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Treatment of aquaculture wastewater contaminated with metronidazole by advanced oxidation techniques

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ABSTRACT

This work analyses the treatment of ornamental aquaculture wastewater contaminated with the antibiotic metronidazole (MTZ) using a reactor with supported TiO_2. Preliminary photolysis and hydrolysis studies revealed inefficient elimination of this pollutant under the study conditions.

The activity of various photocatalysts in suspension in the elimination of 40 $mg{\cdot}L^{-1}$ of MTZ was studied, as well as the degradation performance in different aqueous matrices using UV-A radiation. Process efficiency was strongly and negatively affected by the presence of ions in solution, with a 20% decrease in mineralization. The highest reaction rates was observed with the Evonik-P90 (0.0625 min^{-1}) versus Hombikat (0.0078 min^{-1}).

A number of configurations were evaluated to optimise the performance of the reactor with immobilized catalyst in MTZ degradation. Different types of illumination (UV-A and UV-C) were tested as well as the positions of both lamp and catalyst inside the reactor. Various configurations were able to completely eliminate 10 $mg{\cdot}L^{-1}$ of MTZ. A greater efficiency was observed in general in the degradation processes with the catalyst immobilized on the outer tube with the internal UV-C lamp ($k_{E.UVC}$; 0.042 min^{-1}), compared UV-A lamp ($k_{E.UVA}$; 0.022 min^{-1}). The best configuration was catalyst immobilized on the outer with the internal UV-C lamp and hydrogen peroxide ($k_{E.UVC*}$; 0.055 min^{-1}).The deposited catalyst was also successfully subjected to continuous re-runs using the optimised configuration with no catalyst deactivation observed. Despite a decrease in photocatalytic activity of 24% after the sixth re-run, 100% MTZ elimination was still achieved. The degradation pathway of metronidazole using TiO_2 photocatalysis has also been proposed and detoxification of the samples after the photocatalytic treatment was evaluated using *V. fischeri* bacteria test.

1. Introduction

The aquaculture industry has grown considerably in recent years. Some 600 aquatic species are currently bred in captivity worldwide. The number of ornamental fish that are marketed is rising annually with, for example, an increase between 2006 and 2011 of 16.3 million tonnes (FAO, 2012).

One of the risks inherent in the marketing of aquaculture species is the propagation of pathogens. It is known that the commercialisation of ornamental fish can result in the introduction of exotic diseases into the country of destination, as well as sudden changes in the pattern of endemic diseases or the appearance of previously unknown diseases (FAO, 2007). Infection as a result of these pathogens is common in ornamental fish, particularly in some of the most sensitive and expensive species such as, for example, *Symphysodon discus* (Untergasser, 1991).

In consequence and as a protective measure, exporters of ornamental fish will often treat their specimens with drugs. One of the most commonly used treatments in the ornamental aquaculture industry involves the use of metronidazole (MTZ), an antibiotic derived from the nitroimidazoles typically prescribed for the treatment of infections caused by anaerobic protozoa and bacteria such as *Hexamita* and *Amyloodinium* (Harms, 1996). In general, compounds such as MTZ are highly soluble in water, have low biodegradability (Alexy et al., 2004) and are a potential health hazard as they are both mutagenic and carcinogen (Carrales-Alvarado et al., 2014). Antibiotics are also considered to be among the so-called emerging pollutants due to their continuous introduction and persistence in the aquatic ecosystem (Homem and Santos, 2011).

Wastewater from the ornamental aquaculture industry can contain

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varying amounts of MTZ and, if left untreated, can contribute to the accumulation of this contaminant in the aquatic medium, as well as to the development of bacterial strains which are resistant to antibiotics (Pereira et al., 2013).

Conventional wastewater treatment does not eliminate MTZ, resulting in its potential accumulation in the aquatic environment (Shemer et al., 2006). It is classified as a category 2 carcinogen according to Regulation (EC) 1272/2008.

Contaminated wastewater of this type is commonly treated by filtering it through activated carbon (Eschliewen, 2006; Méndez-Díaz et al., 2010). However, this does not result in elimination of the contaminant, but simply a change in phase, meaning that the activated carbon itself then becomes a waste material which in turn needs to be specially treated. So-called Advanced Oxidation Processes (AOPs), on the other hand, are able to eliminate such contaminants, transforming them into inert substances for the environment. The AOPs, are based on the production and use of hydroxyl radicals, which are strong oxidizing species that react with most organic contaminants (Giraldo et al., 2010).

Various studies have been undertaken on MTZ elimination using AOPs. These include analyses of the degradation process when using photolysis and UV/H_2O_2 treatments, which revealed low levels of degradation of this contaminant (Shemer et al., 2006; Tong et al., 2011; Dantas et al., 2010; Prados-Joya et al., 2011; Johnson and Mehrvar, 2008). Metronidazole degrades more efficiently by system UV/H_2O_2 rather than by direct photolysis (Shemer et al., 2006). This is due to generation of ·OH radicals by photolysis of the peroxidic bond which attack the molecules of MTZ. Other MTZ degradation studies performed employing the Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (UV/H_2O_2/Fe^{2+}) processes have given better results (Shemer et al., 2006; Rodríguez-Gil et al., 2010; Cheng et al., 2013). It was reported that this process is optimal at pH values below 3 and that particulate Fe(III) is formed at pH values above 5, with the resulting sludge requiring further treatment (Cheng et al., 2013). Process efficiency in these cases is therefore highly dependent on pH and the iron salts can be considered a source of contamination (Shemer et al., 2006). The inefficiency of the process at pH 7 (Cheng et al., 2013) makes it unsuitable for the treatment of wastewater from the ornamental aquaculture industry which has a natural pH of around 7. Also, the ozonation (Kermani et al., 2013; Sánchez-Polo et al., 2008) and zero valent iron (Fang et al., 2011) processes have been used to degrade MTZ. Both systems were effective in the degradation of MTZ.

