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Enhanced bioelectricity generation and azo dye treatment in a reversible photo-bioelectrochemical cell by using novel anthraquinone-2,6-disulfonate (AQDS)/MnO_x-doped polypyrrole film electrodes



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HIGHLIGHTS

• Novel AQDS/Mn/PPy electrode was prepared by one-step electropolymerization method.

• Interaction of AQDS and Mn with PPy exhibited excellent electrocatalytic activity.

• AQDS/Mn/PPy electrode enhanced azo dye treatment and power output in RPBEC.

• Anodic and cathodic reaction were simultaneously improved during polarity reversion.

• RPBEC with AQDS/Mn/PPy electrode explores efficient approach for wastes treatment.

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ABSTRACT

A novel anthraquinone-2,6-disulfonate/MnO_x-doped polypyrrole film (AQDS/Mn/PPy) electrode was prepared by one-step electropolymerization method and was used to improve performance of a reversible photo-bioelectrochemical cell (RPBEC). The RPBEC was operated in polarity reversion depended on dark/light reaction of alga *Chlorella vulgaris* by which sequential decolorization of azo dye and mineralization of decolorization products coupled with bioelectricity generation can be achieved. The results showed that formation of uniform AQDS/Mn/PPy film significantly enhanced electroactive surface area and electrocatalytic activity of carbon electrode. The RPBEC with AQDS/Mn/PPy electrodes demonstrated 77% increases in maximum power and 73% increases in Congo red decolorization products mineralization rate after polarity reversion, respectively, compared to the RPBEC with bare electrode. This was resulted from simultaneous dynamics improvement in half-reaction rate of anode and photobiocathode due to enhanced electron transfer and algal-bacterial biofilm formation.

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1. Introduction

With growing concerns about environmental issues and sustainable energy supply, biological solar energy technologies are gaining increasing attention. Photo-Bioelectrochemical Cell (PBEC) which based on the synergism of exoelectrogens and phototrophic microorganisms provides a new approach to convert organic wastes and sunlight into bioelectricity while simultaneously completing wastes treatment (Xiao et al., 2012). Among the various PBECs, the most reported concept is the integration of dark anode for electron production from organic wastes and photo-biocathode for in-situ cathodic oxygen supply (Xiao et al., 2012; Xiao and He, 2014). This integration shows a number of potential advantages. Oxygen production as a result of photosynthesis in the cathode can eliminate the disadvantage of using mechanic aeration due to unnecessarily high energy consumption, which is the most important consideration in the design of a sustainable PBEC for practical application. Microalgae, ubiquitously present in natural water body, are commonly used in the cathode of the PBECs, such as *Chlorella vulgaris* (Wu et al., 2013), *Chlamydomonas reinhardtii* (Raman and Lan, 2012) and *Spirulina*

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platensis (Lin et al., 2013). Giving an appropriate illumination strength and period, the concentration of dissolved oxygen in a cathode compartment containing microalgae can be comparable to or better than mechanic aeration (Xiao et al., 2012; Wu et al., 2013; Juang et al., 2012). Besides bioelectricity generation, the special redox environment of the anaerobic anode and aerobic biocathode of the PBEC could also create favorable conditions for degradation of some recalcitrant organic pollutants. This has been demonstrated, for example, for azo dye which are needed to be mineralized via sequential anaerobic and aerobic biotreatment (Fernando et al., 2014; Sun et al., 2015; Cui et al., 2012).

Despite the promising potential of PBEC in organic wastes treatment and waste-based bioenergy recovery, the poor power output and the low treatment efficiency of the PBEC are still the bottlenecks restricting its application (Lee et al., 2015). Enhancing the microbial extracellular electron transfer through anode modification with redox mediator, such as anthraguinone-2.6-disulfonic acid disodium salt (AQDS) (Feng et al., 2010a), and cathode modification with transition metal oxides, such as MnO_x, (Mao et al., 2010) has been regarded as an effective strategy for improving performance of bioelectrochemical cell based on its electrochemical essence. Recently, one-step electrochemical polymerization of pyrrole to form highly conductive polypyrrole/dopant composite film on the surface of the electrode has been explored as a convenient approach towards electrode modification (Feng et al., 2010b). Composite electrode by electropolymerizing pyrrol with redox mediator or metal oxides on carbon material for enhancing anodic electrons transfer and cathodic oxygen reduction in BEC have been domenstrated, respectively (Feng et al., 2010a; Grover et al., 2014). Nevertheless, synthesizing a ternary composite electrode with both of the redox mediator and transition metal oxide in the polypyrrole film for simultaneous improvement of anodic and cathodic performances in a PBEC with polarity reversion are still unexplored.

