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## OPTIMIZATION OF A CONSTRUCTED WETLAND-MICROBIAL FUEL CELL SYSTEM FOR Cr(VI) REMOVAL FROM WASTEWATER AND POWER GENERATION PERFORMANCE

A new type of bioelectrochemical system features a constructed wetland (CW) coupled with a microbial fuel cell (MFC) to treat Cr(VI) wastewater while generating electricity. The optimal operating parameters for treating wastewater containing Cr(VI) are discussed. The results show that the CW-MFC system is more effective in the treatment of Cr(VI)-containing wastewater and generating electricity. A COD concentration of 300 mg/dm<sup>3</sup> corresponded to the greatest COD and Cr(VI) removal rates with a maximum power density of 505.62 mW/m<sup>3</sup>, whereas a Cr(VI) concentration of 80 mg/dm<sup>3</sup> yielded the greatest COD removal rate, with a maximum power density of 484.43 mW/m<sup>3</sup>. A hydraulic retention time (HRT) of 3 days yielded the largest pollutant removal rates with a maximum power density of 479.21 mW/m<sup>3</sup>. Considering that the comprehensive operating conditions of CW-MFC are based on planting plants, the COD concentration is 300 mg/dm<sup>3</sup>, the Cr(VI) concentration is 80 mg/dm<sup>3</sup>, and the HRT is 3 days. The abundance of electrogenic bacteria *Geobacter* and metal dissimilatory reducing bacteria *Acinetobacter* in CW-MFC is higher than that in the control group. The results of this study provide theoretical guidance for determining the optimal operating conditions and energy recovery of the CW-MFC system for treating chromium wastewater.

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## 1. INTRODUCTION

Chromium has been widely used in the welding, tanning, mining, electroplating, and pigment industries. However, it is one of the primary toxic heavy metals of concern [1]. Industrial wastewater contains significant amounts of chromium. It is present in water bodies mainly as Cr(VI) and Cr(III) ions; however, Cr(VI) toxicity is approximately 100 times greater than that of Cr(III) [2]. Long-term exposure to Cr(VI) may cause serious health problems such as stomach and skin tumors and an increased risk of liver and kidney damage. It may interfere with the DNA transcription process [3]. Unlike some organic pollutants, Cr(VI) does not readily biodegrade and can persist in the environment for a long time. For these reasons, most countries generally designate Cr(VI) as a pollution control priority [4].

At present, some treatment technologies can convert toxic Cr(VI) into less toxic Cr(III) by using, for example, conventional methods such as ion exchange, adsorption, membrane filtration, chemical precipitation, chemical oxidation, and reduction [5]. However, various disadvantages are associated with most of these treatment methods, including high energy consumption, high operating costs, excessive consumption of chemicals, and secondary pollution. The research results clarified the performance of the planting constructed wetland (CW) coupled with a microbial fuel cell (MFC) system in treating chromium wastewater under various conditions and provided theoretical guidance for determining the optimal operating conditions and energy recovery of the system for treating chromium wastewater. Activated carbon used as an auxiliary agent can be prepared from different raw materials to achieve Cr(VI) conversion by adsorption under different adsorption conditions while the total chromium level in aqueous solution is recorded [6]. Studies have shown that the use of composite materials such as carbon fibers to adsorb Cr(VI) makes the process more complex in terms of cost assessment and eco-friendliness [7]. Kazemi et al. [8] prepared a new type of photocatalytic thin-film nanocomposite membrane to remove Cr(VI) from water, but this may produce secondary pollution and cost more. Therefore, it is of great significance to explore a low-cost and sustainable method for treating Cr(VI)-containing wastewater.

In recent years, the ability of CW-MFC systems to provide low-cost electricity while treating heavy metal wastewater is an environmentally sustainable characteristic that makes it increasingly favored by researchers [9]. Compared with a traditional CW, CW-MFC can further improve the removal rate of metal ions in wastewater while generating electricity [10]. Wang et al. [11] found the CW-MFC systems possessed higher Zn and Ni removal efficiencies as compared to CW. A removal study of Pb(II) by CW-MFC displayed that the removal rate was up to 85% with a maximum power density of 7.432 mW/m<sup>3</sup> [12]. In addition, the CW-MFC system is expected to be used to treat Cr(VI) wastewater.

Substrate concentration, hydraulic retention time (HRT), and plants were considered important parameters for optimizing CW-MFCs. Fang et al. [13] studied the effect

of the ratio of glucose and ABRX3 azo dye and the concentration of COD on electricity production and ABRX3 degradation characteristics of CW-MFC. Zhong et al. [10] studied the performance of CW-MFC under varying HRTs (7.6, 4.0 and 2.8 days). Plant roots were capable of removing pollutants directly from wastewater by adsorption and enrichment. However, detailed information about the pollutants removal from Cr(VI) wastewater by CW-MFCs based on optimized substrate concentration, HRT, and plants, is still scarce. Hence, CW-MFC was proposed to treat Cr(VI) wastewater through bioelectrochemical reduction, adsorption on the substrate, and the comprehensive effect of microorganisms in this work. The effects of chemical oxygen demand (COD), Cr(VI) concentration, HRT, and the presence of plants on pollutant removal and power generation in the CW-MFC system were also explored and determined the best operating conditions for the treatment of chromium wastewater. The research results clarified the performance of the planting CW-MFC system in treating chromium wastewater under different conditions and provided theoretical guidance for determining the optimal operating conditions and energy recovery of the CW-MFC system for treating chromium wastewater.

## 2. EXPERIMENTAL

*Construction of the CW-MFC system.* A vertical upward-flow CW-MFC sewage treatment system was constructed for this study. The main part consists of a reactor made of UPVC pipes with a diameter of 30 cm, a height of 70 cm, and an effective height of 60 cm (Fig. 1).

