



## H<sub>2</sub>O<sub>2</sub>/UV-C and Photo-Fenton treatment of a nonylphenol polyethoxylate in synthetic freshwater: Follow-up of degradation products, acute toxicity and genotoxicity

Akin Karci<sup>a</sup>, Idil Arslan-Alaton<sup>b,\*</sup>, Miray Bekbolet<sup>a</sup>, Gul Ozhan<sup>c</sup>, Buket Alpertunga<sup>c</sup>

<sup>a</sup> Bogazici University, Institute of Environmental Sciences, 34342 Bebek, Istanbul, Turkey

<sup>b</sup> Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34469 Maslak, Istanbul, Turkey

<sup>c</sup> Istanbul University, Faculty of Pharmacy, Department of Pharmaceutical Toxicology, 34116 Beyazit, Istanbul, Turkey

### HIGHLIGHTS

- H<sub>2</sub>O<sub>2</sub>/UV-C and Photo-Fenton treatment of a nonylphenol polyethoxylate was studied.
- Rapid, complete surfactant and high TOC removals were obtained in synthetic freshwater.
- Serial polyethoxy chain shortening, carboxylic acid and formaldehyde formation occurred.
- Degradation intermediates were more genotoxic than the original nonionic surfactant.
- A positive correlation existed between nonylphenol monoethoxylate and genotoxicity.

### ARTICLE INFO

#### Article history:

Received 27 September 2013

Received in revised form 3 December 2013

Accepted 6 December 2013

Available online 12 December 2013

#### Keywords:

Acute toxicity

Degradation products

Genotoxicity

H<sub>2</sub>O<sub>2</sub>/UV-C treatment

Nonylphenol polyethoxylates

Photo-Fenton treatment

### ABSTRACT

H<sub>2</sub>O<sub>2</sub>/UV-C and Photo-Fenton treatment of a nonylphenol polyethoxylate surfactant was investigated in synthetic freshwater. H<sub>2</sub>O<sub>2</sub>/UV-C treatment outperformed Photo-Fenton treatment in terms of mother pollutant abatement kinetics as well as overall organic carbon removal efficiencies. Short polyethoxy-chain nonylphenol polyethoxylates, polyethylene glycols, formic acid, acetic acid and formaldehyde were identified as the common degradation products of the nonionic surfactant. Monocarboxylated polyethylene glycols and oxalic acid were detected during H<sub>2</sub>O<sub>2</sub>/UV-C oxidation, whereas a degradation product resulting from the hydroxyl radical attack of the tertiary alkyl chain and the aromatic ring was detected during Photo-Fenton treatment. Based on the liquid chromatography–mass spectrometry results, it was suggested that the polyethoxy chain of the surfactant was more susceptible to degradation with the H<sub>2</sub>O<sub>2</sub>/UV-C treatment process, while the alkyl chain and aromatic ring were more prone to Photo-Fenton oxidation. Acute toxicity analysis employing the photobacteria *Vibrio fischeri* indicated that the inhibitory effect of the surfactant increased from 10% to 30% and 19% during the early stages of H<sub>2</sub>O<sub>2</sub>/UV-C and Photo-Fenton treatment, respectively. At the end of the treatment period, the inhibitory effect of the surfactant dropped back to less than 10%. According to the umu-genotoxicity test conducted with *Salmonella typhimurium* TA1535/pSK1002 strain, the genotoxic effect followed an increasing trend during the course of H<sub>2</sub>O<sub>2</sub>/UV-C treatment. A positive correlation was evident between the intensity of the nonylphenol monoethoxylate product ion and the genotoxic effect observed during H<sub>2</sub>O<sub>2</sub>/UV-C treatment. The genotoxic effect of Photo-Fenton-treated degradation products appeared to be relatively low as compared with those of H<sub>2</sub>O<sub>2</sub>/UV-C treatment.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Among the phenol derivatives of commercial importance, nonylphenol polyethoxylates (NPEO) are among those most ubiquitous in the water environment as a result of anthropogenic input.

