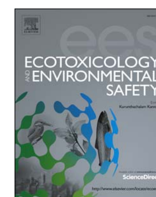
Ecotoxicology and Environmental Safety 140 (2017) 89–95

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Fe(III) and Fe(II) induced photodegradation of nonylphenol polyethoxylate (NPEO) oligomer in aqueous solution and toxicity evaluation of the irradiated solution

Lei Wang[a,*], Junjie Zhang[a], Zhenghua Duan[b], Hongwen Sun[a]

[a] *Ministry of Education Key Laboratory of Pollution Processes and Environmental Criteria/Tianjin Key Laboratory of Environmental Remediation and Pollution Control, Nankai University, Tianjin 300071, China*
[b] *School of Environmental Science and Safety Engineering, Tianjin University of Technology, Tianjin 300384, China*

ARTICLE INFO

Keywords:
Photodegradation
Nonylphenol polyethoxylate (NPEO) oligomer
Ferric/ferrous iron (Fe(III)/Fe(II))
Degradation pathways
Toxicity to luminescent bacteria

ABSTRACT

Photodegradation of nonylphenol tri-ethoxylate ($NPEO_3$) in aqueous solution, and the effects of Fe(III) or Fe(II) were studied. The increasing degradation kinetics of $NPEO_3$ were observed when 500 μM Fe(III) or Fe(II) was present in the solutions. Altered formation of NPEO oligomers with shorter EO chains, including nonyphenol (NP), $NPEO_1$ and $NPEO_2$, was observed in water and in solutions containing Fe(III) or Fe(II). The molar percentage yields of NP and $NPEO_{1,2}$ production from $NPEO_3$ photodegradation were approximately 20% in $NPEO_3$ solution, while $NPEO_3$ solution with Fe(III), this percentage increased to approximately 50%. In solution with Fe(II), the molar balance between the photodegradation of $NPEO_3$ and the production of NP and $NPEO_{1,2}$ was observed. A luminescent bacterium, *Vibrio fischeri*, was used to identify changes in the toxicity of $NPEO_3$ solutions during the photodegradation process under different conditions, while dose addition (DA) model was used to estimate the toxicity of products. Toxicity of $NPEO_3$/water solution increased significantly following the irradiation of UVA/UVB mixture. In contrast, obviously decreasing toxicity was observed when $NPEO_3$ underwent photodegradation in the presence of Fe(III).

1. Introduction

Nonylphenol polyethoxylates (NPEOs) used to be the most commonly used non-ionic surfactants for industrial, agricultural and domestic applications. The annual world-wide production of NPEOs was estimated to be hundreds of thousands of tonnes to several million tonnes (Ohlson, 1998). Approximately 60% of the NPEOs produced were estimated to enter the aquatic environment finally, via various pathways such as municipal and industrial wastewater discharges and sewage treatment plant (STP) effluents (Ying et al., 2002). Even if they have been prohibited in the European Union due to their adverse effects on human health and the environments, NPEOs are still important pollutants in many water environments. In STPs or natural aqueous environments, NPEOs can be biodegraded to their shorter chain homologues, e.g. NP and mono-, di-, and tri-ethoxylates ($NPEO_{1,\ 2,\ and\ 3}$), as well as to nonylphenoxy ethoxy acetic acids (e.g. $NPEC_{1,2}$) (Field and Reed, 1996; Potter et al., 1999; Staples et al., 1999; Jonkers et al., 2003; Samaras et al., 2013; Liu et al., 2017). As important pathways for the abiotic degradation of many organic contaminants, photodegradation and photocatalytical degradation of NPEOs in different aquatic solutions have been studied (Brand et al., 1998; Castillo et al., 2001; Chen et al., 2007; Goto et al., 2004; Karci et al., 2013, 2014; Wang et al., 2009). In these studies, NPEOs were shown to be degradable under UV irradiation, while TiO_2 and ferric iron (Fe(III)) were identified to be effective catalysts for the photo-induced degradation of NPEOs.

