

## Nickel(II) removal from wastewater by Microbial Fuel Cell

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The effect of the high standard electrode potential of copper ions on the anode of microbial fuel cells was demonstrated in a previous study. This paper studied the effect of the low standard electrode potential of nickel ions on the anode, including removal efficiency, migration and distribution. More than 95% of the nickel can be removed in the anode of MFCs (Microbial fuel cells) with influent feed to the anolyte containing Ni<sup>2+</sup>, while the removal mechanism of nickel ions was chemical precipitation, including approximately 75.5% in the anode and approximately 15% in the cathode.

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**Keywords:** Microbial fuel cells; nickel ions; anode; removal mechanism; metal ions

### 1. INTRODUCTION

Microbial fuel cells (MFCs) have been at the forefront of scientific research due to their broad potential applications in metal removal and reduction, while the reactive conditions are mild and clean [1, 2]. The most important component of a MFC is the anodic microorganisms, in which the biofilm on the anode decomposes organic materials and simultaneously generates electricity. To promote microorganism activity and power generation, optimal concentrations of metal ions are required, as they may become inhibiting factors otherwise [2].

Some studies have indicated that the internal resistance, power output, and chemical production in MFCs are affected by metal ions [3]. Additionally, metal ions can participate in anodic or cathodic chemical reactions. Research has shown that Na<sup>+</sup> and K<sup>+</sup> can enhance the conductivity of anolytes and subsequently reduce the internal resistance and increase MFC performance [4-7]. Ca<sup>2+</sup> and Fe<sup>2+</sup> might assist in the establishment of a microbial biofilm [8-10]. V<sup>5+</sup> and Mn<sup>4+</sup>/Mn<sup>2+</sup> could modify anodic materials not only to promote biofilm formation but also to boost electron transfer [11, 12]. Pd<sup>2+</sup> and

$\text{Au}^{3+}$  could be reduced to become nanoparticles by dissimilatory metal reducing bacteria (DMRB) [13, 14].  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$  might work as biosensors due to their toxicity to microbes [15].

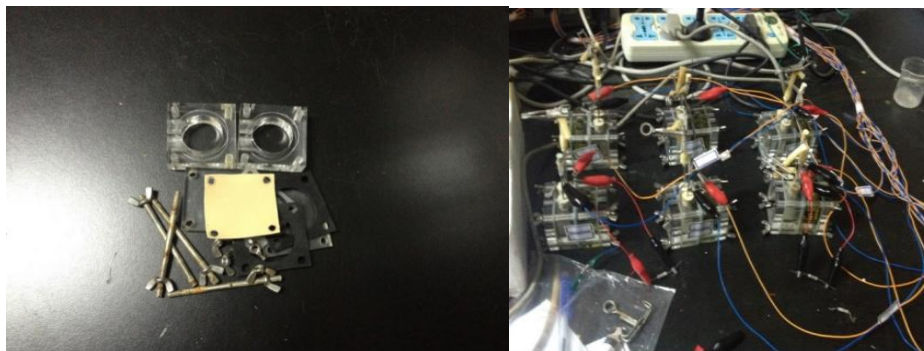
Nickel is a common heavy metal ion that comes from mining and smelting, machinery processing, chemicals, instruments, the textile industry and so on [16]. Nickel accumulates in the human body, which can harm human health and lead to the occurrence of cancer. The traditional methods of removal of nickel include chemical precipitation, ion exchange, reverse osmosis, electrolysis and electroosmosis. However, these methods require large operating costs and generate a large mass of sludge [17,18]. Recently, researchers have focused on the removal of heavy metal ions in bioelectrochemical systems, especially the reduction of heavy metal ions in the cathode [19-23]. MFC cathodes have been reported to remove heavy metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Hg}^{2+}$  and  $\text{V}^{5+}$  using electrons donated from the anodic chamber [24-30]. However, nickel ions belong to low standard potential materials, and the standard electrode potential is -0.25 V for nickel. Based on thermodynamic principles, nickel ions cannot be spontaneously reduced in the cathode of MFCs. This reaction requires external energy. Additionally, many toxic materials have been confirmed to be removed in the anode of MFCs, including heavy metal ions [31-33].