In our previous work, a reversible PBEC (RPBEC) with well acclimatized algal-bacterial biofilm electrodes was developed. The RPBEC can achive simultaneous two-step mineralization of azo dve and production of bioelectricity with additional benefits of simplification of manipulation and buffer minimization (Sun et al., 2015). Despite the difference in reaction mechanisms of the anode and cathode, there is no doubt that electron transfer is a rate-limiting step in both the half-reaction of anode and cathode which directly related to the simultaneous azo dye treatment and bioelectricity generation processes in the RPBEC. In this work, a novel AQDS/Mn-doped polypyrrole film (AQDS/Mn/PPy) electrode was prepared by one-step electropolymerization method and was incorporated into the RPBEC for enhancing simultaneous azo dye treatment and bioelectricity generation. A combination of electrode modification and RPBEC may open the opportunity to construct a high-performance RPBEC for practical application for simultaneous organic wastes treatment and bioelectrical energy production.

2. Materials and methods

2.1. Preparation of AQDS/Mn/PPy electrode

The bare electrode substrate was a piece of graphite felt $(5 \text{ cm} \times 6 \text{ cm} \times 0.5 \text{ cm})$ connected to an external circuit by an embedded titanium wire. Prior to use, graphite felt were soaked in acetone and nitric acid solution (1 N) for 12 h successively, then boiled it in deionized water for overnight. The one-step electropolymerization of AODS/Mn-doped polypyrrole film on the graphite felt surface was conducted in a three-electrode electrochemical cell containing 0.1 M pyrrole (Aldrich), 5 mM

AQDS (Aldrich) and 5 g/L MnSO₄, with saturated calomel electrode (SCE) as reference electrode and a Pt foil (1 cm \times 2 cm) as counter electrode. Upon a constant potential of 0.8 V applied by using an electrochemical workstation (Model 2273, Princeton Applied Research), the AQDS/Mn/PPy film was formed on the graphite felt surface and the total charge passed to the working electrode was 0.5 C/cm² (per geometric anode area). The freshly prepared AQDS/Mn/PPy electrode was gently washed with deionized water to remove aqueous components and then thoroughly rinsed in a 0.1 M phosphate buffered solution (PBS, pH 7.0) before further use. For comparison, AODS-doped and Mn-doped PPy film electrode were also prepared by the same method, respectively.

2.2. RPBEC setup and operation

The configuration of the RPBECs was the same to our previous study (Sun et al., 2015). Generally, two identical cubic chambers with internal dimensions of 8 cm × 8 cm × 4 cm (256 mL) were assembled. The anode and cathode were inserted into each chamber and separated by a cation exchange membrane (CEM, Zhejiang Qianqiu Group Co., Ltd. China) with a projected surface area of 16 cm² (4 × 4 cm). The anode and cathode were placed parallel to each other at approximately 1 cm from the CEM and connected with titanium wire via a resistor of 500 Ω unless otherwise specified. In this study, the novel AQDS/Mn/PPy electrodes were used as anode and also as the cathode.

