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Degradation of the antiviral drug zanamivir in wastewater – The potential of a photocatalytic treatment process

Martin Woche [a], Norbert Scheibe [b], Wolf von Tümpling [b], Michael Schwidder [a,*]

[a] Institute of Chemistry, Otto von Guericke University, Magdeburg, Germany
[b] Helmholtz Centre for Environmental Research, Magdeburg, Germany

HIGHLIGHTS

- The photocatalytic degradation of zanamivir was explored.
- The photocatalytic degradation is up to ca. 95 times faster than the photolysis.
- Guanidine, the primary transformation product of zanamivir, cannot be transformed.
- A rough cost estimation gives a value of 1.30 € per m^3 of wastewater.

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ABSTRACT

The antiviral drug zanamivir counteracts the influenza A and B viruses by preventing the infection of further healthy cells. In pandemic cases, large amounts will be administered and will therefore enter the wastewater. For this reason the potential of a photocatalytic wastewater treatment process aiming at the degradation of zanamivir was explored using aqueous solutions of zanamivir and the primary transformation product guanidine, which were irradiated with UV light under various conditions in the presence of TiO_2 as a photocatalyst. By studying the transformation behavior of these substances it can be demonstrated that using TiO_2 as a photocatalyst can accelerate the transformation of zanamivir. Simultaneously, however, this leads to a decrease of photon efficiency due to turbidity. Based on these findings, an optimization of the amount of TiO_2 suspended in aqueous zanamivir solutions during irradiation and a first rough cost estimate were carried out. Further results show that guanidine cannot be transformed using UV radiation and TiO_2 as a photocatalyst.

1. Introduction

Pharmaceuticals and their metabolites are able to enter the wastewater stream due to elimination from patients and inappropriate waste removal. Especially in the case of a pandemic, the extreme rise in consumption of pharmaceuticals leads to an increase in drug concentration in wastewater systems [1]. Not all of these substances are biodegraded in wastewater treatment plants and the application of modern processes like ozonation, photolysis with UV radiation, or adsorption and filtration by activated carbon is still not mandatory due to the high energy input and instrumentation costs connected with these methods [2]. As a consequence, concentrations of frequently administered pharmaceuticals and their metabolites in surface and drinking water have been shown to increase [3,4]. Since negative short- or long-term effects on the aquatic environment, caused by these rising concentrations, cannot be excluded, the comprehensive application of processes for the degradation of pharmaceuticals in wastewater treatment plants is required.

Beyond the above-mentioned methods, photocatalytic oxidation over TiO_2 could be an opportunity for drug removal by degradation, implemented in temporary or permanent working advanced wastewater treatment technologies. Compared to the alternative processes for drug degradation it offers several advantages: Besides (i) the chemical resistant and harmless TiO_2 (ii) no further chemicals need to be added to the water; (iii) the photocatalyst is not consumed and has no limited capacity with respect to the oxidized pollutant, and finally (iv) energy consumption is lower compared to UV photolysis as the necessary light intensities are lower. The only requirement that must be fulfilled is that the irradiation must offer sufficient energy for the TiO_2 photocatalyst

* Corresponding author at: Laboratory of Industrial Chemistry, Institute of Chemistry, Otto von Guericke University, Universitätsplatz 2, D-39106 Magdeburg, Germany. Tel.: +49 391 67 52213; fax: +49 391 67 12223.
E-mail address: michael.schwidder@ovgu.de (M. Schwidder).

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(between 3.0 and 3.2 eV; short-wavelength visible or UV light [5]) to overcome the bandgap by promoting electrons from the valence band to the conduction band, resulting in electron–hole-pairs and thereby generating a redox potential [6–8]. In case of several pharmaceuticals, e.g. diclofenac [9], metoprolol [10], or chloramphenicol [11], the feasibility of the photocatalytic degradation with TiO_2 has already been demonstrated. The present study addresses the photocatalytic degradation of the antiviral drug zanamivir, as up to now only the photolytic degradation has been reported [12].

Zanamivir is a neuraminidase inhibitor and counteracts the influenza A and B viruses by preventing the infection of further healthy cells. Since zanamivir is administered by inhalation, only small amounts of the antiviral agent are absorbed by the human body, while the predominant amount is either flushed out of the nasopharyngeal zone or is excreted via urine, since zanamivir is not transformed in the liver. In case of a pandemic caused by a viral infection a concentrated and higher use of zanamivir is to be expected, since some virus strains already show resistance to the alternative active agent oseltamivir [13,14]. Therefore, large amounts of zanamivir would reach the wastewater and, if not decomposed in sewage treatment plants, the ground and surface waters. For oseltamivir, a concentration of up to 12 $\mu g\,l^{-1}$ in the wastewater in pandemic cases has been predicted [15,16]. Assuming comparable amounts of zanamivir administered in the future to those of oseltamivir in the past and considering the lower absorption rate of zanamivir, even higher concentrations of zanamivir are to be expected. Since zanamivir is non-readily biodegradable [17] this would result in unknown ecotoxicological consequences.

