UV/TiO₂/O₃), 0.036 min^{-1} (UV/O₃), and $0.000046 \text{ min}^{-1}$ (UV/TiO₂/O₂). Again the presence of ozone significantly enhanced the TiO₂-photoassisted degradation of the polluting substrate nearly 520-fold. The diclofenac was mineralized at a yield of 36 % TOC loss after 2 hrs of irradiation with the UV/TiO₂/O₂ protocol, whereas UV/O₃ (protocol ii) caused the TOC to decrease by a greater extent (ca. 42 % yield after 2 hrs). By contrast, the use of the UV/TiO₂/O₃ protocol (i) led to a near-quantitative mineralization (ca. 92%) of the dichlofenac pharmaceutical after the 2-hr irradiation period with the Hg lamp light source. Consequently, the simultaneous presence of oxidizing agents (•OH radicals and other ROS species from photoexcited TiO₂ and O₃; see below) in the UV-irradiated dispersion led to the most efficient degradation and mineralization of diclofenac under our experimental conditions.

(Figure 1 here)

The mineralization of diclofenac to CO_2 no doubt proceeded through formation of various intermediate products with concomitant evolution of chloride ions as shown in **Figure 2a**.

The Cl^- ion concentration increased rapidly on employing the UV/ O_3 and UV/ TiO_2/O_3 protocols. Stoichiometric amounts of the chloride ions were evidenced in very short times in accord with the degradation process. The experimental results imply dechlorination was one of the first steps in the degradation and mineralization of the chlorinated aromatic substance. Chloride ion evolution coincided with the decomposition of diclofenac initiated by aromatic ring-opening; the corresponding first-order kinetics being $k = 0.14 \pm 0.04 \text{ min}^{-1}$ (UV/ TiO_2/O_3), $0.056 \pm 0.008 \text{ min}^{-1}$ (UV/ O_3), and $0.0021 \pm 0.0001 \text{ min}^{-1}$ (UV/ TiO_2/O_2).

(Figure 2 here)

The organic nitrogen in diclofenac was transformed into nitrate anions and ammonium cations at a rate somewhat similar to chloride ion evolution by the UV/ TiO_2/O_3 protocol (**Figures 2b, 2c**): the first-order kinetics of formation of NH_4^+ ions are $k = 0.053 \text{ min}^{-1}$ (UV/ TiO_2/O_3), 0.067 min^{-1} (UV/ O_3), and 0.24 min^{-1} (UV/ TiO_2/O_2), whereas the corresponding kinetics of nitrate ion formation are $k = 0.092 \pm 0.011 \text{ min}^{-1}$ (UV/ TiO_2/O_3). Note that for the UV/ TiO_2/O_2 protocol, no nitrate ions formed under our conditions; for the UV/ O_3 protocol the formation of nitrate displayed a lag time of ca. 30 min suggesting that nitrate formed subsequent to complete transformation of the nitrogen into NH_4^+ (compare **Figures 2b** and **2c**).

The results obtained clearly indicate that the highest reaction rate for the mineralization of organic carbon and chloride evolution in diclofenac appears with the use of the TiO_2 photocatalyst in the presence of ozone.

The Clofibric acid case: A similar tendency was obtained for the oxidative degradation of clofibric acid when carried out under otherwise identical experimental conditions to diclofenac (**Figure 3a**). The oxidative mineralizations of the clofibric acid by UV/O₃, by UV/TiO₂/O₂ and by the combination UV/TiO₂/O₃ are displayed in **Figures 3b** (TOC decay), while dechlorination of the substrate is reported in **Figure 3c**. The corresponding reaction kinetics are: for TOC loss, $k = 0.14 \text{ min}^{-1}$ (UV/TiO₂/O₃), 0.010 min^{-1} (UV/O₃) and 0.018 min^{-1} (UV/TiO₂/O₂); for dechlorination the relevant kinetics are $k = 0.065 \text{ min}^{-1}$ (UV/TiO₂/O₃), 0.34 min^{-1} (UV/O₃) and 0.044 min^{-1} (UV/TiO₂/O₂). Evidently, dechlorination of this substrate is fastest under UV/ozonation conditions.

The experimental data definitely show that significant mineralization of clofibric acid took place by the use of the UV/TiO₂/O₃ protocol in comparison with either UV/O₃ or by the TiO₂-photoassisted process in the oxygenated dispersions (UV/TiO₂/O₂). The UV/TiO₂/O₃ protocol has thus proven to be an excellent technique to mineralize these two hydrophilic and persistent pharmaceuticals in aquatic environments.