Chlorella vulgaris (obtained from the Institute of Hydrobiology, Chinese Academy of Sciences) and anaerobic sludge (obtained from Liede domestic wastewater treatment plant, Guangzhou, China) were used as inoculum sources for both the anode and cathode of the RPBEC. Chlorella vulgaris were precultured in sterile BG-11 liquid medium and 20 ml of Chlorella vulgaris cultures in the logarithmic growth phase were added to the PBEC to give an initial concentration of approximately 1×10^7 cell/mL (calculated from the growth curve of Chlorella vulgaris measured at OD 685 nm). Anaerobic sludge was washed three times using deionized water to remove residual carbon sources and then filtered through a 0.25-mm pore size sieve to remove impurities, and added to the RPBEC at a final concentration of 2 g volatile suspended solids per reactor volume. The anode was fed with 10 mM nutrient buffer solution (Sun et al., 2015) containing glucose (500 mg COD/L) and Congo red (300 mg/L). The same medium was used in the cathode except for the replacement of glucose and Congo red by NaHCO₃ (0.4 g/L). The RPBECs were operated in polarity reversion mode. During operation, the anodic chamber was sealed off and covered with aluminum foil while the cathodic chamber was continuous illuminated using a fluorescent lamp (52 W, Philips FBH059). Once voltage decreased below 30 mV, the polarity of the RPBEC was reversed. The previous cathode was switched to anode (supplemented with glucose and covered with aluminum foil) and the previous anode was switched to photo-biocathode (supplemented with NaHCO₃ and continuous illuminated). During this process, sequential decolorization of Congo red and mineralizaton of decolorization products (comprising aromatic amines or their derivatives) in single chamber was achived without needing to transport the decolorization products from the anode to cathode for further mineralization, leads to a sigificant simplification of manipulation. Meanwhile, continuous bioelectricity generation was obtained under extreme low buffer due to self-neutralization of acidity and alkalinity in electrolyte accumulated before polarity reversion, resulting in a sigificant reduction in operation cost. For comparison, the RPBEC with bare electrode was also operated at the same conditions as described above. Schematic diagram of preparation of the AQDS/Mn/PPy electrode and operation of the RPBEC were shown in Fig. S1.

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2.3. Analytics and calculations

2.3.1. Electrode surface characterization

The surface morphologies of the bare, AODS-doped, Mn-doped and AQDS/Mn/PPy electrodes were examined by using a SEM (XL-30, Philips, Holland).

The analyses of surface elements of the AQDS/Mn/PPy electrode and bare electrode were performed by X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific Co., USA) with a monochromatic Al Koxsource, and the XPS data for each atom was fitted with the 'XPS peak' software.

The electrochemical properties of the bare, AODS-doped, Mndoped and AQDS/Mn/Ppy film electrodes were measured by cyclic voltammetry (CV) on electrochemical workstation (Model 2273, Princeton Applied Research) using the same three-electrode setup used for electropolymerization. The CVs were recorded between -2.0 and 1.0 V (vs. SCE) in either N₂- or air-saturated PBS solution (100 mM) at room temperature with a scanning rate of 5 mV/s.

2.3.2. Evaluation of performance of the RPBEC

2.3.2.1. Electricity genearation. The cell power density curves and the electrode polarization curves were measured by varying the external resistor over the range from 50 to 5000 O when the performance of RPBEC approached steady state. At each fixed resistance, voltage was collected by a high-precision data acquisition system (Model 2700, Keithly Instruments, USA) when a relatively constant value was reached. Current density (I) was calculated as I = V (cell voltage)/R (external resistance), and power density (P) was calculated as P = V × I. Both I and P were normalized to the geometric anode surface area. The anode potentials were collected by inserting a SCE electrode into the anode chamber. The cathode potentials were calculated as the sum of the anode potential and the cell voltage.

2.3.2.2. Dye degradation. Congo red decolorization and decolorization rate were measured and calculated according to previous study (Sun et al., 2015). The extent of mineralization of Congo red was estimated in terms of chemical oxygen demand (COD) removal which was measured by dichromate oxidation described in standard method (APHA et al., 1998). Degradation rate constants (h⁻¹) were deduced from the slopes of $-\ln [C_t/C_0]$ vs. reaction time (t) and by performing linear regression, where C_0 is the initial dye concentration or COD, C_t is the dye concentration or COD at reaction time t. Each data point represented the mean value of three values obtained from replicate tests.

