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Effects of pH and water matrix on photoinduced degradation of antibiotic cefdinir

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Abstract **-** In this paper, photolytic and photocatalytic degradation of cephalosporin antibiotic cefdinir dissolved in MilliQ water and in synthetic municipal wastewater are described. Both degradation processes were based on UV-A and UV-C radiation. The UV-A-based oxidation processes have been less efficient in terms of irradiation time required for complete degradation of cefdinir than the UV-C-based processes. The effect of pH value was observed for photocatalytic processes in terms of slower degradation under basic conditions than acidic and neutral conditions. It was also confirmed that different wastewater components could significantly reduce the degradation rate of cefdinir in UV-A-based processes. Although UV-A radiation experiments need more time than UV-C experiments for complete degradation of cefdinir, they have a potential for practical use since such reactor configuration could use natural solar radiation as a source of UV-A radiation and therewith significantly reduce the costs of pharmaceuticals degradation treatment step.

Keywords**:** Photolysis, Photocatalysis, Titanium dioxide film, Pharmaceuticals, Cephalosporines, Cefdinir, Wastewater

1. Introduction

Pharmaceuticals are considered as emerging contaminants because the risk to human health and the environment associated with their presence, frequency of occurrence, or source are not fully known. An increasing number of studies have confirmed their presence in different environmental compartments: wastewater effluents, surface, ground and drinking waters, river sediments, wastewater sludge and soil [1]. Pharmaceuticals are released into the environment by many routes [1], but it has been confirmed that they are mainly introduced in the environment through wastewater treatment plants, suggesting that their upgrade and implementation of advanced treatment technologies are required [2].

Under different possibilities for the treatment of water polluted with pharmaceuticals, advanced oxidation processes (AOPs) have obtained promising results for the degradation of pharmaceuticals by producing more biologically degradable and less toxic degradation products. AOPs are based on the generation of highly reactive hydroxyl radicals used for the unselective oxidation of pollutants. In the most of photocatalytic studies, the TiO_2 suspension/slurry was used. Efficiency of the suspended TiO_2 catalyst has proved to be superior to the same catalyst immobilized on the substrate, which could be attributed to the enhanced mass transport in suspended form [3]. However, the cost of the catalyst recovery makes the slurry system impractical for practical purposes.

Cefdinir is a semi-synthetic, broad-spectrum third generation cephalosporin. It has broad spectrum of activity and excellent therapeutic action against susceptible Gram-positive and Gram-negative bacteria [4]. The cefdinir has been approved for the treatment of community acquired pneumonia, acute exacerbations of chronic bronchitis, acute maxillary sinusitis, treatment of respiratory and urinary tract infections, and for uncomplicated skin and skin structure infections [5].

Therefore, the aim of this study was to evaluate photolytic and photocatalytic degradation processes of cefalosporine antibiotic cefdinir in aqueous solution using two different lamps as the light sources (UV-A and UV-C lamp). In photocatalytic experiments, TiO_2 was used as a catalyst in the form of a nanostructured thin film. The effects of water pH value and water composition on photoinduced degradation were evaluated.

2. Materials and methods

2.1. Materials and chemicals

Analytical standard of cefdinir (CAS: 91832-40-5) (Sigma-Aldrich, Saint Louis Missouri, USA) with high purity (> 97%) was used. Cefdinir stock solution (1 mg L^{-1}) was prepared by weighing accurate mass of cefdinir standard and dissolving it in buffer pH 7. Buffer pH 7 was consisted of analytical grade reagents 0.1 M disodium phosphate and 0.1 M potassium monophosphate in the ratio of 2:1 (v/v). Prepared stock solution was kept in the dark at 4 °C. Chemicals used for the preparation of mobile phase were acetonitrile and methanol (J. T. Baker, Deventer, Netherlands), tetramethyl-ammonium hydroxide (Sigma-Aldrich, Saint Louis Missouri, USA) and EDTA disodium salt (Merck Millipore, Burlington, Massachusetts, USA). All solvents used were HPLC-grade. Ultrapure water was prepared by a Millipore Simplicity UV system (Millipore Corporation, Billerica, MA, USA). To investigate the effect of water matrix components, synthetic municipal wastewater (MWW) was used. The MWW was prepared in tap water by dissolving 32 mg L^{-1} of peptone, 22 mg L^{-1} of meat extract, 6 mg $L^{-1}$of urea, 28 mg L^{-1} of K_2HPO_4, 4 mg L^{-1} $CaCl_2{\cdot}2H_2O$, 7 mg L^{-1} NaCl and 2 mg L^{-1} $Mg_2SO_4{\cdot}7H_2O$. The pH value of the MWW was 7,5 and TOC was 10 mg mL^{-1}.

