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Kinetics and degradation pathways of photolytic and photocatalytic oxidation of the anthelmintic drug praziquantel

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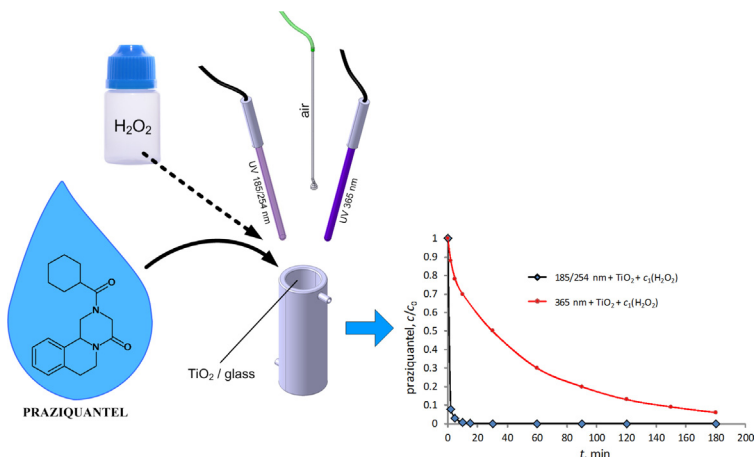
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HIGHLIGHTS

- Degradation of scarcely investigated anthelmintic praziquantel (PZQ) was studied.
- UV photolysis and photocatalytic oxidation on TiO₂ film with H₂O₂ were used.
- UV-C/TiO₂/H₂O₂ process yielded the highest degradation rate of PZQ.
- Five degradation products were detected during the performed experiments.
- Tentative structural formulae for degradation products were proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, an anthelmintic drug, praziquantel (PZQ), was degraded using the direct photolysis, photocatalysis, and oxidation processes including UV radiation, TiO₂ film, and hydrogen peroxide. The photolytic degradation with predominant wavelengths of 185/254 nm (UV-C) proved to be more efficient with a half-life of 3.13 min compared to the radiation of 365 nm (UV-A) where the degradation did not occur. In order to enhance the rate of PZQ photolytic degradation, H₂O₂ was added, which resulted in two to three times higher degradation rates. In the photocatalytic degradation, TiO₂ film was used as catalyst. The degradation was ten times faster in the photocatalytic experiments where UV-C light ($k=0.2390 \text{ min}^{-1}$) was used than in those with UV-A ($k=0.0201 \text{ min}^{-1}$). Comparing the results from all performed experiments it can be concluded that the UV-C/TiO₂/H₂O₂ process yielded the highest degradation rate and complete degradation of PZQ was obtained in less than 7 min. The degradation of PZQ followed the first order kinetics in all the experiments. The photo degradation

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was inhibited in the presence of methanol. The degradation pathways and the structural formulae of five degradation products (m/z 273, 269, 189, 147, 132) were proposed based on the liquid chromatography tandem mass spectrometry analysis.

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1. Introduction

Over the past decade, pharmaceuticals have been considered as emerging pollutants due to their continuous input and persistence in the aquatic ecosystems even at low concentrations. Since they could have a great impact on the environment and on human health, public and scientific concern has progressively increased [1–4]. Veterinary pharmaceuticals are substances that are widely used for treating domestic animals and those in intensive animal farming. Some of important applications of these compounds are the treatment and prevention of infectious diseases, the management of reproductive processes and production, and the control of parasites and of non-infectious diseases [5]. Veterinary pharmaceuticals enter the environment mainly through the direct discharge of aquaculture products, through substances in the urine and feces of livestock and through washing off the topical medication applied to livestock. The contribution of the manufacturing process is probably low due to the strict control of environmental discharge. Pharmaceuticals that are used for treating humans reach the environment in low concentrations either via excretion or as unused drugs. Once pharmaceuticals are released into the environment, they could produce adverse effects on the environment and living organisms [3,4,6].

Anthelmintics are drugs that are used for the protection against helminth infections. They are administered to livestock, to animals in animal husbandry and to aquatic organisms in aquaculture as well as to humans. The estimated total annual production in 2005 was 200 t [7], which included the use in the human and the veterinary medicine. Due to their wide application, anthelmintics are expected to have impacts on the terrestrial and aquatic environments. Exposure to low concentrations of anti-parasitic agents such as anthelmintics in the environment may also stimulate the development of resistant strains of parasites. Unfortunately, regardless of the high usage of anthelmintics and their potential impact on living organisms in water, soil and sediment, the information on their concentrations in the environmental waters is scarce. Their presence in the environment in low $\mu\text{g L}^{-1}$ concentrations has been reported in [8–12] but despite the reported low concentrations, their ongoing input into the environment attracts interest. In that sense, it is necessary to develop more effective wastewater treatment technologies to prevent the emission of pharmaceuticals such as anthelmintics into the environment.