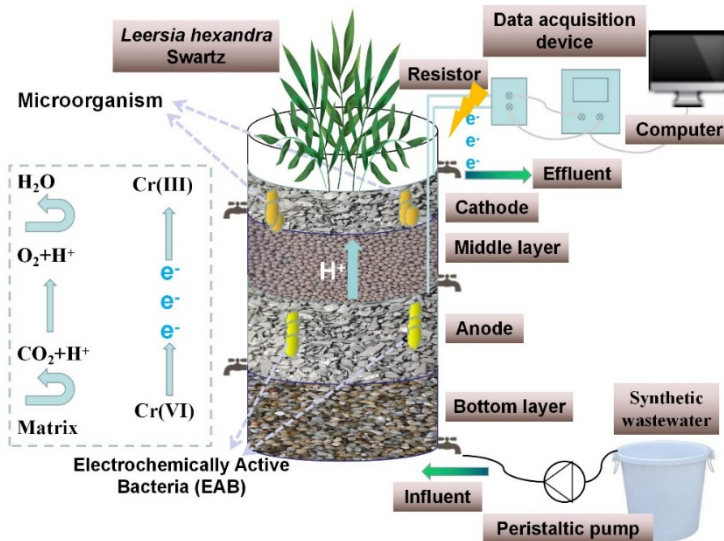


Fig. 1. Scheme of the coupled constructed wetland-microbial fuel cell system installation

A water inlet is located at the bottom of the system, and its outlet lies near the top at a height of 60 cm. The system is composed of a bottom layer (zeolite), an anode layer (activated carbon), and a middle layer (ceramsite), as well as a cathode layer (activated carbon). The anode and cathode are composed of 100-mesh stainless steel wrapped with activated carbon. The anode and cathode wires are connected by a copper wire and an external resistance box (Fuyang Precision Instrument Factory, Hangzhou, China). The resistance was 1000  $\Omega$ , and the voltages were collected using a data acquisition card (NI USB-6009, Suzhou Fuyutong Electronics Co., Ltd., China). The system used artificially prepared Cr(VI) wastewater with *Leersia hexandra* Swartz as wetland plants, and the nonplanted system was also experimented with under the same conditions. Then a peristaltic pump connected the inlet reservoir with the reactor (BT100-2J, Baoding Lange Constant Flow Pump Co., Ltd., China). The cathode and anode of the system control group were not connected to the resistance box. The HRT of the system was changed by controlling the speed of the peristaltic pump.

*Sludge inoculation and wastewater composition.* The inoculation source was a concentrated anaerobic sludge from Liquan Brewery in Guilin. The retrieved sludge was first cultured under anaerobic conditions in the laboratory for one week and then connected to the reactor. The system initially used simulated Cr(VI) wastewater. Its composition is given in Tables 1 and 2.

Table 1

Major components of the experimental solution

Component	Concentration [mg/dm <sup>3</sup> ]	Component	Concentration [mg/dm <sup>3</sup> ]
C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub>	300	NaHCO <sub>3</sub>	200
NH <sub>4</sub> Cl	75	MgSO <sub>4</sub> ·7H <sub>2</sub> O	10
KH <sub>2</sub> PO <sub>4</sub>	5		

Table 2

Trace components of the experimental solution

Component	Concentration [mg/dm <sup>3</sup> ]	Component	Concentration [mg/dm <sup>3</sup> ]
CaCl <sub>2</sub> ·6H <sub>2</sub> O	130	ZnCl <sub>2</sub>	70
FeCl <sub>3</sub>	1000	MnSO <sub>4</sub> ·H <sub>2</sub> O	100
H <sub>3</sub> BO <sub>3</sub>	6	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	206
AlCl <sub>3</sub>	50	CoCl <sub>2</sub>	238
NiCl <sub>2</sub>	24		

Chromium in synthetic wastewater was introduced as potassium dichromate. In the early experiment stage, artificial wastewater was transported to each CW-MFC reactor through a peristaltic pump. After preliminary experimental simulation, the Cr(VI), chemical

oxygen demand (COD), ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ ), and total phosphorous (TP) concentrations of the wastewater system were  $80\pm 5$ ,  $300\pm 10$ ,  $75\pm 5$ , and  $5\pm 0.5$   $\text{mg}/\text{dm}^3$ , respectively, and pH was 6.5–8.0. The HRT was 3 days. When one of the concentrations in the experiment was changed, the others were kept constant at optimum. After sufficient growth of the *Leersia hexandra* Swartz root system, the pollutant purification status and chromium concentration in the effluent become stabilized, at which point the reactor start-up is completed. The nonplanted system only needs the purification state of pollutants and the effluent chromium concentration to be stable. The effects of different operating conditions (Cr(VI), COD concentrations, and HRT) on the performance of the device were investigated. The influent Cr(VI) concentrations were 40, 60, 80, 100, and 120  $\text{mg}/\text{dm}^3$ . The COD concentrations were 100, 200, 300, 400, and 500  $\text{mg}/\text{dm}^3$ . The HRTs were 1, 2, 3, 4, and 5 days, respectively. The corresponding effluent quality and electricity generation performance were determined by changing Cr(VI) or COD concentration or HRT and controlling other operating conditions.

*Analyses and calculations.* After the system stabilized, samples were taken periodically from each reactor according to the experimental conditions. COD was determined by the dichromate water quality determination method (HJ828-2017). Ammonia nitrogen was determined by Nessler's reagent spectrophotometry method (HJ535-2009). Total phosphorus was determined using the ammonium molybdate spectrophotometric method (GB11893-89), and Cr(VI) by the 1,5-diphenylcarbohydrazide spectrophotometric solid waste determination method (GB7467-87). The pollutant removal rate ( $R_E$ ) can be calculated using the following equation:

$$R_E = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \quad (1)$$

where  $C_{\text{in}}$  is the CW-MFC pollutant influent concentration, and  $C_{\text{out}}$  is its effluent concentration.

The data acquisition card (NI USB-6009, Suzhou Fuyutong Electronics Co., Ltd., China) collected voltage information and was connected to a computer for real-time online monitoring. The current in the circuit was calculated using Ohm's law.

Power density and polarization curves were established by reducing the resistance from 10 000  $\Omega$  to 10  $\Omega$  every 15 min. The voltage ( $U$ ) was recorded at each resistance ( $R$ ) value. The current density  $I_V$  and power density  $P_V$  were calculated according to the following formulas, which were used to plot the power density and polarization curves

$$I_V = \frac{U}{RV} \quad (2)$$

$$P_v = \frac{UI}{V} \quad (3)$$

where  $V$  is the effective volume of the anode,  $\text{m}^3$ . For this study, the internal resistance of the CW-MFC was determined from the slope of the linear section of the polarization curve.

*Microbial community analysis.* The system filler was sampled as per the experimental requirements, 16S rRNA gene sequencing, and 454 high-throughput sequencing technology were used to analyze the microbial community structure. The filler samples were extracted and placed in sampling bottles, stored in ice packs during transportation to the laboratory, and then stored in a  $-80\text{ }^\circ\text{C}$  refrigerator for sequencing by Sangon Biotech (Shanghai) Co., Ltd. After sampling, the kit was first used for DNA extraction, followed by amplification and purification of the 16sRNA gene fragment in the V3-V4 region, and finally 454 high-throughput sequencing. The sequences after sequencing analysis were evaluated for OTUs, Ace, Chao1, Shannon, and Simpson indices in Trimmomatic software according to RDP classifier Bayesian algorithm, and the composition of microbial community structure was analyzed [14].

