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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.

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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.

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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 technol-

ogies (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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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 (Ultrax 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 20Ω 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 ($96.2 \pm 1.8\%$ vs. $84.9 \pm 3.8\%$) and SA formation efficiency ($96.0 \pm 0.9\%$ vs. $84.4 \pm 0.8\%$) 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

Fig. 2. Degradation performance of the integrated system in comparison with biocathode BES and anaerobic sludge reactor (ASR), including (A) AO7 decolorization, (B) SA formation within 7 h, and (C) COD removal within 24 h (100 mg L⁻¹ AO7 under applied voltage of 0.5 V).

(Fig. 2A and B), it could not conclude that the anaerobic sludge was inefficient at this moment. The COD removal within 24 h in the biocathode BES was only $2.32 \pm 1.3\%$ mostly due to the unmineralized AO7 products, while in the integrated system with anaerobic sludge, the COD removal was increased to be $27.2 \pm 1.1\%$ (Fig. 2C). It suggested that the anaerobic sludge had a major contribution to the COD removal in the integrated system, which was dominated important to the wastewater treatment. Further considering the difference between the integrated system and BES, both the nature of the treatment process and the mechanism of the azo dye degradation were also different. In the BES, the mechanism of azo dye degradation was that the azo bond was cleaved at cathode by receiving the electrons from anode to realize reductive decolorization, which was actually a pretreatment process in the wastewater treatment. It reflected the BES role in pretreatment, while the intermediate products were still existing in the water. In the integrated system of BES and anaerobic sludge, there were not only the cleavage of azo bond under catalytic BES but also the further degradation of intermediate products under anaerobic sludge. It was a set of pretreatment and treatment processes in one reactor.

It can be concluded that the individual anaerobic sludge reactor could potentially be improved with the employment of BES module. When they worked together as an integrated system, the azo bond was cleaved at cathode, resulting in the easy degradation and finally COD removal under anaerobic sludge.

3.2. The electrochemical characterization of the integrated system

After demonstrating the better azo dye degradation in the integrated system, it is essential to investigate the bioelectrochemical characterization of the integrated system to demonstrate the bioelectrochemical stimulation, with biocathode BES as control.

Results showed that the presence of anaerobic sludge could shorten the startup time and benefit to the startup of reactor. It took about two days in the integrated system to reach the condition of stable electrode potentials (-0.479 ± 0.023 V for anode potential and -0.979 ± 0.023 V for cathode potential with 0.5 V applied voltage), while that was four days for the biocathode BES (Fig. 3A and B). Faster startup in the integrated system was possibly due to that the anaerobic sludge at the bottom of the reactor could accelerate the microbial cells attachment on cathode and benefit to the formation of biofilm, which would result in the rapid decrease of cathode potential and anode potential.

Although the integrated system and biocathode BES had the similar anode potential and cathode potential, the integrated system could obtain better current production with the maximum current of 0.028 ± 0.002 A than that in biocathode BES (0.020 ± 0.003 A), which was 1.4-fold increased. Moreover, integrated system could stabilize the current at a value of at least 0.016 ± 0.004 A, while that for biocathode BES was only 0.006 ± 0.002 A (Fig. 3C). The higher current in the integrated system may be attributed to a more efficient electron transfer or a lower cathode resistance (Liu et al., 2014). It would cause the stronger stress to induce a higher electrochemical activity based on the electrons interaction between biofilm and the electrode, and resulted in the higher electrochemical reaction kinetics in the integrated system (Kong et al., 2014a), which was consistent to the decolorization results.

EIS analysis indicated that the cathode resistance could be improved with the integrated system compared to biocathode BES. Results showed that the cathode resistance of the integrated system was 5.8Ω , which was 1.6-fold lower than the biocathode BES (9.0Ω). The ohmic resistance (R_{ohm}) of the integrated system was only 0.358Ω compared to biocathode BES of 1.384Ω , indicating the enhanced electron transfer process in the integrated system. The corresponding charge transfer resistance (R_{ct}) was 1.245 and 3.349 Ω , respectively (Fig. 3D). Smaller R_{ct} in the integrated system indicated the rapid biofilm formation and the stability of electrode biofilm. The BES module may act as solid media to form a hybrid attached/suspended growth system in an integrated fixed-film-activated sludge process (Zhang et al., 2013), which could reduce the electron transfer and charge transfer. Decreasing the cathode resistance could give rise to a high current production and thus a rapid decolorization, suggesting that the integrated system was superior to the BES in cathode performance.

3.3. Potential and challenge

It is of great interest to explore alternative technologies for the integration of anaerobic sludge reactor (ASR) and bioelectrochemical system (BES). This study developed an integrated system of BES and anaerobic degradation by embedding a BES module with surrounding electrode deployment into an anaerobic sludge reactor (Fig. 1). The feasibility of the improved azo dye degradation in the integrated system demonstrated that the removal of pollutants in the anaerobic system can be enhanced with addition of

Fig. 3. Electrochemical characterization of the integrated system compared with biocathode BES for 10 cycles, including (A) anode potential, (B) cathode potential, (C) current, and (D) cathode resistance, performed with 100 mg L^{-1} AO7 under applied voltage of 0.5 V.

BES module (Fig. 2). In the integrated system, electric reduction still dominated the total integrated system performance and the anaerobic sludge could contribute to the COD removal, suggesting that the electrochemical reduction could serve as a potential pre-treatment unit for the treatment of azo dye wastewater. Moreover, such BES module as a choice in the integrated system has proven to be a good structure in many studies (Huang et al., 2011; Jacobson et al., 2011; Kong et al., 2013). It can compress the distance between electrodes, increase the utilization of the membrane, thus effectively reduce the electron and ion transfer resistance and finally improve the BES performance (Fig. 3). This design of embedding BES module into anaerobic reactor could be scale-up as the imagination exhibited (Fig. 1D) and also would be scalable with successive modules embedding into the existing treatment facilities. This study may offer a new sustainable approach and useful information for the efficient and cost-effective treatment of azo dye.

There are still some challenges for this technology application, including the optimization of the integrated system, the interaction between the BES module and anaerobic sludge, and the tolerance issues in the integrated system. Besides, further effort is still needed to study new modification in electrodes and to explore low-cost membranes, which is essential to develop a successful integration. Future progress in the above aspects will not only improve the wastewater treatment performance in integrated system but also have high theoretical research value and practical significance in the construction and application of the integrated process.

4. Conclusions

Integrating bioelectrochemical system (BES) module with anaerobic sludge reactor can enhance the azo dye treatment on

the cooperation of bioelectrochemical technology and anaerobic process. The cleavage of azo bond can be strengthened by more electrons supplied through the BES module and its products can also be degraded through anaerobic sludge, resulting in the COD partial removal. It will provide a theoretical basis for the development of integrated system, which is critical to accelerate the popularization and application of this technology in practical refractory wastewater.

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