Effects of different cathode conditions on electricity generation and removal of heavy metal pollutants in CW-MFC

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Abstract: The effect of treating copper-containing wastewater by CW-MFC technology was discussed. The power generation and wastewater purification efficiency of CW-MFC are affected by electrode spacing, cathode electrode area and influent copper concentration. Smaller electrode spacing may destroy the anaerobic environment in the wastewater, while larger electrode spacing will increase the total internal resistance of the system, resulting in a decrease in electricity generation efficiency. With the increase of cathode area, the removal efficiency of pollutants in wastewater will be improved. However, when the cathode area is too large, it will increases the internal resistance of the system, which will affect the electric production performance. When the best electrode spacing is 10 cm and the cathode electrode area is 75 cm², CW-MFC shows the best power generation and wastewater purification effect. When the concentration of copper in the wastewater increases, the power generation and wastewater purification efficiency of the system will also increase. When the copper concentration reaches 50 mg/L, the system shows the best effect, its open circuit voltage reaches the maximum, and the removal rate of copper and total nitrogen is also the highest. When the concentration of copper in wastewater reaches 100 mg/L, the microbial activity is inhibited, resulting in a significant decline in the performance of CW-MFC.

1. Introduction

Copper ions in water bodies come from a wide range of sources, mainly from the wastewater produced in ore mining, electroplating, chemical industry and other industrial production. Trace amounts of copper are essential elements for biological growth. However, excessive amounts of copper ions have direct or indirect toxic effects on human body and other organisms[1]. There are many methods to treat copper-containing wastewater, the common ones include ion exchange, membrane filtration, chemical precipitation and electrochemical analysis [2-5]. However, these methods require energy consumption and are expensive. Finding efficient, low-energy ways to treat copper-containing wastewater has become particularly important.

Microbial fuel cell is a new kind of pollutant purification and production technology[6], which uses microorganisms attached to the electrode surface to degrade the pollutants in the wastewater and convert the chemical energy contained in the organic matter into electricity. It has been proved that microbial fuel cells can remove, recover and generate electricity continuously by using heavy metal ions in wastewater as electron acceptors [7]. In microbial fuel cells, organic matter is oxidized at the anode to produce protons and electrons, and most Cu²⁺ is reduced to Cu at the cathode, according to the following formula:

anode:CH₃COO⁻+4H₂O → 2HCO₃⁻+9H⁺+8e⁻
cathode:4Cu²⁺ + 8e⁻ → 4Cu(s)
overall:CH₃COO⁻ + 4Cu²⁺ → 2HCO₃⁻ + 9H⁺ + 4Cu(s)

The maximum voltage and power density in soil MFC studied by Wang et al were 539 mV and 65.77 mW/m², respectively, and copper enrichment was achieved in cathode soil [8]. These studies have investigated the feasibility and performance of removing copper wastewater with two-compartment MFC. However, few studies have been conducted on the effects of different copper ion concentrations on the performance and microbial community of single-compartment MFC. In this study, single-compartment CW-MFC was used to treat copper wastewater, and the effects of different electrode spacing and different electrode areas on the electricity generation and Cu²⁺ removal of copper wastewater treated by CW-MFC were compared. The reasons for the influence of different electrode conditions on the treatment of copper wastewater by CW-MFC were explored, and the removal mechanism and final destination of Cu in CW-MFC were clarified.