*Statistical analysis.* Analysis of variance (ANOVA) was performed to illustrate the statistical significance ( $p < 0.05$ ) of the impact of investigated factors on the CW-MFC system performance and was followed by a Duncan post hoc test ( $p < 0.05$ ). Differences between means were tested for significance ( $p < 0.05$ ) by Tukey's test. All of the statistical analyses were conducted using SPSS and Origin software.

### 3. RESULTS AND DISCUSSION

#### 3.1. EFFECT OF COD CONCENTRATIONS ON WASTEWATER TREATMENT AND POWER GENERATION IN A CW-MFC SYSTEM

For a COD concentration of  $300\text{ mg/dm}^3$ , the removal rates of COD, Cr(VI),  $\text{NH}_4^+\text{-N}$ , and TP in the experimental group were 93.73, 97.77, 86.18, and 93.23%, respectively, whereas those of the control group were 86.60, 93.57, 81.96, and 90.71%, respectively (Fig. 2). Similar phenomena were observed under other conditions. The reason for this difference may be that the existence of an external circuit promotes the transfer of electrons, thereby increasing the rate of oxidation–reduction reactions. In particular, phosphorus removal in CWs mainly depends on filler adsorption, plant absorption, and microbial utilization [15].

For COD concentrations in the range of  $100\text{--}500\text{ mg/dm}^3$ , the COD concentrations significantly ( $p < 0.05$ ) affected the removal rate of pollutants, the maximum COD removal rate was 93.73% ( $300\text{ mg/dm}^3$ ) (Fig. 2).

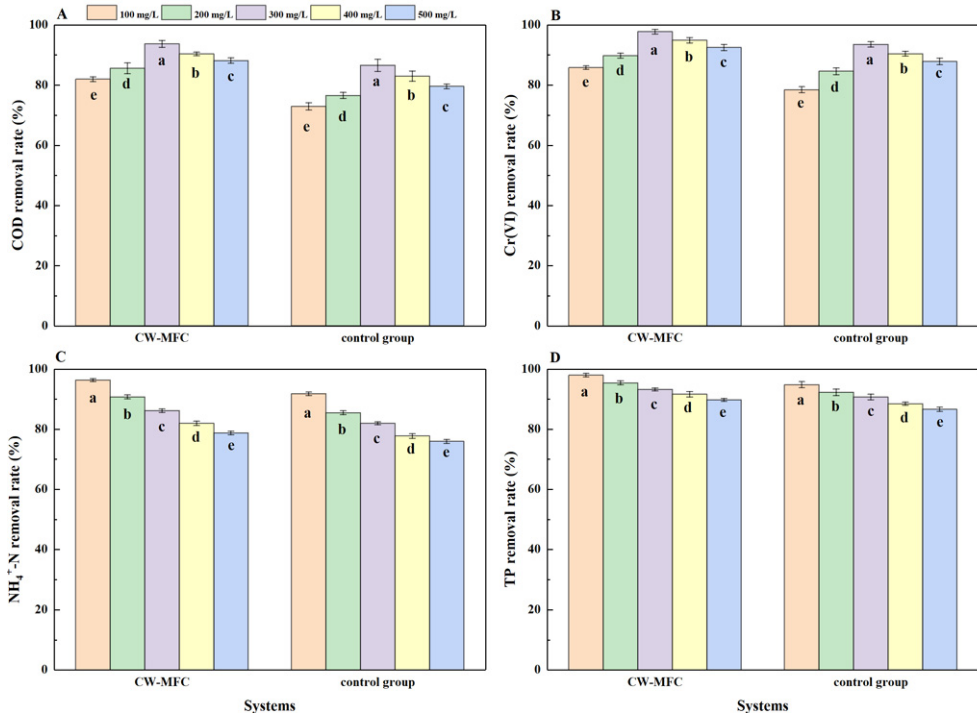


Fig. 2. COD (a), Cr(VI) (b), NH<sub>4</sub><sup>+</sup>-N (c) and TP (d) removal rates for various COD concentrations at initial concentrations of TP, NH<sub>4</sub><sup>+</sup>-N, and Cr(VI) of 5±0.5, 75±5, 80±5 mg/dm<sup>3</sup>, respectively, HRT was 3 days. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ )

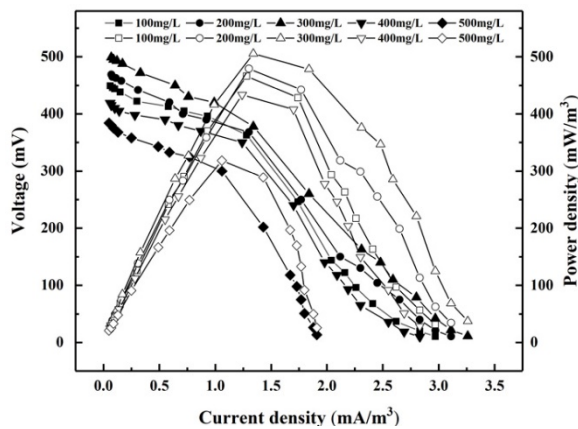


Fig. 3. Power density and polarization curves for various COD concentrations at initial concentrations of TP, NH<sub>4</sub><sup>+</sup>-N, and Cr(VI) of 5±0.5, 75±5, 80±5 mg/dm<sup>3</sup>, respectively