Very few studies have been published on the photocatalytic degradation of MTZ using immobilized (Khataee et al., 2013) or suspensions photocatalysts (Farzadkia et al., 2014; Aoudjit et al., 2015; Farzadkia et al., 2015; Wang et al., 2010; Dong et al., 2014; El-Sayed et al., 2014; Okhovat et al., 2015).

In view of this and the fact that wastewater from this industry is ideally suited for treatment using photocatalytic techniques as a result of its low organic matter concentration and the small volumes involved (Domènech et al., 2001), the present study will focus on MTZ degradation by heterogeneous TiO_2 photocatalysis.

One of the drawbacks of using TiO_2 photocatalysis is the need to subsequently separate the catalyst from the treated wastewater by a filtering process when the catalyst is used in suspension. One way of resolving this problem involves supporting the catalyst on an inert material, thereby immobilising it. Among the different immobilisation techniques that can be employed, dip-coating is a very simple procedure which has shown suitable efficacy (Guillard et al., 2002; Legrand-Buscema et al., 2002).

In view of the fact that very few studies have considered an economic evaluation of the application of AOPs (Lucas et al., 2010; Muñoz et al., 2008; Jordá et al., 2011), it was decided to consider this aspect after the determination of the optimum configuration.

The aim of this work is therefore to propose a photocatalytic reactor, with immobilized catalyst, for the treatment of wastewater from the ornamental aquaculture industry. For this purpose, a synthetic wastewater containing the dissolved contaminant was produced for the purpose of studying the photolysis and photocatalytic processes. The degradation pathway of metronidazole using TiO_2 photocatalysis has also been proposed. Moreover, the toxicity of the reaction samples has been evaluated by *V. fischeri* bacteria test for the best of the studied photocatalysts.

2. Experimental

2.1. Chemical reagents

Commercial MTZ ($C_6H_9N_3O_3$) was supplied by Acofarma S.L. pH was adjusted with aqueous solutions of H_2SO_4 and NaOH. The synthetic water was created using calcium chloride (Panreac, 95%) magnesium sulphate heptahydrate (Panreac, 99%), sodium nitrate (Riedel-de Haën, 99.5%), anhydrous disodium hydrogen phosphate (Panreac, 99%), sodium bicarbonate (Fluka, 99%), potassium chloride (Panreac, 99.5%) and sodium chloride (Panreac, 99%). Ethanol (Panreac, ≥ 99.5%) was used as TiO_2 dispersion agent. When required, hydrogen peroxide (H_2O_2) at 30% (w/v) was used, supplied by Scharlau. The properties of the different TiO_2-based catalysts used in this study are shown in Table 1.

The ECT 1023t catalyst was synthesised in the laboroatory following a sol-gel procedure (Araña et al., 2010).

2.2. Preparation of TiO_2 film

A KSV DX2S Dip Coater for specialised fine-layer coating was used in this study. All supports were coated at an immersion rate of 500 mm min^{-1}, with submersion time of 120 s, removal rate of 120 mm min^{-1} and a period of 240 s outside the liquid (Espino-Estévez et al., 2015), and the cycle was repeated 80 times in all cases. A 16 g L^{-1} suspension of commercial catalyst in ethanol was used. Deposited TiO_2 mass was measured with an analytic balance (A & D HR-200, accuracy 1 mg ± 0.1). The catalyst was deposited on borosilicate and quartz supports. After the substrate had been coated, the dispersant (ethanol) was evaporated in an oven at 100 °C. The catalyst was subsequently calcined at 450 °C for 2 h, with a temperature ramp of 30 °C min^{-1}.

Coating adhesion was evaluated by vigorous washing with ultrapure water. Catalyst mass detachment was determined with a calibration curve of turbidity vs. catalyst concentration (Santiago et al., 2015; Qiu and Zheng, 2007).

2.3. Configuration of reactors

Two photocatalytic systems were used according to the type of

Table 1
Catalyst properties.

Properties		Evonik-P25	Evonik-P90	ECT 1023t	Hombikat-UV100
Anatase (A)/Rutile (R) (%)		80 A/20 R	86 A/14 R	89–94 A/ 6–11 R	100 A
Crystal domain size (nm)	A	22	13	57	7
	R	25	–	86.3	–
Band gap (eV)		3.18	3.29	2.97	3.22
Aggregate size (μm)		3.9	–	30.1	–
Surface area ($m^2 \cdot g^{-1}$)		52	100	15.8	280
pH_{PZC}		6.5	7.8	5.2	5.8
References		Araña et al. (2010)	Santiago et al. (2015)	Araña et al. (2010)	Araña et al. (2010)