Numerous studies have reported the removal of heavy metals in the anodic chamber of MFCs. When studying the effects of chemical toxins on MFC-based biosensors, Stein observed a lower effluent concentration of  $\text{Ni}^+$  than that of the influent, suggesting the removal of  $\text{Ni}^+$  in the anodic chamber [34]. Some researchers noted that while producing electricity, single-chamber MFCs could also remove low standard potential  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  through biosorption and sulfide precipitation [35]. In our previous paper, the effect of  $\text{Ni}^{2+}$  concentration on voltage output was reported, and we found that removing  $\text{Ni}^{2+}$  in the anode of MFCs is a good solution [36]. This paper intends to study the behavior of nickel ions on the anode of MFCs, including the migration and distribution, as well as the removal efficiency. The characterization of nickel species on biofilm was determined by XPS and EDS. The removal mechanism was also discussed.

## 2. EXPERIMENT

### 2.1 MFC construction

The MFC consisted of two cubic organic glasses with a volume of 15 mL (Beijing physical chemical, Beijing) that were separated by CEM (cation exchange membrane, 7 cm<sup>2</sup>, CMI7000, DuPont, USA) (shown in Fig. 1). The membrane was submerged in  $\text{H}_2\text{SO}_4$  solution (1 mol/L) for 24 h and later washed with deionized water and dried in air. The anode was made using graphite felt (Jixing Shengan, China) with a working area of 4 cm<sup>2</sup> (2 cm×2 cm), while the cathode was made using a graphite plate with a working area of 4 cm<sup>2</sup> (2 cm×2 cm). The external resistance was 10,000 Ω in the starting-up period, the whole circuit was connected via titanium wires (Sanxin Metal Co. Ltd., China, 1.0 mm), and both graphite materials connected with titanium wires were fixed with plastic screws. Four reactors were constructed accordingly, as mentioned above, and marked as FC (abiotic, as control), MFC-1, MFC-2 and MFC-3 (as a parallel test).



**Figure 1.** H-type MFCs consisting of two chambers with a volume of 15 mL. The two chambers were separated by CEM. Titanium wires were used to connect the two electrodes with an external resistance of 5,000  $\Omega$ .

### 2.2 MFC inoculation and operation

The MFCs were inoculated with an anaerobic sludge from Wrigley Confectionery (China) Limited. The anodic nutrient medium contained (per liter): 1.64 g NaAC, 0.5 g  $\text{NH}_4\text{Cl}$ , 0.1 g  $\text{MgSO}_4$ , 0.08 g  $\text{CaCl}_2$ , 0.1 g  $\text{KCl}$ , 0.125 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , 0.03 g  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , 18.875 g/L PIPES and 1.0 mL trace elements [37] (pH=7.2). The nutrient medium was purged with  $\text{N}_2$  for 15 min to maintain anaerobic conditions [21]. The catholyte consisted of 32.92 g  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , 2 g/L  $\text{NaCl}$  and 18.875 g/L PIPES (per liter, pH=7.2). The MFCs were operated under a water bath at a temperature of  $30 \pm 1^\circ\text{C}$ .

After starting up, the internal resistance was determined to choose the external resistance. Nickel ions (in 2.93, 5.87, 8.80, 11.7, 14.7, 17.6, 20.5, 23.5 and 26.4 mg/L) were added to the anode of MFCs to investigate the removal of nickel.

### 2.3 Analysis

The nickel concentrations were measured by AAS (atomic absorption spectrometry) (novAA400, Analytic Jena AG, Germany). A drop of nitric acid solution (with 50% water) was added to the influent and effluent samples to maintain the ionic form, and the nickel ion removal efficiencies were calculated according to  $(C_i - C_e) \times 100 / C_i$ , where  $C_i$  and  $C_e$  are the nickel ion concentrations in the influent and effluent of the MFCs. To determine the distribution of nickel in MFCs, the MFC reactors were disassembled after the experiments. The effluents in the anode and cathode were measured by AAS directly, and the CEM, cathode graphite plate, anode graphite felt, reactor wall and precipitates were soaked in 1 mol/L nitric acid for 24 h and analyzed by AAS.