2. Materials and methods

2.1 Experimental equipment

The CW-MFC reactor used in the experiment was made of a polycrylic plastic bucket with a height of 350 mm and an inner diameter of 150 mm. The electrodes are...
composed of two square sheets of carbon felt (20 mm thick, Tianjin Carbon Factory, China) with stainless steel wire mesh (16 mesh, Taizhou Subei Laboratory Supplies, China). The carbon felt was soaked with 1 mol of sodium hydroxide and 1 mol of concentrated nitric acid before use to eliminate possible metal ion contamination. The carbon felt and stainless steel wire mesh are fixed by titanium wire (Anhui Zhengying Scientific Research, China) with a diameter of 0.5 mm, and the leading device is used as a wire. The reactor structure includes a support layer, an anode layer, a spacer layer and a cathode layer. The support layer and spacer layer are filled with 20 mm pebbles to achieve insulation and support functions. The anode and cathode layers are filled with 5mm pebbles. The cathode is located at the top of the device, the anode is buried in the anode layer, connect 1000 Ω resistors to a closed loop with copper wires. CW-MFC has a total volume of 1.9 L and a net volume (liquid volume) of 0.9 L. Cannaindica L. was planted in the cathode with a plant length of 30-40 cm, which was collected from Xuzhou aquatic plant Base in Jiangsu Province, China. After 30 days of culture with nutrient solution, the plants were rinsed with distilled water and transplanted to the cathode layer of CW-MFC unit.

2.2 Sludge inoculation

The sludge used in the experiment (taken from the anaerobic sludge of Xi’an No. 4 Sewage Treatment Plant) was acclimated for more than 10 days before being inoculated into the anode chamber. The microbial nutrient solution consisted of 5 mM phosphate buffer. Glucose (0.8 g/L), NH₄Cl (0.15 g/L), KCl (0.13 g/L), MgSO₄*7H₂O (0.025 g/L) and 1 mL/L trace elements. In the experiment, the nutrient solution to the unit at a rate of 0.3 ml per experiment, during this process, use a pump to deliver the nutrient solution regularly. During the experiment, deionized water was replenished to compensate for evaporation losses.

2.3 Experimental Operation

Five wetland plants of Canna 80.5 g were used in the experiment. Each group of devices included three parallel devices, and the fresh weight of plants in each device was kept the same as far as possible. A group of plant-free CW-MFC was also set as a comparison. The intermittent mode was adopted in the experiment, and the wastewater was mixed by nutrient solution and CuSO₄•5H₂O. At the time of sampling, a syringe was used to take 0.5 ml of samples from each of the spacer layer, anode layer and cathode layer of the device and mix them. The sample to be measured is then filtered through the microporous filter head to remove the solid residue. After the experiment officially started, samples were taken every hour for analysis.

2.4 Analysis and calculation

After stabilizing the voltage to the highest value, connect the variable resistance box to the CW-MFC and change the value from 10,000 Ω to 5 Ω. Measure the potential of the cathode and anode using a silver chloride reference electrode (Ag/AgCl, 0.198 V vs. SHE). The power and current are calculated by dividing the effective area of the anode to obtain the power density (mW/m²) and current density (mA/m²) of CW-MFC, respectively.

Cu²⁺ was determined by spectrophotometric method HJ 485-2009 (in ammonium solution (pH=8 ~ 10), copper reacted with sodium diethyl dithiocarbamate to form a yellow-brown complex, which can be extracted with carbon tetrachloride or trichloromethane. Absorbance color can be stable for 1 h when measured at 440 nm wavelength).

After the end of the experiment, the cathode and anode carbon felt were removed, and the samples were treated with a vacuum device to remove water. The morphology of the reduction products on the cathode surface was observed by scanning electron microscopy (SEM), and use energy dispersive spectrometer (EDS) analyzed the composition and proportion of the elements contained in the reduced substances attached to the electrode surface. Finally, the plants were taken out completely, divided into above-ground and underground parts, dried at 60°C for 24 h in an electric constant temperature oven (101-2A, Tianjin Testing Instrument Co., LTD.), weighed and ground. The plant tissue after grinding was accurately weighed to 1 g and dissolved in HNO₃/HClO₄ (3/1) mixed acid. Then ICP-OES was used to determine the Cu content in the digestion solution. The Cu content of negative and anode carbon felt was determined by a similar method. The proportion of Cu in the water phase can be calculated by formula (1), the total Cu in the solid phase is calculated according to (2), and the contribution ratio of plant absorption plantη, cathodic reduction cathode η and anode precipitation anode η Cu²⁺ removal is calculated according to (3), (4) and (5).

