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Sequential reduction/oxidation of azo dyes in a three-dimensional biofilm electrode reactor

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HIGHLIGHTS

- Sequential reduction/oxidation of azo dye were satisfactorily acquired in 3D-BER.
- Multiple electron transfer means significantly enhanced azo dye degradation.
- Electro-generated H_2 was a key electron donor for bioreduction of azo dye.
- Bioelectrochemical mechanisms of azo dye degradation in 3D-BER were discussed.
- Most of toxic aromatic amines formed at biocathode were mineralized at bioanode.

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ABSTRACT

By combining sequential anaerobic-aerobic reactor and penetrable cathode-anode operation, a novel anaerobic/aerobic sequencing three-dimensional biofilm electrode reactor (3D-BER) was developed to evaluate the degradation of azo dye reactive brilliant red X-3B (RBRX-3B). In the bottom cathodic region, anaerobic reductive conditions and H_2 were produced for the bioreduction of azo dyes; in the top anodic region, aerobic oxidative conditions and O_2 were produced for the mineralization of dye intermediates. Due to the supply of electrical power, electrons could be mediated via electrolysis of water or directly transfer between electrodes and microbe cells. The biofilm immobilized on the surface of the cathode utilized electrode or H_2 as electron donors and accelerated the rate of RBRX-3B reduction, and the decolorization rate was significantly increased 2.6–3.7 fold, reaching at 2.52–3.39 mol/m^3/d at an energy consumption of 0.15 kWh/mol RBRX-3B. RBRX-3B was reductively cleaved into aromatic amines at the biocathode and these amines were effectively removed at the bioanode. Acute toxicity tests showed that the intermediates of RBRX-3B were more toxic when compared with the initial influent, and the 3D-BER effluent exhibited much lower toxicity (5% inhibition of bioluminescence of *Vibrio fisheri*) than the electrochemical and biological effluent (65% and 30% inhibition, respectively). These findings suggest the novel 3D-BER may provide a promising alternative to remove azo dyes in dyeing wastewater.

1. Introduction

Synthetic dyes are widely used in textile, leather, paper, cosmetics, food and pharmaceutical industries, and it is estimated that 10–15% of these dyes are lost during the dyeing process and released as effluents (Stolz, 2001). Azo dyes account for approximately 70% of all dyestuffs used worldwide by weight, making them the largest group of dyes released into the environment (Saratale et al., 2011; Brillas and Martinez-Huitle, 2015). Moreover, azo dyes consist of one or more azo bonds (−N=N−) in the structure, which are the most labile portions that can be reduced and cleaved resulting in mutagenic or carcinogenic intermediate products (dos Santos et al., 2007; Saratale et al., 2011). Therefore, it is essential to remove azo dyes and intermediate products completely from dye effluent prior to their final discharge to the environment.

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Over the past decades, a range of physicochemical methods have been reported to treat dye containing effluents (Verma et al., 2012; Brillas and Martinez-Huitle, 2015; Sathishkumar et al., 2017). Coagulation/flocculation methods are used most extensively, but they have the inherent drawbacks of requiring significant quantities of chemicals, generating notable amounts of sludge and being ineffective in decolorization of soluble reactive azo dyes. Adsorption and membrane techniques are excellent in removal of a wide variety of dyes, but the regeneration or disposal of spent absorbents is costly, while the application of membrane filtration is rather limited due to the high cost and frequent membrane fouling. Advanced oxidation processes (AOPs) (e.g., UV/H_2O_2, Fenton, ozonation and electro-peroxone process) can be quite effective for color removal but are highly expensive, furthermore, the mineralization effectiveness often varies widely with the type of constituents present in the wastewaters (Yao et al., 2016). Compared to conventional physical and chemical methods, microbial method is considered as an eco-friendly and promising way for dyeing wastewater treatment as it has the following advantages: (1) resulting in partial or complete bioconversion of azo dyes to stable and nontoxic end products, (2) being cost-competitive, (3) being under moderate temperature and pH conditions, (4) without adding potentially toxic chemical oxidants and catalysts (dos Santos et al., 2007; Saratale et al., 2011).

Owing to the recalcitrant and hydrophilic characteristics, reactive azo dyes generally resist biodegradation and cannot be precipitated with the sewage sludge in conventional sewage treatment plants (Stolz, 2001; dos Santos et al., 2007). However, microbial degradation of reactive azo dyes can be achieved by a sequenced anaerobic–aerobic treatment (Shaw et al., 2002; Khan et al., 2012). In the first step, the azo bonds of dye molecules are cleaved under anaerobic conditions, resulting in the generation of aromatic amines (Mu et al., 2009; Li et al., 2010), while the second step involves the microbial metabolism of aromatic amines in a subsequent aerobic process leading to their complete mineralization (van der Zee and Villaverde, 2005; Frijters et al., 2006). Unfortunately, the unspecific anaerobic reduction of azo dyes is a relatively slow process because the transfer of reducing equivalents from the electron-donating primary substrate to the electron-accepting dye is often a rate-limiting step (van der Zee and Villaverde, 2005; Cui et al., 2016), and long retention times should be required to obtain complete dye removal. This time-determining restriction, however, can easily be overcome by adopting electron shuttles to mediate reducing equivalents (Thrash and Coates, 2008). In a recent study, we have tested the enhancement of anaerobic biodecolorization of azo dyes in the presence of H_2 evolution at cathode in biofilm electrode reactors (BERs) (Liu et al., 2015), as the in-situ H_2 can be utilized as an electron donor for the bioreduction of azo dyes (van der Zee et al., 2001; Li et al., 2014; Shen et al., 2015). So it has been suggested that electrolysis of water can be used as a strategy to mediate electrons (Van der Zee and Cervantes, 2009) which will significantly accelerate azo dye degradation.