NPEO are synthetic compounds belonging to the class of nonionic surfactants and have been designed to have both hydrophilic and hydrophobic properties [1]. NPEO have been used in cleaning products, paints, ink dispersants, textile and leather processing, manufacture of pulp and paper, metalworking, cosmetics and personal care products. However, many of these applications are now restricted by the European Commission [2] due to the raising concerns regarding the environmental safety of NPEO and its metabolites. It has been reported that the aerobic/anaerobic

\* Corresponding author. Tel.: +90 212 285 37 86; fax: +90 212 285 65 45.

E-mail addresses: [arslanid@itu.edu.tr](mailto:arslanid@itu.edu.tr) (I. Arslan-Alaton), [bekbolet@boun.edu.tr](mailto:bekbolet@boun.edu.tr) (M. Bekbolet), [gulozhan@istanbul.edu.tr](mailto:gulozhan@istanbul.edu.tr) (G. Ozhan).

biotransformation products of NPEO are more inhibitory and estrogenic than the original surfactant [3–5]. Despite the above-mentioned restrictions regarding the use of NPEO, these products still appear in several industrial applications where they cannot be replaced by alternative chemicals due to technical and economic reasons. Consequently, NPEO and its degradation products have been reported in water bodies associated with continuing discharges from industrial and municipal treatment plants [6,7].

The scientific literature on the fate of NPEO in water resources reinforces the idea that more efficient, alternative treatment processes are needed for its elimination from natural waters. Ozonation has been most extensively studied as an alternative for the treatment of NPEO-bearing waters as evidenced from the review articles on this issue [8–10]. So-called advanced oxidation processes (AOP) on the other hand take advantage of using hydroxyl radicals ( $\text{HO}^\bullet$ ) which react with most environmental pollutants at diffusion-limited reaction rates [11]. Among the currently existing AOP,  $\text{H}_2\text{O}_2/\text{UV}$  and Photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ ) processes have attracted considerable interest since these exhibit relatively high treatment performances for surfactants removal [12,13]. Furthermore, although a reasonable body of information about the metabolites of NPEO exists in the scientific literature [7,14,15], degradation products arising from advanced oxidation of NPEO have been rarely published so far [14].

The extensive follow-up of degradation products and toxicity is important to ensure economically and ecologically safe applications of AOP. The ecotoxicological characterization of AOP during their application to treat industrial pollutants has attracted significant interest recently. The marine photobacterium *Vibrio fischeri* remains the most popular organism for the easy and rapid measurement of cytotoxicity in water and wastewater samples being subjected to AOP [16]. Although *V. fischeri* is very sensitive and hence useful for obtaining a preliminary idea about the inhibitory effect of pollutants and their degradation products, it does not give information about the specific mode of action [17,18]. Therefore, it should always be complemented by another bioassay targeting specific toxicological features to capture cases where degradation products have lost their nonspecific mode of inhibitory effect. Among the specific adverse effects developed by degradation products, genotoxicity is of special concern because it may cause reproductive damage to organisms or even lead to their extinction [19]. Aquatic genotoxicity studies are also of interest since epidemiological investigations have shown a link between genotoxic drinking water intake and a rise in cancer cases [20]. Being a simple, sensitive and fast bacterial colorimetric assay to determine genotoxic potential of environmental waters influenced by anthropogenic input, the umu-test has the theoretical advantages that it is based on one of the standard Ames strains and uses the same S9 mix and the practical advantages of high throughput capacity [21]. The umu-test has been previously applied for several research groups to evaluate various water treatment options [22–24]. Considering these facts, evaluating the umu-test as a potential tool to assess the genotoxic effect of NPEO and its degradation products during  $\text{H}_2\text{O}_2/\text{UV-C}$  and Photo-Fenton treatments deserves particular attention.