\[
\eta_{\text{effluent}} = \frac{C_{\text{Cu-\text{influent}}}}{C_{\text{Cu-effluent}}} \times 100\% \\
W_{\text{Cu-solid}} = W_{\text{Cu-\text{plant}}} + W_{\text{Cu-cathode}} + W_{\text{Cu-anode}} \\
\eta_{\text{plant}} = (1 - \eta_{\text{effluent}}) \times 100\% \\
\eta_{\text{cathode}} = (1 - \eta_{\text{effluent}}) \times 100\% \\
\eta_{\text{anode}} = (1 - \eta_{\text{effluent}}) \times 100\% 
\]

Where \( C_{\text{Cu-influent}} \) and \( C_{\text{Cu-effluent}} \) respectively represents the copper content of inlet and outlet water. \( W_{\text{Cu-plant}} \), \( W_{\text{Cu-cathode}} \), \( W_{\text{Cu-anode}} \) respectively represents the copper content of plant, cathode carbon felt, anode carbon felt.
3. Results and discussion

3.1 Electric generation performance of different electrode areas

Figure 1 shows that the voltage and power density of CW-MFC with three different cathode areas are very different at the same current density. The open circuit voltages of CW-MFC with cathode areas of 100 cm$^2$, 75 cm$^2$ and 25 cm$^2$ are 642 mV, 650 mV and 589 mV, respectively, this suggests that increasing the area of the cathode may be beneficial for increasing the cathode potential and battery voltage. As the current density gradually increases, the voltage output shows the following trend: 75 cm$^2 > 100$ cm$^2 > 25$ cm$^2$, and the maximum power density of CW-MFC with cathode area of 25 cm$^2$, 75 cm$^2$ and 100 cm$^2$ is 17.8 mW/m$^2$, 31 mW/m$^2$ and 21.9 mW/m$^2$, respectively. Therefore, it can be concluded that when the cathode area is 75 cm$^2$, the electrical production performance of CW-MFC is the best.

As the current density gradually increases, the voltage output sequence is as follows: 75 cm$^2 > 100$ cm$^2 > 25$ cm$^2$, and the maximum power density of CW-MFC with cathode area of 100 cm$^2$, 75 cm$^2$ and 25 cm$^2$ is 21.9 mW/m$^2$, 31 mW/m$^2$ and 17.8 mW/m$^2$. Therefore, according to the experimental results, when the cathode area is 75 cm$^2$, the electrical production performance of CW-MFC is the best.

According to the data shown in Figure 2, as the area of the cathode expands of CW-MFC, the removal rate of Cu$^{2+}$ is accelerated. At 9h, When the cathode area is 25 cm$^2$, the removal efficiency of Cu$^{2+}$ reaches 66.4%, when the cathode area of CW-MFC is 75 cm$^2$ and 100 cm$^2$, the removal efficiency of Cu$^{2+}$ reaches 72.1% and 75.6%. As the surface area of the cathode increases, the material transfer rate in the system will increase, thus improving the removal efficiency of Cu$^{2+}$. In addition, a larger cathode area can provide a larger living place for microorganisms, increasing the number of catalytic bacteria, thus significantly reducing the activation internal resistance (i.e., cathode activation loss) of biological cathodes. In addition, the assimilation and dissimilation processes of heavy metal ions in microorganisms are promoted because the microbial population increases. Therefore, CW-MFC with larger cathode area has a more significant removal effect on Cu$^{2+}$.

3.3 Electric generation performance of different electrode spacing

According to the results in Figure 3, under open circuit conditions, when the electrode distance is 5cm, 10cm and 15cm, its open circuit voltage is 607 mV, 680 mV and 500 mV, respectively. With the increase of current density, the battery voltage of CW-MFC decreases, and the battery voltage output sequence at different electrode distances is: 10 cm > 5 cm > 15 cm. When the electrode distance is 10 cm, the maximum power density of CW-MFC reaches 30.8 mW/m$^2$, which is much higher than the maximum power density at 5 cm (21.5 mW/m$^2$) and 15 cm (15.0 mW/m$^2$). When the electrode spacing is too large, the internal resistance of CW-MFC increases, this impedes the flow of electrons and mass transfer, thereby reducing power output efficiency. Therefore, at an electrode distance of 10 cm, CW-MFC achieves the highest power output. Zhou et al. studied the effect of electrode distance (1 cm, 2 cm, 3 cm and 4 cm), the results show that it has the highest power density, 35.4 mW/m$^2$[9], when the electrode distance was 2 cm.

