



Treatment of solutions containing nonylphenol ethoxylate by photoelectrooxidation



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ABSTRACT

In this work the photoelectrooxidation (PEO) was applied in the treatment of a solution containing nonylphenol ethoxylate surfactant (NP_nEO). The use of different lamps (125 and 250 W), current density (5 and 10 mA cm⁻²) and treatment time (0, 60, 120, 180 and 240 min) were investigated. The samples were characterized by UV/Vis, total organic carbon (TOC), gas chromatography associated to mass spectroscopy (GC/MS) and ecotoxicity. The reaction kinetics were calculated and the light flux and pH were measured. The results of analysis by UV/Vis show that there is degradation of nonylphenol ethoxylated in the treatment time of 240 min for all configurations, and the configurations that used a 250 W lamp and a current density of 10 mA cm⁻² obtained better results, with a reduction of 83% in TOC, indicating a high mineralization of the surfactant. It was further found in the GC/MS that the configurations that used the 125 W lamp promoted a smaller incident light flux on the solution, and, regardless of the applied current density, it was generated the reaction intermediate nonylphenol, more toxic than the parent compound. The opposite can be observed when a 250 W lamp was used, which produced a higher incident light flux. Based on the degradation products detected, a simplified mechanism for degradation of nonylphenol ethoxylate was proposed. Although a treatment time of 240 min with photoelectrooxidation with different configurations was not effective in the complete mineralization of the compound, a promising process was developed with the treatment using a lamp of 250 W and a current density of 10 mA cm⁻², which generated a solution with less toxicity than the original one.

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1. Introduction

Nonylphenol ethoxylate (NP_nEO, where n is the degree of ethoxylation) is a nonionic surfactant that is obtained by reacting nonylphenol (NP) with ethylene oxide (EO). Depending on the degree of ethoxylation, products are obtained that exhibit different hydrophile–lipophile balance values, which enables a wide range of applications at relatively low costs (Mcleese et al., 1981; Ciabatti et al., 2009). This surfactant has a chain that follows the Poisson distribution, and a recalcitrance that increases with the decrease in the number of ethoxylate groups (Kim et al., 2005).

Because of the extensive use of NP_nEO it reaches effluents and water treatment plants in substantial quantities. Here it can be biodegraded to more recalcitrant compounds than the precursor. Different authors have studied the biodegradation mechanism for the alkylphenols ethoxylates (APEOs). NP and short-chain NP_nEOs, as well as octilphenol and *p*-nonylphenol, were identified as biodegradation intermediates (Jobling and Sumpter, 1993; Jonkers et al., 2001; Chang et al., 2004; Lu et al., 2008). Besides these compounds, alkylphenol ethoxycarboxylates, organic acids, benzoquinone, ethylene glycol and alcohols can be generated (Ahel et al., 1994; Kim et al., 1996; Brown and Reinhard, 2003). The impact of NP on different environmental niches is mainly controlled by the physicochemical properties of the compounds, the vapor pressure and Henry's law constant for NP are 2.07 × 10⁻² Pa and 8.39 × 10⁻¹ Pa m³ mol⁻¹, suggesting that this is a semi-volatile

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organic compound that is capable of performing a water/air exchange. Once NP reaches the atmosphere, it can be transported to aquatic and terrestrial means by wet deposition (Azevedo et al., 2001; Rudel et al., 2003; Fries and Püttmann, 2004).

NP is an endocrine disruptor that mimics the natural 17β -estradiol hormone and that can compete for the binding site of the receptor's natural estrogen because of their structural similarity, disrupting the endocrine system of animals by inhibiting or stimulating it (White et al., 1994). 17β -estradiol influences the development and maintenance of female sexual characteristics and is also involved in the neuroendocrine and skeletal system (Lee and Lee, 1996).

Conventional treatment of water and effluents, such as physicochemical treatment followed by biological processes, is not efficient in the complete degradation of these recalcitrant compounds. The use of more efficient processes for the removal and/or improvement of the biodegradability of these compounds and their metabolites have become urgent and necessary.

In this context, Advanced Oxidation Processes (AOPs) have been proposed as a suitable option for the degradation of recalcitrant compounds (Karci et al., 2013). Among different processes, photoelectrooxidation (PEO) can be applied to the degradation of these compounds (Bertoldi et al., 2012). PEO is the combination of two processes: electrolysis and heterogeneous photocatalysis. That is, it is the application of a potential or current density in combination with an ultraviolet radiation source, which radiates the anode surface. In this process, the photon and electron are the only reactants. In the photocatalytic process, the semiconductor species are photoexcited by promoting an electron from the valence band (VB) to the conduction band (CB). The region between the two bands is called the bandgap. With promotion of the electron to the CB and the generation of the gap (h^+) in the VB, reducing and oxidizing sites are created that are capable of catalyzing chemical reactions. The electrochemical process is based on applying a current density or a potential to reduce or oxidize the substrates of interest.