2.3.3. Biofilm characterization

Electrochemical activity and electrochemical impedance behavior of the biofilm electrode were evaluated by CV and electrochemical impedance spectroscopy (EIS) in three-electrode mode, with the anode (or cathode) as working electrode, the cathode (or anode) as counter electrode and a SCE inserted into the anode (cathode) chamber as reference electrode. CVs were performed within a potential window between -1.0 and 0.3 V (vs. SCE) at a scan rate of 5 mV/s. EIS measurements were carried in a frequency range of 100 kHz to 5 mHz with an ac signal of 10 mV amplitude, and the data obtained were fitted and simulated by ZSimpWin3.10 software (Echem., US) based on predetermined equivalent electrical circuit. Both the CV and EIS tests were performed under open circuit voltage (OCV). The morphologies of the biofilm electrode were examined using a SEM (XL-30, Philips, Holland). Before observation, samples were collected and fixed overnight with paraformaldehyde and glu-taraldehyde in a buffer solution (0.1 M cacodylate, pH 7.5, 4 °C), followed by washing and dehydration in water/ethanol. Samples were then coated with Au/Pt before SEM observation.

3. Results and discussion

3.1. Characterization of AQDS/Mn/PPy electrode

3.1.1. Surface morphologies

Surface morphologies of the AQDS/Mn/PPy, AODS/PPy, Mn/PPy and bare electrodes were visualized by SEM (Fig. S2). It can be seen that the surface of the bare electrode is relatively clean and smooth (Fig. S2A). After electropolymerization, the surfaces of carbon fibers were uniformly covered by the PPy film with various dopants, which are compact and continuous (Fig. S2B-S2D). The SEM images at high magnifications distinctly observed that AQDS and sheet-like MnO_x were fully mixed with PPy to form a uniform composite film with an average thickness of approximately 14 µm on the surface of carbon fibers (Fig. S2D), implying that the AQDS/ Mn/PPy electrode was successfully synthesized by the one-step electropolymerization method. Among the three components, the PPy could play a key role in the formation of uniform composite film since the PPy can serve as a template for uniform dispersion of AQDS and MnO_x (Lu et al., 2013). It was noted that electropolymerization of AQDS/Mn/PPy composite film gave rise to a more rougher surface of electrode surface than bare electrode, leading to an increase in electrode surface area.

3.1.2. Chemical composition and structure

XPS was employed to analyze the chemical composition and structure of the AQDS/Mn/PPy electrode (Fig. S3). The XPS spectra clearly show the characteristic peaks of C, N, O, and Mn at around 284.4, 398.3, 530.4 and 641.8 eV, respectively, confirming the presence of the four elements on the surface of the electrode (Fig. S3A) (Jia et al., 2016; Burkitt et al., 2016; Zhou et al., 2016). The C1s core-level spectrum can be fitted into four peaks (Zhou et al., 2016). The dominant peak at 284.4 eV can be attributed to the C-C bond of the sp2 graphitic carbon, whereas the peak at 285.1 eV can be attributed to the C-N bond which are most likely originated from porrole or PPy since no additional nitrogencontaining compounds is added during the electrodeposition process. The peaks at 286.0 and 288.3 eV are associated with C-O and C=O bonds, respectively (Fig. S3B). The origin of the two peaks is probably related to the oxygen-containing functional groups in AQDS molecule (Fig. S3F). The N1s peak has only one contribution around 400.0 eV and can be associated with -NH- groups in PPv (Fig. S3C, S3F) (Sha et al., 2014; Ilton et al., 2016), indicating that the porrole monomers are oxidized during electropolymerization process to form PPy. In the high resolution XPS spectrum of Mn2p, Mn2p_{3/2} and Mn2p_{1/2} have been deconvoluted into four components peaks (Fig. S3D). In this case, 639.8 and 651.1 eV are attributed to Mn³⁺, while 641.5 and 652.5 eV are attributed to Mn⁴⁺, suggesting that there are mixed valence states of Mn³⁺ and Mn^{4+} in the composite film (Liu et al., 2014; Pan et al., 2016). The existence of MnO_x and AQDS in the composite film electrode are also reflected in the O1s core level spectrum, as shown in Figure S3E. The peak with highest intensity indicates Mn–O–Mn oxide which is predicted at 529.4 eV (Liu et al., 2010). Two minor peaks at 531.0 eV and 533.0 eV corresponding to C-O (or S-O) and COOH species, repectively, confirming the presence of AQDS molecule (Lim et al., 2014).