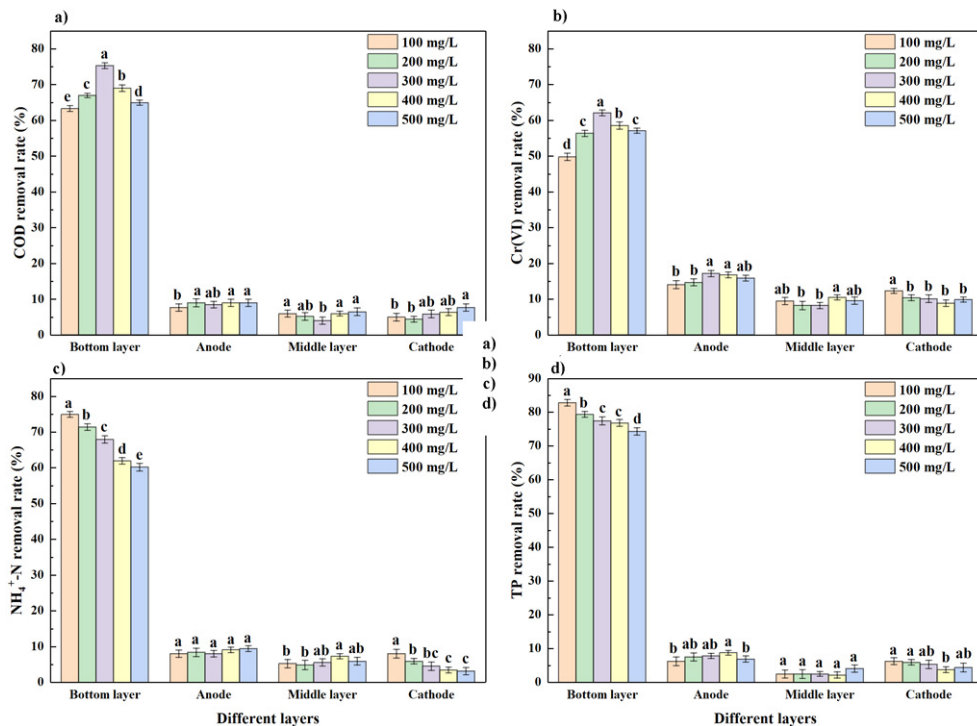


Fig. 4. COD (a), Cr(VI) (b),  $\text{NH}_4^+\text{-N}$  (c) and TP (d) removal rates for layers of various thickness and COD concentrations at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , and Cr(VI) of  $5 \pm 0.5$ ,  $75 \pm 5$ ,  $80 \pm 5$   $\text{mg}/\text{dm}^3$ , respectively, HRT was 3 days. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ ).

At this point, the maximum voltage of the system was 499 mV with a maximum power density of  $505.61 \text{ mW}/\text{m}^3$  (Fig. 3). When the COD concentration was  $500 \text{ m}/\text{dm}^3$ , the removal rate of Cr(VI) dropped to 92.54%, and the  $\text{NH}_4^+\text{-N}$  removal rate gradually decreased to 78.81%, but there was little change in the TP removal rate. Removal of pollutants mainly occurred within the bottom layer, the COD concentrations significantly ( $p < 0.05$ ) affected the removal rate of pollutants at the bottom layer of each system (Fig. 4). Within a certain concentration range, organic matter is initially decomposed into smaller molecules and then degraded by electrochemically active bacteria (EAB) and other bacteria on the CW-MFC anode [16]. With gradually increasing influent COD concentrations, microorganisms can obtain enough food to use for multiplying, oxidizing more organic matter, and generating abundant electrons with improved pollutant removal rates and the ability to generate electricity. However, beyond a certain COD concentration, too much organic matter may cause organic acids to accumulate in bacterial cells, thereby inhibiting the activity of microorganisms and reducing electrical



energy generation. Microorganisms have a limited ability to decompose and utilize organic matter, resulting in decreasing pollutant removal rates. Wen et al. [17] confirmed that increased COD concentration resulted in improved system bioelectricity outputs.

### 3.2. INFLUENCE OF Cr(VI) CONCENTRATION ON CW-MFC WASTEWATER TREATMENT AND POWER GENERATION

For Cr(VI) concentrations in the range of 40–120 mg/dm<sup>3</sup>, the Cr(VI) concentrations significantly ( $p < 0.05$ ) affected the removal rate of pollutants. The maximum removal rates of COD, Cr(VI), NH<sub>4</sub><sup>+</sup>-N, and TP were 94.67%, 98.31%, 97.05%, and 96.38%, respectively (Fig. 5), with a maximum system voltage of 370 mV and a maximum power density of 484.43 mW/m<sup>3</sup> (Fig. 6).

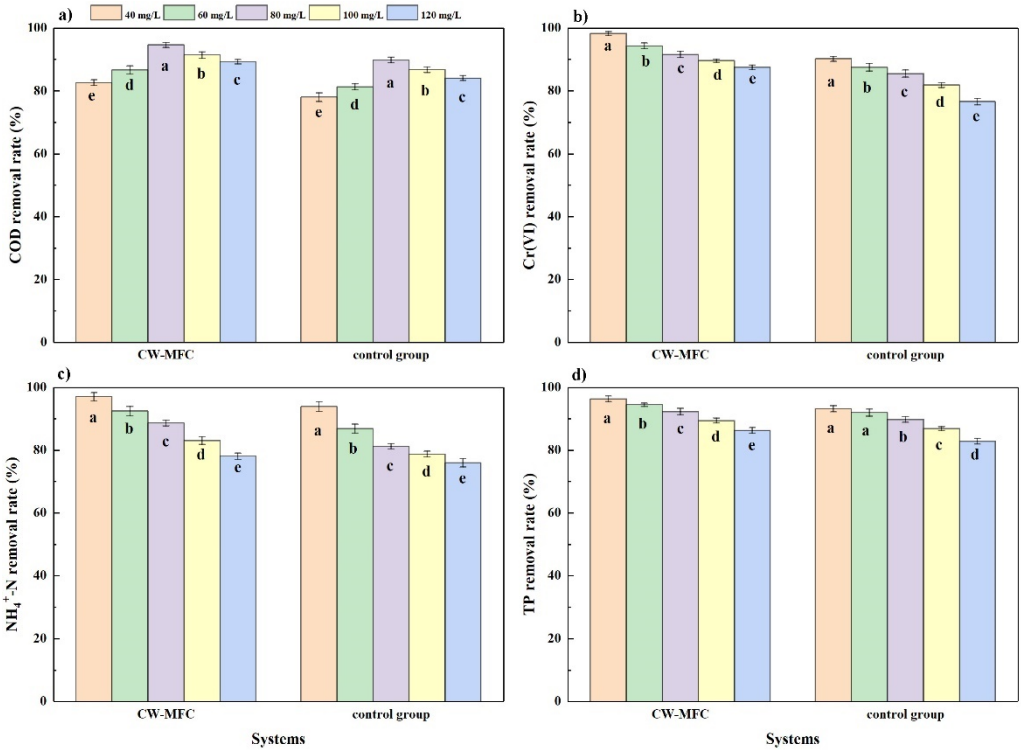


Fig. 5. COD (a), Cr(VI) (b), NH<sub>4</sub><sup>+</sup>-N (c) and TP (d) removal rates for various Cr(VI) concentrations at initial concentrations of TP, NH<sub>4</sub><sup>+</sup>-N, COD of 5±0.5, 75±5, 300±10 mg/dm<sup>3</sup>, respectively, HRT was 3 days. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ )

