



Electrodegradation of naphthalenic amines: Influence of the relative position of the substituent groups, anode material and electrolyte on the degradation products and kinetics

A.S. Rodrigues, M.J. Nunes, A. Lopes*, J.N. Silva, L. Ciríaco, M.J. Pacheco

FibEnTech-UBI Research Unit and Department of Chemistry, Universidade da Beira Interior, 6201-001 Covilhã, Portugal

HIGHLIGHTS

- Sulfonated aminonaphthalenes can be electrodegraded with BDD or Ti/Pt/PbO₂ anodes.
- Amino and sulfonic groups in same aromatic ring confer stability towards oxidation.
- For all the studied amines, DOC removal is higher at BDD than at Ti/Pt/PbO₂.
- Amines' degradation follow a first order kinetics in both electrolytes and anodes.
- Amines' degradation kinetics is 10–40 times higher in chloride than in sulfate.

ARTICLE INFO

Article history:

Received 20 January 2018

Received in revised form

24 March 2018

Accepted 13 April 2018

Available online 18 April 2018

Keywords:

Aminonaphthalene sulfonate

BDD

Ti/Pt/PbO₂

Electrolysis

Aromatic amines

ABSTRACT

The electrodegradation of the 4-aminonaphthalene-1-sulfonic acid (4AN1S), 5-aminonaphthalene-2-sulfonic acid (5AN2S) and 8-aminonaphthalene-2-sulfonic acid (8AN2S) was studied, using two electrode materials as anode, BDD and Ti/Pt/PbO₂, and two different electrolytes, sodium sulfate and sodium chloride. The highest COD removal rates were obtained at BDD: for 5AN2S and 8AN2S results were similar in both electrolytes; for 4AN1S, results were better in sodium chloride. The lowest COD removal rates were obtained at the system Ti/Pt/PbO₂-sodium sulfate, for all the studied amines. The dissolved organic carbon (DOC) removal was much higher at BDD for all the amines, in sulfate for 5AN2S and 8AN2S and in chloride for 4AN1S. Nitrogen removal was always almost irrelevant in sulfate medium but higher than 60%, after 6-h assays, in chloride. The highest combustion efficiencies were attained at the system BDD-sodium sulfate and were: 4AN1S-75%; 5AN2S-84%; 8AN2S-74%. HPLC results show that total degradation of the studied aminonaphthalene sulfonates is attained at both anode materials, utilizing any of the electrolytes, with a first order kinetics. However, kinetic constants obtained with the variation of the amines concentration in time are 10–40 times higher in chloride, being slightly higher at Ti/Pt/PbO₂ than at BDD. Regarding the presence of carboxylic acids during the degradation assays, it was observed that the electrolysis of the amines 5AN2S and 8AN2S always lead to higher amounts of oxalic acid and lower quantities of acetic acid than the electrolysis of the amine 4AN1S.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Aromatic amines are chemical compounds with one or more aromatic rings in their molecular structure and at least one amino substituent. Their structure ranges from as simple as aniline, up to highly complex molecules, with conjugated aromatic or

heterocyclic structures and several substituents, such as one or more sulfonate groups that increases solubility in aqueous medium (Pinheiro et al., 2004). They are a very important class of compounds for the chemical industry, since they are used in the manufacture of many chemical products, namely, azo dyes, detergents, dispersants, pesticides, polymers, wetting agents, concrete plasticizers, among others (Lange et al., 2000; Riediker et al., 2000; Shiyun et al., 2002; Panizza et al., 2006). Given their wide application, many aromatic amines, particularly mono- and disulfonated aminonaphthalenes, can be released to the aquatic

* Corresponding author.

E-mail address: analopes@ubi.pt (A. Lopes).

environment. In fact, several naphthalene sulfonate compounds have been identified in textile and tannery wastewaters, leachates and plumes from landfills, and even in rivers (Song et al., 2005). Sulfonated aminonaphthalenes are, in general, very toxic pollutants and some are known human carcinogens (Sharma et al., 2007; Brillas and Martínez-Huitle, 2015). Since these chemicals represent a risk to human health, namely due to their persistence in the environment, some have been listed as priority pollutants (Shiyun et al., 2002). Thus, European and US-EPA regulations are getting stricter in terms of the environmental impact of aromatic sulfonated amines, becoming necessary to find effective alternatives to degrade the aromatic amines and the metabolites originated during their degradation.

Although simple aromatic amines can be mineralized under methanogenic conditions, the same does not happen under aerobic conditions, where the aromatic sulfonated amines are not easily degraded (Pandey et al., 2007). However, there are some studies, mentioned in the literature, where biological treatments were applied with success in the degradation of the original molecule, although, in most of these treatments the aromatic rings remain intact (Nörtemann et al., 1986, 1994; Zürrer et al., 1987; Haug et al., 1991; Tan et al., 2005; Panizza et al., 2006; Nicoletta et al., 2007; Juárez-Ramírez et al., 2012). An example is the biodegradation process of azo dyes (one of the main sources of aminonaphthalene sulfonates in the aquatic environment), where, through the azo bond cleavage, the initial molecule is reduced to the corresponding colorless aromatic sulfonated amines (Tan et al., 2005). After the azo bond cleavage, the by-products can lose sulfonic and amino groups, through oxidative deamination, hydroxylation and oxidation, given origin to hydroxyl naphthalene compounds (Puvanewari et al., 2006; Singh and Ramesh, 2013; George et al., 2014; Nidheesh and Gandhimathi, 2014; Shah, 2014; Adnan et al., 2016; Naik et al., 2017).