3.1.3. Electrochemical characterization

CVs were performed to evaluate electrocatalytic activity of the AQDS/Mn/PPy electrode. As shown in Fig. 1, the voltammetric responses of the bare electrode were flat in both O_2 and N_2 -saturated PBS solution. By contrast, distinctive reduction peaks were observed with the AQDS/PPy, Mn/PPy and AQDS/Mn/PPy electrode in O_2 -saturated PBS solution, because of oxygen reduc-



Fig. 1. CVs for the bare electrode and PPy film electrodes with dopants in O₂-saturated and N₂-saturated PBS solution (100 mM, pH7).

tion on these electrodes (Fig. 1A). Specially, the catalytic activity of the AQDS/Mn/PPy film electrode for ORR was much higher as compared to the Mn-doped polypyrrole film because of more than 3fold increases in peak current (0.014 vs. 0.06 A) but is slightly lower than that of the AODS-doped polypyrrole film electrode (with a peak current of 0.07 A). Slight decrease in ORR catalytic activity for AQDS/Mn/PPy electrode compared to the AODS/PPy electrode could be ascribed to higher redox of AODS than that of MnO_x. However, the application potential of the AODS/Mn/PPy electrode in RPBEC is doubtless because the transition metal oxides are thought to be necessary for enhancing biocatalyzed oxygen reduction in biocathode of the BEC due to facilitated electrons transfer from oxygen to cathodic electrode (Mao et al., 2010; Rosenbaum et al., 2011). In addition, the AQDS/Mn/PPy electrode also resulted in much larger current responses when compared to the bare electrode in the scan range between -2.0 V to 1.0 V in N2-saturated PBS solution (Fig. 1B), indicating that AQDS/Mn/ PPy play an important role in increasing the electroactive surface area (Schröper et al., 2008). The enhancement of electrocatalytic activity for the AQDS/Mn/PPy electrode should be mainly from the synergistic catalytic effect of AQDS, MnO_x and PPy, i.e. PPy not only provides more electrochemically active sites for electron transportation but also serves as a template for uniformly dispersing of AQDS and Mm with large surface, while the presence of AQDS and MnO_x in PPy matrix on the other hand helps in bypassing the chain defects to further enhance the conductivity and catalytic activity of PPy (Grover et al., 2014) The CV results further confirmed the successful synthesis of the AQDS/Mn/PPy electrode and domenstrated excellent electrocatalytic activity of the composite electrode.

3.2. RPBEC performance with AQDS/Mn/PPy electrode

3.2.1. Electricity generation

The novel AQDS/Mn/PPy electrodes were incorporated into and used as anode and cathode in a RPBEC for enhancing simultaneous azo dye treatment and bioelectricity generation. Fig. 2 shows a comparison of the power output and electrode polarization between the RPBEC with AQDS/Mn/PPy electrodes and the RPBEC with bare electrodes. It can be seen that the RPBEC with AQDS/Mn/PPy electrodes generated substantially larger power densities versus the RPBEC with bare electrodes (Fig. 2A). The maximum power density of the RPBEC with AQDS/Mn/PPy electrodes was 29.46 mW/m² before polarity reversion and 84.58 mW/m² after polarity reversion, increased by 77% (16.68 mW/m²) and 198% (28.35 mW/m²), repectively, as compared with the RPBEC with bare electrodes.