In BERs, cathode electrode (direct electron transfer) and in-situ electro-generated H_2 (via electrolysis of water) can be utilized as electron donors for the microbial catalytic reduction of azo dyes (Cui et al., 2017), but the preponderant electron donor (or transfer way of reducing equivalents) for bioreduction of azo dyes is unknown and needed to be further investigated. Moreover, the intermediates (e.g., aniline, sulfanilic acid and 1-amino-2-naphthol) (Mu et al., 2009; Li et al., 2010) produced from the reductive fission of azo dyes cannot be effectively removed in a single anaerobic bioelectrochemical system, and many of them are known or possible toxic, carcinogenic and mutagenic substances that need be further treated or detoxified.

Due to the limited electrochemical surface area of cathode in traditional BERs, the removal efficiency of contaminant is relatively low, and long hydraulic retention time (HRT) is normally required. For example, Liu used an anaerobic BER to degrade azo dye reactive brilliant red X-3B (RBRX-3B), however they observed that the decolorization efficiency was relatively low (only 79.77% when dye concentration was of 100 mg/L) and decreased gradually with the increase of dye loading (Liu et al., 2015). To improve the performance of BERs, a novel three-dimensional (3D) BER has been developed by introducing activated carbon (or other media) as a third bipolar electrode which can provide large effective area for biofilm formation and hydrogen gas yield (Zhou et al., 2007). Recently, the 3D-BERs have been demonstrated to be very effective in removal of nitrate and organic pollutants from groundwater (Zhou et al., 2009), Fe(II)EDTA-NO (Zhou et al., 2012; Xia et al., 2016), nitrate from municipal wastewater (Hao et al., 2013), and sulfamethoxazole and tetracycline (Zhang et al., 2016). Enlightened by these results, in the present work, a novel anaerobic/aerobic (biocathode/bioanode) sequencing 3D-BER was proposed, with an aim to achieve the goal of highly efficient decolorization and detoxification of azo dyes.

In this research, activated carbon fiber (ACF) attached to stainless steel mesh (ACF/SSM) was applied to 3D-BER cathode, and activated carbon fiber attached to titanium mesh (ACF/Ti) was applied to 3D-BER anode. Granular activated carbon (GAC) filled into the cathode chamber acted as a third bipolar electrode. RBRX-3B was chosen as a representative of reactive azo dyes, and the decolorization performances in 2D-BER, 3D-BER, three-dimensional biological reactor (3D-BR) and three-dimensional electrochemical reactor (3D-ER) were compared. The affecting parameters including glucose concentration and electrical current were systematically investigated, and the preponderant electron donor for bioreduction of RBRX-3B was also analyzed. Based on intermediates detected in the biocathode effluent and bioanode effluent, a probable azo dye degradation pathway in the 3D-BER was proposed. Finally, the toxicity evaluation at different areas of the 3D-ER, 3D-BR and 3D-BER were carried out based on the bioluminescence test.

2. Materials and methods

2.1. Reactors and materials

The experimental reactors (see Fig. S1) were made of polycarbonate plastic and divided by the hydraulic distribution board into a conical inlet chamber and a cylindrical electrochemical cell ($\Phi 150 \times 250$ mm). The electrochemical cell contained four layers (from lower to upper): (1) a 20-mm ACF/SSM cathode, (2) a 150 mm GAC (3–5 mm in diameter with a specific area of 500–900 m^2/g) layer, (3) a 20 mm ACF/Ti anode. The distance between GAC (upper surface) and ACF/Ti anode (lower surface) was 20 mm. The total volume of the whole container was 4.7 L, with an effective liquid volume of 2.8 L.

RBRX-3B (analytical grade) was purchased from Jiaying Chemical Co. Ltd., China. General characteristics of RBRX-3B are presented in Table S1. Methanol, methylene chloride, and aniline were chromatographic grade supplied by Sigma-Aldrich. All other chemicals were of analytical grade.

2.2. Inoculation and procedure

Four reactors were constructed as follows: (1) 3D-BER, as shown in Fig. S1; (2) 2D-BER, reactor similar with that of the 3D-BER except the absence of the filled GAC; (3) 3D-ER, reactor without biological sludge; (4) 3D-BR, reactor with biological sludge but no