Multiple studies have reported bio- and abio- degradation of NPEOs (Castillo et al., 2001; Chen et al., 2007; da Silva et al., 2015; Gori et al., 2010; Karci et al., 2013, 2014; Lu et al., 2007; McAdam et al., 2011; Ömeroglu and Sanin, 2014; Ying et al., 2002; Zhang et al., 2008). However, knowledge of the degradation pathways and the ecological risk of the intermediates and products formed during the NPEOs photodegradation is still insufficient. Moreover, a mixture of NPEO polymers was used in the majority of the previous studies, which resulted in difficulty in most cases to distinguish the parent NPEO from an intermediate. Although many different intermediates and products have been proposed (Brand et al., 1998; Castillo et al., 2001; Chen et al., 2007; Wang et al., 2009), the proportion of NPEO photodegradation following different pathways under various conditions have not been qualified. Besides, all available results on NPEO degradation

* Correspondence to: Nankai University, 38 Tongyan Road, Tianjin, China 300071.
E-mail address: wang2007@nankai.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.ecoenv.2017.02.021
Received 29 October 2016; Received in revised form 11 February 2017; Accepted 14 February 2017
Available online 27 February 2017
0147-6513/ © 2017 Elsevier Inc. All rights reserved.

focused on NPEOs with relatively high degrees of polymerization (i.e. with long EO chain). In contrast, little is known on the photochemical degradation of NPEO oligomers with low polymerization degrees, even if it has been well documented that the ecological risk of NPEO homologues increases with a decreasing degree of polymerization (Goto et al., 2004; Lu et al., 2007; Ying et al., 2002). Different degradation pathways, such as EO shortening and cleavage of the aromatic ring (Chen et al., 2007; Różalska et al., 2010; Zhang et al., 2008), will lead to different toxic changes compared with the parent compounds. Fe species are natural water substances with photochemical activity (Wu and Deng, 2000). The degradation of NPEOs photoinduced by Fe(III) aquacomplexes has been identified (Brand et al., 1998). In the photoinduced reaction of Fe(III), formation of Fe(II) was documented (Bajt et al., 2001; Faust and Hoigné, 1990). It also involved in degradation process of NPEOs, as a reducing agent (Brand et al., 1998). However, studies on the direct effect of Fe(II) presence on NPEOs degradation are still scarce. In addition, quality balance between NPEO degradation and the formation of products through different pathways is far from being established. Therefore, it is necessary to assess the ecological risk resulting from different degradation processes.

In the present study, effects of Fe(III) or Fe(II) presence in aqueous solutions on the degradation of $NPEO_3$ and the formation of $NPEO_{0-2}$ under two types of UV irradiations were determined. In addition, the toxicity of $NPEO_3$ solutions during photoinduced degradation was tested using a luminescent bacterium. The aim of the study is to evaluate the contribution of an EO shortening pathway to the photodegradation of short chain NPEO oligomers and the effects of iron species on photoinduced degradation, and to assess the toxicity of the intermediates and products formed during $NPEO_3$ photodegradation under different conditions.

2. Experimental methods

2.1. Chemicals

Nonylphenol (NP, technical grade) standard was purchased from Tokyo Chemical Synthesis Ind. Company, Japan. The individual standards of $NPEO_{1,\ 2,\ \text{and}\ 3}$ were purchased from Hayashi Pure Chemical Ind. Company, Japan. Stock solutions of Fe(III) and Fe(II) were made by dissolving $FeCl_3{\cdot}6H_2O$ (A.R.) and $FeCl_2$ (A.R.) in water. Water used in this study was prepared using a Milli-Q system (Millipore, Bedford, MA).

2.2. Photodegradation experiments

Experiments were carried out in 150 mL open pyrex glass vessels, containing 100 mL of 2.0 μmol L^{-1} $NPEO_3$. To study the effects of Fe (III) and Fe(II), 500 μmol L^{-1} of Fe(III) or Fe(II) was added originally in some cases. The initial pH was adjusted to 3.1 ± 0.1 with 0.1 M HCl before the experiments. Experiments were conducted in water bath shakers equipped with a UV lamp. Vessels were placed symmetrically under the lamp to receive direct irradiation, and shaken at 150 rpm. The vertical distance from the lamp to the liquid surface was approximately 7.0 cm, and the light intensities on the solution surface of each beaker were tested with a radiometer (UV-A/UV-B types, Photoelectric Instrument Factory of Beijing Normal University, China) to ensure the consistency and stability of irradiation throughout the experiment. Two types of UV irradiation, namely UV-1 and UV-2, were used in this study. A 30-W UVA lamp (Nanjing Electronic Vacuum Devices Company, China) was used as UV-1 for 48 h irradiation. The light intensity of the main wavelength of UVA irradiation on the solution surface was measured to be approximately 0.67 mW cm^{-2} (365 nm). Milli-Q water was added at interval of 12 h to maintain a volume of 100 mL. A 400-W medium pressure mercury lamp (Tianjin Yingze Technology Company, China) was used as UV-2 in the 60 min irradiation experiment, with light intensities of 3.97 (at 302 nm), 4.20 (at 313 nm) and 9.82 mW cm^{-2} (at 365 nm).

