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EVALUATION OF INTEGRATED UFCW-MFC REACTOR FOR AZO DYE WASTEWATER TREATMENT AND SIMULTANEOUS BIOELECTRICITY GENERATION

An up-flow constructed wetland (UFCW) incorporating a novel membrane-less air-cathode single-chamber microbial fuel cell (MFC) was designed to treat dye wastewater and simultaneously generate bioelectricity. The performance of UFCW-MFC was evaluated via Methyl Orange (MO) and chemical oxygen demand (COD) removal rates and the output voltage. For comparison, the performance of a single UFCW was also assessed. A repeatable and stable voltage output of about 0.44 ± 0.2 V was obtained in UFCW-MFC. The MO and COD removal rates in UFCW-MFC were 93.5 and 57.2%, respectively, significantly higher than those in single UFCW (75.4 and 42.6%, respectively), suggesting the obvious enhancement of electrodes on MO and COD removal. The anode zone of UFCW-MFC made the most contribution to MO and COD removal compared with other layers. The oxidation-reduction potential (ORP) and dissolved oxygen (DO) profiles showed that the anaerobic environment was well developed in the lower part of UFCW-MFC (0–24 cm) and the upper part (41–42 cm) had a good aerobic environment, thus greatly contributing to the MO anaerobic reduction and aerobic degradation of breakdown products. These results obtained here suggest that the UFCW-MFC may provide an effective alternative for the treatment of dye wastewater and simultaneous bioelectricity generation.

1. INTRODUCTION

Azo dyes are extensively used in various branches of industries (such as textiles, cosmetics, and food), constituting 60–70% of all dyestuff produced [1] which are synthetic aromatic compounds with one or more typical azo chromophore groups ($-N=N-$). During dyeing processes, ca. 40–50% of the azo dyes were released into wastewater [2]. Azo dyes and their breakdown intermediates (such as aromatic amines) are commonly car-

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cinogenic and mutagenic in nature [3], probably causing a series of serious environmental and/or public health problems. Thus, the treatment of wastewater containing azo dyes is crucial before discharging into the water environment.

Nowadays, many methods have been employed for azo dyes wastewater treatment, mainly including physical/chemical and biological technologies [4–6]. The physical/chemical techniques have certain drawbacks including high energy requirement and operational cost as well as the generation of a large amount of sludge [7]. By contrast, biological processes are regarded as cost-effective, environment-friendly and sustainable methods [8]. Although biodegradation of complex azo dyes is rather difficult under natural aerobic conditions due to their low BOD/COD ratios (less than 0.1) [9], azo dye wastewater can be effectively treated using a sequential anaerobic-aerobic process [1]. Reductive cleavage of azo linkages can occur in anaerobic condition and the breakdown products (such as aromatic amines) after breakage of azo bonds can be mineralized under aerobic conditions [10]. Therefore, a combination of the sequential anaerobic-aerobic environment is necessary for the treatment of azo dyes in various wastewater treatment processes.

Constructed wetland (CW) is an emerging technology and has been increasingly used to remove pollutants from wastewater treatment worldwide due to its simple construction, minimal energy requirement, and low operation and maintenance cost. In a CW, wastewater can be treated by a complex combination of physical, chemical and biological behavior [11]. Moreover, microbial fuel cell (MFC) has demonstrated as an innovative technology that also successfully gained attention from many research groups worldwide [12, 13] due to its potential for contaminants removal from wastewater and simultaneous bioelectricity production. An MFC consists of an anode and cathode electrode similar to any battery. In an MFC, organic matter was oxidized by electrochemically active microorganisms at the anode, where electrons and protons were generated. And then the electrons are transported to the cathode via an electrical circuit, which would be consumed for oxygen reduction.

Notably, both CW and MFC consist of anaerobic and aerobic regions, in which reduction and oxidation processes can take place, respectively [14]. These would provide the possibility of azo dye wastewater treatment by the combination of CW with MFC. What is more, the bacteria play a major role both in the CW and MFC, which are the other base of the combination of the two processes. The anode region in MFC (similar to the bottom of CW) should maintain in an anaerobic environment to reduce azo bonds and release electrons and protons. Oxygen, an aerobic condition, would react with electrons and protons at the cathode (similar to the upper part of CW) [15]. Moreover, the upper region of CW is also capable of biodegradation of breakdown products from azo dye reduction.

