Journal of Hazardous Materials 282 (2015) 241–248

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

# Degradation of the commercial surfactant nonylphenol ethoxylate by advanced oxidation processes

Salatiel Wohlmuth da Silva[a], Cláudia Regina Klauck[b], Marco Antônio Siqueira[b], Andréa Moura Bernardes[a,*]

[a] *Universidade Federal do Rio Grande do Sul (UFRGS) – Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGEM), Av. Bento Gonçalves, 9500, Porto Alegre, RS, Brazil*
[b] *Universidade Feevale, Campus II ERS-239, 2755, Novo Hamburgo, RS, Brazil*

## HIGHLIGHTS

- $NP_4EO$ in industrial effluents can be treated before reaching water reservoirs.
- Advanced oxidation processes are proposed for the degradation of $NP_4EO$.
- The degradation rate depends mainly on the light intensity.
- The mineralization rate depends mainly on the current density.
- Photo-assisted electrochemical oxidation showed the best degradation results.

## ARTICLE INFO

*Article history:*
Received 10 June 2014
Received in revised form 4 August 2014
Accepted 11 August 2014
Available online 19 August 2014

*Keywords:*
Nonylphenol ethoxylate
Emerging organic pollutants
Advanced oxidation process

## ABSTRACT

Four different oxidation process, namely direct photolysis (DP) and three advanced oxidation processes (heterogeneous photocatalysis – HP, eletrochemical oxidation – EO and photo-assisted electrochemical oxidation – PEO) were applied in the treatment of wastewater containing nonylphenol ethoxylate ($NP_nEO$). The objective of this work was to determine which treatment would be the best option in terms of degradation of $NP_nEO$ without the subsequent generation of toxic compounds. In order to investigate the degradation of the surfactant, the processes were compared in terms of UV/Vis spectrum, mineralization (total organic carbon), reaction kinetics, energy efficiency and phytotoxicity. A solution containing $NP_nEO$ was prepared as a surrogate of the degreasing wastewater, was used in the processes. The results showed that the photo-assisted processes degrade the surfactant, producing biodegradable intermediates in the reaction. On the other hand, the electrochemical process influences the mineralization of the surfactant. The process of PEO carried out with a 250 W lamp and a current density of 10 $mA/cm^2$ showed the best results in terms of degradation, mineralization, reaction kinetics and energy consumption, in addition to not presenting phytotoxicity. Based on this information, this process can be a viable alternative for treating wastewater containing $NP_nEO$, avoiding the contamination of water resources.

## 1. Introduction

The alkaline degreasing step of the electroplating process uses nonylphenol ethoxylate ($NP_nEO$), a non-ionic surfactant that is part of the alkylphenol polyethoxylates ($APEO_S$) group. $NP_nEO$ in the environment or in biological treatment plants is biodegraded into its more toxic metabolites, $NP_{4\text{-}1}EO$ and NP (nonylphenol) [1], persisting in aquatic environments and entering the water cycle [2]. NP is considered an emerging organic pollutant (EOP) that mimics the natural hormone 17 β-estradiol, competing for the receptor binding site of natural estrogen due to their structural similarity and disrupting the hormonal system of animals [3–6]. Conventional treatments, such as physical-chemical followed by biological processes, are not efficient in the complete degradation of these emerging organic pollutants. As such, the use of more efficient processes for removing or improving the biodegradability of these compounds has become necessary.

In this context, direct photolysis (DP) [7] may be used for the dissociation of complex organic pollutants through a radiation source.

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* Corresponding author at: Av. Bento Gonçalves, 9500 – Setor 4 – Prédio 74 – Sala 109, Porto Alegre, Rio Grande do Sul, Brazil. Tel.: +55 51 3308 9428; fax: +55 51 3308 9475.
*E-mail addresses:* salatielws@gmail.com (S.W. da Silva), claudiark@feevale.br (C.R. Klauck), marcor@feevale.br (M.A. Siqueira), amb@ufrgs.br (A.M. Bernardes).

http://dx.doi.org/10.1016/j.jhazmat.2014.08.014
0304-3894/

Ultraviolet radiation (UV) is an important parameter for the photo-mediated processes. This radiation belongs to the electromagnetic spectrum, situated in the wavelength ($\lambda$) range of 40–400 nm. In fact it can be divided into: vacuum UV – 40 to 200 nm, UV C – 200 to 280 nm, UV B – 280 to 315 nm and UV A – 315 to 400 nm. Among the different sources of radiation, mercury vapor lamps are widely used because of their low cost, ease of operation, good energy efficiency (proportion of electrical power converted into radiation) and good spectral efficiency (proportion of radiation emitted as UV). In the same line follow the advanced oxidation processes (AOPs), that are characterized by the degradation of organic contaminants in $CO_2$, $H_2O$ and inorganic anions through reactions involving transient oxidant species, especially the hydroxyl radical (HO•)[8], which has a high oxidation potential (2.8 V).

Heterogeneous photocatalysis (HP) can be highlighted among the AOPs. This consists in the catalysis of photochemical reactions on the surface of a catalyst, usually a semiconductor, and involves two simultaneous reactions: the oxidation by gaps in the valence band (VB) and the reduction by photogenerated electrons in the conduction band (CB) of the semiconductor. These reactions develop oxidation–reduction processes, generating the HO• radical by water dissociation.