The solution temperature under UV-1 irradiation was 20 °C controlled by the water bath. In UV-2 irradiation experiment, the samples were placed in an ice-water bath due to the higher power of the medium pressure mercury lamp used. The solution temperature was determined to be 7.5 ± 2.5 °C during the 60 min experiment. Vessels covered by aluminum foil were used as a dark control, while the loss of $NPEO_3$ after 48 h was less than 2% in water solutions as well as in solutions containing Fe(III) or Fe(II).

At the desired time, i.e. 0 h, 4 h, 12 h, 24 h, 48 h for UV-1 irradiation and 0 min, 10 min, 20 min, 30 min, 60 min for UV-2 irradiation, ten milliliters of the solution in each vessel was taken out to test the toxicity to luminescent bacteria, according to the process described below. The residual 90 mL of solution were concentrated by solid phase extraction (SPE) using a Waters Oasis™ HLB cartridge (3cc) and then analyzed by high-performance liquid chromatography coupled with a fluorescence detector (HPLC-FL). The detailed procedure for SPE as well as the extraction recoveries is described in Text S1 in the Supplementary material. Experiments were carried out in triplicate to determine the experimental variability (RSD < 15% in each triplicates). Average values of the triplicates were applied in the statistical analysis.

2.3. Chemical analysis and quality assurance/quality control

$NPEO_n$ (n = 0–3) was separated by a Waters 1525 HPLC system using a Waters W2108N007 NH_2 normal phase column (μBondapak™ 3.9 mm i.d. × 300 mm × 5 μm, Waters Corp., Ireland), and detected with a Waters 2475 fluorescence detector (Waters Company, USA). *n*-hexane/isopropanol (98/2, v/v) and isopropanol/water (98/2, v/v), named as solvent A and B, respectively, were used as the mobile phase. The mobile phase was ramped linearly from 95% A to 80% A in 10 min, and the flow rate was 1.0 mL min^{-1}, with detailed chromatogram shown in our previous work (Wang et al., 2009). Excitation and emission wavelengths of the fluorescence detector were 233 and 302 nm, respectively. The method detection limits for $NPEO_{0-3}$ were 0.48 (for NP), 0.80 (for $NPEO_1$), 0.68 (for $NPEO_2$), and 0.60 nmol L^{-1} (for $NPEO_3$), which were calculated based on 3 times the valid lowest acceptable calibration standard and a water sample volume of 90 mL. Duplicate analyses were conducted for each sample and the average response was calculated. Instrumental calibration was verified by injection of 10 calibration standards with regression coefficients (R) higher than 0.99 for all calibration curves.

Potential sample contamination by $NPEO_n$ during experiments and extraction was evaluated by running solvent blanks and procedure blanks. No NPEO analytes were detected in these blank samples.

2.4. Toxicity test with Vibrio fischeri

Different biomarkers have been used in assessing eco-toxicity, i.e., *Allium cepa* (Iqbal et al., 2015a, 2015b, 2017; Iqbal and Nisar, 2015), Vicia faba (Iqbal, 2016), and luminescent bacterium (Lechuga et al., 2016). Luminescent bacterium test has been applied for a long time to evaluate the toxicity of aquatic environments (Bulich et al., 1981; Lechuga et al., 2016; Parvez et al., 2006; Zhang et al., 2015). According to a standard method recommended by the Chinese EPA (Water quality-determination of the acute toxicity-luminescent bacteria test. GB/T 15441-1995), *Vibrio fischeri* freeze-dried powder (the Institute of Soil Science, Chinese Academy Sciences (ISSCAS), Nanjing, China) was selected as the test luminescent bacteria. Before the test, 0.5 g of the bacteria were reactivated in 1 mL 3% NaCl solution for 30 min and stored in an ice water bath. Fixed amounts of $NaH_2PO_4{\blacksquare}H_2O$ (1.21 g) and Na_2HPO_4 (1.75×10^{-1} g) were added into 10 mL of a standard solution or samples from the photodegradation experiments, to adjust pH to 6.0. Two milliliters of the water solution were transferred into a

Download English Version:

https://daneshyari.com/en/article/5747691

Download Persian Version:

https://daneshyari.com/article/5747691

Daneshyari.com