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Review

Degradation models and ecotoxicity in marine waters of two antifouling compounds: Sodium hypochlorite and an alkylamine surfactant

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ABSTRACT

Industrial wastes have a substantial impact on coastal environments. Therefore, to evaluate the impact of cooling water discharges from coastal power plants, we studied the kinetics of the degradative processes and the ecotoxicity of two antifouling products: (1) a classic antifouling product; sodium hypochlorite (NaClO) and (2) an alternative one; aliphatic amines (commercial under the registered trade mark Mexel®432). To assess the persistence of both compounds the decay of sodium hypochlorite and the primary biodegradation rate of Mexel®432 were determined in natural seawater at 20 °C. The results indicated a more rapid decay of NaClO than Mexel®432. The degradation behavior of both chemicals was described following a logistic model, which permitted calculating kinetic parameters such as t_{50} or t_{90}. The t_{50} was 1 h and 2 d for NaClO and Mexel®432, respectively. To evaluate the potential risks of the aforementioned treatments to marine organisms, the acute toxicity of both antifouling products was studied on the microalgae *Isochrysis galbana* and *Dunaliella salina*, and on the invertebrate *Brachionus plicatilis*, using growth inhibition and death tests as toxic response, respectively. For *I. galbana*, the 96-h EC_{50} values were 2.91 ± 0.15 mg/L of NaClO and 4.55 ± 0.11 mg/L of Mexel®432. *D. salina* showed values of 96-h EC_{50} of 1.73 ± 0.16 mg/L of NaClO and 7.21 ± 0.1 mg/L of Mexel®432. *Brachionus plicatilis* showed a 24-h LC_{50} of 1.23 ± 0.1 mg/L of NaClO and 3.62 ± 0.37 mg/L of Mexel®432. Acute toxicity was highly dependent on the chemical and species tested. NaClO presented more toxic effects than Mexel®432, also *B. plicatilis* was the most sensitive species in both cases. The lowest NOECs obtained, 0.25 mg/L for NaClO and 2.12 mg/L for Mexel®432, were similar to the theoretical residual concentrations of these biocides in cooling water discharges. Therefore, these discharges can cause undesirable negative effects upon the aquatic organisms present.

Contents

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1. Introduction

The formation of fouling in heat exchangers in coastal power stations using seawater for cooling purposes has special economic significance. In order to minimize this undesirable phenomenon, biocides are usually employed as antifouling agents for reducing deposit accumulation (Nebot et al., 2006). Sodium hypochlorite (NaClO) is one of the most widely used antifouling agents due to its low cost (often electrolytically generated from seawater) and high effectiveness (Characklis, 1990). NaClO solutions are unstable and strong oxidants. Heat, light, storage time, and impurities such as iron accelerate product degradation. NaClO reacts with water to form hypochlorous acid (HClO) which readily dissociates into hydrogen ions (H^+) and hypochlorite ions (ClO^-) (Grasso, 1996). Such chlorination by-products (CBPs) can be further subdivided into four categories: free halogens, haloamines, trihalomethanes (THMs) and organohalogenated compounds (OX). Free halogens are compounded with "free chlorine" (HClO and ClO^-) and "free bromine". In seawater, free chlorine reacts with bromide ion and releases "free bromine" composed of hypobromous acid (HBrO) and hypobromite (BrO^-). In the presence of ammonia or organic amines, free halogens give haloamines (chloramines and bromamines). THMs are the most volatile organic compounds generated by chlorination of natural waters, and in chlorinated seawater. These compounds are mainly composed of bromoform and bromochloromethanes. Free halogens react with organic matter present in water to form OX (halogenated phenols, haloacetonitriles and haloacetic acids) (Jenner et al., 1997).

On the other hand, the organic biocide Mexel®432 (EPA Registration No. 69100-1) is a mixture of aliphatic amine surfactants, in which the main active ingredient is (alkylamino)-3 aminopropane (1.7%). The alkylamine acts as a surfactants or "filming amine" and adheres to wetted metal, plastic, concrete, and glass surfaces to form a film thus, preventing biofouling organisms from forming an attachment (Sprecher and Getsinger, 2000).

The impact of pollutants on aquatic organisms is related to the time that these compounds take to degrade. The determination of the kinetic equations that describe the degradation process provides the necessary data to study the negative effects of a chemical product on an ecosystem. The kinetics of degradation and biodegradation has been described by a variety of mathematical expressions, increasing in complexity as they include more variables as temperature, concentration, microorganism, light, etc. Numerous researches have studied the kinetics of the degradative process of surfactants such as linear alkylbenzene sulphonate (LAS), sodium dodecyl sulfate (SDS) and alkyl ethoxysulphate (AES) (e.g. Quiroga et al., 1999; Perales et al., 2006; Sibila et al., 2008). On the other hand, although there is plenty of literature dealing with models employed to predict chlorine decay in municipal and grey waters, namely March et al. (2005) and Hua et al. (1999), little information is available for sea water (Wang et al., 2008).