The biofilm was imaged and observed using SEM (Scanning Electron Microscopy, JSM-6360LV, JEOL, Japan). EDS (Energy dispersive X-ray spectroscopy, Falcon, EDAX, USA) was used for elemental analysis of the biofilm. XPS (X-ray photoelectron spectroscopy, ESCALAB 250Xi, Thermo Fisher, USA) was employed to determine the nickel species in the biofilm.

### 3. RESULTS AND DISCUSSION

#### 3.1 MFC start-up

Through 30 days of inoculation and acclimatization, the voltage output increased to 0.68~0.7 V, and the open-circuit voltage reached 0.77 V. To obtain good contrast, the selected external resistance was 5000  $\Omega$  [1].

#### 3.2 Removal of nickel in MFCs

The nickel concentration in the effluents of the cathode and anode were measured in the first 18 batches. The removal of nickel in FC was less than 10%, mostly because of adsorption to the anode, CEM and reactor wall. The results for the MFCs are shown in Table 1. The nickel concentrations in the effluents in almost all batches were lower than 0.3 mg/L, which were lower than the national standard of the integrated wastewater discharge standard of China. The removal rates were nearly greater than 96%. The effluent  $\text{Ni}^{2+}$  concentrations slightly increased as the influent  $\text{Ni}^{2+}$  concentrations increased, but they were still lower than 0.5 mg/L. Some studies have reported that nickel can be removed by electrochemical methods, such as electrocoagulation, but the concentration in the effluent is higher than 4 mg/L[38,39]. MFCs are suitable to remove nickel at low concentrations. The efficiency was also higher than that of other biological methods, such as biosorption[40].

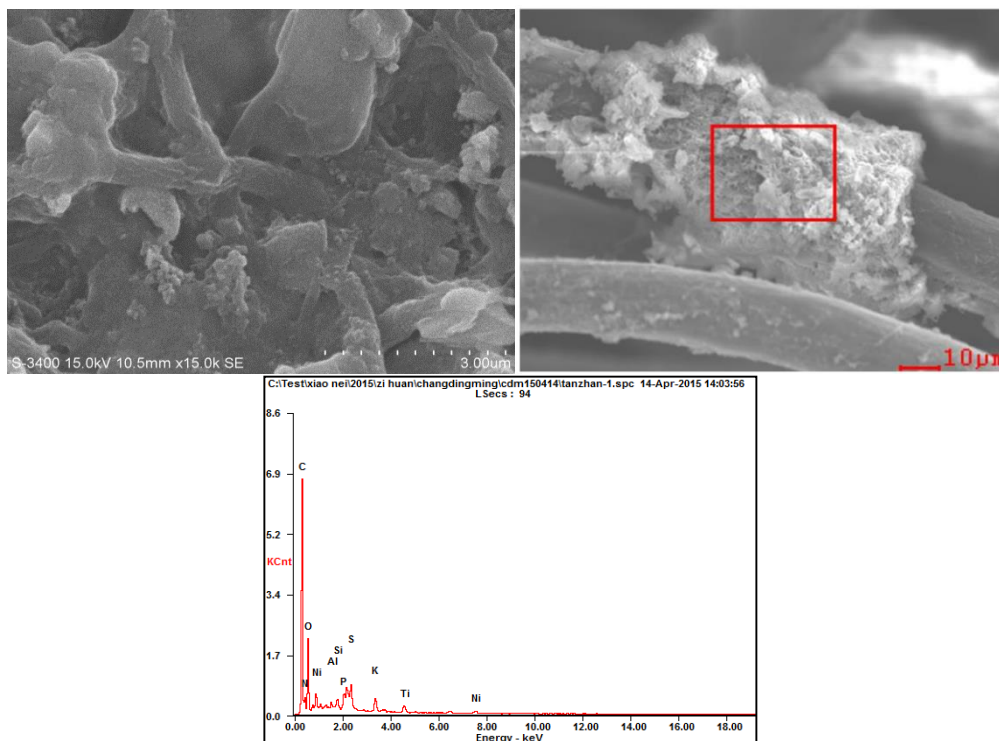
**Table 1.** Effluent concentration of  $\text{Ni}^{2+}$  and removal rate in 18 batches of each experimental test

