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Aqueous phototransformation of zinc pyrithione Degradation kinetics and byproduct identification by liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry

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Abstract

The photochemical behavior of the antifouling agent zinc pyrithione (ZnPT) was studied in aqueous media of different composition under simulated solar irradiation using a xenon light source. The influence of important constituents of natural water (dissolved organic matter and nitrate) was also examined using a multivariate kinetic model. It was found that photodegradation proceeds via a pseudo first-order reaction. Kinetic experiments were monitored by LC–MS and photolytic half-lives ranging between 9.2 and 15.1 min have been observed. The increasing concentration of dissolved organic matter (DOM) accelerates the photolysis reaction, while the effect of nitrate ions was also positive since it increased the degradation rate, but to a lesser extent. Irradiation of the aqueous ZnPT solutions gave rise to several transformation products that were isolated by means of solid-phase extraction using poly(styrene-divinylbenzene) extraction disks. These byproducts were identified using liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry. Besides 2-pyridinesulfonic-acid, other degradation products formed included pyridine-*N*-oxide, 2-mercaptopyridine, 2,2′-dithiobis(pyridine-*N*-oxide), 2,2-dipyridyl disulfide and the pyridine/pyrithione mixed disulfide, 2,2′-dithiobispyridine mono-N-oxide (PPMD).

Keywords: Photodegradation; Zinc pyrithione; Dissolved organic matter; Fate

1. Introduction

New alternative antifouling paint formulations (based mainly on organic booster biocides) have been developed and introduced in the market as a result of the ban introduced on the organotin compounds due to their negative impact on marine environment. Worldwide around 18 compounds are currently used as booster biocides in antifouling products (the most widely used are: chlorothalonil, dichlofluanid, diuron, Irgarol 1051, Sea-Nine 211, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine (TCMS-pyridine), (thiocyanomethylthio)benzothiazole (TC-MTB), zinc and copper pyrithione, zineb, folpet, mancozeb, thiram, ziram) for amateur and professional use [1]. The continued input of these biocides from the painted hulls of boats directly onto the foreshore has led to reports of elevated concentrations in areas of high yachting activity and low water exchange rates such as marinas [2,3].

Besides used as additive in antifouling paint formulations, the majority of ZnPT (Fig. 1) (*bis*(2-pyridylthio)zinc 1,1′-dioxide) produced has been used as the active ingredient in anti-dandruff shampoo or as an additive in cosmetics and dermatitis treatments. Therefore, two distinct routes into the aquatic environment exist for ZnPT that depend principally upon the mode of usage.

Given the potential human and wildlife health risks associated with toxic pollutants in surface waters, it is important to determine the probability that a certain chemical will persist in the environment by examining the various reactions of the

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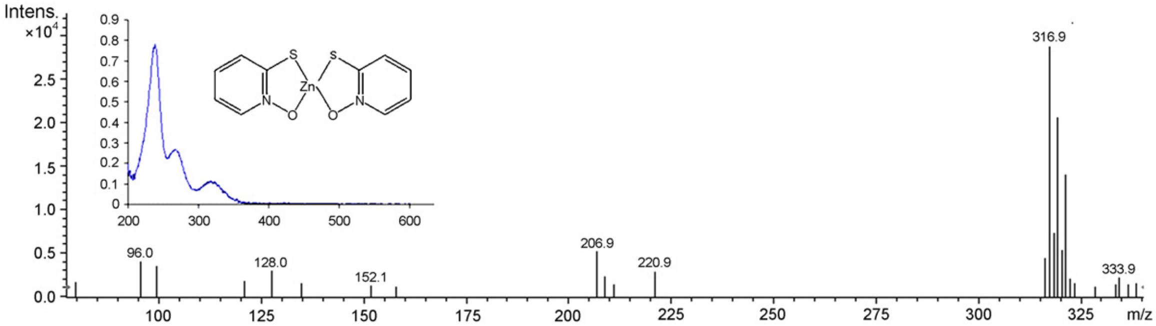

Fig. 1. Structure, UV–vis and APCI–MS spectrum of ZnPT.

molecule. Direct and indirect photochemical reactions are of the most important abiotic processes that may contribute to the degradation of organic micro-pollutants under environmental conditions.