In this work the feasibility of a photocatalytic process for zanamivir degradation in wastewater was evaluated by irradiating suspensions of a commercially available TiO_2 photocatalyst in solutions of zanamivir and guanidine under varying conditions. The latter was identified to be the primary photocatalytic transformation product of zanamivir in preliminary examinations. Since economic aspects also have to be considered for such a process in terms of engineering applications, a first rough cost estimate based on the results obtained is also given.

2. Experimental

2.1. Materials

Aqueous solutions of zanamivir and guanidinium nitrate were prepared using zanamivir and guanidinium nitrate (Sigma–Aldrich, 98%) as pure substances and purified water (Merck Millipore, spec. resistivity: 18.2 MΩ cm, total organic carbon: 5–10 ppb). AEROXIE® TiO_2 P25 (Evonik Industries) was used as a photocatalyst. This material was chosen because it is commercially available in large quantities and is known for its high performance in photocatalytic degradation reactions.

2.2. Methods

Irradiation experiments were performed using a water-cooled mercury vapor lamp immersed in a quartz reactor (Peschl Ultraviolet UV lab reactor system 1, irradiance: 2700 $W\,m^{-2}$, volume: 400 ml), as well as an irradiation chamber (Hönle UVACUBE 400) equipped with a mercury vapor lamp (irradiance: 495 $W\,m^{-2}$) and a radiation filter producing simulated sunlight. A comparison of the light sources' emission spectra can be found in Fig. 1. The immersed lamp in the quartz reactor shows a discrete spectrum with several peak intensities, while the lamp installed in the irradiation chamber supplies a continuous spectrum in the range of UV and visible light. Both of the light sources show an intensity peak between 380 and 420 nm, which is necessary for the activation of the photocatalyst.

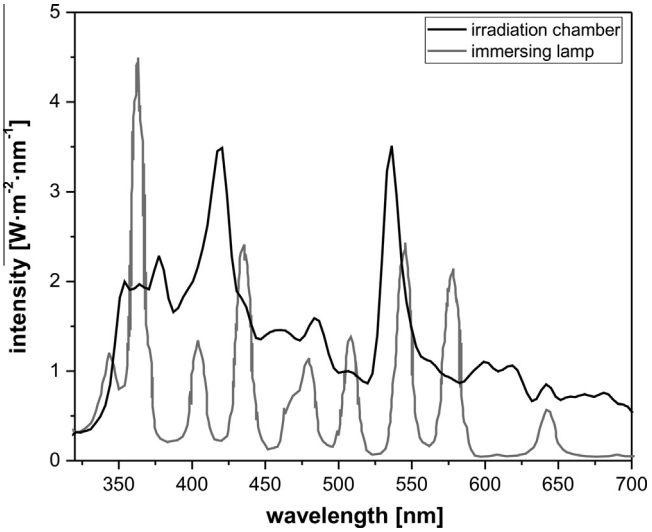

Fig. 1. Emission spectra of the irradiation sources used.

In all experiments 400 ml of a solution of zanamivir or guanidinium nitrate with an initial concentration of 100 $\mu g\,l^{-1}$ were used, which can be viewed as a realistic concentration for wastewater dominated surface waters in pandemic cases.

The standard amount of TiO_2 was 3.05 mg, which gives a ratio of 76.38 mg of the photocatalyst per mg zanamivir/guanidinium nitrate, corresponding to the conditions applied by Calza et al. [9]. For comparison, irradiation experiments without adding TiO_2 were also performed. Standard experiments were carried out at room temperature. When using the irradiation chamber, the solution was filled into a quartz flask. Before starting irradiation of the TiO_2 suspensions, the radiation sources were given 30 min operating time to reach a constant level of intensity. In the case of the quartz reactor, this was accomplished by igniting the immersing lamp outside of the reactor, while the irradiation chamber was equipped with a shutter. The extent of substance conversion under radiation was determined by taking samples after defined reaction time intervals, where the starting time was defined as the beginning of irradiation.

Prior to the irradiation experiments, identical measurements with and without the addition of TiO_2 were performed without irradiation to determine the extent of adsorption of zanamivir and guanidine on the photocatalyst as well as on the quartz vessels and sampling system used. Additional experiments were carried out by varying the TiO_2 amounts (1, 3, 5, 7, and 10 mg).

2.3. Analytical procedure

Concentrations of zanamivir or guanidine in the samples taken during irradiation were determined by HPLC–MS/MS (TSQ Quantrum Ultra, Thermo Fisher Scientific). The samples were eluted through the column (Hypersil GOLD HILIC (100 × 2.1 mm), Thermo Fisher Scientific) using a program with gradient concentrations of two different eluents (see Fig. 2) as the mobile phase.

The transfer of the sample components into the ionization chamber of the mass spectrometer occurred by H-ESI electrospray injection (3.5 kV, 647 K). Concentrations were determined by the guanidinium cation (m/z = 60.04, see Fig. 3), conducted in the SRM-modus [18,19]. The standard process variation of the analytical procedure is 10.7% and the limit of quantitation amounts to 6.3 $\mu g\,l^{-1}$.