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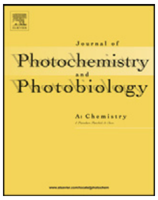

Photodegradation of the endocrine-disrupting chemicals 4*n*-nonylphenol and triclosan by simulated solar UV irradiation in aqueous solutions with Fe(III) and in the absence/presence of humic acids

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ABSTRACT

4*n*-Nonylphenol (4*n*-NP) and triclosan (TCS) are endocrine disrupters that are used widely in personal care products. They are mainly transported in domestic sewage, which can eventually reach natural waters (rivers, lakes or reservoirs). In this work, the photodegradation of 4*n*-NP and TCS using a solar simulator (300–800 nm) at two different pH levels, two different concentrations of ferric ion, Fe(III), and in the absence/presence of humic acids (HAs) were investigated. A Xe lamp (250 W m^{-2}) was employed as the light source. The conditions were chosen to simulate a natural aquatic environment. The experiments were performed using a factorial design for three factors with eight combinations of the factors studied. Experiments performed in ultrapure water showed that the degradation of 4*n*-NP was faster than that of TCS. The data showed that first-order reaction kinetics describe the degradation of both compounds well; the half-lives of TCS and 4*n*-NP were 5.4 h and 2.3 h, respectively. For TCS, the results indicated that the oxidation rate increases in the presence of Fe(III) and at basic pH levels; however, the rate it decreased in the presence HAs. In the case of 4*n*-NP, synergistic effect was observed for presence of Fe(III) and HAs. The best conditions were a basic medium (pH 9) and an Fe(III) concentration of 2 mg L^{-1} without HAs for TCS and a pH of 9, an Fe(III) concentration of 2 mg L^{-1} and a HAs concentration of 1 mg L^{-1} for 4*n*-NP. The results of photodegradation of both compounds in water from two reservoirs showed that the photodegradation was highly dependent on the conditions of the aquatic environment.

1. Introduction

Several studies have proved the presence of emerging contaminants in rivers, lakes and reservoirs that can cause adverse effects on the environment, and such contamination is becoming a worldwide concern [1–3]. The occurrence of these contaminants is usually a result of municipal and industrial wastewater discharge as these compounds are not completely removed during treatment [4]. Two emerging contaminants: 4*n*-nonylphenol and triclosan are used in a wide range of personal-care products, and they are mainly transported in domestic sewage, which eventually reaches rivers and reservoirs. These compounds are considered as endocrine disruptors, and they have been found in various sources of water [5–11]. 4*n*-Nonylphenol (Fig. 1a) is a degradation product of alkylphenol ethoxylates that is produced under both aerobic and anaerobic conditions [12]. 4*n*-Nonylphenol is used as a precursor in the manufacture of nonionic surfactants for use in detergents, dispersive agents, emulsifiers, pesticide formulations, paints and personal-care products [13–16]. Because of its physicochemical characteristics, such as its low solubility and high hydrophobicity, it accumulates in different environmental compartments characterized by a high organic content [17]. Triclosan (Fig. 1b) is one of the most studied emerging contaminants because it is a widely employed antimicrobial agent [18]. Triclosan is highly toxic to some aquatic organisms, especially fish, and it can bioaccumulate [19]. This compound has been detected in wastewater and surface water (rivers and lakes) and is mainly transported in domestic sewage [8,11,20].

Photolysis is a degradation pathway for many contaminants in surface waters. This process may affect both, the environmental fate of this compounds and the ecological risk that they represent [21]. Solar phototransformation may proceed via a direct pathway, where photodecomposition after the absorption photons from solar radiation occurs or via an indirect pathway induced by hydroxyl free radicals (•OH); these free radicals result from the interaction of sunlight and light-absorbing organic substances [22]. For indirect photolysis in natural aquatic environments, iron and humic substances (HSs) play a significant role because these substances are ubiquitous in aquatic environments, absorb solar radiation to reach an excited state, and subsequently generate free

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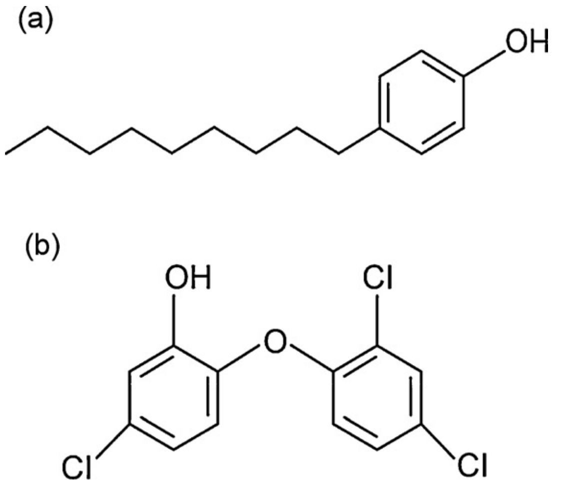

Fig. 1. Chemical structure of (a) triclosan and (b) 4*n*-nonylphenol.

radicals composed of reactive oxygen species [23–25]. The degradation time of these organic compounds in the environment may vary depending on various environmental parameters [26].