3.2 Influence of different electrode areas on the treatment effect of heavy metals

According to the data shown in Figure 2, as the area of the cathode expands of CW-MFC, the removal rate of Cu$^{2+}$ is accelerated. At 9h, When the cathode area is 25 cm$^2$, the removal efficiency of Cu$^{2+}$ reaches 66.4%, when the cathode area of CW-MFC is 75 cm$^2$ and 100 cm$^2$, the removal efficiency of Cu$^{2+}$ reaches 72.1% and 75.6%. As the surface area of the cathode increases, the material transfer rate in the system will increase, thus improving the removal efficiency of Cu$^{2+}$. In addition, a larger cathode area can provide a larger living place for microorganisms, increasing the number of catalytic bacteria, thus significantly reducing the activation internal resistance (i.e., cathode activation loss) of biological cathodes. In addition, the assimilation and dissimilation processes of heavy metal ions in microorganisms are promoted because the microbial population increases. Therefore, CW-MFC with larger cathode area has a more significant removal effect on Cu$^{2+}$.
In order to explain the difference of electrical properties of CW-MFC at different electrode distances, the total internal resistance of three kinds of CW-MFC was calculated by linear quasi-summation of polarization curves. The results show that the total internal resistance of CW-MFC at the electrode distance of 10 cm is the lowest, which is only 314.6 Ω. In contrast, the internal resistance of 5 cm and 15 cm electrodes was 62% and 111% higher than that of 10 cm, 508.7 Ω and 662.9 Ω, respectively. In the process of increasing the electrode spacing from 10 cm to 15 cm, the main reason for the increase of the total internal resistance is the increase of the transmission distance between the anode and the cathode of the protons generated by the degradation of organic matter, which leads to the increase of the mass transfer resistance inside the system.

3.4 Influence of different electrode spacing on the treatment effect of heavy metals

The Figure 4 shows the removal effect of different electrode spacing on Cu²⁺. CW-MFC with electrode spacing of 10 cm has the highest removal efficiency for Cu²⁺, which is 71.3%, then the electrode distance is 5 cm (70.4%). However, the removal rate of Cu²⁺ in CW-MFC with electrode distance of 15 cm is the worst, only 68.2%. The results show that when the electrode distance is 10 cm, the removal efficiency of Cu²⁺ and electricity generation is the best.

![Figure 4 Removal efficiency of Cu²⁺ in CW-MFC system at three electrode spacing](image)

3.5 Electric generation performance of CW-MFC system with different Cu²⁺ concentration

According to the data in Figure 5, CW-MFC systems exhibit different voltage and power density curves under different influent Cu²⁺ concentrations. As the influent Cu²⁺ concentration increases, the maximum voltage and power density of the CW-MFC system both increase. When the influent Cu²⁺ concentration is 0 mg/L, the maximum voltage obtained is 630.6 mV, and when the influent Cu²⁺ concentration is increased to 50 mg/L and 50 mg/L, the maximum voltage obtained is 630.6 mV. The maximum voltage obtained by CW-MFC system is 641.4 mV and 666.2 mV, respectively. However, when the influent Cu²⁺ concentration reaches 100 mg/L, the maximum voltage and power density begin to drop dramatically. According to the calculation of polarization curve, the total internal resistance of CW-MFC with influent Cu²⁺ concentration of 0 mg/L, 15 mg/L and 50 mg/L is lower than 400 Ω, while that of CW-MFC with influent Cu²⁺ concentration of 100 mg/L is as high as 1557 Ω. This indicates that the high concentration of heavy metals will inhibit the activity of electrogenic microorganisms, resulting in the increase of the activated internal resistance of the system[10], therefore, this will have an impact on the voltage and power output.

