Research on treatment of wastewater containing heavy metal by microbial fuel cell

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Abstract. With rapid development of social economy, serious problem has been caused by wastewater containing heavy metals, which was difficult to be treated by many kinds of traditional treatment methods, such as complex processes, high cost or easy to cause secondary pollution. As a novel biological treatment technology, microbial fuel cells (MFC) can generate electric energy while dealing with wastewater, which was proposed and extensively studied. This paper introduced the working principle of MFC, the classification of cathode, and the research progress on the treatment of wastewater containing Cr(VI), Cu(II), Ag(I), Mn(II) and Cd(II) by MFC. The study found that different cathode, different heavy metals anddifferent hybrid systems would affect the performance of the system and removal effect for heavy metal in MFC. MFC was a highly potential pollution control technology. Until now, the research was still in the laboratory stage. Its industrial application for recovery of heavy metal ion, improving the energy recovery rate and improvement or innovation of system were worthy of further research.

1. Introduction

Treatment of industrial wastewater has always been the research focus at home and abroad. Industrial wastewater contains a variety of heavy metals which is not only difficult to be degraded in the natural environment, but also can transfer into human bodies, accumulated in human organs through the food chain, and caused a serious threat to human health. At present, the main methods for treating wastewater containing heavy metal can be divided into three types, including physical methods, chemical methods[1]and biological methods[2]. Although physical methods and chemical methods have high efficiency, they need large investment and are easy to cause secondary pollution, while biological method has the advantages of low cost and without producing secondary pollution. Microbial fuel cell is a novel biological technology that can degrade waste water by electrogenesismicroorganism, which can simultaneously produce electricity and treating wastewater, and has been paid more and more attention by researchers at home and abroad.

In recent years, MFC technology has shown wide application prospects in the field of pollution control and their research grow exponentially each year. Numerous studies are focusing on improving

the power density of MFC, reducing the internal resistance, optimizing the structure of the reactor and so on.As a novel technology that combined wastewater treatment with biological electricity generation, its structure can generally divide into anode chamber and cathode chamber. The organic substrate in the anode chamber was degraded by microorganisms to produce protons and electrons, then the protons were transferred to the cathode chamberfrom the anode chamber via the proton membrane and the electrons were transferred to the cathode through a outer wire, and finally the oxygen (or other expensive species) located at the cathode was reduced as an electron acceptor to complete the internal charge transfer[3]. Some heavy metals have strong reducibility, which can be as good electronic acceptors for MFC to produce electricity. This paper briefly introduced the principle of reducing heavy metal by MFC and relative configurations of MFC. Recent improvement in the study of MFC for treating wastewater containing heavy metal, such as Cr(VI), Cu(II), Ag(I), Mn(II) and Cd(II), was systematically introduced, and the prospects of combining MFC with other new technology were also discussed.

2. Principle of reducing heavy metal by MFC

Protons produced in the anode chamber are transferred to the cathode chamber trough a separator which is one of the important parts in MFCs. Some MFCs are membrane-less. Without a separator, the diffusion of oxygen and substrate would increase, and thus lower the coulombic efficiency and the catalytic activity of anode microorganisms [4]. Proton exchange membrane (PEM), for example, is a kind of common separator. In recent studies, ion exchange membranes (IEMs), size-selective separators and salt bridge, have been explored to be used as separators in MFC [4]. In the cathode chamber, electrons and protons being transferred from the anode were used for reduction reaction and heavy metal ions were acted as electron acceptors. The heavy metal ions were removed as solids, transformed into non-toxic state, etc. For example, toxic Cr(VI) was reduced to less toxic Cr(III) in MFC[5]. Ag(I) ion was reduced to Ag (0) as solid in MFC[5].The heavy metal pollutants were removed, and then continuously generated and transferred electrons to form the current. Because of the existence of over potential, mass transfer resistance and other influence factors, the cathode redox potential of MFC should be at least 0.3 V higher than that of anode[6]. At present, the studies of heavy metal ions as electron acceptors in cathode, were focused on hexavalent chromium, silver ion and divalent copper ion, and so on, which have higher redox potential. The reaction equation of MFC with glucose as substrate of reaction in the anode chamberisas follows:

$$\text{Anode: } C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

The reaction equation for heavy removal in the cathode and the redox potential were shown in table 1.