Several studies have dealt with ZnPT photodegradation in distilled and seawater, respectively, mainly in terms of degradation kinetics that have been reviewed before [4]. Zinc pyrithione photodegradation is a rapid procedure with half-lives ranging from minutes to hours depending on the light source and the aqueous matrix [5–7].

Previous research has identified dissolved organic matter (DOM), NO_3^-, and HCO_3^-/CO_3^{2-} as significant participants in the photochemical degradation of organic micropollutants in surface waters [8,9]; accordingly, identifying their effect on ZnPT degradation was of interest. The role these constituents play in photochemical degradation is concentration dependent; and can simultaneously respectively decrease and increase photochemical reactions [10,11]. In order to meet these requirements we examined the aquatic photochemical degradation of ZnPT under simulated solar irradiation. A multivariate kinetic model of aqueous ZnPT photodegradation was developed as a function of DOM, and nitrate at concentrations that bracket those commonly observed in natural waters.

Few studies have dealt with the fate of ZnPT in the aqueous environment [12,13]. On the other hand, reports on the development of analytical methods for determining ZnPT residues are still scant due to the lack of sufficient analytical methods for its determination (despite concerns of considerable environmental toxicity at ultra-trace concentrations) and only a few studies have been presented accomplishing their determination [14–16]. Since the study of the photochemical behavior of a contaminant is a key issue in terms of the formation of toxic transformation products; in this context, we now attempt to extend the analytical utility of LC methods towards the investigation of this chemical and the determination of phototransformation intermediates formed.

In a wider context, the aim of the present study is two-fold. First, it strives to decipher the prime mechanisms involved in the fate and environmental behavior of ZnPT and examine the simultaneous effect of natural occurring constituents. Second, isolate and characterize the intermediate products, which are produced during the phototransformation process.

2. Materials and methods

2.1. Chemicals

ZnPT, purity above 90% was purchased from Wako (Tokyo, Japan). 2-Mercaptopyridine-*N*-oxide (POS) and pyridine-*N*-oxide (PO) were obtained from Aldrich (Tokyo, Japan). 2-Mercaptopyridine (PS) and 2,2′-dipyridyl disulfide $(PS)_2$ were purchased from Tokyo Kasei (Japan). 2-Pyridinesulfonic acid (PSA) was from Synchem and 2,2′-dithiobispyridine-*N*-oxide $[(POS)_2]$ was provided from Chem Service (USA). Sodium hydrogencarbonate ($NaHCO_3$) and sodium nitrate ($NaNO_3$) were purchased from Junsei (Tokyo, Japan) while humic acids (HA) were provided by Wako. Pesticide analysis grade solvents were purchased from Pestiscan (Labscan, Dublin, Ireland). HPLC analysis grade solvents were obtained from Merck (Darmstadt, Germany). Poly(styrene-divinylbenzene) (PS-DVB) extraction disks (47 mm) were purchased from 3M Empore (St. Paul, MN, USA), and a conventional filtration apparatus was supplied from Supelco (Bellefonte, PA, USA). $NaNO_3$ and HA stock solutions were diluted to achieve the respective NO_3^- and DOM concentrations outlined in the experimental section. Natural water samples used in the experiments were collected from the Epirus region of N.W. Greece with the following physicochemical characteristics: seawater (Ioanian sea) DOM = 2.1 mg/L, nitrate = 3.3 mg/L, lake water (Pamvotis lake) DOM = 11.0 mg/L, nitrate = 10.3 mg/L.

2.2. Chromatographic conditions

LC–MS was performed under the same conditions optimized in our previous work during the direct analysis of ZnPT by LC–MS [14]. An Agilent 1100 series HPLC system was used, equipped with a quaternary pump, a diode-array detector, an autosampler, and a column compartment. The LC system was coupled to a LC ion trap mass spectrometer complete with an atmospheric pressure chemical ionisation source operated under positive polarity.

The samples were separated on a Unison UK-Phenyl column (50 mm × 3.0 mm) supplied by Imtakt (Kyoto, Japan). For the separation of the degradation products a mobile phase consisted of methanol (A) and water containing 20 mM ammonium acetate