Humic substances, the largest component of dissolved organic matter (DOM) are formed during the abiotic and microbiological transformations of plant and animal materials, and they can be categorized as humic acids (HAs), fulvic acids or humin depending on their solubility [27]. Humic acids are the important constituent of HSs; they are light-absorbing species in natural waters that can generate free radicals that cause the photooxidation of organic contaminants [28]. These photochemical processes are often associated with transition-metal ions because HAs have a strong affinity toward metal cations, especially iron. The iron, which is a ubiquitous element in natural waters, is involved in many redox reactions, including those with hydrogen peroxide, organic matter and trace metals [29]. The photochemical processes play an important role in the photodegradation of pollutants in natural waters that contain Fe(III) and DOM. The interaction of trace organic pollutants with reactive species may induce the indirect photolysis of the pollutant and therefore influence its photochemical fate and persistence in natural waters [30].

The environmental behavior and fate of these compounds is of significant interest. Because of its endocrine-disrupting effect and the potentially important environmental and human health implications of these compounds, the study of their photochemical behavior in aqueous solutions is necessary. Because the presence of humic acids and Fe(III) significantly affects natural aquatic environments, studies of the influence of these factors on the photodegradation of triclosan and 4*n*-nonylphenol to predict the transport and fate of these contaminants in natural waters are necessary. The goal of this study was to simulate the degradation process of triclosan and 4*n*-nonylphenol under solar irradiation to investigate the influence of pH and natural photosensitizers, such as Fe(III) and humic acids (HAs), on this reaction in ultrapure water using an experimental design. Other experiments were performed to allow a comparison of the results obtained for ultrapure water with those obtained for reservoir water.

2. Experimental

2.1. Chemicals

Triclosan (99.5%) and 4*n*-nonylphenol (99.0%) were purchase from Dr. Ehrenstorfer (Audgsburg, Germany). Isotopic triclosan-d_3 (98.5 atom%, 0.05 g) was purchased from CDN Isotopes (Quebec, Canada). The derivatizing agent *N*,*N*-trimethylsilyl trifluoroacetamide (MSTFA) was purchased from Restek (Bellefonte, USA). Fuming hydrochloric acid (HCl, 37%) was purchased from Merck (Frankfurter, Germany). Sodium hydroxide (NaOH) was purchased from Carlo Erba (Rodano, Italy). Dichloromethane (DCM) and pesticide-grade methanol (MeOH) were purchased from Honeywell B&J. Acetone was purchased from J.T. Baker (Teugseweg, Deventer, The Netherlands). Ultrapure water was produced using a Milli-Q system from Millipore (Watford, UK).

Analytical-grade ferric chloride ($FeCl_3 \cdot 6H_2O$) was purchased from Carlo Erba (Rodano, Italy). Suwannee River humic acid of reference grade 2S101H was acquired from the International Humic Substances Society (IHSS) (Standard II, Atlanta, GA, USA). HAs stock solution with a concentration of 1 mg L^{-1} of carbon was prepared by dissolving 24 mg of HAs in 10 mL of ultrapure water. Individual stock solutions of triclosan and 4*n*-nonylphenol solutions were prepared by dissolving 10 mg of the solute in 10 mL of acetone to achieve a final concentration of 1000 mg L^{-1}; these solutions were stored at 4 °C and were protected from light. For GC/MS analyses, the individual stock solutions were mixed and diluted with acetone to a final concentration of 100 mg L^{-1} and were subsequently diluted with dichloromethane or acetone to obtain working mixed solutions. An individual stock solution of isotopically labeled internal standard triclosan-d_3 was also prepared in acetone, and a mixed working solution with a concentration of 5 mg L^{-1} was used as an internal standard.

2.2. GC/MS analyses

The analytical method used in this study was based on a methodology previously developed in our laboratory [31]. The concentrations of triclosan and 4*n*-nonylphenol were measured by gas chromatography on an Agilent Technologies 7890A equipped with an Agilent Technologies 7693 (Wilmington, DE, USA) mass selective detector (MSD). Chromatographic separations were performed on a HP MSi, 30 m × 0.25 μm ID column with a film thickness of 25 μm (Agilent, Wilmington, DE, USA) using helium as the carrier gas at a flow rate of 1 mL min^{-1}. The chromatographic conditions used were: pulsed splitless injection mode; an injection volume of 0.5 μL; an injection-port and transfer-line temperature of 290 °C. The oven program was an initial temperature up to 100 °C for 2 min; 15 °C min^{-1} to 180 °C; 6 °C min^{-1} to 250 °C; and 50 °C min^{-1} to 320 °C. The analysis run time was 20.4 min. A single-quadrupole mass spectrometer with electron-impact ionization (EI, 70 eV) was used. The optimization of the retention times was initially performed in scan mode at a concentration of 2 mg L^{-1}. The mass spectrometer was operated in a mass range of 50–400 amu. An ion was selected for each analyte in single-ion monitoring (SIM) mode: $m/z = 279$, $m/z = 345$ and $m/z = 350$ for 4*n*-nonylphenol, triclosan and triclosan-d_3, respectively. The compounds were identified based on their retention times, and the identifications were confirmed by comparison of their mass spectra with those of the standards. The quantification of the samples was performed using a calibration with the triclosan-d_3 isotopically labeled internal standard; thus, relative areas were used for quantification purposes. For gas chromatographic analyses, a derivatization process was necessary. MTSFA (*N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide) was selected as a derivatizing reagent to form trimethylsilyl (TMS) derivatives. For this process, 150 μL of the extract was collected, and 10 ng of internal standard (20 μL of a solution to 5 μg mL^{-1} TCS-d_3) and 20 μL of MSTFA were added in excess to ensure that the compounds derivatized completely [32]. The samples were then allowed to react 40 min at 60 °C. After derivatization, the sample was injected into the GC/MS. For quantification, six standards in dichloromethane