Electrochemical oxidation (EO) consists in the application of a potential or current density to an electrochemical cell composed of one or more pairs of electrodes (cathodes and anodes). The pairs of polarized electrodes act in the reduction occurring at the cathode and the oxidation reactions that occur at the anode. This, by itself, is not characterized as an AOP. However, with the use of special materials, such as metal electrodes coated with metal oxide semiconductors, known as dimensionally stable anodes (DSA®), the generation of HO• can occur during the electrolysis of water. The anodic oxidation of organic contaminants in an aqueous medium may occur in two ways: electrochemical conversion, where the non-biodegradable compounds are transformed into biodegradable compounds, and electrochemical combustion, where all organic contaminants are mineralized.

Recent research has pointed to the use of combined processes that take advantage of different methods and their synergistic effects. Electrochemical oxidation (EO) can be assisted by heterogeneous photocatalysis (HP) when the electrode surface presents photo-activity, i.e., provided that the cell has a type DSA®. One such method has been extensively studied, the photo-assisted electrochemical oxidation (PEO) [9–11].

In PEO, the semiconductor can be used as a photoanode and, in the presence of a counter electrode, it can be polarized, minimizing recombination of the pair $e^-/h^+$ and increasing photocatalytic efficiency for the oxidation of organic pollutants [12]. The polarization of the electrode favors the oxidation reactions on the surface, resulting in a concentration gradient that promotes the diffusion of the species in solution to the surface of the photocatalyst, increasing the efficiency of the oxidation reaction [13–16]. Such processes are an alternative in the degradation of EOP [17] and have been studied in the degradation of 1-amino-8-hydroxynaphthalene-3,6-disulfonic acid [18] and 4-chlorophenol [19], among others [11].

The objective of this paper was to investigate the degradation of the emerging organic pollutant $NP_4EO$ by the above-mentioned processes, comparing them in terms of degradation efficiency, mineralization, reaction kinetics, energy efficiency and phytotoxicity.

## 2. Experimental

### 2.1. Solution

A solution was prepared as a surrogate of the wastewater of the alkali degrease step in the electroplating industry by diluting the commercial product ULTRANEX NP40® in distilled water to a final concentration of 51 mg/L. It was assumed that if the wastewater is treated in order to degrade $NP_4EO$ before discharge into the environment, then the risks associated to this pollutant should be smaller.

The solution obtained does not have enough conductivity for the proposed electrochemical treatments. It was therefore necessary to add 0.25 mg/L of supporting electrolyte sodium sulfate ($Na_2SO_4$).

### 2.2. Direct photolysis (DP)

The reactor used in the DP trials was a jacket borosilicate glass reactor with a capacity of 3 L, operated in batch mode with recirculation and connected to an ultra-thermostatic bath to control the temperature. 125 W and 250 W high-pressure commercial mercury vapor lamps, without the glass bulb and inside a quartz tube, were used as source of UV radiation, with a negative irradiation geometry. The experimental system of the HP process is shown in Fig. 1A.

### 2.3. Heterogeneous photocatalysis (HP)

The process used the same reactor with the addition of two catalysts: one composed of $Ti/Ru_{30\%}Ti_{70\%}O_2$ and another composed of $Ti/TiO_2$. The catalysts were placed concentrically around the lamp, remaining under UV radiation, with a negative irradiation geometry. The experimental system of the HP process is shown in Fig. 1B.

### 2.4. Electrochemical oxidation (EO)

The experimental system of the EO process is shown in Fig. 1C and in this case the radiation source has been removed and a current (*CEL P-6000*) was applied between the electrodes (One DSA® composed of $Ti/Ru_{30\%}Ti_{70\%}O_2$ and one cathode composed of $Ti/TiO_2$).

### 2.5. Photo-assisted electrochemical oxidation (PEO)

The experimental system of PEO is shown in Fig. 1D and consists of the combination of the earlier processes.

### 2.6. Oxidation experiments

For all experiments, 5 L of the working solution was placed in the reservoir that feeds the reactor with an average flow rate of 1 L/min with the aid of a peristaltic pump. The configurations of the processes are shown in Table 1.

All assays were replicated five times, and samples were collected every 60 min until a final time of 240 min.

**Table 1**
Configuration of DP, HP, EO and PEO process.

| Configuration | Lamp power (W) | Current density (mA/cm$^2$) | Anode | Cathode | Catalyst |
|---|---|---|---|---|---|
| DP1 | 250 | – | – | – | – |
| DP2 | 125 | – | – | – | – |
| HP1 | 250 | – | – | – | DSA® and $Ti/TiO_2$ |
| HP2 | 125 | – | – | – | DSA® and $Ti/TiO_2$ |
| EO1 | – | 5 | DSA® | $Ti/TiO_2$ | – |
| EO2 | – | 10 | DSA® | $Ti/TiO_2$ | – |
| PEO1 | 250 | 5 | DSA® | $Ti/TiO_2$ | – |
| PEO2 | 125 | 5 | DSA® | $Ti/TiO_2$ | – |
| PEO3 | 250 | 10 | DSA® | $Ti/TiO_2$ | – |
| PEO4 | 125 | 10 | DSA® | $Ti/TiO_2$ | – |