To overcome the difficulty of sulfonated aromatic amines biodegradation, various other oxidation techniques for the degradation of these amines were studied, namely, ozonation (Shiyun et al., 2002, 2003), photochemical oxidation (Sørensen and Frimmel, 1997) and photoelectrochemical oxidation (Socha et al., 2005). Electrochemical oxidation was also applied for the degradation of sulfonated aromatic amines with good results (Casero et al., 1997; Socha et al., 2005; Panizza et al., 2006; Santos et al., 2010; Pacheco et al., 2011; Liu et al., 2013). This oxidation process is affected by experimental conditions, such as electrode material, support electrolyte, applied current density, pollutant molecular structure and temperature, amongst others. These factors have an impact in the selectivity and efficiency of the process, and in the degradation mechanism and consequent by-products. The oxidation of pollutants in the electrochemical cell can be carried by direct or indirect anodic oxidation. In the direct process, the pollutants oxidation is carried at the electrode surface, by direct electron transfer, whereas in the indirect process, the oxidation is mediated through electrogenerated species such as the hydroxyl radical. The latter yields better results for decontamination processes, leading from partial to total pollutants degradation (Martínez-Huitle and Brillas, 2009; Nidheesh et al., 2013; Martínez-Huitle et al., 2015).

The influence of the pollutant chemical structure in the degradation mechanism is also an important factor to be evaluated during the degradation process. Some studies shown a correlation between the molecular structure and the type and position of substituents with the oxidation efficiency of some dyes, which can be corroborated through the identification and monitoring of intermediates (Martínez-Huitle and Brillas, 2009; Araújo et al., 2014).

This paper aims to bring some enlightenment on the understanding of the electro-oxidation of naphthalene sulfonated amines, namely on the influence of the relative position of the

amino and sulfonic groups. The influence of the anode material, BDD and Ti/Pt/PbO₂, and of the electrolyte, sodium sulfate and sodium chloride, were also investigated. These anode materials were selected because they both present extraordinary mechanical, chemical and electrochemical properties, being excellent candidates for anodic oxidation in industrial applications, namely as tertiary treatment for effluents containing persistent organic pollutants. The chosen compounds were 4-aminonaphthalene-1-sulfonic acid (4AN1S), 5-aminonaphthalene-2-sulfonic acid (5AN2S) and 8-aminonaphthalene-2-sulfonic acid (8AN2S). These three pollutants were already found in industrial effluents (Alonso and Barceló, 1999; Alonso et al., 2005). 4AN1S was also detected as a metabolite during degradation studies of dyes, namely, Acid Red 27 (Adnan et al., 2016) and Amaranth dye (Naik et al., 2017).

2. Experimental

The aromatic amines 4-aminonaphthalene-1-sulfonic acid (sodium salt hydrate, x.H₂O; >97%), 5-aminonaphthalene-2-sulfonic acid (>95%) and 8-aminonaphthalene-2-sulfonic acid (>97%) were purchased from Sigma Aldrich and used without further purification. Their structures are represented, as insets, in Fig. 1a. The electrolyte salts used in the degradation assays were sodium sulfate (Carlo Erba, 99%) and sodium chloride (V. Reis, 99.8%).

Cyclic voltammetry (CV) studies were performed in a three electrodes cell with an Ag/AgCl, KCl_{sat} reference electrode, a Pt plate counter electrode and a Si/BDD (1 cm²) or a Ti/Pt/PbO₂ (1 cm²) working electrode. Aqueous sodium sulfate or sodium chloride solutions, 5 g L⁻¹, were used in the absence and in the presence of the different amines (1000 mg L⁻¹ for 4AN1S and 5AN2S and saturated solution for 8AN2S). The electrochemical cell was connected to a potentiostat/galvanostat VoltaLab 40, model PGZ301. Voltammograms were recorded in the potential region from approximately 0.2 to 3.2 V (vs. NHE), at potential sweep rates varying from 10 to 1000 mV s⁻¹.

The electrodegradation assays were run in a batch cell, with magnetic stirring (200 rpm). The aqueous solutions, 220 mL, contained 200 mg L⁻¹ of the amine and 5 g L⁻¹ of the electrolyte. Two different anodes were used: a 10 cm² Si/BDD plate, purchased from Adamant (now Neocoat); and a 10 cm² Ti/Pt/PbO₂ plate, prepared as described elsewhere (Andrade et al., 2008; Ciríaco et al., 2009). In both cases, the cathode was a stainless steel plate (10 cm²), with an inter-gap between electrodes of 1.2 cm. A GW, Lab DC, model GPS-3030D (0–30 V, 0–3 A), was used as power supply to guarantee an applied current density of 30 mA cm⁻² in all the electrodegradation assays. The resulting potential differences were measured and the variation during the assays was the following: for BDD, 11 ± 1 V to 9.8 ± 0.8 V; for Ti/Pt/PbO₂, 11 ± 2 V to 10 ± 1 V.

The degradation assays had a duration of 6 h and were monitored every 30 min during the first two hours and hourly for the remaining 4 h. To perform the kinetic studies, samples were collected every 15 min for assays run with sodium chloride as electrolyte. Assays were run at least in triplicate and results presented are mean values.

The organic load decay was followed by chemical oxygen demand (COD), dissolved organic carbon (DOC), total nitrogen (TN) and UV–Vis. spectrophotometry. These determinations were performed according to standard procedures (Eaton et al., 2005). For the COD determinations, the closed reflux titrimetric method was used. The DOC and TN contents were measured in a Shimadzu TOC-VCPH analyzer combined with a TNM-1 unit. Before DOC and TN determinations, samples were filtered through 1.2 μm glass microfiber filters.

The amines concentration was determined by reversed-phase high-performance liquid chromatography (RP-HPLC) using a

Download English Version:

<https://daneshyari.com/en/article/8851175>

Download Persian Version:

<https://daneshyari.com/article/8851175>

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