The motivation of the present work was to comparatively evaluate  $\text{H}_2\text{O}_2/\text{UV-C}$  and Photo-Fenton treatment of NPEO in synthetic freshwater (SFW) with special emphasis placed on the identification of degradation products as well as changes in genotoxicity patterns during the application of AOP. The commercially important nonionic surfactant NP-10 was selected as a model pollutant and typical member of the NPEO family. In order to elucidate degradation products of NP-10 in SFW and to propose a reaction pathway for its treatment with  $\text{H}_2\text{O}_2/\text{UV-C}$  and Photo-Fenton processes, high performance liquid chromatography (HPLC) and liquid chromatography-electrospray ionization-mass spectrometry

(LC–ESI–MS) techniques were employed. Besides acute toxicity assessment of NP-10 and its degradation products employing the *V. fischeri* bioassay, temporal evolution of genotoxic effects during  $\text{H}_2\text{O}_2/\text{UV-C}$  and Photo-Fenton treatment of NP-10 was examined with the umu-test protocol using a *Salmonella typhimurium* TA 1535/pSK 1002 strain. To the best of our knowledge, this is the first study investigating the genotoxicity pattern of freshwaters contaminated with alkylphenol polythoxylates being subjected to advanced oxidation.

## 2. Materials and methods

### 2.1. Materials

NP-10 was obtained from a local chemical company and used as received.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Merck) and  $\text{H}_2\text{O}_2$  (35% w/w; Merck) were used in the photochemical experiments. Methanol ( $\text{CH}_3\text{OH}$ , Merck), anhydrous  $\text{Na}_2\text{SO}_4$  (Merck) and methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ , Sigma–Aldrich) were used to prepare HPLC mobile phases. HPLC-gradient grade acetonitrile ( $\text{CH}_3\text{CN}$ , Sigma–Aldrich), LC–MS grade formic acid ( $\text{HCO}_2\text{H}$ , Sigma–Aldrich) and  $\text{NH}_4\text{OH}$  (25%; Merck) were used to prepare LC–ESI–MS mobile phases. Distilled water was used throughout the experiments, except high purity water having a conductivity of less than  $0.056 \mu\text{S cm}^{-1}$  (Arium 611UV, Sartorius AG) that was employed for HPLC and LC–ESI–MS analyses.

### 2.2. Photoreactor and UV light source

All experiments have been conducted at room temperature in a 3250 mL capacity, cylindrical quartz batch photoreactor covered with stainless steel (length: 84.5 cm; diameter: 8.0 cm). The UV-C light source was a 40 W, low pressure mercury vapour lamp located in the center of the photoreactor. Due to the fact that the UV-C light source was a low pressure lamp, it did not warm up during the experiments and hence no cooling device was required through the photochemical runs. During photochemical treatment, the photoreactor was mixed with a peristaltic pump at a flow rate of  $170 \text{ mL min}^{-1}$ . The incident photon flux at 253.7 nm was determined by means of  $\text{H}_2\text{O}_2$  actinometry as  $7.9 (\pm 1.8) \times 10^{-2} \mu\text{E cm}^{-2} \text{ s}^{-1}$  [25]. Samples were regularly withdrawn from the photoreactor by means of a three-neck valve and prepared for the analytical procedures as described below.

### 2.3. Experimental procedures

All experiments were performed in SFW that was prepared in accordance with Standard Methods [26] and composed of a mixture of inorganic salts at typical concentrations encountered in moderately hard freshwaters. SFW with the same composition has been used in related work [27,28] and simulates the potential effects that are expected from ubiquitous inorganic constituents (such as carbonate, sulfate and chloride) in natural freshwater [29,30]. SFW was spiked with NP-10 prepared from a stock solution of  $4 \text{ g L}^{-1}$  (6 mM) under constant agitation. At the beginning of all experiments, the initial pH value of SFW spiked with NP-10 was adjusted to 7.0 for  $\text{H}_2\text{O}_2/\text{UV-C}$  and to 3.0 for Photo-Fenton treatment by using  $\text{H}_2\text{SO}_4$  solution at varying concentrations. Before adding  $\text{H}_2\text{O}_2$  to the reaction solution, an original sample was taken to confirm the prepared initial NP-10 concentration by HPLC and total organic carbon (TOC) analyses. Following the addition of 10 mM  $\text{H}_2\text{O}_2$ , the photoreactor was filled with the sample by means of a peristaltic pump. Before turning on the UV-C lamp in the  $\text{H}_2\text{O}_2/\text{UV-C}$  process a  $t = 0$  sample was taken. In the case of Photo-Fenton treatment, the addition of 0.2 mM  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  from

Download English Version:

<https://daneshyari.com/en/article/147566>

Download Persian Version:

<https://daneshyari.com/article/147566>

[Daneshyari.com](https://daneshyari.com)