Table 1. The electrode potential of reduction of heavy metals by MFC

Pollutant	Equation of reduction	Electrode potential of reduction/V
Cr(VI)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (2)	+1.33V
Cu(II)	$Cu^{2+} + 2e^- \rightarrow Cu$ (3)	+0.337V
Ag(I)	$Ag^+ + e^- \rightarrow Ag$ (4)	+0.799V
Mn(VII)	$MnO^{4-} + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ (5)	+1.70V
Cd(II)	$Cd^{2+} + 2e^- \rightarrow Cd$ (6)	-0.40V

3. Classification of Cathode

Previous studies on MFC were mostly focused in theanode.With the in-depth study, optimized functions of cathode are also attracted in recent years. At present, the cathode for treating wastewater containing heavy metal can be divided into two types of non-biological cathode and biological cathode.

3.1. Non-biological cathode

In general, in a traditional non-biological cathode MFC, wastewater containing single heavy metal was used as electron acceptor of cathode, and the other materials with catalytic properties were used to modify cathode for catalyzing reaction on the cathode. Base materials of the cathode are graphite, carbon cloth, carbon paper, carbon felt, etc. Studies had shown that stainless steel mesh, foam nickel

and other metals could also be used as base materials for the cathode[7-9].The catalyst on the base materials was favorable for the occurrence of redox reactions.Activated carbon, Pt, transition metals (CoTMPP[10], Fe[11]) and their complexes (e.g. FeEDTA[12]) were commonly used as catalysts in the researches. In recent years, with the appearance of grapheme, the focus of research has turned to the combination of conductive polymers and grapheme. Some studies have referred that Nitrogen-doped grapheme (NG)[13], modified Graphene/Polyaniline[14] and composites of Graphene/Co-Mo carbide[15] having the advantages of simple preparation and low cost.

The aeration for wastewater containing heavy metal in MFC can improve the energy output of MFC system, which has been demonstrated by comparing exposed nitrogen cathode with aerating wastewater containing Cr(Ⅵ) in the cathode. It was inferred that the following reaction occurs in the air cathode[16-17]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O(7)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2(8)$$

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + O_2(9)$$

The rate of Cr(Ⅵ) removal could be accelerated by the mid product H_2O_2.At the same time, electricity production was improved by reducing internal resistance and cathodic polarization[18].

3.2. Biocathode

Microorganisms were used as catalysts in the cathodes, which were usually divided into aerobic and anaerobic. Aerobic type is the microorganism in the cathode directly or indirectly using oxygen as an electron acceptor for redox reaction. Anaerobic type is under anaerobic conditions that the nitrate[19-21], sulfate[22-24], fumarate[25], carbon dioxide[26-27]etc, as electrons acceptors instead of oxygen. Compared with the aerobic type, the anaerobic type can avoid the oxygen diffuse from cathode to the anode chamber, thus maintaining the anaerobic environment of the anode chamber.

Biofilm is the key to producing electricity and process in gpollutants. Therefore, it is important to form an enriched electron-accepting (electrotrophic) biofilm via microorganism acclimatization on the surface[28] before starting the reactor. Anaerobic sludge digestion solution and suitable heavy mental wastewater could be used as inoculation sources for acclimatization of microorganism[29]. In addition, local microorganisms in heavily polluted areas were directly used asinoculums in there searches[30].Besides, a new acclimatization method by firstly enriching an exoelectrogenic biofilm on a MFC anode, then following directly inverting the anode to function as the biocathode, had been established[31].

Biological cathode had the characteristics of faster reduction rate, lower price, milder working conditions etc, which was beneficial to operate the MFC continuously and economically. At the same time, it was a good method to avoid the shortcoming of inactivation of Pt and other metal catalyst[32]. If the biocathode was used in heavy metal wastewater treatment, pre-domestication is an important step. Wastewater containing heavy metals may have an effect on the growth and reproduction of microorganisms, therefore, screening out the microorganisms in the wastewater containing heavy metal is the prerequisite to start the reactor. Moreover, how to maintain the activity of microbes during the later run is worthy of attention.

