Bioresource Technology 175 (2015) 624–628

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Improved azo dye decolorization in an advanced integrated system of bioelectrochemical module with surrounding electrode deployment and anaerobic sludge reactor

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HIGHLIGHTS

- Integrated system with BES module and ASR was developed for azo dye treatment.
- It improved decolorization and electrochemical performance without co-substrate.
- COD can be removed after cleavage of the azo bond, different from biocathode BES.
- Cooperation of cathode, biofilm, and sludge played an important role in treatment.

ARTICLE INFO

Article history:
Received 19 August 2014
Received in revised form 13 October 2014
Accepted 18 October 2014
Available online 25 October 2014

Keywords:
Integrated system
Bioelectrochemical system (BES)
Anaerobic sludge reactor (ASR)
Decolorization
Azo dye

ABSTRACT

A new integrated system, embedding a modular bioelectrochemical system (BES) with surrounding electrode deployment into an anaerobic sludge reactor (ASR), was developed to improve azo dye decolorization. Results demonstrated that the AO7 decolorization and COD removal can be improved without co-substrate in such system. The kinetic rate of decolorization (0.54 h^{-1}) in integrated system was 1.4-fold and 54.0-fold higher than that in biocathode BES (0.39 h^{-1}) and ASR (0.01 h^{-1}), respectively. COD can be removed after cleavage of azo bond, different from biocathode BES. The combined advantages of this integrated system were achieved by the cooperation of biocathode in modular BES and sludge in ASR. Biocathode was a predominant factor in AO7 decolorization, and anaerobic sludge contributed negligibly to AO7 reduction decolorization but mostly in the COD removal. These results demonstrated the great potential of integrating a BES module with anaerobic treatment process for azo dye treatment.

1. Introduction

Bioelectrochemical system (BES) has great potential in wastewater treatment especially in refractory wastewater because of its sustainability and bioenergy benefit (Kong et al., 2014b,c; Sun et al., 2011). Previous studies have focused on the BES improvement to promote its application in practice (Liu et al., 2014; Oliveira et al., 2013). Although BES technology has the potential to replace traditional treatment technologies (Janicek et al., 2014), it may not be sufficient as a stand-alone wastewater treatment technology to achieve high effluent quality (Malaeb et al., 2013) and may be better used in conjunction with current technologies (Janicek et al., 2014; Zhang et al., 2013). The reported coupled systems are summarized as the following three categories: linking BES as a separate process with other treatment system (Ren et al., 2014; Wang et al., 2014), introducing electrode into the treatment system (Cui et al., 2014; Malaeb et al., 2013), and inserting BES as a individual component into treatment system (Zhang et al., 2013).

Considering the anaerobic sludge processes are widely used in wastewater treatment (Solís et al., 2012), the combination of BES with anaerobic sludge reactor for wastewater treatment may be a great potential application, especially with BES module embedding into the traditional anaerobic sludge reactor. This integrated process will allow electrons produced at anode to be a driving force for removing pollution at cathode as a part of the energy saving process. It has been found that the performance in desalination, decolorization and metal removal can be improved when BES with surrounding electrode deployment was employed, with the advantages of the compact structure, small electrode spacing, large

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http://dx.doi.org/10.1016/j.biortech.2014.10.091
0960-8524/

proton exchange area and low internal resistance (Huang et al., 2011; Jacobson et al., 2011; Kong et al., 2013). Therefore, it would be meaningful if employed this surrounding electrode deployment BES as a BES module in developing an advanced integrated system with anaerobic process to treatment wastewater.

Further taking into account the important role of BES in azo dye decolorization (Mu et al., 2009) as well as the limited cleavage of azo bond in anaerobic sludge reactor (Solís et al., 2012), this work developed an advanced integrated system, embedding a modular BES with surrounding electrode deployment into anaerobic sludge reactor, to achieve improved azo dye degradation. This study aimed to realize the enhanced pretreatment of azo dye through BES module and further treatment through anaerobic sludge.

2. Methods

2.1. Integrated system setup

The integrated reactor (Fig. 1C) was developed by inserting a BES module with surrounding electrode deployment into an anaerobic sludge reactor (ASR, ID 8 cm × 10 cm, Fig. 1A) with the anaerobic sludge (1/5 total volume) at the bottom. The BES module was constructed as three cathode electrodes surrounding the anode electrode, separated by a cation exchange membrane (Ultrex CMI7000, Membranes International Inc., USA) pasted on the inner tube (full of holes, ID 3 cm × H 10 cm). The working volume for the inner anode chamber was 70 mL, resulting in the working volume for cathode to be 210 mL as the module inserted. Both anode and cathode electrode materials were carbon brush (ID 3 cm × 8 cm) displaced to be surrounding deployment as described previously with the electrode ratio of 1:3 (Kong et al., 2014a). When the BES module was inserted without anaerobic sludge, it became a sleeve-type BES reactor (Fig. 1B) (Kong et al., 2013).

