Degradation of azo dye wastewater by the combination process of 3D BER and CW-MFC

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Abstract. The treatment of azo dye wastewater has become a hot issue in the area of water pollution control. In this paper, a novel combined process of constructed wetland-microbial fuel cell (CW-MFC) and three dimensional biofilm electrode reactor (3D BER) was carried out for treatment of reactive brilliant red X-3B dye wastewater. Decolorization rate, COD removal rate and electricity generation in the combination process were studied, and the main factors affecting the system’s performance were also investigated. The results showed that the decolorization rate of combination process (3D BER-CW-MFC) was over 96%, and closed-circuit CW-MFC had better decolorization effect than open-circuit CW-MFC. COD removal rate of the combination process was far higher than the 3D BER and CW-MFC operated alone (78.9%~90.8% and 50.6%~66.2%, respectively). With the increase of influent dye concentration in the 3D BER, Cell voltages of the CW-MFCs all increased firstly and then decreased. The cell voltage reached the maximum at influent dye concentration of 600 mg L\(^{-1}\), and then decreased by 6.42%~14.34% after the dye concentration increased to 1000 mg L\(^{-1}\). In addition, cell voltage could be enhanced by increasing the cathode area of CW-MFCs, due to improved cathode potential and reduced total internal resistance of the system.

1. Introduction

With the rapid development of industry and agriculture, the gradually increased dye wastewater discharge has become a serious threat to human’s health and environment. Generally, Azo dyes are formed by the coupling of aromatic amines which has been diazotized, and active methylene compounds in phenols and aromatic amines [1]. The extremely stable chemical properties and potential harm of azo dye molecules in wastewater make it the recognized refractory organic pollutant.

Presently, physical, chemical, biological, ultrasonic, photocatalytic and electrocatalytic methods have been used for azo dye wastewater treatment. Vishwakarma [2] found the decolorization rate reached to 99% within 18 hours, when dye wastewater (direct blue) was treated with immobilized enzyme. Munagapati and Kim [3] found that the maximum adsorption capacity of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder was estimated to reach 163 mg/g. Li’s [4] studies on carbonate-activated hydrogen peroxide (CAP) oxidation processes obtained well AO7 decolorization performance. When H\(_2\)O\(_2\) concentration increased from 5 mM to 50 mM, the decolorization efficiency increased linearly from 5.95±0.32% to 94.03±0.39%. Harichandran [5] demonstrated that Fenton and Sono-Fenton methods could decolor DR81 dyes effectively under higher dye wastewater. However, these single traditional methods have been difficult to satisfy with
the increasing environmental protection requirements. Therefore, more efficient and harmless methods for refractory dye wastewater treatment should be developed imminently. The results of azo dye wastewater treated by a mixed anaerobic digestion (AD) bioreactor with a built-in bioelectrochemical system (BES) [6] showed that the quality of the effluent was further improved after the BES joined. Long [7] established a combined system with microbial fuel cell-photoelectrocatalytic cell (MFC-PEC) to treat azo dye wastewater, and the results displayed that the joined PEC promoted COD removal and dye decolorization in MFC. Therefore, combining electrochemical methods with other methods, or increasing pretreatment often can be used to improve the biodegradability of dye wastewater. Biofilm electrode reactor (BER) uses micro-current to stimulate the metabolic activities of microorganisms fixed on electrode surface, and makes pollutants degradation faster under the double effects of electrochemical reactions and microbial metabolic activities [8]. Kang [9] compared COD removal rate during the degradation of 4-Amino-dimethyl-aniline Hydrochloride by electrochemical method and BER, and the results demonstrated that the COD removal rate was only 74.81% when the indirect electro-oxidation was used, while the COD removal rate of BER reached 100% after operating 5 hours with a current of 2 mA.