In this context, an up-flow constructed wetland (UFCW) incorporating together with a novel membrane-less air-cathode single-chamber microbial fuel cell (MFC) was proposed in this study for treatment the dye wastewater and simultaneously generate bioelectricity. Generally, double-chamber MFC is the most commonly adopted in studies, where a membrane used as a physical separator could function to allow only protons

to pass through it from anode to cathode region and to avoid the diffusion of oxygen from cathode to anode region in MFC. However, MFC consisting of a membrane may cause biofouling, high internal resistance as well as high operation cost [16]. Moreover, double-chamber MFC is hard to implement in practice [17]. Thus, a membrane-less single-chamber MFC was conducted here. In addition, aerobic microorganisms rather than other materials (such as manganese dioxide, platinum and lead dioxide, etc.) were used as catalysts (i.e., air biocathode), greatly contributing to cost savings, environmental protection and more effective utilization of oxygen adopted as an electron acceptor. The performance of UFCW-MFC was evaluated in terms of ability to MO and chemical oxygen demand (COD) removal rates and the capability to generate bioelectricity. For comparison, the performance of single UFCW was also assessed. The UV-visible spectra were analyzed to investigate the change of molecular and structural characteristics during the MO treatment by using MFC. This study may contribute to the application of UFCW-MFC technology for the treatment of dye wastewater or non-biodegradable industrial wastewater and simultaneous bioelectricity generation.

2. MATERIALS AND METHODS

UFCW-MFC set up and operation. A lab-scale UFCW-MFC was designed in this study. The reactor was fabricated by using polyvinyl chloride with a total working volume of 3.3 dm³, 42 cm in height and 10 cm in inner diameter. Figure 1 shows the schematic diagram of UFCW-MFC. The bottom of the reactor was layered with 16 cm in height of gravel (4–5 mm in diameter) to support the anode and cathode and eliminate the DO possible existence in influent. The electrodes materials employed here were granular activated carbon (GAC, 4–7 mm in diameter, Taiyuan Huasheng, Co., Ltd., China) and stainless steel mesh (SSM, wire diameter of 0.4 mm, mesh No. 12, Jiangsu Changzhou Metal Products Factory, Co., Ltd., China). The anode and cathode zones were packed with 8 and 2 cm, respectively, in height of GAC, where an SSM was placed at the center of anode region. The isolation layer was also packed with gravel 16 cm in height between the anode and cathode.

Prior to use, the anode and cathode regions were inoculated with concentrated activated sludge (20 g/dm³ of mixed liquid suspended solids (MLSS)), collected from an oxidation ditch configuration (Fengyang Municipal Wastewater Treatment Plant, Anhui, China), for 90 days to immobilize the specific microorganisms on the surface. There were two sampling points (anode and cathode, i.e., effluent) from the bottom to the upper of the reactor. The UFCW-MFC was operated for 90 days in a continuous mode with a variable speed peristaltic pump (BT100J-1A, Beijing Huiyu Fluid Equipment, Co., Ltd., China).

Synthetic wastewater. The synthetic wastewater consisted of carbon sources, nutrients and buffer solutions, and its composition was as follow: MO (100 mg/dm³), sodium

acetate (0.1 g/dm^3), NH_4Cl (0.31 g/dm^3), KCl (0.13 g/dm^3), K_2HPO_4 (3.4 g/dm^3), KH_2PO_4 (4.4 g/dm^3), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 g/dm^3) and NaCl (0.116 g/dm^3).

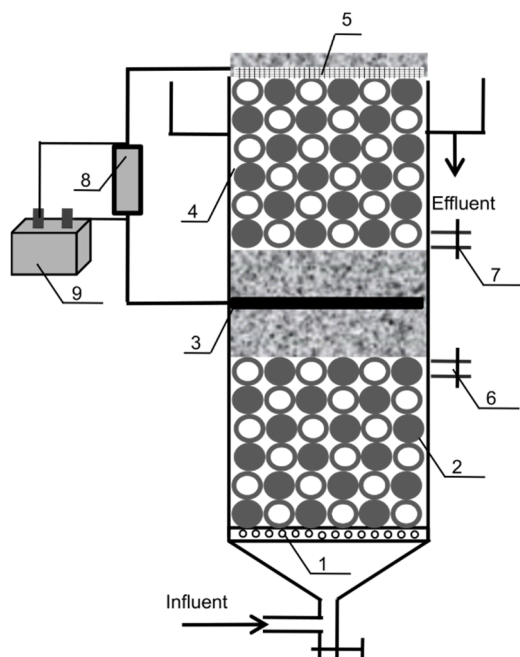


Fig. 1. The schematic diagram of UFCW-MFC: 1 – water distribution, 2 – support layer, 3 – anode, 4 – isolation layer, 5 – cathode, 6, 7 – sample points, 8 – variable external resistor, 9 – voltage data collector