2.2. Inoculation and operation

Activated sludge as described was used as the inoculum of the anode and cathode (Kong et al., 2014a). Sodium acetate (1 g L^{-1}) was used as the sole electron donor in the anode chamber, and azo dye, acid orange 7 (AO7, 100 mg L^{-1}), was used as the electron acceptor in the cathode chamber. Experiments were performed to investigate the decolorization performance in the integrated system compared to the individual biocathode BES and ASR.

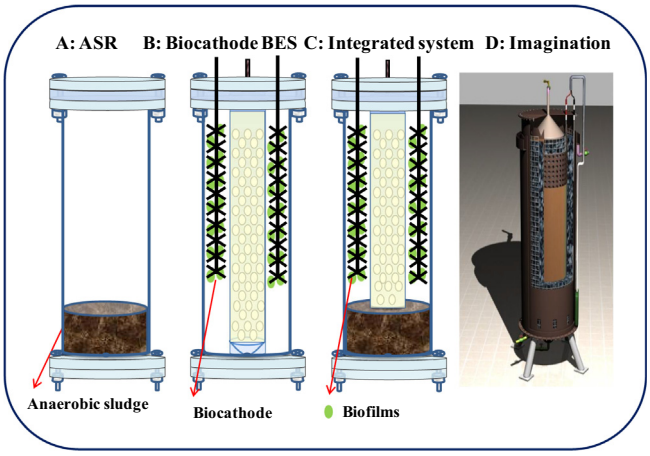

Fig. 1. Schematic of (A) anaerobic sludge reactor (ASR), (B) biocathode BES with surrounding electrode deployment, (C) integrated system of the biocathode BES and ASR by embedding the modular BES into the anaerobic sludge reactor (ASR), and (D) the imagination of the integrated system acceptable for application.

2.3. Analysis and calculation

AO7 concentration and its products were measured as (Mu et al., 2009). AO7 decolorization efficiency, sulphanilic acid (SA) formation efficiency and chemical oxygen demand (COD) removal were calculated and modeled according to (Fernando et al., 2012). Anode and cathode as well as the reference electrode were connected to a data acquisition unit (Keithley 2700, Keithley Co., Ltd., USA) with external resistance of 20 Ω to record electrode potential and current every 10 min. Electrochemical impedance spectroscopy (EIS) were carried using electrochemical workstation (model-660D, CH Instruments Inc., USA) as previously described (Kong et al., 2013).

3. Results and discussion

3.1. The azo dye degradation in the integrated system

To examine the feasibility and clarify the contribution of BES module and anaerobic sludge for AO7 decolorization in the integrated system, the individual biocathode BES and ASR were considered and compared, with the AO7 degradation in nature as control.

Decolorization results indicated that with such an integrated process, AO7 decolorization was improved without co-substrate. The decolorization was found to be under first-order kinetic model in each reactor but reaction rates varied greatly. The kinetic rate in integrated system was 0.54 h^{-1} which was 1.4 and 54.0-fold higher than that in biocathode BES (0.39 h^{-1}) and ASR (0.01 h^{-1}), respectively (Fig. 2A). The improved decolorization in the integrated system probably resulted from the synergistic effects of the possible functional structures in the reactor, including cathode electrical stimulation, cathode biofilm catalysis and the anaerobic sludge degradation.

It has been reported that the AO7 was firstly initiated by the cleavage of —N=N— in the BES, with sulphanilic acid (SA) and 1-amino-2-naphthol (AN) as the possible intermediates (Kong et al., 2013; Mu et al., 2009). The anaerobic treatment of this type of dye might be also with the cleavage of the azo bond by a reduction reaction when there was no co-substrate added. The azo bond might be destroyed with the aid of an anaerobic azo reductase and electron transfer by a redox mediator that acted as an electron shuttle between the extracellular dye and the intracellular reductase (Solís et al., 2012). However, anaerobic reduction of azo dye was limited by the transference rate of the reducing equivalents to the azo bond (Solís et al., 2012), which might be the reason for low decolorization in ASR. In this study, SA was found nearly equimolar concentration based on the AO7 decolorization in the integrated system, similar to the biocathode BES (Fig. 2B), indicating that the AO7 decolorization in the integrated system was also completely reduced and not adsorbed by the sludge or electrode. However, the other aromatic amine resulting from the cleavage of the azo bond (AN) was not directly observed most likely because of its low stability and autoxidation even in a low oxygen amount (Mu et al., 2009). Further considering the relative low kinetic rate in ASR compared to that in the biocathode BES (Fig. 2A), it was not the anaerobic sludge but the biocathode of the BES module played an important role in AO7 decolorization of the integrated system. Azo dye could perform relative easy cleavage of azo bond at cathode due to efficient electrons produced from anode, especially with the catalysis of biofilm at cathode.

Although the AO7 decolorization efficiency (96.2 ± 1.8% vs. 84.9 ± 3.8%) and SA formation efficiency (96.0 ± 0.9% vs. 84.4 ± 0.8%) in the integrated system were not significantly different from that in biocathode BES, which were mostly due to the improvement room for degradation in the batch mode within 7 h