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Degradation pathways of aniline in aqueous solutions during electro-oxidation with BDD electrodes and UV/H_2O_2 treatment

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HIGHLIGHTS

- Electro-oxidation and UV/H_2O_2 reach aniline mineralization >85%.
- Two different degradation routes were observed during aniline oxidation.
- Electro-oxidation using BDD electrodes has lower operational cost.

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ABSTRACT

In this work, it has been studied the mineralization of aniline, a toxic substance of low biodegradability typically found in many industrial wastewaters, through electro-oxidation using boron doped diamond (BDD) electrodes and photo-oxidation (UV photolysis and UV/H_2O_2 treatments). It was observed that in electro-oxidation and UV/H_2O_2, it was feasible to reach aniline mineralizations higher than 85%. Two different degradation routes have been observed during the aniline oxidation in these two treatments. The first route was the mineralization pathway, in which aniline was oxidized to CO_2, water and nitrate. The second route was the polyaniline pathway in which polyanilines of high molecular weight are formed. The intermediate compounds involved in both degradation routes are different depending on the treatment used. In the electro-oxidation, denitrification processes were also observed. From an economical point of view, electro-oxidation of aniline using BDD electrodes is more interesting than UV/H_2O_2 due it has an 87% lower operational cost. So, electro-oxidation using BDD electrodes seems to be a more suitable technique for the mineralization of wastewater containing aniline than UV or H_2O_2 based technologies.

1. Introduction

Aniline is an important compound in the petrochemical industry, used primarily for the synthesis of isocyanate, an intermediate for the manufacture of polyurethane. Its derivatives are also key precursors for the production of accelerators and antioxidants in the rubber industry, herbicides and pharmaceuticals (Chen and Huang, 2015). Aniline is a toxic recalcitrant substance of low biodegradability which has been listed as one of the 129 priority pollutants by the U.S Environmental Protection Agency (U.S.EPA) (Zhang et al., 2013). It is estimated that the emission amount of aniline into the environment is 30 000 tons per year by accidental spills, the illegal release of industrial and municipal wastewater, and excessive use of pesticides (Orshansky and Narkis, 1997).

There are many studies regarding the different alternatives that exist to treat wastewaters polluted with aniline, such as oxidation (Chen and Huang, 2015; Faria et al., 2007), extraction (Fazylova et al., 2015), biodegradation (Hu et al., 2014) and adsorption (László, 2005; Li, 2010; Orshansky and Narkis, 1997; Valderrama et al., 2009; Wu et al., 2012; Xiao et al., 2015; Xie et al., 2007; Yao et al., 2008). Up to day, all these treatments present different problems in terms of efficiency, cost or feasibility. Among all the treatments, advanced oxidation processes (AOP) seems to be one of most promising techniques able to degrade recalcitrant organic compounds in water (Brillas and Martínez-Huitle, 2015; Chaplin, 2014; Oturan and Aaron, 2014; Santos et al., 2010). AOP processes

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consist of the generation of $OH^\bullet$ which oxidize organic compounds into shorter molecules and finally convert them mainly into CO_2 and H_2O (mineralization). AOPs involve combinations of chemical agents such as H_2O_2, O_3, transition metals and metal oxides, and also auxiliary energy sources as UV radiation, electric current, γ-radiation or ultrasound (Petrovic et al., 2011). The mineralization degree will strongly depend on the chemistry of each organic compound, the constituents of the wastewater and the type of AOP. In the case of aniline, there are previous studies where different AOPs have been used, such as Fenton (Anotai et al., 2006; Ratanatamskul et al., 2011), photo-Fenton (Brillas et al., 1998; Ratanatamskul et al., 2011), photocatalysis (Egzar et al., 2013; Shahrezaei et al., 2012), ozonation (Jing et al., 2015), ultrasounds (Bi and Huang, 2013), UV-H_2O_2 (Krystyn, 2014) and electro-oxidation (Matsushita et al., 2005; Mitadera et al., 2004) in which was shown that aniline could be effectively degraded by AOP.

In the last years the use of boron doped diamond (BDD) anodes has been studied in the electrochemical remediation of wastewaters containing organic pollutants (Dos Santos et al., 2015; Moreira et al., 2014; Oturan et al., 2015; Panizza, 2014; Panizza et al., 2001a,b; Tissot et al., 2012). BDD anodes are interesting materials in electro-oxidation because they have a wide potential window in aqueous solutions, low background current, inertness to adsorption, extreme robustness and high resistance to corrosion (Bi and Huang, 2013; Chaplin, 2014; Krystyn, 2014; Matsushita et al., 2005; Montilla et al., 2002). Mitadera et al. used BDD electrodes to oxidize aniline in water (Mitadera et al., 2004). This work was focused mainly on voltammetry studies, the effect of pH on the voltammetry behavior and aniline removal and mineralization (Mitadera et al., 2004). They concluded that acidic media and high anodic potential was favorable to oxidize aniline. They mentioned that the mineralization degree reached in their experiments was 80%. However, this study did not pay attention on the byproducts formed during the oxidation neither on the economic costs of the process.