Analysis of electrode polarization curves found that increases in power ouput were attributed to performance improvement of the anode and photo-biocathode (Fig. 2B). The slop of both the anodic and photo-biocathodic polarization curve of the RPBEC with AQDS/ Mn/PPy electrodes showed more gentle decreases as compared to that of the RPBEC with bare electrode with increasing current density, evidently indicating alleviative polarization (or lower driving force for the bio-electrochemical reaction at high currents) in the anode and photo-biocathode. Such improvements are likely to be attributed to an increase in efficiency of electron transfer from algal-bacterial biofilm to the anode and from the biocathode to oxygen in the presence of AQDS and MnOx which kinetically promoted the reaction rates of substrate oxidation and electric energy conversion at anode, and oxygen reduction at biocathode in the RPBEC. It was worth noting that the extent of improvement in electrode performance after polarity reversion was more notable than that before polarity reversion. Previous study has shown that accumulated protons at the anode and hydroxyl at the cathode before polarity reversion can be used as their respective reactants after polarity reversion, resulting in rate enhancements of halfreaction for the anode and cathode (Cheng et al., 2010; Strik et al., 2010). In addition, the decolorization products of Congo red can also serve as redox mediator to accelerate electrons transfer from cathodic electrode to oxygen after polarity reversion (Sun et al., 2011). The enhancement resulted from polarity reversion and Congo red decolorization could be further amplified by the AQDS/Mn/PPy electrode due to further dynamics improvement in half-cell reaction rate in the RPBEC. These results indicated that the AQDS/Mn/PPy can significantly enhance the bioelectrochemical performance of the anode and photo-biocathode simultaneously in the RPBEC.

Complementary to electrode polarization measurements, EIS is an effective technique for probing the electrochemical features of surface-modified electrode, which provides useful information on redox reaction resistance and equivalent series resistance of the electrode (He and Mansfeld, 2009). Fig. 3 shows the representative impedance spectra (Nyquist plots) of both the anode and cathode for the RPBEC with AQDS/Mn/PPy electrode and the RPBEC with bare electrode before and after polarity reversion. As clearly indicated by the results of the Nyquist plots, charge-transfer resistance (R_{ct}) , which is reflected by the diameter of the semicircular arc of the curve (He and Mansfeld, 2009) overwhelmed the anode and cathode impedance of the RPBEC with bare electrodes, which were estimated to be 82 and 371Ω before polarity reversion, and decreased to 44 and 147 Ω after polarity reversion, respectively, by fitting the impedance data with the equivalent circuit (Fig. S4). In contrast, the anode and cathode of the RPBEC with



Fig. 2. Comparison of performance of RPBEC with bare electrodes and with AQDS/Mn/PPy electrodes in term of power output (A) and electrode polarization (B).



Fig. 3. Nyquist plot for anodic (A) and cathodic (B) biofim in the RPBEC with bare electrodes and the RPBEC with AQDS/Mn/PPy electrodes.

AQDS/Mn/PPy electrode exhibit much smaller semicircle in high frequency region (with R_{ct} of 24 and 7 Ω before polarity reversion, and 8 and 3 Ω after polarity reversion calculated by fitting the impedance data with the equivalent circuit shown in Fig. S5), and a nearly vertical warburg curve, indicating much lower R_{ct} at electrode/electrolyte interface and better charge propagation behavior (Si et al., 2011) This observation suggests that the rate of the anodic and cathodic bioelectrochemical reaction is considerably improved by AQDS/Mn/PPy electrode, to be consistent with the results of the electrode polarization test.

CVs were performed to reveal the effect of AQDS/Mn/PPy modification on biocatalytic activities of the electrode biofilms in the RPBEC. As is shown in Fig. 4, the voltammograms of AQDS/Mn/ PPy electrodes in the presence of biofilm showed much larger redox current against the bare electrode during the polarity reversion of the RPBEC, which indicated that the half-reaction of anode and cathode were considerably enhanced by AODS/Mn/PPv modification on electrode. It is widely recognized that the outermembrane c-type cytochromes of bacteria play a key role in extracellular electron transfer in bioelectrochemical system (Huang et al., 2011; Yang et al., 2012). The increases in current responses caused by the AQDS/Mn/PPy electrodes were most likely due to enhanced electron-transfer efficiency from intracellular cell to extracellular electrode and final electron acceptor via interaction between the c-type cytochromes with immobilized AQDS and MnO_x. On the one hand, the quinone groups in AQDS allow the heme rings of c-type cytochromes more accessible to electrode surface, which causes more cytochromes available for shuttling electron transfer (Lowy et al., 2006). On the other hand, the cycle of Mn (IV or III) reduction and subsequent reoxidation of Mn (II) via the catalysis of manganese-oxidizing bacteria (involve electrons transfer at the interface between bacteria and MnO_x) enhances the electron transfer from the cathodic electrode to oxygen (Huang et al., 2011; Mao et al., 2010). As a result, enhanced anodic substrate conversion to current and cathodic oxygen reduction were achived simultaneously.