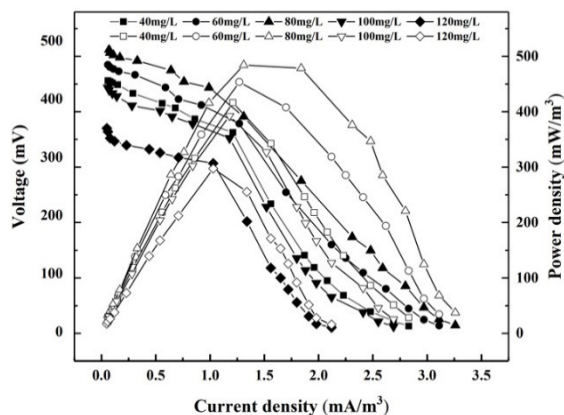


Fig. 6. Power density and polarization curves for various Cr(VI) concentrations at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , COD of  $5\pm 0.5$ ,  $75\pm 5$ ,  $300\pm 10$ , respectively. HRT was 3 days

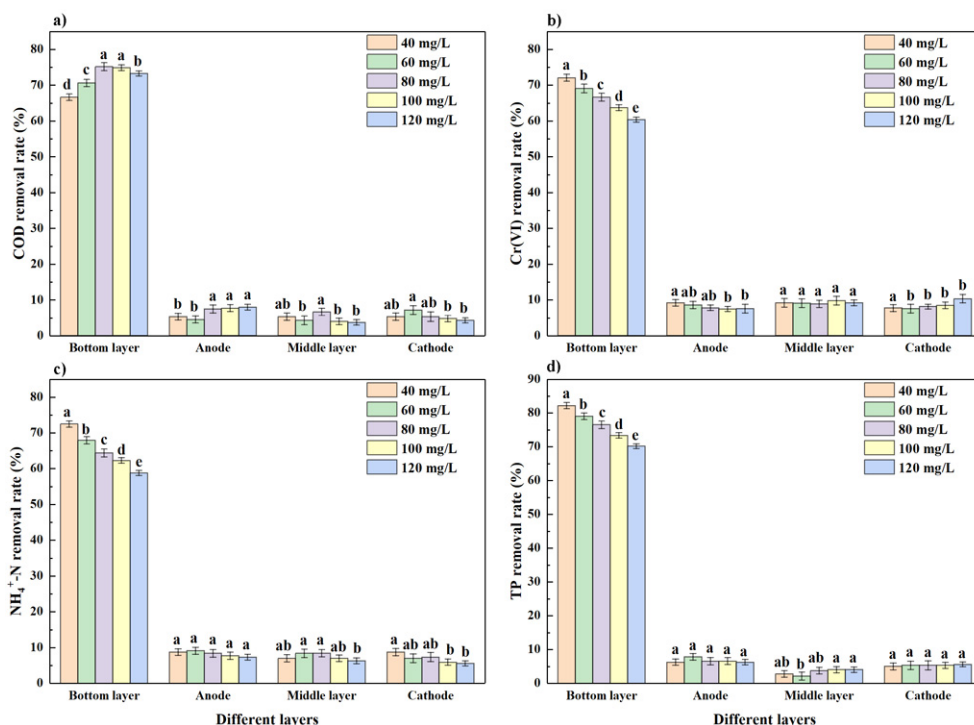


Fig. 7. COD (a), Cr(VI) (b),  $\text{NH}_4^+\text{-N}$  (c) and TP (d) removal rates for layers of various thickness and COD concentrations at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , and COD of  $5\pm 0.5$ ,  $75\pm 5$ ,  $300\pm 10$   $\text{mg/dm}^3$ , respectively. HRT was 3 days. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ )

Figure 7 indicates that pollutant removal occurs in the bottom layer. The Cr(VI) concentrations significantly ( $p < 0.05$ ) affected the removal rate of pollutants at the bottom layer of each system. When the concentration of Cr(VI) increases, Cr(VI) acts as an electron acceptor and hence consumes a large number of electrons, which not only leads to an increase in voltage but also improves the removal rate of Cr(VI) [18]. At relatively high Cr(VI) concentrations, the cathode acceptor accepts more electrons than are produced during the metabolism of the anode [3]. In addition, Cr(VI) concentrations above a certain level start to become toxic to microorganisms, inhibiting their activity, reducing power density, and reducing the removal rate of pollutants [18].

### 3.3. THE EFFECT OF HRT ON CW-MFC SYSTEM WASTEWATER TREATMENT AND POWER GENERATION

For an HRT of 1–5 days, the HRT significantly ( $p < 0.05$ ) affected the removal rate. The maximum removal rates of COD, Cr(VI), TP, and  $\text{NH}_4^+\text{-N}$  were 95.47, 96.91, 98.27, and 97.05%, respectively (Fig. 8). An HRT of 3 days corresponded to a maximum system voltage of 489 mV and power density of 479.21 mW/m<sup>3</sup> (Fig. 9).

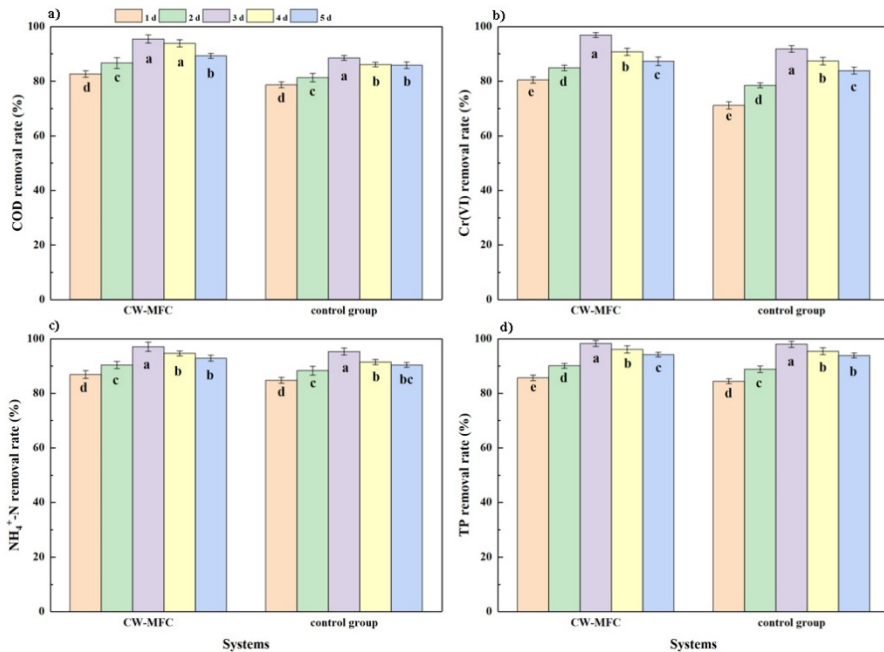


Fig. 8. COD (a), Cr(VI) (b),  $\text{NH}_4^+\text{-N}$  (c) and TP (d) removal rates for various HRT at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , and Cr(VI) of  $5 \pm 0.5$ ,  $75 \pm 5$ ,  $80 \pm 5$  mg/dm<sup>3</sup>, respectively,