The electrolysis and heterogeneous photocatalysis processes involve the generation of hydroxyl radicals (HO^\bullet). This radical has a high oxidizing power ($E_{\text{HO}^\bullet/\text{HO}^-}^\circ \sim +2.8 \text{ V}$, 25°C) and low selectivity, enabling the degradation of a large number of toxic contaminants in a relatively short time (Malato et al., 2002).

The oxidation of organic compounds, represented by RH, RX e PhX, by the HO^\bullet occurs through three basic mechanisms: proton abstraction, electron transfer and radical addition, which are described by Eqs. (1)–(3), respectively.



The final products of the reaction are carbon dioxide, organic acids and inorganic ions. These have lower toxicity and are capable of biodegradation (Augugliaro et al., 1995a,b).

This work was carried out in order to investigate the application of PEO to the degradation of the NP_4EO surfactant. Different power sources (125 and 250 W), resulting in different incident light flux, current densities (5 and 10 mA cm^{-2}) and experimental time (0–240 min) were evaluated. The main objective of this research was the determination of the best experimental conditions associated to a complete degradation of NP_4EO , without the formation of more toxic reaction intermediates. Based on the reaction products detected after the degradation experiments, a degradation pathway will be proposed.

2. Experimental

2.1. Synthetic solution

This work was carried out with a solution containing NP_4EO in a concentration that is a surrogate of the effluent generated in an alkaline degreasing step of the electroplating industry. The reagent Ultralex NP_40° , which is used commercially to prepare alkali-degreasing solutions, was used as the source of NP_4EO . The solution was prepared by dilution and the working solution contained 51 mg L^{-1} of NP_4EO . The high NP_4EO concentration is related to this type of industrial effluent. It was considered that if the effluent is treated to NP_4EO degradation, before discharge to the environment, risks associated to this pollutant would be smaller. As supporting electrolyte additions of 0.25 g L^{-1} of Na_2SO_4 were carried out. The choice of Na_2SO_4 instead of NaCl was based on the fact that NaCl can react with the organic compounds present on the effluent, generating hazardous organochlorines.

Due to the low electrical conductivity of the solution, a high voltage is necessary to achieve the desired current density, which increases power consumption. The addition of a supporting electrolyte to the solution can therefore increase the electrical conductivity by increasing the mass transfer, reducing the energy consumed (Selcuk and Bekbolet, 2008). Na_2SO_4 was selected as the supporting electrolyte because it can provide high levels of sulfate anions (SO_4^-), which can enhance the charge transfer. In addition, SO_4^- can be oxidized to peroxodisulfate anions ($\text{S}_2\text{O}_8^{2-}$), which can work not only as electrolyte supports, but also as oxidizing agents. A concentration of 0.25 g L^{-1} of Na_2SO_4 was added to all initial solutions.

2.2. Experimental

The experimental system is illustrated in Fig. 1. The reactor used in the PEO trials was a jacket borosilicate glass reactor with a capacity of 3 L, operated in batch mode and connected to an ultra thermostatic bath to control the temperature. The anode was dimensionally stable (DSA°) and composed of $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ with surface geometric area of 475.2 cm^2 and the cathode was composed of Ti/TiO_2 with surface geometric area of 118 cm^2 . The anode and cathode are produced by thermal decomposition by De Nora of Brazil $^\circ$. The cathode (TiO_2) has crystalline anatase and rutile structure, the first being more photoactive (Gomes, 2009; Alves, 2010). The anode has TiO_2 with the same characteristics as that of the cathode and RuO_2 with a rutile crystal structure (Hu et al., 2012).

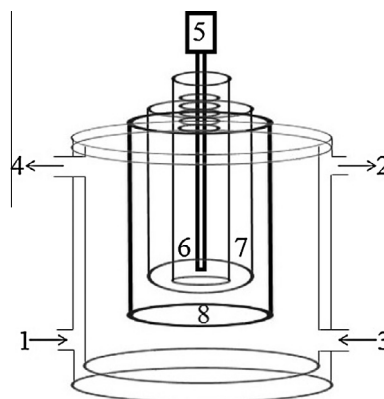


Fig. 1. Batch Reactor used in the PEO process, where 1 is the entrance for the refrigeration fluid into the glass reservoir, 2 is the exit of the refrigeration fluid, 3 is the entrance of the effluent, 4 is the exit of the effluent, 5 is the mercury-vapor lamp, 6 is the quartz tube, 7 is the Ti/TiO_2 cathode and 8 is the $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode.

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