



Electrochemical mineralization pathway of quinoline by boron-doped diamond anodes



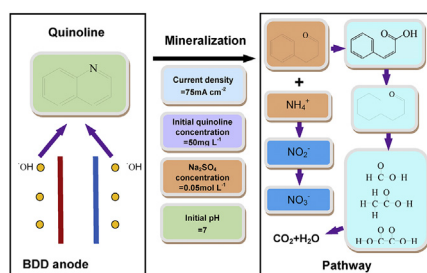
Chunrong Wang^{*}, Keke Ma, Tingting Wu, Min Ye, Peng Tan, Kecheng Yan

School of Chemical and Environmental Engineering, China University of Mining and Technology (Beijing), Beijing 100083, PR China

HIGHLIGHTS

- BDD anodes were effective in quinoline mineralization.
- A new plausible reaction pathway for quinoline mineralization was proposed.
- Quinoline degradation starts with pyridine ring opening, with NH_4^+ release.
- After pyridine ring cleavage, NH_4^+ is partially converted to NO_3^- .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 9 November 2015

Received in revised form

24 January 2016

Accepted 25 January 2016

Available online 6 February 2016

Handling Editor: E. Brillias

Keywords:

Boron-doped diamond anode

Quinoline

Mineralization

Pathway

ABSTRACT

Boron-doped diamond anodes were selected for quinoline mineralization, and the resulting intermediates, phenylpropyl aldehyde, phenylpropionic acid, and nonanal were identified and followed during quinoline oxidation by gas chromatography-mass spectrometry and high-performance liquid chromatography. The evolutions of formic acid, acetic acid, oxalic acid, NO_2^- , NO_3^- , and NH_4^+ were quantified. A new reaction pathway for quinoline mineralization by boron-doped diamond anodes has been proposed, where the pyridine ring in quinoline is cleaved by a hydroxyl radical giving phenylpropyl aldehyde and NH_4^+ . Phenylpropyl aldehyde is quickly oxidized into phenylpropionic acid, and the benzene ring is cleaved giving nonanal. This is further oxidized to formic acid, acetic acid, and oxalic acid. Finally, these organic intermediates are mineralized to CO_2 and H_2O . NH_4^+ is also oxidized to NO_2^- and on to NO_3^- . The results will help to gain basic reference for clearing intermediates and their toxicity.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

As one of the most important nitrogen-containing organic compounds, quinoline is a common organic pollutant in coal gasification wastewater. He and Wang (2015) reported that the organic pollutants in coal gasification wastewater were primarily

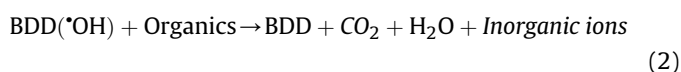
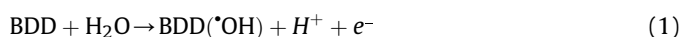
phenols, accounting for 53.3%, and second, quinoline and its derivatives accounted for 27.4% of the pollutants, based on the data from the South African Sasol Company. At present, many studies have reported the removal of phenols from waste water, while relatively few studies have reported on the removal of quinoline and its derivatives. Moreover, quinoline and other nitrogen-containing heterocyclic derivatives present a significant threat to the environment. It is important to remove them from the wastewater before it is discharged into the environment because of their toxicity, carcinogenicity, teratogenicity, and mutagenicity in

^{*} Corresponding author.

E-mail address: wcrzgz@126.com (C. Wang).

humans. These compounds also undergo bioaccumulation in various organisms of the food chain, and have thus attracted increasing attention from researchers (Cui et al., 2003). In addition, Yu et al. (2005) reported that quinoline, as a common and significant proportion of the heterocyclic aromatic hydrocarbons in coal gasification wastewater, has been listed as a priority pollutant by the US Environmental Protection Agency.

Currently, biological and chemical treatment technologies are used to remove quinoline and its derivatives from waste water. In biological treatments, the dominant strains that are efficient in the degradation of quinoline are screened, cultured, and reproduced to quickly biodegrade quinoline. Chemical treatments use redox reactions, where quinoline is mineralized by adding strong oxidants into the wastewater or producing strong oxidizing substances *in situ*. In these chemical treatment technologies, electrochemical oxidation is one of the most promising advanced oxidation processes because of its high efficiency and environmentally friendly methodology (García-Segura and Brillas, 2011). In particular, electrochemical oxidation technology using boron-doped diamond (BDD) anodes appears to be a suitable technology because of its wide potential window and low background current (Jeong et al., 2009; Panizza and Cerisola, 2005). BDD has a robust oxidation capacity, which originates from its ability to oxidize pollutants by a combination of direct electron transfer reactions at anode surface and indirect oxidation via hydroxyl radicals ($\cdot\text{OH}$) produced by water oxidation (see Equations (1) and (2)) (Chaplin et al., 2009, 2010; El-Ghenymy et al., 2013; Oturan et al., 2012; Uranga-Flores et al., 2015). This has led to BDD anodes being used for the degradation of different organic pollutants, such as phenol and its derivatives (Azevedo et al., 2011; Pacheco et al., 2007; Pereira et al., 2012; Rabaaoui et al., 2013), oxalic and oxamic acids (García-Segura and Brillas, 2011), salicylic acid (Rabaaoui and Allagui, 2012), sulfanilic acid (El-Ghenymy et al., 2012), herbicides (Alves et al., 2012), dyes (Costa et al., 2009), reverse osmosis concentrate (Bagastyo et al., 2013; Chaplin et al., 2010), and landfill leachate (Anglada et al., 2011).