4. Treatment of heavy metal by MFC

4.1. Cr removal by MFC

A classic double chamber MFCs, which used carbon paper as anode and cathode, had been used for the treatment of Cr(VI) (200 mg/L) in cathode electrolyte, with glucose as the anode solution. According to the result, the lowest concentration of Cr(Ⅵ) could only reach 160 mg/L and the treatment efficiency was about 20 %. The reason why removal rate was only 20 % is that proton transport capacity of double chamber MFCs connected by salt bridge was much less than double chamber MFCs connected by membrane (PEM)[33]. Another reason is that the nutrient solution (glucose) was consumed by the growth of microorganism rather than producing electricity. In order to

study Cr(Ⅵ) removal efficiency of the MFCs, anaerobic sludge with glucose nutrient solution had been used as the anode substrate. At the same time, it had been found that the removal rate of Cr(VI) could reach 100% at pH 2,because this reaction strongly depended on pH[34]. The result was that lower pH might make the reaction more favorable. The study proved that the MFCs had great potential applications for synchronously treating wastewater containing Cr(VI) and producing electricity[35]. In general, treatment of MFC contain in gchromium is a conversion of toxic Cr (VI) to less-toxic Cr (III), but the separation of Cr (III) from the reactor is still a challenge.

4.2. Cu(II) removal by MFC

It had been demonstrated that surplus sludge from the municipal sewage treatment plant could be used as an anode substrate to remove copper from cathode solution containing $CuSO_4$, and a highest removal efficiency of 97.8% for Cu(II)could be reached, at the same time the surplus sludge in the municipal sewage could be disposed[36]. Cu(II)removal efficiency could be significantly affected by the pH value of the aqueous solution in the MFC. X-ray diffraction analysis confirmed that copper solids as metal copper and Cu_2O in a cathode were deposited on the copper electrode with simultaneous electricity generation by using glucose as the cathode substrate. High Cu(II) removal efficiency (>99%), which being below 1.3mg/L of the US Environmental Protection Administration (USA EPA) maximum contaminant level for drinking water, and maximum power density could be reached at the initial 196.2±0.4mg Cu(II) and the pH value of 4.7 under the condition of having no external resistor or external resistor of 15Ω. A sustainable Cu(II) removal efficiency over 96% of MFCs were confirmed via eight cycles of batch experiments[37]. Sediment microbial fuel cell(SMFC) was constructed to treat organic wastewater and copper-contained wastewater in the anode and cathode chamber respectively with mixed bacteria in activated sludge as anode microbial inoculation. The maximum power density and electric current density of 81.7 mW/ m^2 and 980.0 mA/m^2 could be achieved with the catholyte of 3000mg/L $CuSO_4$, and the highest removal efficiencies of COD and Cu(II)could reached 74.3% and 96.6%, respectively. The SMFC had great potential removal effect for the treatment of wastewater containing Cu(II)[38].Wastewater containing copper is just a simple simulated wastewater in the laboratory. However, printing and dyeing wastewater containing copper is more complex. Therefore, we should give further study on the impact of other complex components of copper wastewater on electricity production mechanism.

4.3. Ag (I) Removal by MFC

MFCs had been used to treat wastewater containing $AgNO_3$ with external resistance of 1000Ω and initial concentration being between 50-200mg/L. Through a continuous reaction of 8h, the $AgNO_3$ removal efficiency in the aqueous water could arrive at 99.9%. Meanwhile, maximum power density, output voltage and current could reach 4250mW/m^2, 0.75V and 5.67A/m^2, respectively, corresponding with 69.9kg of silver per 1kW·h energy being produced by the system[39]. 99.9% of $[AgS_2O_3]^-$could be recovered and 83%COD could be removed by the two chamber MFCs. In comparison with two chamber MFCs and biological adsorption for treating wastewater containing $[AgS_2O_3]^-$, MFCs achieved advantages of higher recovery efficiency, higher selective and possibility of electrical power producing under the condition of the concentration of the $[AgS_2O_3]^-$ being less than 20mg/L, though biological adsorption having good economy[40].These studies have made a further exploration for the recovery of precious metals.

4.4. Mn (II) removal by MFC

Permanganate had been used in a two-chamber MFC as the cathodic electron acceptor, which recover much more electrical power than using hexacyanoferrate and oxygen. It had been demonstrated that a higher open circuit potential (OCP) could be provided by permanganate, which could harve stenergy power of 0.116mW/m^2. Manganese dioxide(MnO_2) was the main reduced product of the permanganate at pH 3.6 in a MFC, which had been demonstrated by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS)[41].A microbial fuel cell had been operated with

glucose and Klebsiellapneumoniae in the anodic compartment, together with $KMnO_4$and Leptothrixdiscophora in the cathodic compartment. In order to facilitate the electron transfer from glucose to the graphite electrode, a redox mediator of 2-hydroxy-1,4-naphthoquinone had been added in the microbial fuel cells. It had been showed that biomineralized manganese oxides could get 2 orders higher current density than oxygen when used as cathodic reactants in microbial fuel cells. After operating for 500h, the system could achieved-441.5 ±31 and +384.5 ± 64mVscE for anodic and cathodic potentials, respectively. A peak power density of 126.7 ±31.5 mW/m^2 could be achieved with an external resistance of 50Ohms[42].

