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Photodegradation kinetics and transformation products of ketoprofen, diclofenac and atenolol in pure water and treated wastewater

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HIGHLIGHTS

- Direct UV photolysis of 3 pharmaceuticals in pure and waste water was investigated.
- Ketoprofen has higher photodegradion kinetics, followed by diclofenac and atenolol.
- MP/UV photodegradation products were identified for the 3 compounds.
- Photodegradation pathways were proposed to explain the obtained products.
- The persistent photoproducts were identified for each compound.

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ABSTRACT

Pharmaceutical compounds such as ketoprofen, diclofenac and atenolol are frequently detected at relatively high concentrations in secondary effluents from wastewater treatment plants. Therefore, it is important to assess their transformation kinetics and intermediates in subsequent disinfection processes, such as direct ultraviolet (UV) irradiation. The photodegradation kinetics of these compounds using a medium pressure (MP) lamp was assessed in pure water, as well as in filtered and unfiltered treated wastewater. Ketoprofen had the highest time- and fluence-based rate constants in all experiments, whereas atenolol had the lowest values, which is consistent with the corresponding decadic molar absorption coefficient and quantum yield. The fluence-based rate constants of all compounds were evaluated in filtered and unfiltered wastewater matrices as well as in pure water. Furthermore, transformation products of ketoprofen, diclofenac and atenolol were identified and monitored throughout the irradiation experiments, and photodegradation pathways were proposed for each compound. This enabled the identification of persistent transformation products, which are potentially discharged from WWTP disinfection works employing UV photolysis.

1. Introduction

In the past decade, there has been a growing concern about the discharge of pharmaceutical active compounds (PhAC) from wastewater treatment plants (WWTPs) [1,2]. These compounds are designed to have an impact on life and are often resistant to biological degradation in the secondary treatment of conventional WWTPs. Therefore, it is important to assess the fate of PhACs in the tertiary treatment step of WWTPs where physical/chemical methods are often used.

UV irradiation is often employed for disinfection of drinking water and municipal WWTP [3], and it has also been demonstrated to effectively reduce the concentration of recalcitrant organic compounds [4,5]. However, this process can also generate photodegradation intermediates that are more recalcitrant or toxic than the parent compounds. Low pressure (LP) mercury

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lamps – that emit monochromatic light at 254 nm – are known by their high disinfection efficiency since they irradiate at a wavelength in the range of the maximum absorption of DNA (240–260 nm). Medium pressure (MP) mercury lamps that emit light over a wider range of wavelengths have been reported as an effective alternative to LP lamps (e.g. [6]) and may be preferred in compact treatment systems, since the UV intensity per lamp is higher than in LP systems [3].

The compounds selected for this study were widely used pharmaceutical compounds with different chemical structures: ketoprofen, diclofenac (non-steroidal anti-inflammatory drugs), and atenolol (a β-blocker). These compounds were found in relatively high concentrations (up to 21.6 $\mu g\,L^{-1}$ [7,8]) in the effluent of the secondary settler of municipal WWTPs, thus reaching a subsequent disinfection process. The photolysis of ketoprofen, diclofenac and atenolol has been previously investigated, mostly in distilled water and surface water matrices (e.g. [4,9–11]). Baeza and Knappe [12] recently studied the kinetics of diclofenac using low pressure (LP) direct and indirect UV photolysis in ultrapure water, lake water and also in wastewater effluent and found that the degradation rate was similar across all matrices. Good LP/UV photodegradation of ketoprofen and diclofenac in treated wastewater was demonstrated by Kim et al. [13], although atenolol only showed medium removal. Also Rosario-Ortiz et al. [5] reported low atenolol removal in WWTP effluent through LP/UV photolysis. Nevertheless, very few studies reported the effect of treated wastewater on photodegradation using MP lamps.

The objective of this study was to investigate the degradation kinetics and extent of transformation of selected PhACs by UV radiation used for wastewater disinfection purposes (i.e. direct photolysis). UV photolysis can be strongly affected by the presence of other organic compounds (other PhACs or dissolved organic matter), or particulate matter. In the present study, the photodegradation kinetics of ketoprofen, diclofenac and atenolol were assessed in a reactor equipped with a MP lamp, in filtered and unfiltered treated wastewater, and compared to the results obtained in pure water. Moreover, the photodegradation products of each compound were identified and monitored along irradiation time. To the best of our knowledge, this is the first study identifying the transformation products of ketoprofen, diclofenac and atenolol with direct photolysis, which enabled proposing photodegradation pathways for each compound.