However, quinoline oxidation by BDD anodes has only been reported by Xing et al. (2012), and the focus of that report was the degradation kinetics and main intermediates of nitrogen-heterocyclic compounds (including quinoline), and using quantum chemical calculations combined with experimental results to describe the degradation character of nitrogen-heterocyclic compounds at BDD anodes, leaving the oxidation pathway of quinoline to be inferred. Initial studies by our group found that during the oxidation of quinoline by BDD anodes, different gases were released at different times. Wet pH test paper held in the gas stream from electrolysis turned blue at the start, and then gradually turned red as the oxidation proceeded (see Fig. SM-1). The most probable alkaline gas to be released from quinoline was judged to be ammonia from the N in the pyridine ring, and the most likely acidic gas would be CO_2 . Moreover, because the ammonia was released at the beginning, the quinoline oxidation by BDD anodes might proceed through a pathway where the pyridine ring was cleaved first, and released as NH_4^+ instead of NO_3^- , and this would require a completely different pathway from the results presented by Xing et al. (2012).

Based on above sensory phenomena and deduction, the aim of this work was to identify the by-products and intermediates formed during the quinoline abatement process to confirm the

oxidation pathway. And the results will help to gain basic reference for clearing intermediates and their toxicity.

2. Materials and methods

2.1. Experimental system

The experimental system comprised an electrolytic cell, three pieces of BDD (see Fig. SM-2) to act as anodes (purchased from CONDIAS GmbH, German), and two pieces of 312 stainless steel to act as cathodes with an electrode gap of 1.0 mm, a direct-current power supply (DH1716-7A; Dahua Electronics Co., Ltd., China), and a thermostat. The anode and cathode had the same size with length \times width \times thickness of 195 mm \times 26 mm \times 2 mm. The electrolytic cell was made of Plexiglas and had a working volume of 3 L. The current was controlled in constant current mode with an applied current density of 75 mA cm^{-2} . All tests were carried out at 25 ± 1 °C (Wang et al., 2015).

2.2. Instruments and analytical methods

The stable intermediates formed during quinoline mineralization were qualitatively analyzed by gas chromatography-mass spectrometry (GC–MS) (QP2010Ultra/SE, Shimadzu, Japan). GC–MS column oven temperature was held at 50 °C for 3.5 min, ramped at 5 °C min^{-1} to 270 °C, and held there for 10 min. The injection port was held at 270 °C and the ion source at 250 °C. The mass spectra were identified by comparison to the NIFT08 and NIFT08s data libraries. Before the samples were injected into the GC–MS, they were extracted three times at pH 2, 7, and 12, with 50 mL of dichloromethane at each pH. The resulting organic solutions were dried over Na_2SO_4 , filtered, and rotary evaporated to about 2 mL.

High-molecular-weight organics, including phenylpropyl aldehyde and phenylpropionic acid, were qualitatively and quantitatively analyzed by high-performance liquid chromatography (HPLC) (LC-10AD, Shimadzu, Japan) coupled with a Wondasil C18 column. The mobile phase was water-methanol (50/50, v/v) with a flow rate of 0.4 mL min^{-1} . The detection wavelength was 205 nm and 20 μL of each sample was injected.

Low-molecular-weight organic acids, including formic acid, acetic acid, oxalic acid, maleic acid, and fumaric acid, were quantitatively analyzed by ion chromatography (ICS-1100, Dionex, United States) fitted with a Dionex IonPac AS19 anion analytical column (4 \times 250 mm) and guard column (4 \times 50 mm), at 30 °C, using 20 mM KOH at 1.0 mL min^{-1} as the eluent. A Dionex ASRS™ 300 4-mm suppressor was used, set at 50 mA.

Inorganic ions, including NO_2^- and NO_3^- , formed during electrolysis were detected and quantified by ion chromatography (ICS-2100, Dionex, United States) fitted with a Dionex IonPac AG19 anion analytical column, and all other detection conditions was set based on the Standard Method from the Ministry of Environmental Protection of the People's Republic of China (HJ-T 84-2001). NH_4^+ was detected by salicylic acid spectrophotometry (Editorial Board of Monitoring and Analysis Method of Water and Waste Water (2002)).

Prepared electrolyte was divided into 15 equal parts with volume of 3 L, and one of them was control group, other 14 parts were electrolyzed between 5 and 240 min respectively under the same condition, and then the different volume samples were taken out for analysis, in which the qualitative measurements were in duplicate and the quantitative measurements were in triple and the arithmetic averages were taken for calculations and data analysis.

Download English Version:

<https://daneshyari.com/en/article/4407916>

Download Persian Version:

<https://daneshyari.com/article/4407916>

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