Microbial fuel cell (MFC) is a bioelectrochemical device that converts chemical energy in organic matter into electrical energy by catalytic activities of microorganisms [10]. The poor power generation performance and the high cost have hindered its practical application value. Therefore, many researchers have turned their attention to the pollutants degradation performance of MFC. For example, Fang’s [11] studies showed that decolorization rate of methyl orange by constructed wetland-MFC system reached 87.6%, and the degradation rate of decolorization product DMPD was up to 96.33%. In addition, the treatment of azo dye wastewater by MFC can achieve both power generation and decolorization [12].

In this study, a novel constructed wetland-microbial fuel cell combined with three-dimensional biofilm electrode (3D BER-CW-MFC) system was proposed for reactive brilliant red X-3B (RBR X-3B) wastewater treatment. Firstly, the influent with refractory macromolecular organics was converted into simple biodegradable small molecular organics in 3D BER. Secondly, the remaining small molecular organic matter was degraded by CW-MFC and generated electricity to maintain the operation of 3D BER. We mainly examined the decolorization effect, COD removal and electricity production of the combination process, and the main factors affecting the system’s performance were investigated. At last, the combined system’s electricity production was compared with the consumption, and the coulombic efficiencies of the combined system were also calculated.

2. Materials and methods

2.1. The operation and configuration of 3D BER

As schematically shown in Figure 1, 3D BER was operated in continuous upflow mode. The reactor was built with a plexiglass cylinder, 35 cm in height and 15 cm in internal diameter. Activated carbon fiber / stainless steel mesh cathode (ACF / SSM (about 0.5 cm in height)), granular activated carbon (GAC (about 15 cm in height)) and the ACF / Ti mesh anode (about 0.5 cm in height) was filled in the reactor from bottom to top. And the anode was fixed 5 cm from GAC layer.

Anaerobic sludge was inoculated in 3D BER reactor, and nutrients were replenished every 24 h for 5 days, which contained glucose (0.44 g L⁻¹), NaCl (0.33 g L⁻¹), NH₄Cl (0.134 g L⁻¹), KCl (0.184 g L⁻¹), Na₂HPO₄·12H₂O (0.616g L⁻¹), NaH₂PO₄·2H₂O (0.562 g L⁻¹), NaHCO₃ (0.34g L⁻¹) and 1 mL L⁻¹ trace essential elements solution [13]. After the inoculations completed, the continuous inflow was about 3.47 mL min⁻¹, and cultivated voltage was increased gradually from 0.5 V to 2.0 V and then kept constant. When microorganism had grown well, an appropriate concentration of RBRX-3B was added into the influent for domestication.
2.2. The operation and configuration of CW-MFCs

Figure 2 is a schematic of the CW-MFC system. The CW-MFCs reactor was built with polycrystalline plastic cylinder (400 mm in height and 100 mm in diameter). Cathode (constructed with granular activated carbon-stainless steel wire mesh), 200 mm layer of gravel (diameter of 3-6 mm), anode (built with 100 mm thick GAC), and 200 mm layer of gravel was filled in the reactor from bottom to top.

The anode of CW-MFCs were inoculated with anaerobic sludge collected from a wastewater treatment plant. The nutrient solution was consisted of 5 mM phosphate buffer solution (PBS) with glucose (0.20 g L\(^{-1}\)), KCl (0.13 g L\(^{-1}\)), NH\(_4\)Cl (0.15 g L\(^{-1}\)), NaHCO\(_3\) (3.13 g L\(^{-1}\)), and 1 mL L\(^{-1}\) trace essential elements solution [14]. The bio-cathode were inoculated using aerobic sludge with a similar nutrient without glucose. Both the anode and bio-cathode were inoculated under batch-feed operation. After the inoculations completed, the nutrient solution was fed continuously into the CW-MFCs at a flow rate of 0.52 mL min\(^{-1}\).

2.3. Configuration and operation of BER / CW-MFC

Connect effluent from 3D BER to four CW-MFCs (Firstly, the differences were: CW-MFC 0 was an open-circuit with a cathode working surface area of 78.5 cm\(^2\); CW-MFC 1 was a closed-circuit with a cathode working surface area of 706.5 cm\(^2\); CW-MFC 2 and CW-MFC 3 were the exactly same system, both were closed-circuit with a cathode working surface area of 78.5 cm\(^2\). Secondly, 1000 Ω external resistances were connected to the closed-circuits).