For that reasons, it has been carried out a comprehensive study of the aniline removal from water through electro-oxidation using BDD electrodes analyzing the byproducts formed during the process as well as the economic costs associated with the electrical consumption. The results were compared with the UV photolysis, UV/H_2O_2 treatment and with H_2O_2 oxidation.

2. Materials and methods

2.1. Experimental set-up

Electro-oxidation experiments were conducted in a single compartment electrochemical cell manufactured by Waterdiam (DiaCell 106). BDD on silicon was used as anode and cathode and both were circular with a surface area of 70 cm^2 each one with 1 mm gap. The electric power required during the electro-oxidation experiments was provided by a power supply (Diaclean-PS 220VAC-48VDC) that had a maximum output of 30 A and 48 V. The electrochemical cell was operated in batch mode. The wastewater was stored in a glass tank and circulated in a close circuit through the electrochemical cell by a peristaltic pump (See supplementary material Fig. SM-1a). Continuous pumping of the water and the electro-oxidation process caused a temperature increase so, a cooler was used to keep constant the wastewater temperature.

Photo-oxidation experiments were carried out with the UV Laboratory Reactor System 3 from UV-Consulting Peschl® which consists of an immersion-type photochemical reactor (Fig. SM-1b) with a working volume of approximately 550 mL. The UV lamp used was a 15 W Heraeus Noblelight TNN 15/32 low-pressure mercury vapor lamp emitting at 254 nm. Potassium ferrioxalate actionometry was used in order to characterize the intensity light of the UV lamp, resulting in an irradiance of 0.049 W cm^{-2} (Hatchard and Parker, 1956).

2.2. Advanced oxidation experiments

Synthetic wastewater solutions were prepared using deionized water and aniline (Sigma-Aldrich; > 99.5% purity). Initial aniline concentration in all experiments was 250 mg L^{-1} and pH was 7.5.

Electro-oxidation experiments were performed during 4 h with 1 L of synthetic wastewater. The current density was kept constant at values ranging from 9 mA cm^{-2} to 60 mA cm^{-2} and the flow rate of the cell was adjusted to 120 L h^{-1}. The experiments were conducted at 25 ± 2 °C. During the experiments, samples were periodically collected from the feed tank.

Photo-oxidation batch experiments were carried out during 4 h using 500 mL of synthetic wastewater. Once the water was placed in the photoreactor, H_2O_2 was added and the UV lamp turned on. The H_2O_2 concentrations used in this work ranged from 1 to 5 g L^{-1} and it was added stepwise in order to maintain the H_2O_2 concentration constant. The experiments were conducted at 28 ± 5 °C. Samples were taken at different times and sodium thiosulfate was added stoichiometrically as a quencher to stop the reaction. Afterwards, H_2O_2 concentration was measured. Experiments without H_2O_2 and experiments with only H_2O_2 were also carried out in order to see the influence of these parameters.

During all the tests, samples were taken periodically and filtered with 0.45 μm filter to analyze pH, oxidation reduction potential (ORP), total dissolved solids (TDS), dissolved organic carbon (DOC), aniline concentration, turbidity, UV–Vis spectra, ammonium, nitrate and total nitrogen concentration.

2.3. Analytical methodology

A multiparameter waterproof meter HI 98194 from HANNA instruments was used to measure pH, ORP, TDS and temperature. Turbidity was determined with a 6035 turbidimeter from Jenway.

Aniline concentration was measured by an Alliance 2695 HPLC system (Waters) equipped with a LiChrosorber® 100 RP-18 (5 μm) Hibar® RT 125-4 Merck Millipore column. The mobile phase was composed by water:methanol (55:45 V/V) with a flow-rate of 1.0 mL min^{-1} and 30 °C. The detection of aniline was performed with a UV-DAD detector at 230 nm.

An UPLC-MS/MS (Acquity H-Class) equipped with an Acquity BEH C18 2.1 mm × 50 mm 1.7 μm column was used in order to separate and identify the byproducts produced during the oxidation. The eluents were 0.2% (v/v) formic acid/MilliQ water and methanol operating in gradient mode. The flow and temperature were 0.5 mL min^{-1} and 45 °C respectively. A Waters Xevo TQSmicro MS system has been used to detect the degradation byproducts obtaining their molecular weights. The acquisitions have been done using polarity switching, proceeding by positive [ESI+] and negative [ESI-] modes, and scanning from a range between $m/z = 50$ to $m/z = 1000$.

DOC was determined with a TOC-V CSH/CSN analyzer from SHIMADZU. UV–Vis spectra of the samples were obtained using an UV-1280 spectrophotometer from Shimadzu. Total nitrogen was measured by the TNT Persulfate Digestion Method from Hach. NH_4^+-N concentration was determined with an ISENH418101 ammonium probe from Hach and NO_3^--N concentration was determined by the chromotropic acid method from Hach. H_2O_2 concentration was analyzed by a spectrophotometric method using titanium (IV) oxysulfate (DIN 38 402 H15 method), which forms a yellow complex with H_2O_2 (maximum absorption at 410 nm) (Shahbazi et al., 2014).