2. Materials and methods

2.1. Reagents

The PhACs used in this study were atenolol, diclofenac and ketoprofen (Discovery CPR, Sigma–Aldrich, Portugal). Atrazine (Discovery CPR, Sigma–Aldrich, Portugal) was used for actinometry of the UV MP lamp. The mobile phases used in high performance liquid chromatography (HPLC) were acetonitrile (HPLC grade, Panreac, Portugal) and ultra pure water obtained from Milli-Q50 system water purification (Millipore, Bedford, USA), acidified with formic acid (analytical grade, Merck, Portugal). The derivatisation reagent used for gas chromatography (GC) analysis was MSTFA (N-methyl-N-(trimethylsilyl)trifluoro-acetamide) (GC grade, Sigma–Aldrich, Portugal).

2.2. UV irradiation experiments

2.2.1. Photolysis with UV mercury vapour lamp, low pressure (LP)

LP/UV photolysis experiments were conducted in a collimated beam bench-scale reactor (Trojan Technologies Inc., Canada) using a LP Hg lamp that emits mainly monochromatic light at 254 nm.

100 mL of pure water were spiked with the appropriate volume of stock solutions of each pharmaceutical to a concentration of 1 $mg\,L^{-1}$. 50 mL were placed in a Petri dish and continuously stirred underneath the lamp. The remaining 50 mL were used as a control and kept in the dark under identical experimental conditions to determine possible PhACs losses due to evaporation or adsorption to the Petri dish. All experiments were conducted at room temperature ($21 \pm 2\,^{\circ}C$). The lamp irradiance was measured using a calibrated radiometer (IL1700, International Light, Newburyport, MA) which was placed at the same height of the water level in the Petri dish and the solution transmittance was measured by a UV photometer (P254C, Trojan Technologies Inc.). UV fluences of 0, 100, 500, 750, 1000 and 1500 $mJ\,cm^{-2}$ were selected to establish the corresponding exposure times when 200 μL of sample were taken for analysis of the PhACs through HPLC.

2.2.2. Photolysis with UV mercury vapour lamp, medium pressure (MP)

The photodegradation tests were carried out in a pear-shaped glass reactor with a volume of 300 mL, using a MP Hg lamp Heraeus Noblelight model TQ 150 (nominal power 150 W) which emits radiation between 200 and 450 nm. The lamp was covered with a quartz cooling jacket, where pure water (with negligible light adsorption in the wavelength range of emitted radiation) was used as an optical filter and to maintain a temperature of $25 \pm 1\,^{\circ}C$.

300 mL of pure water (pH 6.4) was spiked with atenolol, ketoprofen or diclofenac, separately or in a mixture of all three compounds, to get a concentration of 1 $mg\,L^{-1}$ of each compound. The photolysis of a mixture of the three PhACs was also carried out in 300 mL of filtered (through 0.45 μm glass fibre filters (Whatman, Portugal)) and unfiltered secondary effluent of a biological WWTP (Fernão Ferro, Portugal).

2-mL samples were taken throughout the experiments to assess the photolysis of the PhACs in the different experimental conditions through HPLC analysis. Samples for identification of photolysis transformation products were taken at critical points of the photodegradation experiments (ketoprofen, LP – 2.5 h; ketoprofen, MP – 7.5 min; diclofenac – 1.5 min; atenolol – 17.5 min), where the highest relative area of new chromatographic peaks was detected. Once identified, the transformation products were monitored in all other samples taken along photolysis time.

Fluence rates under MP/UV irradiation were determined by chemical actinometry using 4.6 μM aqueous atrazine, following the procedure described in Canonica *et al.* [4], i.e. assuming a wavelength-independent quantum yield and using the emission spectrum of the MP Hg lamp:

$$E_p^0(200-450\,\text{nm}) = \frac{k_{\text{atr}}}{2.303\phi_{\text{atr}}\sum_{200\,\text{nm}}^{450\,\text{nm}}(f_{p,\lambda}\varepsilon_{p,\lambda})} \quad (1)$$

where E_p^0 (200–450 nm) (einstein $m^{-2}\,s^{-1}$) is the photon fluence rate determined through atrazine actinometry in the wavelength interval of 200–450 nm, k_{atr} (s^{-1}) is the pseudo-first-order rate constant of atrazine depletion, Φ_{atr} is the quantum yield of atrazine depletion (=0.046 mol einstein^{-1} [4]), $f_{p,\lambda}$ is the emission spectrum of the lamp based on the photon flux and normalised to the chosen wavelength interval, i.e., $\sum_{200\,\text{nm}}^{450\,\text{nm}}(f_{p,\lambda}) = 1$, and $\varepsilon_{\text{atr},\lambda}$ ($M^{-1}\,cm^{-1}$) is the molar absorption coefficient of atrazine at wavelength λ (=3860 $M^{-1}\,cm^{-1}$ [4]).

2.3. Analytical procedures

2.3.1. HPLC-DAD analysis

High performance liquid chromatography (HPLC) with a diode array detector (DAD) was used to monitor diclofenac, ketoprofen, atenolol and atrazine degradation kinetics according to the method