4.5. Cd (II) removal by MFC

Double microbial fuel cells (d-MFC) were arranged to remove cadmium, which were constituted by acathode chamber with Cd(Ⅱ)solution (Cd-MFC) and another cathode chamber with Cr(Ⅵ) solution (Cr-MFC). It had been demonstrated that the voltage and energy generated by the Cr-MFC could not only be used to replenish the need of operating the Cd-MFC, but also ensure the normal operation of the Cd-MFC with the removal efficiency of Cd(Ⅱ) reaching 90%.By using the optimized cathode with sulfate buffer, the highest maximum utilization power density of Cr(VI)-MFC is 22.5W/m^2, whichwas11.3times of power density being supplied to Cd(II)-MFC. In comparison to the system without a passage, Cr(VI)-MFC could produced 4 times power with the additional passage, corresponding with 4.2times higher current density in contrast with without the additional passage at the same maximum power point (38.0AW/m^2vs. 9.0AW/m^2). It had been demonstrated that quickly removing electrons generated by microorganisms can accelerate the rate of electron–hole pair formation. Coupling MFCs can achieve a higher moval efficiency for treating the wastewater containing cadmium[43].

5. Heavy metal removal by hybrid MFCs

As a new process technology for treating wastewater, lots of researches were carried through on the field of optimizing the performance of MFCs. Furthermore, researches on combing MFCs with other processes had also constantly operated in order to have a better development for MFCs. Reduction of Cr(Ⅵ), Cu(Ⅱ) and Cd(Ⅱ) by two-chamber MFCs and microbial electrolysis cells(MECs) combination process had been studied with the reduction rates of Cr, Cu and Cd being (56.4 ± 0.5)%, (52.7 ± 3.5)%, (41.4 ± 2.2)%, respectively. It had been demonstrated that Cr(VI), Cu(II) and Cd(II) could be simultaneously removed from the aqueous solution by the combing system of MFCs and MECs. The structure of MEC was roughly the same as MFC, except for an external power supply in order to produce hydrogen. At the same time, as the cathodes of MECs, titanium sheet was critical for efficient system performance[44].

A microbial fuel cell-zero-valence iron (MFC-ZVI) coupling process had been constituted for treating trivalent arsenic in the aqueous solution. ZVI could directly use the low voltage electricity produced by MFC, and MFC-ZVI system could greatly improve the iron corrosion rate and arsenite removal rate. During the power generation process, the maximum steady voltage output of 0.52V and the Columbic Efficiency of 4.59% had been gained in the hybrid system. 72.74% of current efficiency was achieved and the pH value increased from 8.0 to 8.5 after several days running in the MFC-ZVI system. The reasons of causing different efficiency for arsenite removal were regarded as the amount difference of hydrous ferric oxides(HFOs) and the species difference of the iron corrosion products in the two systems[45].

It had found that bio-electro-Fenton process was an effective and economical method for As(III) oxidation, which was performed in a dual-chamber microbial fuel cell under neutral pH conditions. In this system, microbial-driven electro-reduction ofO_2 and γ-FeOOH produced H_2O_2 and Fe (II) in situ, respectively, without an electricity supply. The results indicated that an apparent As(III) depletion first-order rate constant of 0.208h^{-1} was found in As(III) oxidation. The apparent oxidation current efficiency of 73.1%had been gained in the bio-electro-Fenton system. The γ-FeOOH dosage in the cathode was an important factor to determine the performance of the system[46].

6. Conclusions

As an innovative technology for wastewater treatment and electricity generation, MFC has been paid close attention. However, MFCs are still in the laboratory stage, and there are still many problems in the industrial applications, such as expanding the scale of the reactor, increasing the power density etc. In the cathode, especially in the biological cathode, further study on the mechanism of electron production and transmission, domesticating the appropriate microorganism and maintaining activity are worthy of attention.Study on how to recover heavy metal ions from wastewater containing heavy metal in the MFC and improve the energy recovery rate should be strengthened, while further developing applications of heavy metal wastewater treatment by MFC, which were believed to certainly have a breakthrough in progress in future.

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