Chemical analyses. All water samples were filtered through a $0.22 \mu\text{m}$ Millipore filter and then placed at 4°C before the analysis. Chemical oxygen demand (COD) and MLSS were measured by standard methods (APHA, 2005). MO concentration and wavelength scan were analyzed by using UV-3600 (Shimadzu). The degradation of MO was monitored at 463 nm . ORP and DO were measured by the meter analyzers (YSI 100 and YSI 5100-230, respectively). Anode was connected to cathode with titanium wires and a fixed external resistor of $1 \text{ k}\Omega$. The voltage output generated from UFCW-MFC was recorded with a data logger (R6100, Hangzhou Excon Technology, Co., Ltd., China) every 5 min.

3. RESULTS AND DISCUSSION

3.1. STARTUP OF UFCW-MFC

As shown in Fig. 2, after 90 days, repeatable and stable voltage output of about $0.44 \pm 0.2 \text{ V}$ ($R_{ex} = 1000 \Omega$) was obtained in UFCW-MFC with additions of 100 mg/dm^3 of sodium acetate and 100 mg/dm^3 of MO, displaying that the MFC operated smoothly and performed well for electricity production. It was noted that slight fluctuation of

output voltage was observed during the day/night cycles, which may be due to the difference in temperature between day and night. A similar result was also reported by Villasenor et al. [18] that the light/darkness changes had a direct impact on the voltage variations with the temperature fluctuations ranging from 18 to 30 °C.

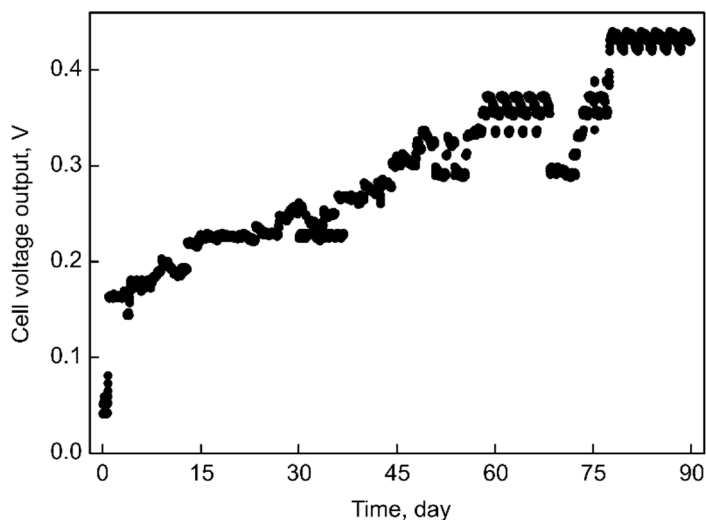


Fig. 2. Variations of voltage output with time during the UFCW-MFC startup period

3.2. MO REMOVAL

The MO removal performances in water samples collected from four different sites, namely support layer, anode zone, isolation layer and effluent for UFCW-MFC and UFCW were averaged and are shown in Fig. 3. The total MO removal rates were 93.5 and 75.4% in UFCW-MFC and UFCW, respectively, and it was mostly contributed by microbes in anode zone, where removal rate of MO reached 59.5% in UFCW-MFC significantly higher than that in UFCW (41.9%). This strongly suggests the enhancement of electrodes on MO removal. Research indicated the electric field of UFCW-MFC can enhance the degradation of organics by changing the physiological characteristics of microorganisms, thereby promoting the azo bond reduction reaction by increasing the number of electrons [19]. Compared with the UFCW, the UFCW-MFC anode acts as an insoluble terminal electron acceptor, which could increase the metabolic rate of microorganisms and accelerated the degradation of sodium acetate, thus providing more electrons for the MO reduction in an anaerobic environment [10].