Advanced oxidation processes (AOPs) have proven to be among the most effective techniques for removing personal care products [13] and pharmaceuticals from water samples [14–18]. These processes can be broadly defined as aqueous phase oxidation methods in which highly reactive species such as hydroxyl radicals are (primarily, but not exclusively) responsible for the destruction of target pollutants. Depending on the properties of the waste stream to be treated, AOPs can be employed either alone or coupled with other physicochemical and biological processes [19]. They have also proved to be efficient in the removal of contaminants from wastewaters as a tertiary treatment [20]. Besides AOPs, membrane processes, particularly reverse osmosis and nano-filtration [21], can be used for the removal of pharmaceuticals, including praziquantel (PZQ). As there is only a limited amount of data on the presence of praziquantel in the environment and on its removal from it, one

can use the available predicted data on the PZQ removal during the waste water treatment. In the predicted data a total removal of 2.89% is reported [22].

The most extensively investigated AOPs used for the degradation of pharmaceuticals include the UV irradiation combined with H_2O_2 as a strong oxidant, the Fenton and the photo-Fenton oxidation, and the heterogeneous photocatalysis [19]. Titanium dioxide or titania (TiO_2) was used in photocatalytic oxidation experiments as the most suitable photocatalyst [23,24]. It crystallizes in three polymorphic forms: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The most common phases of photocatalysts are anatase and rutile. Titanium dioxide in the form of aqueous suspensions has been commonly used as a photocatalyst for water purification. However, the main disadvantage of using the suspended TiO_2 is the need of separating TiO_2 nanoparticles from the treated water after the reaction and of their reuse. Therefore, the immobilization of TiO_2 onto a supporting substrate would be required for industrial applications. One of the methods suitable for the TiO_2 film deposition is sol-gel dip coating. This method is most frequently used for the synthesis of TiO_2 film used for the degradation of different organic pollutants. Titanium dioxide is characterized by low processing costs, photochemical stability, simplicity, nontoxicity, excellent homogeneity, and it offers a possibility for tailoring the film properties [25–29].

Few reports on the degradation of PZQ found in the literature [30] have shown that PZQ is a photolabile drug when directly exposed to sunlight in aqueous media over a very long period (a few months). Havlikova and co-authors [31] investigated the photocatalytic degradation of PZQ in the aqueous TiO_2 suspension. According to the available literature, there are not many studies that deal with the removal of PZQ from waters. PZQ is a pharmaceutical drug whose presence in the environment poses a threat to human and animal health. This research will contribute to the amount of data on the removal of PZQ from water matrices, but it also has a novelty value as, to our knowledge, the TiO_2 film-based photocatalysis of PZQ has not been investigated yet.

Therefore, the main objective of the present study was to determine whether the photolytic degradation (UV-C only and UV-A only), photocatalytic degradation (UV-C/ TiO_2 and UV-A/ TiO_2) and other advanced oxidation methods (UV-C/ H_2O_2 , UV-A/ H_2O_2 , UV-C/ $\text{TiO}_2/\text{H}_2\text{O}_2$, UV-A/ $\text{TiO}_2/\text{H}_2\text{O}_2$) can be used for the degradation of PZQ. The degradation kinetics and degradation pathways of the PZQ degradation were also investigated. As sources of UV radiation, two different UV lamps were used—a lamp with predominantly 185/254 nm wavelengths (UV-C) and a lamp with a predominant radiation wavelength of 365 nm (UV-A). The degradation of PZQ in the presence of a low concentration of organic solvents such as methanol or acetonitrile in aqueous solutions as helping agents for a better dissolution of PZQ was also monitored and analyzed. In aqueous solutions of organic matter, there is competitiveness between the direct oxidation (by means of holes on the TiO_2 surface), the electrons, and the indirect oxidation (by means of $\cdot\text{OH}$ radicals) [32–34]. Since methanol has proved to be a radical scavenger and a hole scavenger, this study is also focused on the comparison between the degradation efficiency and its kinetics in the experiments with acetonitrile and methanol. Formation and degradation of PZQ degradation products and degra-

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