Batches	Reactors	Influent $\text{Ni}^{2+}$ concentration mg/L	Effluent $\text{Ni}^{2+}$ concentration mg/L	Removal rate %
1~2	MFC-1	2.93	$0.098 \pm 0.038$	$96.6 \pm 1.3$
	MFC-2		$0.123 \pm 0.002$	$95.8 \pm 0.1$
	MFC-3		$0.149 \pm 0.014$	$94.9 \pm 0.5$
3~4	MFC-1	5.87	$0.098 \pm 0.004$	$98.3 \pm 0.1$
	MFC-2		$0.191 \pm 0.016$	$96.7 \pm 0.3$
	MFC-3		$0.168 \pm 0.013$	$97.1 \pm 0.2$
5~6	MFC-1	8.80	$0.297 \pm 0.022$	$96.6 \pm 0.3$
	MFC-2		$0.309 \pm 0.008$	$96.5 \pm 0.1$
	MFC-3		$0.214 \pm 0.002$	$97.6 \pm 0.3$
7~8	MFC-1	11.7	$0.295 \pm 0.033$	$97.4 \pm 0.3$
	MFC-2		$0.229 \pm 0.005$	$98.0 \pm 0.1$
	MFC-3		$0.257 \pm 0.024$	$97.8 \pm 0.2$
9~10	MFC-1	14.7	$0.293 \pm 0.000$	$98.0 \pm 0.0$
	MFC-2		$0.233 \pm 0.030$	$98.4 \pm 0.2$
	MFC-3		$0.265 \pm 0.031$	$98.2 \pm 0.2$
11~12	MFC-1	17.6	$0.322 \pm 0.001$	$98.2 \pm 0.0$
	MFC-2		$0.263 \pm 0.021$	$98.5 \pm 0.1$
	MFC-3		$0.232 \pm 0.019$	$98.7 \pm 0.1$
13~14	MFC-1	20.5	$0.276 \pm 0.033$	$98.6 \pm 0.2$
	MFC-2		$0.252 \pm 0.030$	$98.8 \pm 0.2$

	MFC-3		$0.228 \pm 0.012$	$98.9 \pm 0.1$
	MFC-1		$0.186 \pm 0.079$	$99.2 \pm 0.3$
15~16	MFC-2	23.5	$0.196 \pm 0.025$	$99.2 \pm 0.10$
	MFC-3		$0.295 \pm 0.003$	$98.7 \pm 0.0$
	MFC-1		$0.236 \pm 0.003$	$99.1 \pm 0.0$
17~18	MFC-2	26.4	$0.237 \pm 0.014$	$99.1 \pm 0.1$
	MFC-3		$0.297 \pm 0.008$	$98.9 \pm 0.0$

### 3.3 Morphology of nickel ions on anodic biofilms of MFCs

The anodic biofilms of the MFCs were characterized by SEM-EDS, and the results are shown in Fig. 2 and Table 2. It can be seen from Fig. 2 that microorganisms and many other materials were absorbed on the anodic biofilms of the MFCs. According to the EDS analyses, only 3.4% (by weight) of the nickel ions existed on the anodic biofilms. This was different from those of other metal ions absorbed on the anodic biofilms, which were approximately 24%~34% (by weight) of copper ions present on the biofilms and 20% of platinum[2, 41, 42]. The reason for these differences was the low standard electrode potential of nickel, and the nickel ions are hard to reduce in biofilms. It can be inferred from EDS that nickel ions may exist as nickel sulfide or nickel phosphate. A small amount of the adsorption on the anodic biofilms of the MFCs was from the anaerobic atmosphere.