Cooling water discharges from power plants can have negative effects on organisms at different levels of their biological organization: cell, tissue, organ system, organism, population and community. In the marine environment, phytoplankton and zooplankton are very important components of biological communities and the significance of their toxicity data has been internationally recognized. Standardized toxicity tests with microalgae are usually static tests, wherein the algae are cultivated and exposed to different toxic chemical concentrations under controlled conditions of light and temperature (Pereira et al., 2005; Garrido-Pérez et al., 2008; Sibila et al., 2008). At the same time, zooplankton is frequently used to detect anthropogenic contamination because of their sensitivity to various toxicants and their important role in the ecosystem. Rotifers are common members of zooplankton communities. The use of rotifers in ecotoxicological studies has been on the rise, and such an interest can be attributed especially to their commercial availability as well as their small size and fast reproduction rate (Preston and Snell, 2001; Marcial et al., 2005; Schamphelaere et al., 2006).

Although abundant toxicological information has been provided by related literature, no comprehensive literature on persistence and toxic properties of the two antifouling agents mentioned earlier has been made available.

Therefore, the aim of this study was twofold: a) to determine the degradation rate of the inorganic chemical sodium hypochlorite and the biodegradation rate of the anionic surfactant Mexel®432 and, b) to examine the acute toxicity of the aforementioned chemicals to marine organism, namely the microalgae *Isochrysis galbana* and *Dunaliella salina,* and the invertebrate *Brachionus plicatilis*. The results obtained in the present work will hopefully help to estimate the risk assessment of these antifouling biocides in the marine environment.

2. Materials and methods

2.1. Degradation tests

2.1.1. Decay of NaClO

Chlorine decay in seawater was evaluated using a modified version of the shake flask method described in the OPPTS (Office of Prevention, Pesticides and Toxic Substances) 835.3160 "Biodegradability in sea water" guidelines, proposed by the United States Environmental Protection Agency (1998). 1.5 L glass bottles were used for the degradation test. Prior to the experiment, the equipment was cleaned with hydrochloric acid (HCl 10%) and rinsed with deionised water in order to avoid contamination. Natural seawater collected from the south coast of Spain was filtered through a 0.45 µm glass microfibre filter (Whatman®) to eliminate the particulate matter and then introduced in the glass bottles. After that, the water was chlorinated using a NaClO 10% w/v solution from Panreac Química S.A. (Spain) at an initial concentration of 0.3 mg/L and tested in triplicate.

The experimental bottles were introduced in a climatic test chamber to reach the suitable temperature of 20 ± 1 °C. Control parameters as Eh, pH and conductivity were measured at the beginning of the experiment. Chlorine decay was followed for 28 h. Total residual chlorine (TRC) was measured every 30 min, duplicated, following the colorimetric DPD (*N, N*-diethyl-*p*-phenylenediamine) method suggested by APHA et al. (1995).

2.1.2. Biodegradation of Mexel®432

Primary degradation of the alkylamine surfactant Mexel®432 was tested following the shake flask method described in the OPPTS 835.3160 "Biodegradability in sea water" (USEPA, 1998) guidelines. For this experiment, 2.5 L glass bottles were used and cleaned following the same procedure as for the NaClO experiment. In this case, natural sea water was filtered through a 1.0 µm glass microfibre filter (Whatman®) to remove the high amount of particulate matter though retaining the microorganisms present. After this procedure, stock solutions of mineral nutrients were added. The following are the instruments used for the experiment: 1 control glass bottle filled with seawater only; 3 glass bottles which contained the test substance at an initial concentration of 12 mg/L of Mexel®432; and, 1 glass bottle containing a biodegradable reference substance; 20 mg/L of dissolved organic carbon (DOC) of sodium benzoate. A more detailed description of the protocols can be consulted in Sibila et al. (2008).

The experiment was carried out under the same conditions of light and temperature as for the NaClO decay experiment. Mexel®432 biodegradation was monitored for 40 d. DOC was periodically measured using samples filtered through 0.45 µm Whatman® GF/F glass microfiber filters, and employing a Shimadzu TOC-5050 TOC analyzer. Every day, Mexel®432 was analyzed by methyl orange measurement after extraction with dichloro-1,2-ethane according to Crompton (1985).

2.1.3. Kinetic models

The NaClO and Mexel®432 degradation courses were adjusted to the different kinetic models such as first, second and double first order