3.2.2. Dye treatment

The removal of Congo red for an initial concentration of 300 mg/ L in the RPBEC with AQDS/Mn/PPy electrodes was examined and compared with the RPBEC with bare electrodes. The Congo red was first decolored at dark anode and resulting decolorization products were further mineralized after the anode reversed to the photo-bicathode. The results clearly show that the two-step degradation of Congo red in the RPBEC was significantly enhanced by the AQDS/Mn/PPy electrodes (Fig. 5). The decolorization and mineralization of Congo red occurred much faster in the RPBEC with AQDS/Mn/PPy electrodes compared to the RPBEC with bare electrodes at any given time during entire degradation period (Fig. 5A1, B1). Furthermore, the degradation kinetics of Congo red fitted well to the pseudo first-order kinetics model, which also showed higher k of Congo red degradation for the RPBEC with AQDS/Mn/PPy electrodes, compared to that of the RPBEC with bare electrodes (Fig. 5A2, B2). The k value of Congo red decolorization and decolorization products mineralization for the RPBEC with AQDS/Mn/PPy electrodes were 0.178 and 0.0031 h⁻¹, which represent increases of 73% and 138%, in comparison with the RPBEC with bare electrodes (0.103 and 0.0013 h^{-1}), respectively. Enhancement in Congo red decolorization in the anode of the RPBEC should be expected since AODS can efficiently mediate electron transfer from bacteria to azo dye, resulting in accelerated reductive decolorization of Congo red (Silva et al., 2012). However, the reason for enhanced mineralization of decolorization products by the AQDS/Mn/PPy electrodes in the RPBEC might be complicated. Our previous study showed that the mineralization of decolorization products of azo dye (comprising aromatic amines or their derivatives) in the aerobic biocathode was not a currentdependent process and could be largely dependent on the presence



Fig. 4. CVs for anodic (A) and cathodic (B) biofilm in the RPBEC with bare electrodes and AQDS/Mn/PPy electrodes.



Fig. 5. Decolorization (A) and mineralization (B) of Congo red in the RPBEC with bare electrodes and the RPBEC with AQDS/Mn/PPy electrodes.

of aromatic amines-degrading bacteria which can utilize the aromatic amines as sole carbon source (Sun et al., 2011). In addition, a partial aromatic amines could be subjected to photodegradation due to photoreaction in the presence of algae (Norvill et al., 2016; Liu and Liu, 1992). As stated previously, SEM clearly observation the formation of compact AQDS/Mn/PPy film on surface of carbon fiber which created a rough surface and provided much higher specific surface area for accommodating more functional bacteria, such as aromatic amines-degrading bacteria, and algae on the surface of the electrodes in the RPBEC.

Moreover, enhanced extracellular electron transfer by the AQDS/Mn/PPy film could also contribute to enhance formation of electrochemically active biofilm on electrode since extracellular electron transfer is a general mechanism whereby microorganisms generate energy for cell growth (Rosenbaum et al., 2011; Zhao et al., 2016). Therefore, the most likely reason for the enhanced mineralization of decolorization products by the AQDS/Mn/PPy electrodes could be due to the increases in algal-bacterial biofilm biomass on electrode surface. In order to confirm the speculation, the surface morphologies of the biofilm was also observed by SEM (Fig. S6), which clearly evidenced a more compact algal-bacterial biofilm formed on the surface of the AQDS/Mn/PPy electrode, compare to that of the bare electrode.

4. Conclusion

The RPBEC performance in terms of bioelectricity generation and azo dye treatment was significantly improved by using novel AQDS/Mn/PPy electrode prepared by one-step electropolymerization method. Electropolymerization enabled AQDS and MnO_x to fully mix with PPy to form uniform composite film on carbon electrode, and synergetic effect of AQDS, MnO_x and PPy contributed to increased electroactive surface area and enhanced electrocatalytic activity of carbon electrochemical reaction dynamics of anode and photo-biocathode in the RPBEC due to enhanced electron transfer and algal-bacterial biofilm formation, resulting in increased power output and enhanced two-step biodegradation of azo dye.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.11. 038.

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