HRT was 3 days. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ )

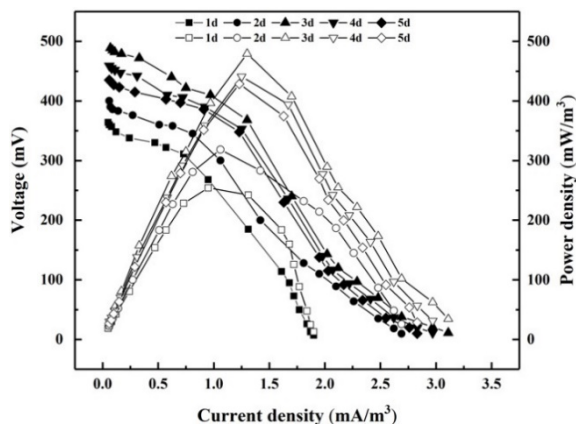


Fig. 9. Power density and polarization curves for various HRT values at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , COD, and Cr(VI) of  $5\pm 0.5$ ,  $75\pm 5$ ,  $300\pm 10$ , and  $80\pm 5$   $\text{mg}/\text{dm}^3$ , respectively

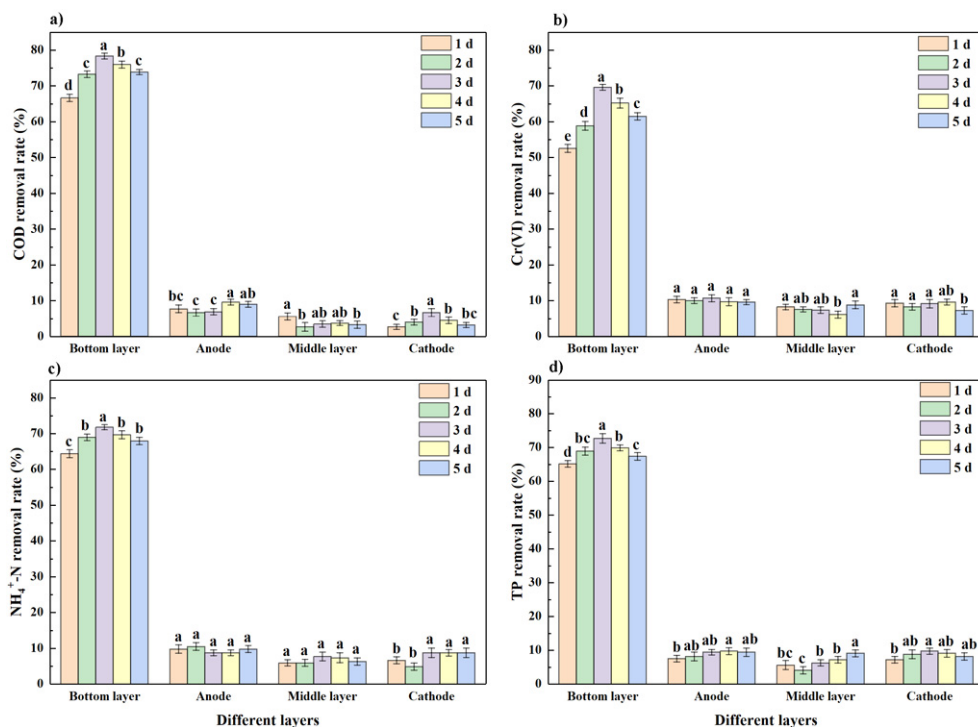


Fig. 10. COD (a), Cr(VI) (b),  $\text{NH}_4^+\text{-N}$  (c) and TP (d) removal rates for layers of various thickness and various HRT at initial concentrations of TP,  $\text{NH}_4^+\text{-N}$ , COD, and Cr(VI) of  $5\pm 0.5$ ,  $75\pm 5$ ,  $300\pm 10$ , and  $80\pm 5$   $\text{mg}/\text{dm}^3$ , respectively. Error bars indicate standard deviation. Letters a–e indicate significant differences between different treatment groups ( $p < 0.05$ ). The same letters suggest that there was no significant difference between different treatment groups ( $p > 0.05$ )

Figure 10 shows that pollutant removal mainly occurs through the physical and chemical effects of the substrate. The HRT significantly ( $p < 0.05$ ) affected the removal rate of pollutants at the bottom layer of each system. With increasing HRT, the electricity-producing bacteria have sufficient time to degrade organic matter and further their proliferation through anabolism, increasing the number of microorganisms and further increasing the rate of organic matter degradation. However, an excessively long HRT leads to an insufficient supply of organic matter, aggravates the anaerobic environment of the system, and is not conducive to aerobic degradation of organic matter or ammoniating and nitrification reactions. At this time, the activity of the electrogenic bacteria on the anode surface is decreased, thereby reducing the power generation performance of the system [19]. This study found the most suitable HRT to be 3 days, which is consistent with the results of Feng et al. [20].

#### 3.4. INFLUENCE OF PLANTS ON CW-MFC SYSTEM WASTEWATER TREATMENT AND POWER GENERATION

Tables 3 and 4 ( $p < 0.05$ ) demonstrate that in the planted (nonplanted) CW-MFC systems, the removal rates of COD,  $\text{NH}_4^+$ -N, TP, and Cr(VI) were 94.67 (87.20), 92.49 (84.07), 96.38 (89.13), and 98.31% (85.36%), respectively.