The influent RBR X-3B concentration in the 3D BER was sequentially increased to 100, 200, 400, 600, 800, and 1000 mg L\(^{-1}\) (running 6 days per concentration), the dye and COD concentration both from 3D BER and CW-MFC effluent were measured, and the electrochemical indicators of each CW-MFC were calculated.

2.4. Analysis and calculation

The decolorization rate of dye was RC = (A\(_1\)−A\(_2\)) / A\(_1\)×100%, A\(_1\) and A\(_2\) were the absorbance of influent and effluent measured at 538 nm respectively. Chemical oxygen demands (COD) in the water was determined by the potassium dichromate titration method.

The cell voltage of the CW-MFC was recorded every 15 minutes through a voltage data collector (DAM-3058R and DAM-3210, Art Technology Co. Ltd., China). The coulombic efficiency (CE) which represents the ratio of electrons used for electricity generation versus the theoretical electrons provided by the consumed organic matter was calculated.
3. Results and discussion

3.1. The dye decolorization effect of combined system
Table 1 indicated that dye decolorization rate of the combination process of 3D BER and CW-MFCs were all over 96%. The dye decolorization rate in the 3D BER increased first and then decreased with the increase of dye concentration. CW-MFC showed little synergistic decolorization effect on 3D BER at the influent dye concentration lower than 200 mg L\(^{-1}\). When dye concentration was higher than 400 mg L\(^{-1}\), the decolorization rate of CW-MFC increased by 62%, but the decolorization rate of 3D BER decreased to 86.3%–96.5%, mainly because more azo dye and reduction products inhibited the microorganisms’ activities in 3D BER, thus reducing the dyes’ degradation [15]. Therefore, the combination of 3D BER and CW-MFC could ensure a high dye decolorization effect in high-concentration organic wastewater. Besides, closed-circuit CW-MFC had a better decolorization effect, while the cathode area size had little effect on dye decolorization.

3.2. The COD removal effect of combined system
As shown in Figure 3, the COD removal effect of 3D BER was poor (50.55%–66.21%) and decreased with the increase of dye concentration, however, the COD removal effect of the subsequent CW-MFCs all improved (COD removal rate of CW-MFC 0, CW-MFC 1, CW-MFC 2 and CW-MFC 3 were 78.9%, 81.59%, 80.7% and 80.6 %, respectively), mainly because the 3D BER converted refractory azo dyes into micro-molecular organics that was easily degraded and the BOD/COD in the dye wastewater increased. Besides, the COD removal effect of closed-circuit CW-MFC was better than that of the open-circuit CW-MFC, and the larger cathode area CW-MFC had a higher COD removal rate. Li [16] suggested that the larger cathode area accelerated the reaction on cathode, then the faster consumption of electrons and protons on the cathode led to the acceleration of electrons transfer from the anode to the cathode, and as a result the more organic matter was degraded.

3.3. The influence factors on electricity production of combined system
As shown in Figure 4, the cell voltages of CW-MFCs changed significantly with the dye concentration. The cell voltage of CW-MFCs reached the maximum when the influent dye concentration was increased to 600 mg L\(^{-1}\), and the average cell voltage of CW-MFC 0 with open circuit was about 0.763V, and the average output voltage of CW-MFC 1, CW-MFC 2 and CW-MFC 3 was 0.551 V, 0.461 V and 0.479 V, respectively. When dye concentration increased to 1000 mg L\(^{-1}\), the cell voltages of the CW-MFCs all decreased by about 6.42%–14.34%. The reasons were as follows: the weight of organic matter transformed by 3D BER at low influent dye concentration could not satisfy with the demand of electrogenic bacteria on the anode of CW-MFC; however, too much organic matter transformed by the 3D BER at the high influent dye concentration could not be degraded completely in the CW-MFC anode chamber, and it would consume dissolved oxygen after flow into the cathode chamber and then resulted in cathode potential decline.