Although the volume of anode zone was only 19% of the whole UFCW-MFC volume, the MO removal rate in the anode region was significantly higher than others zones and it was 21.2, 59.5, 10.5 and 2.3% in the support layer, anode zone, isolation zone, and cathode zone, respectively. The increase of the MO removal rate was greater in the

lower part of reactors (0–24 cm) than in the upper part of reactors (25–42 cm). Two possible reasons were responsible for this. One is that the anaerobic environment, which can favor the reductive cleavage of $-N=N-$ bond contained MO, has developed in the support layer and anode zone. The other reason may be that high concentration sodium acetate in the lower half of UFCW-MFC can serve as a co-substrate. The co-substrate degradation can donate the electron to support the $-N=N-$ reductive cleavage [20].

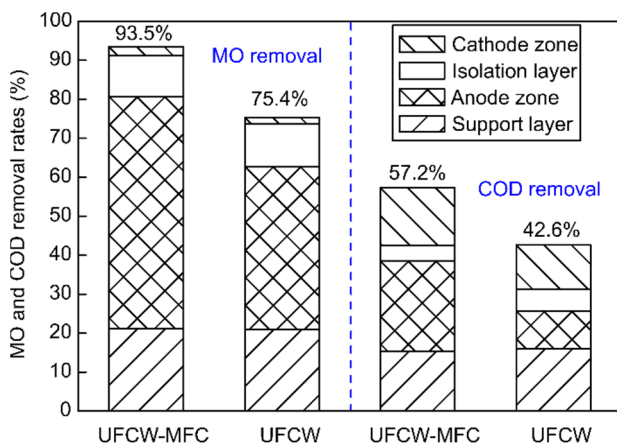


Fig. 3. MO and COD removal performance in UFCW-MFC and UFCW

3.3. COD REMOVAL

It is clear from Fig. 3 that the anode zone also made the most contribution to COD removal in UFCW-MFC and UFCW and the total COD removal rate in UFCW-MFC was higher (57.2%) than that in UFCW (42.6%). Without the presence of electrodes in UFCW, the decrease of COD was solely dependent upon the microbial metabolism, thus displaying a rather low COD removal rate compared with UFCW-MFC, while COD removal by the biomass could be enhanced by the electric current in UFCW-MFC. In this way, the synergistic effect between electrochemistry and microorganisms accelerated the organics degradation reaction. Moreover, the UFCW-MFC and UFCW exhibited very low COD removal rates as compared to the color removal rates mentioned above. This may be attributed that the decolorization products of MO cannot be oxidized sufficiently.

In the UFCW-MFC, the COD removal rate was 15.3, 23.2, 4.0 and 18.7% in the support layer, anode zone, isolation zone, and cathode zone, respectively. The lower half of the reactor may contribute to the degradation of most of the sodium acetate and the decolorization products of MO removal may mainly occur in the upper half of UFCW-MFC. Generally, the co-substrate (sodium acetate) is more biodegradable than MO intermediates. Many intermediates of azo dyes could not be further degraded by

anaerobic treatment but could be treated in the aerobic environment [21]. Therefore, an anaerobic/aerobic system was commonly adopted for the degradation of azo dyes [22].

3.4. DO AND ORP STATE

The anaerobic and aerobic conditions of the UFCW-MFC and UFCW could be well distinguished from the monitoring of ORP and DO. Generally, ORPs higher than 100 mV and lower than -100 mV are regarded as aerobic and anaerobic environments, respectively [23]. The full profiles of ORP and DO in the two reactors are shown in Table 1.

Table 1

ORP and DO in UFCW-MFC and UFCW

	DO concentration [$\text{mg O}_2/\text{dm}^3$]		ORP [mV]	
	UFCW-MFC	UFCW	UFCW-MFC	UFCW
Support layer	0.32	0.26	-182	-179
Anode zone	0.19	0.22	-196	-193
Isolation layer	0.95	1.20	55	68
Cathode zone	2.98	3.23	143	172

There was no significant difference in ORP and DO between the UFCW-MFC and UFCW apart from the upper parts of the two reactors. In the two reactors, the low ORP of from -179 to -196 mV and DO at 0.32 – 0.19 $\text{mg O}_2/\text{dm}^3$ at 0 – 24 cm height indicated the good anaerobic environment. Furthermore, the relatively high ORP of 143 – 172 mV and DO of 2.98 – 3.23 $\text{mg O}_2/\text{dm}^3$ were recorded at the surface layer (at 40 – 42 cm), which were attributed to the dissolution of oxygen in the air. In a cathode of UFCW-MFC, besides microbial aerobic respiration consumed oxygen, it was also reduced by the cathode half reaction ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$) [20]. Thus, there seems to exist a competition mechanism between the degradation of MO decolorization products and the cathode for the DO [24]. As a result, the cathode zone of UFCW-MFC had a lower DO level (2.98 $\text{mg O}_2/\text{dm}^3$) than that in the surface layer of UFCW (3.23 $\text{mg O}_2/\text{dm}^3$).