Table 3

The effect of plants on pollutant removal rates

Sample	Growth condition	Removal rate (mean $\pm$ SD) [%]			
		COD	$\text{NH}_4^+$ -N	TP	Cr(VI)
CW-MFC	planted	94.67 $\pm$ 1.10	92.49 $\pm$ 1.14	96.38 $\pm$ 1.32	98.31 $\pm$ 1.22
	nonplanted	87.20 $\pm$ 1.20	84.07 $\pm$ 1.51	89.13 $\pm$ 0.99	85.36 $\pm$ 0.94
Control group	planted	89.87 $\pm$ 1.15	86.88 $\pm$ 0.99	93.23 $\pm$ 1.27	90.25 $\pm$ 1.32
	nonplanted	84.27 $\pm$ 0.95	80.91 $\pm$ 0.87	88.82 $\pm$ 1.41	80.29 $\pm$ 1.67

Initial concentrations of TP,  $\text{NH}_4^+$ -N, COD, Cr(VI) were 5 $\pm$ 0.5, 75 $\pm$ 5, 300 $\pm$ 10, 80 $\pm$ 5 mg/dm<sup>3</sup>, respectively, and HRT = 3 days.

The planted system exhibited a maximum voltage and maximum power density of 490 mV and 484.43 mW/m<sup>3</sup>, respectively, whereas the nonplanted system displayed values of 384 mV and 295.54 mW/m<sup>3</sup>, respectively (Fig. 11). The higher degradation rate of pollutants in the plant system is attributed to reduction reactions of heterotrophic and electroactive microorganisms in the root zone and absorption by the plants in the system. Studies have supported that the diversity and richness of the functional bacteria with the ability to remove C, N, and P are enriched in the rhizospheres of the planted CW-MFC [21]. Wetland plants provide organic matter to the rhizosphere, which is then

degraded by EAB to generate electricity. Previous researchers noted that plants enhance bioelectricity by increasing the biodiversity of bacteria in CW-MFC systems (especially EAB) [22]. Plant physiological activities, including the root organic matter secretion and oxygen secretion, can typically influence the bioelectricity production of CW-MFC.

Table 4

Table 4. The effect of plants on pollutant removal rates (mean±SD) [%]

Site	Planted				Nonplanted			
	COD	NH <sub>4</sub> <sup>+</sup> -N	TP	Cr(VI)	COD	NH <sub>4</sub> <sup>+</sup> -N	TP	Cr(VI)
Bottom layer	75.20±1.09	67.93±0.95	76.54±0.85	72.12±1.00	70.67±0.77	60.91±1.12	72.44±1.26	63.93±0.86
Anode	82.67±1.12	77.05±1.07	85.35±0.97	81.34±0.80	77.33±0.80	70.04±0.97	81.26±0.89	72.23±1.00
Middle layer	89.33±1.13	85.47±1.24	91.34±0.93	90.56±0.75	81.07±1.00	78.46±0.88	85.35±0.75	79.33±0.97
Cathode	94.67±0.79	92.49±0.88	96.38±1.15	98.31±0.96	87.20±0.74	84.07±1.14	89.13±0.92	85.36±1.23

Initial concentrations of TP, NH<sub>4</sub><sup>+</sup>-N, COD, Cr(VI) were 5±0.5, 75±5, 300±10, 80±5 mg/dm<sup>3</sup>, respectively, and HRT = 3 days.

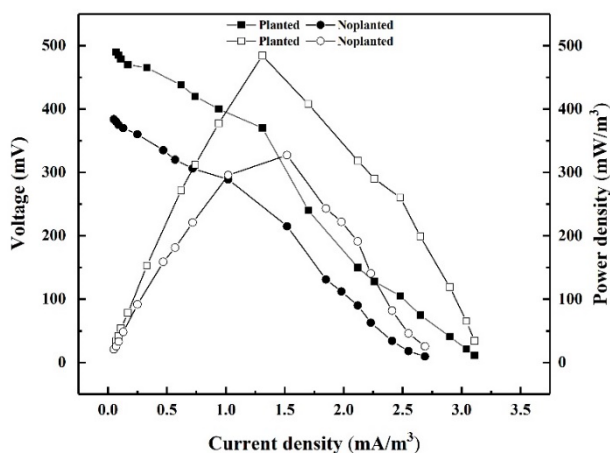


Fig. 11. Power densities and voltage vs. current density in relation to plant presence at initial concentrations of TP, NH<sub>4</sub><sup>+</sup>-N, COD, Cr(VI) of 5±0.5, 75±5, 300±10, 80±5 mg/dm<sup>3</sup>, respectively, and HRT of 3 days

#### 4. ANALYSIS OF THE MICROBIAL COMMUNITY STRUCTURE

As shown in Table 5, the higher Chao1 and Ace indices indicated the microbial community was more abundant. The higher the Shannon index, the lower the Simpson index, and the higher the community diversity is. The analysis of alpha diversity index

demonstrates that bioelectricity production in the CW-MFC system is more conducive to the growth and reproduction of microorganisms, as well as has a positive effect on the increase of community diversity.

Table 5

Statistics of the alpha diversity index

Sample	OTUs	Shannon	Chao1	Ace	Simpson
CW-MFC	1457	5	1748.26	1713.75	0.03
Control group	1325	4.59	1256.55	1287.06	0.06

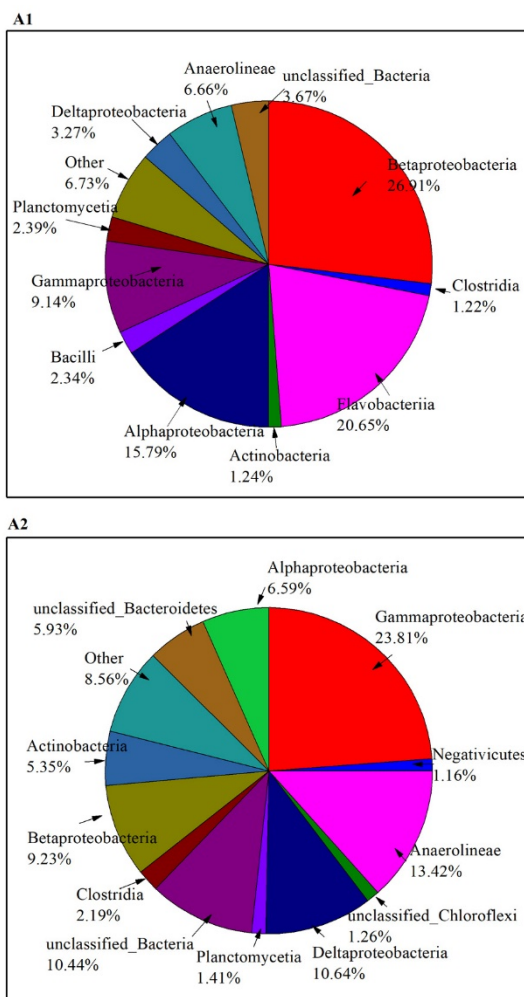


Fig. 12. Relative abundance map of microbial community composition at CW-MFC (A1) and control group class levels (A2)