2.2. Photolytic and photocatalytic experiments

All experiments were carried out in two 0.11 L borosilicate glass cylinders: one with the TiO_2 film, for photocatalytic experiments, and the other one, without the TiO_2 film, for photolytic experiments. UV radiation lamps were placed in the middle of each reactor. Photolytic/photocatalytic experiments were performed using two radiation sources (UVP, Upland, CA, USA): (a) model Pen-Ray CPQ-7427, with λ_{max}=365 nm and (b) model Pen-Ray 90-0004-07, with λ_{max}=185/254 nm. Experiments were performed at a temperature of (25±0.2) °C, with continuous purging with air. One-milliliter aliquots were withdrawn at regular time intervals and analyzed directly by liquid chromatography with diode array detector (HPLC-DAD). For all photolytic and photocatalytic experiments, cefdinir solution concentration of 1 mg L^{-1} was used.

2.3. Chromatographic analysis

Liquid chromatography analysis was performed using an Agilent chromatograph (Santa Clara, CA, USA) series 1100 coupled to a diode array detector. Chromatographic separation was achieved using a Supelcosil LC-18-DB (250 mm×4.6 mm, particle size 5μm) supplied by Supelco (Bellefonte, PA, USA). Mobile phase consisted of acetonitrile (60 mL), methanol (40 mL), tetramethyl-ammonium hydroxide (900 mL) and EDTA disodium salt (0.4 mL). The isocratic elution was used with the mobile phase flow rate of 1 mL min^{-1}. Injection volume was 100 μL and column temperature was 40 °C. The chromatogram was monitored at absorbance wavelength of 287 nm. The total analysis time was 12 min. Instrument control, data acquisition and evaluation were done using the Agilent ChemStation software. Linearity was obtained in the concentration range from 0.005 mg L^{-1} to 1.6 mg L^{-1} with R^2=0.9999. The limit of quantification determined as the lowest concentration of calibration curve was 5 μg L^{-1}.

3. Results and discussion

The results of photolytic/photocatalytic degradation study are shown on Fig.1 and 2. The results from the “dark” control demonstrated the absence of cefdinir degradation in the absence of radiation (Fig. 1) during the photocatalytic experiment (reactor with TiO_2 film). Under UV-C radiation, similar degradation rates were obtained for both photolytic and photocatalytic experiments. The degradation processes were very fast with complete degradation of cefdinir obtained in less than 9 min (Fig. 2). Significantly slower degradation was observed in the solution irradiated with UV-A light (Fig. 1), when complete degradation was not obtained even after 360 min. Photocatalytic process was much faster and complete degradation was achieved after 120 min (Fig. 1). Experiments under UV-A radiation at pH=7 were performed in duplicate and estimated pooled standard deviations were 0.007 and 0.158 for photolysis and photocatalysis, respectively.

The pH value may play an important role in the photolytic and photocatalytic degradation of organic pollutants. Most pharmaceutical compounds have acidic and/or basic functionalities, their ionization state is controlled by both solution pH and acid dissociation constants. Cationic, neutral, or anionic forms of substances often have vastly different properties with respect to water solubility, volatility, UV absorption, and reactivity with chemical oxidants [6]. Cefdinir structure contains carboxylic, amino and hydroxyl groups that can release a proton resulting in negatively charged molecule. These groups correspond to three dissociation constants (2.73, 7.91 and 12.48 [7]). Accordingly, single charged molecule of cefdinir will exist in the pH range 2.73 to 7.91, while at higher pH values (7.91 to 12.48) double negatively charged ionic structure will occur. Furthermore, during the photocatalytic degradation of organic pollutants pH of solution influences the surface-charge properties of the catalysts.

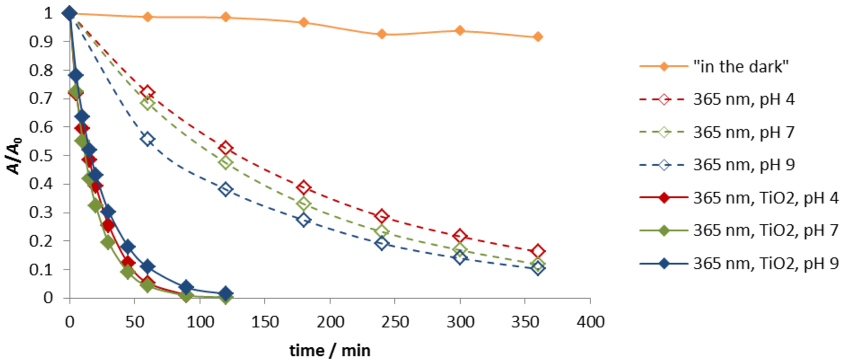

Fig. 1: Photolytic and photocatalytic degradation profiles of cefdinir under UV-A radiation.