(Figure 3 here)

Results illustrated in **Figures 1-3** can best be understood by considering all the possible oxidizing agents present in the aquatic solutions (or dispersions). Past experience has taught us that the strongly oxidative •OH radical species, generated according to reactions 1–10, attack the electron-rich moieties in the organic substrates. It is noteworthy that formation of the •OH radicals tends to be most effective in the presence of O₃ [18].

Once formed, the $\cdot\text{OH}$ radical species attack the moieties having the higher electron density such as the aromatic ring, which is then followed by formation of hydroxylated aromatic intermediates. The aromatic ring is subsequently cleaved to form aldehydes and/or carboxylic acid derivatives by further UV illumination. Finally, CO_2 gas is evolved as evidenced by the loss of TOC in the aqueous degraded dispersions/solutions.

3.2 Laboratory experiments – Lipophilic pharmaceuticals

The Ethynylestradiol case: Remediation of an aquatic system contaminated with the lipophilic (water-insoluble) ethynylestradiol was also carried out by the three different protocols. Addition of ethynylestradiol (296 mg) to 500 mL of water followed by stirring yielded an emulsion. If the substrate was totally soluble in water, its concentration would have corresponded to about 1 mM. In fact, however, its concentration in the reactant emulsion or dispersion tended to be quite low (ca. 10 ppm of TOC).

(Figure 4 here)

Figure 4a shows the temporal profile of the photodegradation of ethynylestradiol whose concentration appeared to increase immediately during the initial period of ozone bubbling. Once the benzene ring was hydroxylated, the ethynylestradiol became hydrophilic (water-soluble) so that the quantity of TOC in the emulsion/solution tended to increase. Hydroxylated intermediates were identified through an analysis of the reactant solution by TOF-MS (JEOL TOF CS JMS-T100CS mass spectrometer). The hydrophilic intermediates adsorbed on the surface of the hydrophilic TiO_2 following which further oxidation proceeded toward their mineralization. Increase and decrease of TOC were faster under the UV/ TiO_2/O_3 protocol conditions. To confirm the effect of the presence of the TiO_2 photocatalyst in the mineralization of ethynylestradiol, in another experiment ozone bubbling was continued in the aqueous dispersion under UV irradiation for 2 hrs, after which TiO_2 was added and UV irradiation continued. As illustrated in **Figure 4b**, TOC loss was complete within 2 hrs of irradiation subsequent to addition of TiO_2 .

The Indomethacin case: The TiO_2 -photoassisted ozonation (UV/ TiO_2/O_3 protocol) of this lipophilic pharmaceutical was carried out using 179 mg of indomethacin in aqueous media (500 mL) that also contained 500 mg of TiO_2 . The resulting dispersion was subjected to UV irradiation with constant ozone bubbling. A tendency otherwise similar to that observed for ethynylestradiol was seen as shown in **Figure 5**. Complete photodegradation ($k = 0.012 \pm 0.002 \text{ min}^{-1}$) was also confirmed by the stoichiometric formation of Cl^- ions upon dechlorination of the indomethacin ($k = 0.030 \pm 0.006 \text{ min}^{-1}$). In such TiO_2 -photoassisted oxidations, it is essential that the organic substrate in water be adsorbed on the surface of the metal oxide so that the $\bullet\text{OH}$

radicals formed may have a chance to oxidatively decompose these otherwise water-insoluble organic substrates.

(Figure 5 here)

Clearly, even such lipophilic organics can be photodegraded and mineralized using simultaneously both ozone and the TiO_2 photocatalyst.

3.3 Natural Sunlight – outdoor experiments

The results in the laboratory experiments led us to examine the mineralization of diclofenac and clofibric acid outdoors under irradiation with natural sunlight using the combined UV/ TiO_2/O_3 protocol that proved most efficient under irradiation by the more conventional Hg lamp. To achieve this objective, we examined aqueous dispersions of the two hydrophilic substrates at a concentration of 0.10 mM. The experiments were performed with a photoreactor consisting of 120 Pyrex glass tubes (inner diameter, 1.76 cm; length, 145 cm; total area subjected to sunlight irradiation, 3.1 m^2) connected in series as illustrated in **Figure 6a**. The photograph of the experimental setup is shown in **Figure 6b**. A peristaltic pump (PR-KV2, Furue Science Co.) ensured the re-circulation of the large volume (300 L) of reactant solution between the feed tank and the photoreactor. As the reactor consisted of glass tubes connected in series, the reactant dispersion could be re-circulated at a relatively high flow rate (7.5 L min^{-1}) that provided turbulent flow conditions.