Figure 12 shows the microbial community composition of CW-MFC and the control group at the class level. The microbial proportions of CW-MFC and control group are *Gammaproteobacteria* (26.91% and 23.81%), *Deltaproteobacteria* (20.65%, 10.64%), *Alphaproteobacteria* (15.79%, 6.59%), *Betaproteobacteria* (9.14%, 9.23%), and *Anaerolineae* (6.66%, 5.93%). As EABs, *Alphaproteobacteria*, *Betaproteobacteria*, *Gammaproteobacteria*, *Deltaproteobacteria*, and *Anaerolineae* have been reported to be relatively abundant. *Alphaproteobacteria* and *Gammaproteobacteria* were the predominant classes in all CW-MFC system groups, and both of them are conducive to the reduction of nitrates and nitrites.

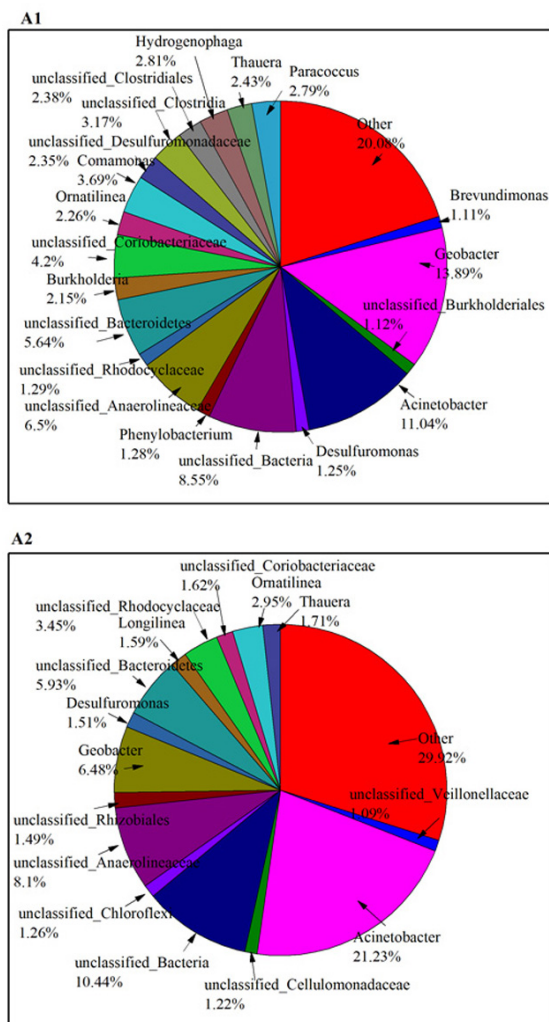


Fig. 13. Relative abundance map of microbial community composition at CW-MFC (A1) and control group genus levels (A2)



Previous studies have shown that *Gammaproteobacteria* can improve the denitrification efficiency and phosphorus removal [23]. *Deltaproteobacteria* include some anaerobic bacteria with other physiological characteristics, such as *Geobacter* [24]. In this study, electricity production and reduction of Cr(VI) can be promoted, which is also the reason for the higher removal rate of Cr(VI) and electricity production in CW-MFC.

The microbial taxa in the system are classified at the genus level (Fig. 13). Common genera identified by CW-MFC and control group primarily included (in %) *Acinetobacter* (11.04, 10.44), *Geobacter* (13.89, 6.48), *Thauera* (2.43%, 1.71), and *Desulfuromonas* (1.25, 1.51%). Pradhan et al. [25] demonstrated that *Acinetobacter*, a bacterium tolerant to many metals and oxygen-consuming pollutants, has been used for Cr(VI) removal and has shown good chromium-reducing ability. *Geobacter* was the most common electrogenic microorganism in MFC, and the energy conversion rate of *Geobacter metallireducens* was as high as 25.8% [26]. *Geobacter's* nanowire structure could achieve direct contact with electrodes and conduct electrons to electrodes, thus reducing electron loss when conducting via other electron mediators, and generating better electricity [27]. Moreover, Wang et al. [28] believed that *Desulfuromonas* were the possible EAB. Therefore, the relative abundance of *Geobacter* in CW-MFC contributed to the high power generation. *Thauera* was an autotrophic denitrifying bacteria. This could explain the high nitrogen removal efficiency of the CW-MFC.

## 5. CONCLUSIONS

The results of this work show that the CW-MFC system successfully promotes Cr(VI) wastewater treatment with simultaneous power generation. A COD concentration of 300 mg/dm<sup>3</sup> corresponded to the greatest COD and Cr(VI) removal rates (93.73% and 97.77%, respectively), with a maximum power density of 505.62 mW/m<sup>3</sup>, whereas a Cr(VI) concentration of 80 mg/dm<sup>3</sup> produced the greatest COD removal rate (94.67%) with a maximum power density of 484.43 mW/m<sup>3</sup>. A HRT of 3 d yielded the largest pollutant removal rate with a maximum power density of 479.21 mW/m<sup>3</sup>. The removal rates of COD, Cr(VI), NH<sub>4</sub><sup>+</sup>-N, and TP in the planted system were 94.67%, 98.31%, 92.49%, and 96.38%, respectively, with a maximum power density of 484.43 mW/m<sup>3</sup>. Therefore, the optimal conditions for water purification and electricity production found in this study are a COD concentration of 300 mg/dm<sup>3</sup>, a Cr(VI) concentration of 80 mg/dm<sup>3</sup>, and the HRT of 3 d in the CW-MFC system containing plants. Microbial community diversity in the CW-MFC was significantly higher than control group. The abundance of electrogenic bacteria *Geobacter* and metal dissimilatory reducing bacteria *Acinetobacter* in CW-MFC is higher than that in control group. The results of this study provide theoretical guidance for determining the optimal operating conditions and energy recovery of the CW-MFC system for treating chromium wastewater. The results of this study indi-

cate that the use of CW-MFC systems is expected to be able to reduce chromium pollution in water bodies. Therefore, CW-MFC can be used to treat industrial wastewater, which contains recalcitrant pollutants such as dyes and metals. CW-MFC produces bioenergy while improving treatment efficiency, but it cannot achieve practical application in power output. Therefore, the system can be further optimized to enhance bioelectricity production.

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