The lowest DO concentration was about 0.19 $\text{mg O}_2/\text{dm}^3$ at the anode zone in UFCW-MFC, indicating that the anode region was in a strong reductive environment. In the surface of UFCW-MFC, i.e., cathode zone, the DO concentration increased sharply and its maximum reached up to 2.98 $\text{mg O}_2/\text{dm}^3$, suggesting that the cathode was in aerobic condition. The increase of DO was attributed to the dissolution of oxygen in the air. The DO of the surface layer in UFCW-MFC was lower than that in UFCW (3.23 $\text{mg O}_2/\text{dm}^3$), which may be due to the different oxygen consumption mechanisms in the two reactors. In the UFCW-MFC, the DO consumption mainly included aerobic microbial reaction and chemical reaction (cathode half-reaction), but the UFCW only contained biodegradation. Generally, the reaction rate of the chemical reaction is higher

than that of biological reaction, as demonstrated by the lower DO recorded in the cathode zone of UFCW-MFC proposed here.

3.5. CHANGE OF UV/VISIBLE ABSORBANCE SPECTRA IN UFCW-MFC

To investigate the change of molecular and structural characteristics during the MO treatment by using UFCW-MFC, the change in representative UV/Visible absorbance spectra were recorded with a hydraulic retention time (HRT) of 3 days before and after oxidation, as depicted in Fig. 4.

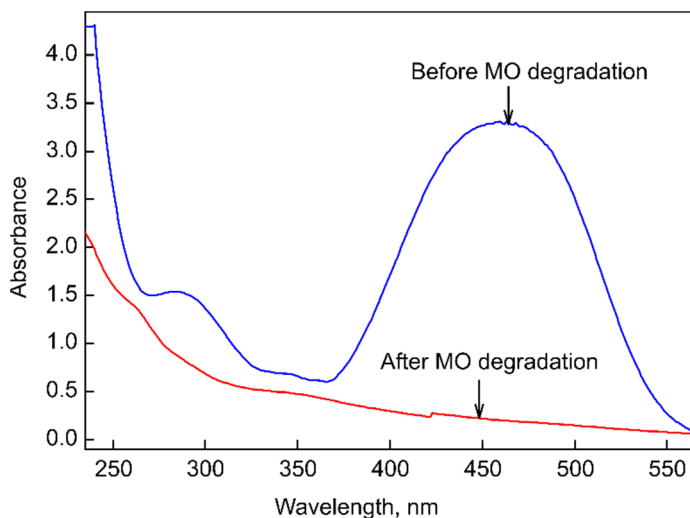


Fig. 4. UV/visible absorbance spectra of MO solution in UFCW-MFC before and after degradation

There was a significant difference in the main absorbance bands in the samples before and after MO degradation. Before degradation, the absorbance spectrum of MO solution was characterized by three main bands, including two in the UV region at 210 nm and 273 nm, respectively, and the other in visible region at 463 nm. The peak at 273 nm is attributed to the aromatic ring contained MO whereas the other peak at 463 nm is associated with the azo bond ($-N=N-$) [25]. After degradation, the absence of a peak at 463 nm showed that the azo bond of MO was cleaved completely, which was also demonstrated via color removal rate described in detail previously. The absorbance in the UV region at 210 nm and 273 nm were found to have decreased to a certain extent, but not completely disappeared, which are in agreement with results mentioned above. The low removal rate of total COD (57.2%) suggested that the breakdown products from MO were only partly removed in UFCW-MFC.

4. CONCLUSIONS

- The UFCW-MFC exhibited a good MO removal and bioelectricity generation. A repeatable and stable voltage output of about 0.44 ± 0.2 V was obtained in UFCW-MFC by continuous operation for 90 days. And, 93.5% of MO was removed from wastewater.

- The MO and COD removal rates in UFCW-MFC were significantly higher than those in single UFCW. The anode zone of UFCW-MFC made the most contribution to MO and COD removal compared with the other layers. The anaerobic and aerobic environments were well developed in the lower and upper of UFCW-MFC, respectively.

- The UFCW-MFC may provide an economical and effective alternative for the treatment of non-biodegradable industrial wastewater and simultaneous bioelectricity generation. Further efforts are required for overall performance improvements in the reactor.

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