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Research Paper

Formation of brominated oligomers during phenol degradation on boron-doped diamond electrode

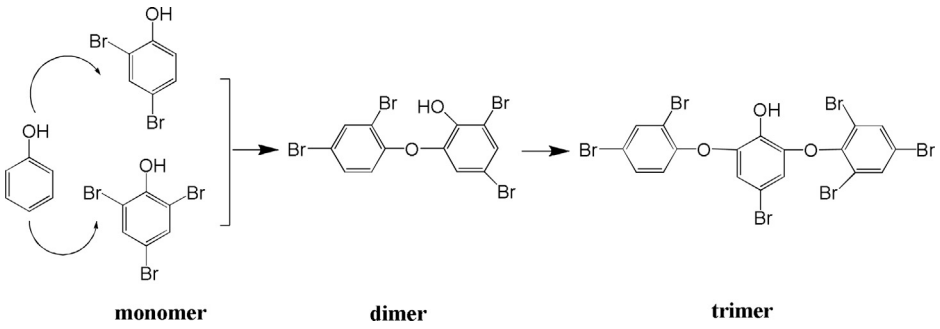
Chunyong Zhang [a,*], Jiahui Xian [a], Min Liu [a], Degang Fu [b]

[a] Department of Chemistry, College of Science, Nanjing Agricultural University, Nanjing 210095, China
[b] State Key Laboratory of Bioelectronics, Southeast University, Nanjing 210096, China

HIGHLIGHTS

- Brominated intermediates from anodic oxidation of phenol are investigated.
- Bromides and chlorides demonstrate different effects toward phenol degradation .
- Dimer and trimer intermediates are generated via coupling reactions.
- Most trimer intermediates are generated only in bromide-rich systems.
- Active bromine exhibits better reactivity and selectivity than active chlorine.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, the brominated oligomers formed during phenol degradation with boron-doped diamond (BDD) anode had been initially studied at three different concentrations of bromide (1, 10 and 100 mM). The results from LC/MS analysis indicated that, brominated monomer, dimer and trimer of phenols resulting from electrophilic substitution and coupling reactions were the important reaction by-products. Specifically, the trimer by-products were generated only in bromide-rich systems. The reaction mechanisms concerning oligomer formations were proposed in detail accordingly. The above results were in well accordance with those recorded in the degradation experiments. As a whole, bromides and chlorides demonstrated quite different effects toward phenol degradation, which deepened our understanding on the reactions involved in BDD anode cells.

1. Introduction

In the past decade, boron-doped diamond (BDD) has been proven to be an outstanding anode material in electrochemical oxidation processes [1]. This is because BDD exhibits many valuable properties, such as high oxygen evolution overpotential, excellent chemical and electrochemical stability, weak surface adsorption and low background current [2]. It is interesting to note that owing to these properties, most supporting electrolytes may display unique roles in BDD anode cells [3]. Specifically, the roles of halide ions (X^-, mainly Cl^- and Br^-) have attracted great research interests [4,5]. As is known, halide ions may react with the quasi-free hydroxyl radicals (•OH) generated on BDD surface, resulting in the formation of reactive halogen species (RHS, i.e. X_2, •X, $•X_2^-$,

* Corresponding author.
E-mail address: zhangchy@njau.edu.cn (C. Zhang).