![Figure 5 Power density curves and polarization curves of Cu²⁺ concentrations in different influents](image)

3.6 Removal efficiency of Cu²⁺ at different Cu²⁺ concentrations

According to the data shown in Figure 6, the removal efficiency of Cu²⁺ by CW-MFC at different influent Cu²⁺ concentrations showed an obvious trend. In CW-MFC with lower influent Cu²⁺ concentration, the removal efficiency of Cu²⁺ is higher. Among them, the removal efficiency of CW-MFC with Cu²⁺ concentration of 50 mg/L reached 94.72% at 8h, followed by CW-MFC with Cu²⁺ concentration of 15 mg/L, at 8h, the removal efficiency was 85.47%. The removal rate of CW-MFC with Cu²⁺ concentration of 100 mg/L was only 78.20%. CW-MFC with influent Cu²⁺ concentration of 15 mg/L and 50 mg/L showed little difference in the remaining Cu²⁺ concentration at hour 8, which was 2.18 mg/L and 2.63 mg/L. As the influent Cu²⁺ concentration increases, the time required for CW-MFC to remove copper ions becomes longer, and the 8 h Cu²⁺ concentration of CW-MFC with influent Cu²⁺ concentration of 100 mg/L is 21.8 mg/L, which is much higher than the first two. This indicates that there are more effective electron acceptors in the CW-MFC system at lower Cu ion concentration, and the electrochemical reaction rate is accelerated with the increase of Cu ion concentration, thus making the removal efficiency of Cu ion higher. However, when the concentration of copper ions is too high (100 mg/L), it exceeds the tolerance of the microorganisms to copper, and the inhibition of the metabolic activity of the microorganisms is more obvious[9], which greatly reduces the removal effect of copper ions in the system.
4. Conclusion

The influence of cathode electrode area on pollutant removal and power generation of CW-MFC was investigated. The device with a cathode area of 75 cm² has the best electrical performance, the best wastewater purification effect, the open circuit voltage of 650 mV, the maximum power density of 31 mW/m², and the lowest internal resistance of the three is only 433.7 Ω. The copper removal rate of the device with cathode area of 75 cm² is slightly lower than that of the device with 100 cm², which is 72.1% and 75.6%, respectively, and the removal efficiency of total nitrogen is 66.2% and 67.9%, respectively, which is much higher than that of the device with cathode area of 25 cm². Therefore, Selecting 75 cm² as the most suitable cathode electrode area.

When the cathode area was controlled to 75 cm², three kinds of electrode spacing were set, 5 cm, 10 cm and 15 cm, and the influence of electrode spacing on the electricity generation and pollutant removal of CW-MFC was explored. Among them, the device with electrode spacing of 10 cm is the best to produce electricity, the maximum open circuit voltage is 680 mV, the maximum power density is 30.8 mW/m², and the removal rate of copper and total nitrogen in wastewater is 71.3% and 67.1%, respectively. Therefore, the electrode spacing of 75 cm² is the best.

Different influent copper ion concentrations have different effects on CW-MFC. Since copper ions can be reduced as electron acceptors at the cathode, when the influent copper ion concentration is small, the electricity generation of CW-MFC increases with the increase of copper concentration, but when the influent copper concentration is too high, the microbial activity is inhibited and the electricity generation of the system is greatly reduced. In the four influent copper concentrations of 0 mg/L, 15mg/L, 50mg/L and 100 mg/L, the power generation of CW-MFC system has been increasing during the process of increasing from 0 mg/L to 15 mg/L and then to 50 mg/L. When the influent concentration is 50 mg/L, the maximum power density reaches 37.1 mW/m². The removal rate of copper was 94.72%. When the influent Cu²⁺ concentration is 100 mg/L, the electricity generation performance decreases sharply, and the maximum power density is only 18.8 mW/m², which is 49.3% lower than that when the influent concentration is 50 mg/L. The removal efficiency of pollutants showed the same trend as that of CW-MFC. When the influent concentration was 50 mg/L, the wastewater purification effect was the best, and the copper removal rate was 94.72%.

References