(Figure 6 here)

In the present study, the electric power for the five peristaltic pumps, the stirrer, the O_3 generator and the personal computer was all supplied by the solar cell for which the energy

source was sunlight. This can significantly reduce running costs when only natural sunlight is used. Ozone can be obtained using oxygen produced from natural air by a column method.

The temperature of the reactant solution was measured at the outlet of the reactor; it increased to *ca.* 45 °C during solar irradiation. The solar irradiance was measured continuously (every second) with a radiometer set at a wavelength of 360 nm. The data obtained were then integrated using a personal computer. As sunlight irradiance is intermittent in certain days and depends on weather conditions, the decrease of TOC during the course of mineralization is then best expressed as a function of accumulated sunlight energy (in units of kJ L^{-1}) incident on the photoreactor per liter of the solution (as the variable), rather than against time. For instance, on a sunny day and at a solar irradiance of 3 mW cm^{-2} during 1 hr of irradiation, the photoreactor harvests an accumulated energy of 330 kJ and thus 1.1 kJ L^{-1} for a 300-L solution.

The solar degradation and mineralization of diclofenac and clofibric acid with ozone in the presence of TiO_2 (loading, 1 g L^{-1}) are depicted in **Figure 7**. Complete mineralization in such a large volume (300 L) of solution containing tens of ppm of the pharmaceuticals was achieved after only *ca.* 4 hrs of sunlight irradiation.

(Figure 7 here)

The operating system depicted in **Figure 6** has thus proven useful for the remediation of contaminated wastewaters. Similar contaminated sites can be detoxified at locations situated far from any electric network, not least of which the method is also favorable in terms of ecological considerations.

4. Concluding remarks

Laboratory indoor experiments have demonstrated that irradiation of the combined TiO₂-photoassisted ozonation protocol (UV/TiO₂/O₃) using a super high-pressure Hg lamp represents an efficient pathway toward the photodegradation and mineralization of non-biodegradable pharmaceuticals, particularly for the lipophilic ones. The outdoor solar experiments further demonstrated that aquatic systems contaminated with pharmaceuticals in large quantities can also be mineralized to carbon dioxide and inorganic ions within a reasonably short time with sunlight providing all the energy necessary to carry out the entire operation without the need to be connected to an electrical network.

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Diclofenac (acid form) **Clofibric acid** **Ethynylestradiol** **Indomethacin**

(Substrates examined)

Figure 1. Time profiles of (a) concentration change and (b) TOC concentration change in the photodegradation and mineralization of diclofenac (initial concentration, 1.0 mM).

Figure 2. Formation of (a) Cl⁻, (b) NH₄⁺ and (c) NO₃⁻ ions in the photodegradation of sodium diclofenac (initial concentration, 1.0 mM).

Figure 3. Time profiles of (a) the concentration changes in the photodegradation of clofibric acid, (b) changes in the TOC concentration, and (c) evolution of Cl⁻ ions during the photodegradation of clofibric acid. Initial concentration: 0.10 mM. Data above the expected quantity of chloride in (c) is due to experimental uncertainty in the determination by the HPLC technique.

Figure 4. Time profiles of (a) ethynylestradiol (derivatives) and (b) TOC changes during the

photodegradation of this lipophilic substrate. In graph (b), TiO_2 was added to the UV/ O_3 system after 2 hrs of UV irradiation in the presence of ozone only.

Figure 5. Time profiles of the (a) concentration changes of indomethacin, (b) TOC changes, and (c) formation of Cl^- ions during the photodegradation of this lipophilic substrate. Initial concentration 1.0 mM.

Figure 6. (a) Schematic illustration of the solar reactor setup; (b) actual photograph of the experimental setup of the solar ozonation system located on the rooftop of the Department of Chemistry, Meisei

University.

Figure 7. (a) Concentration changes of diclofenac and clofibric acid with accumulated light energy; (b) decay of TOC with light energy; and (c) time profiles of the evolution of Cl^- ions against accumulated light energy in the TiO_2 -photoassisted ozonation of these two hydrophilic pharmaceuticals (initial concentrations, 0.1 mM; volume, 300 L).