Moreover, the analysis indicated that the cell voltage increased by 15.03–19.52% as the cathode area of CW-MFC increased from 78.5 cm\(^2\) to 706.5 cm\(^2\) at the influent dye concentration of 600–800 mg L\(^{-1}\). The main reason was that the larger cathode area could greatly increase the contact area between bio-cathode and air, which was advantageous to the improvement of cathode potential.

3.4. Comparison of the combined system's electricity production with consumption
As is shown in Table 2, electrical energy of 0.0168 KWh would be consumed while 1 m\(^3\) dye wastewater was treated by 3D BER. However, the maximum power generated by CW-MFC 1, CW-MFC 2 and CW-MFC 3 was 0.018KWh m\(^{-3}\), 0.012 KWh m\(^{-3}\) and 0.013 KWh m\(^{-3}\), respectively. It can be seen that the coulombic efficiencies of all the CW-MFCs system calculated were less than 10%. Therefore, the combined system would achieve electric consumption self-contained with a high efficiency of azo dye wastewater treatment, if the combined system of 3D BER and CW-MFC was optimized to achieve a higher electron recovery rate.
4. Conclusions

(1) The combined system had better dye decolorization and COD removal effect. The decolorization rate was over 96%, and the COD removal rate of the combined system (78.86%−90.78%) was higher than 3D BER operated alone (50.55%−66.21%).

(2) The circuit state and cathode area of CW-MFC had influence on dye decolorization rate and COD removal rate. The closed-circuit CW-MFC showed better decolorization and COD removal effect, and the cathode area size had less effect on the decolorization rate, but the larger cathode area obtained a higher COD removal rate.

(3) The electricity generated by CW-MFCs could satisfy the demand of energy consumed by 3D BER if the combined system were optimized to achieve a higher electron recovery rate.

Table 1. Dye concentrations in the influent and the dye removal effect of each reactor during the experiment.

| Influent (mg L\(^{-1}\)) | removal rate of BER (%) | removal rate of CW-MFC 0 (%) | removal rate of CW-MFC 1 (%) | removal rate of CW-MFC 2 (%) | removal rate of CW-MFC 3 (%) |
|--------------------------|-------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 102.5                    | 96.1                    | 96.8                        | 97.2                        | 96.8                        | 97.0                        |
| 208.5                    | 98.1                    | 98.3                        | 98.5                        | 98.3                        | 98.4                        |
| 401.4                    | 96.5                    | 98.5                        | 98.8                        | 98.7                        | 98.8                        |
| 607.4                    | 89.3                    | 98.3                        | 98.7                        | 98.4                        | 98.5                        |
| 815.4                    | 88.5                    | 98.1                        | 98.7                        | 98.4                        | 98.5                        |
| 992.6                    | 86.3                    | 97.6                        | 98.5                        | 98.3                        | 98.2                        |

Figure 3. COD concentrations of effluent and COD removal in the 3D BER and CW-MFCs at different initial dye concentrations.

Table 2. The electrical parameters of each unit in the combination process of 3D BER and CW-MFC.

| Reactor | Influent flow (L d\(^{-1}\)) | Applied voltage (Power generation) (V) | Applied current (Generated current) (mA) | Power consumption (Generated electricity) (KWh m\(^{-3}\)) | Current efficiency (Coulomb efficiency) (%) |
|---------|-------------------------------|----------------------------------------|------------------------------------------|----------------------------------------------------------|--------------------------------------------|
| 3D BER  | 5.00                          | 1.000                                  | 3.498                                    | 0.0168                                                   | 563.26                                     |
| CW-MFC 1 | 0.47                          | 0.376                                  | 0.941                                    | 0.0181                                                   | 8.81                                       |
| CW-MFC 2 | 0.47                          | 0.373                                  | 0.621                                    | 0.0118                                                   | 5.96                                       |
| CW-MFC 3 | 0.47                          | 0.391                                  | 0.652                                    | 0.0130                                                   | 6.37                                       |
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