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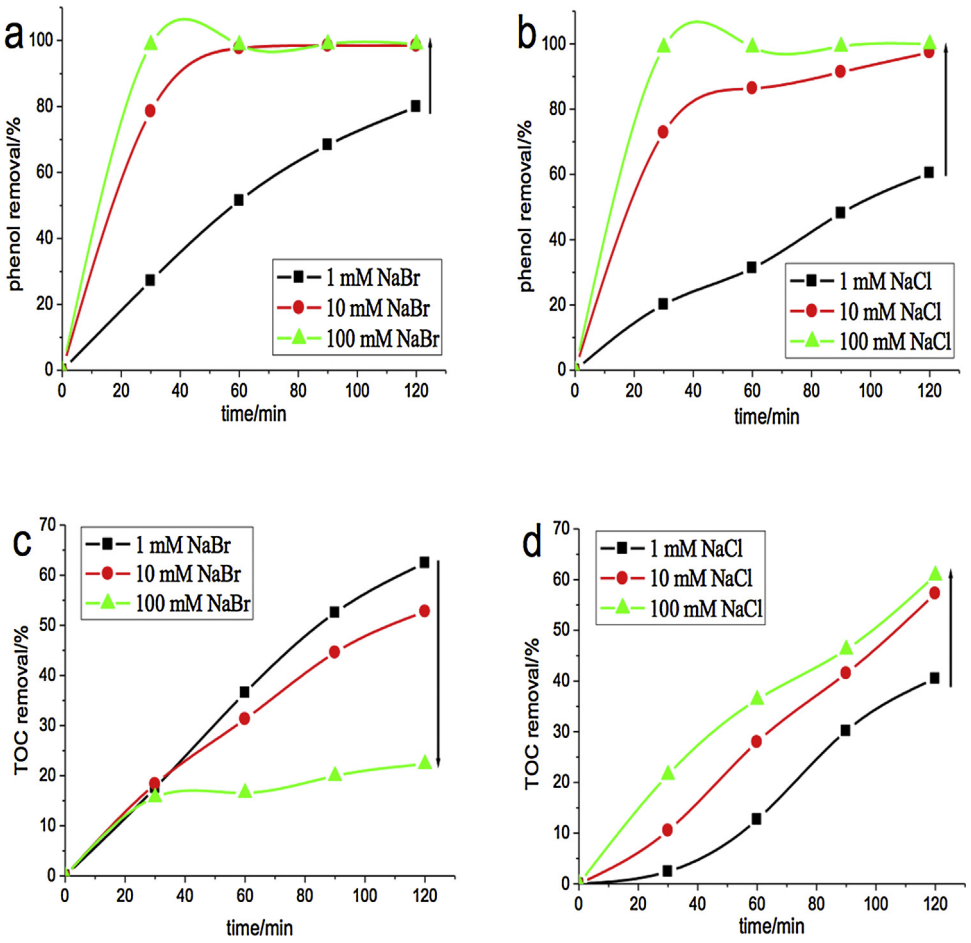

Fig. 1. Effects of initial chloride and bromide concentration on the degradation and mineralization of phenol ($[Phenol]_0$: 50 mg dm^{-3}; flow rate: 400 ml min^{-1} and j_{appl}: 6.46 mA cm^{-2}).

HXO and XO^-) [6]. It has been found that •OH can even transform X^- to higher oxidation states (XO_2^-, XO_3^- and XO_4^-) under suitable operating conditions (e.g., at high halide concentration and high applied current) [7–9]. More importantly, RHS may attack electron-rich organics producing halogenated by-products [10]. In other words, there are also considerable interests in investigating how halogen atoms are incorporated into the molecule of organics during the electrolysis. To our knowledge, most previous studies conducted in this field have focused on chloride ions, and the works concerning bromide ions are scare.

Our interests in this field are mainly triggered from a recent study on the identification of chlorinated oligomers formed during phenol degradation with BDD anodes [11]. It is well known that chlorides and bromides exhibit different redox potentials (E^θ (Cl_2/Cl^-) = 1.36 V, E^θ (Br_2/Br^-) = 1.09 V). As a consequence, bromides are more readily oxidized by •OH to form RHS than chlorides [12]. Unfortunately, till now a correlative work is still lacking in clarifying the role of bromides in BDD anode cells, as well as in identifying the brominated oligomers formed during the electrolytic oxidations.

Thus, to explore the reactions involved in bromide media, we reported herein on a comparative study of how halide concentration affected the degradation and mineralization performance of BDD technology. As expected, a large number of brominated oligomers had been identified by the LC/MS technique. Phenol (C_6H_5OH) was adopted here as a pollutant model to mimic the reactivity of natural organic matter [13]. As a result, some new and characteristic features in the degradation patterns had been observed and properly interpreted.

2. Experimental

2.1. Reagents and materials

All chemicals (C_6H_5OH, NaBr, NaCl and KH_2PO_4) were of the purest available quality from Wako (Japan), and the stock solutions were prepared with purified water from a Milli-Q system. Nb/BDD and Nb/Pt electrodes were both commercial products from Condias (Germany).

2.2. Reactor and experimental procedures

The degradation experiments were carried out in an undivided electrochemical reactor in batch mode (see Fig. SM-1). Nb/BDD and Nb/Pt plates (both with an effective surface area of 77.44 cm^2) were used as anode and cathode, respectively. The electrode spacing was set as 10 mm. For each entry, 500 ml working solution was pumped through the BDD anode cell and then returned to reservoir for recycling. Samples were collected at preset intervals to track the degrees of both degradation and mineralization. Specifically, the roles of chlorides and bromides were comparatively examined under equal operating conditions to evaluate their impacts toward phenol degradation. All entries were conducted in duplicate and the average data were reported. Note that the selections of the operating levels, such as phenol concentration of 50 mg dm^{-3}, flow