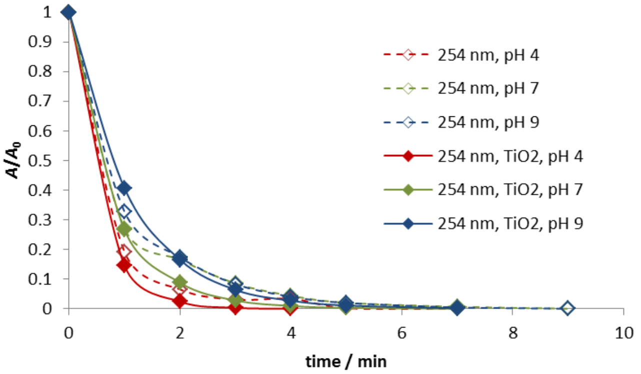

Fig. 2: Photolytic and photocatalytic degradation profiles of cefdinir under UV-C radiation.

The effect of pH on degradation of cefdinir was investigated over a pH range from 4 to 9. For photocatalytic degradation, slower degradation was observed at pH 9 for both light sources (Fig. 1 and 2). This finding might be explained by the amphoteric characteristic of the catalyst and cefdinir. The point zero charge (pH_{ZPC}) of TiO_2 is at pH 6.25. For $pH > pH_{zpc}$ the surface charge of TiO_2 will be negative, and at lower pH ($pH < pH_{zpc}$), the surface charge will be positive [8]. Hence, at pH value of 9, TiO_2 surface is negatively charged leading to repulsion of negatively charged molecule of cefdinir and prevention of their contact. As a result, degradation of cefdinir was slower comparing to neutral and acidic conditions. During the photolytic experiments under UV-A radiation, the fastest degradation of cefdinir was observed at pH 9, comparing to pH 4 and 7. This could be explained by relatively fast hydrolytic degradation of cefdinir under basic conditions [7].

Finally, photolytic and photocatalytic degradation of cefdinir was investigated in municipal wastewater whereas the wastewater contained different matrix components that could influence the efficiency of photoinduced degradation process. For that purpose, the synthetic MWW with a composition similar to that of the municipal wastewater was used. The results are presented in Fig. 3.

Results showed that, under UV-C radiation, photoinduced degradation of cefdinir was not significantly affected by MWW composition. On the contrary, significant slowdown of degradation was observed when UV-A light source was used which could be addressed to matrix effect.

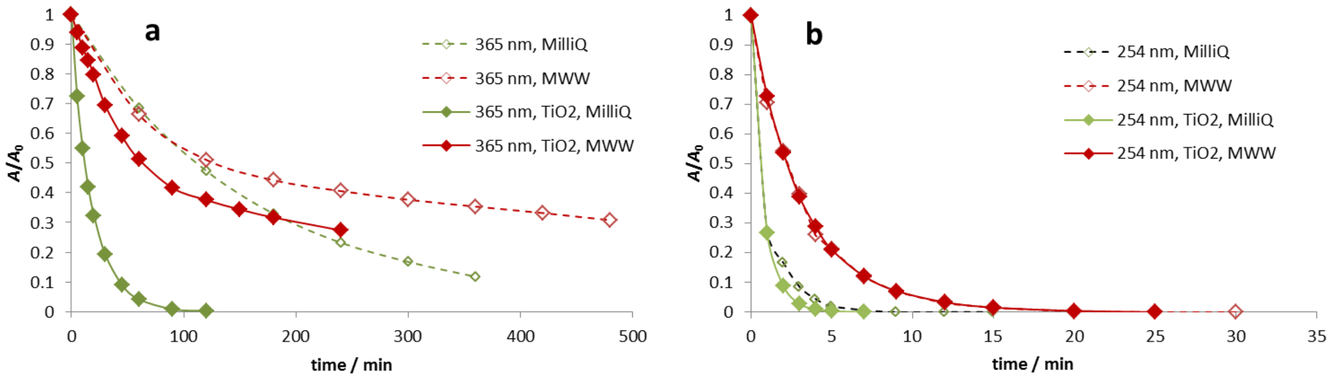

Fig. 3: Photolytic and photocatalytic degradation profiles of cefdinir in MilliQ and municipal wastewater (MWW) under UV-A radiation (a) and UV-C radiation (b).

4. Conclusion

Photolytic and photocatalytic oxidation processes of cefdinir using the immobilized TiO_2 film was investigated in MilliQ water and in synthetic MWW. It has been shown that the presence of TiO_2 nanostructured film enhanced photodegradation under UV-A radiation, while under UV-C radiation significant acceleration of oxidation process was not observed. The effect of pH value on photocatalytic degradation was observed; degradation was faster at acidic and neutral than in the basic conditions. Photolytic degradation under UV-C radiation was faster at basic condition due to faster hydrolysis of cefdinir. The effect of water matrix was observed only during UV-A-based processes, the cefdinir degradation was considerably reduced in MWW due to the effects of different wastewater components.

Acknowledgements

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