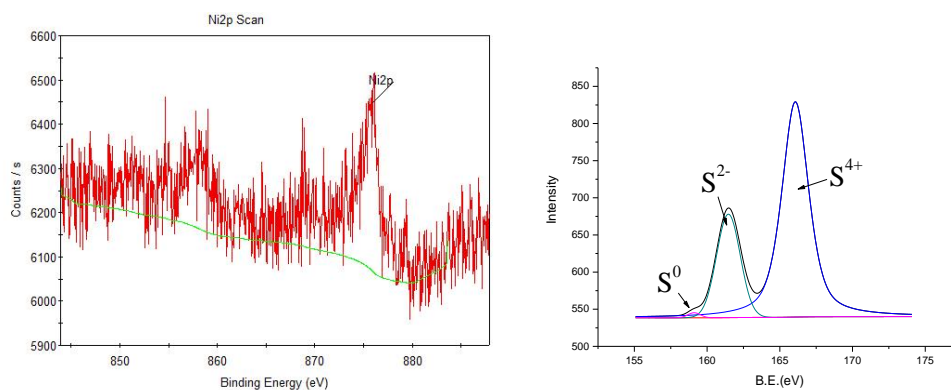


**Figure 2.** Scanning electron micrographs and energy dispersive X-ray spectrographs of the anodic biofilms of the MFCs with influent feed to the anolyte containing  $\text{Ni}^{2+}$ .

**Table 2.** Energy dispersive X-ray spectrographs of the anodic biofilms of the MFCs with influent feed to the anolyte containing Ni<sup>2+</sup>

Element	Wt%	At%
C	54.16	65.22
N	11.20	11.57
O	19.42	17.56
P	01.81	00.85
S	03.22	01.45
K	02.34	00.87
Ni	03.84	00.95

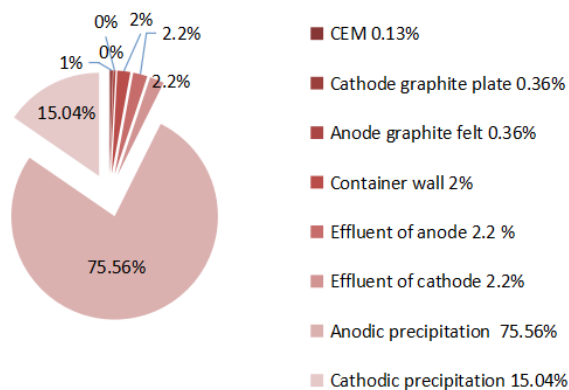
To clarify the valence state of the nickel ions on the anodic biofilms of the MFCs, XPS of the elemental nickel and sulfur was employed. The results are shown in Fig. 3. The peak of nickel was low, which indicated that only a small number of bivalent nickel ions were on the anodic biofilms. While sulfur was detected in three valence states, by comparing the peak areas, the content of S<sup>0</sup> was very low, and the proportions of S<sup>2-</sup> and S(IV) were 1:3. It can be estimated that the atomic percentage of S<sup>2-</sup> was 0.36% by the results of EDS and XPS. While the atomic percentage of nickel ions was 0.95%, there should be some other forms of precipitation besides nickel sulfide, such as nickel hydroxide or nickel phosphates, and similar observations have been reported in a previous study [43].

**Figure 3.** XPS spectrum of Ni and S adsorbed on the biofilms of the MFCs with influent feed to the anolyte containing Ni<sup>2+</sup>.

### 3.4 Distribution and removal mechanism of nickel ions

As shown in Fig. 4, most of the nickel ions were removed by chemical precipitation (93%), including anodic precipitation (75.56%) and cathodic precipitation (15.5%). The total nickel ions in the CEM electrode materials and anodic biofilms were less than 1%. Approximately 4% of the nickel ions were present in the effluent. 30% of the nickel was in ionic form under the PIPES buffer, and some nickel ions migrated to the cathode because of the action of the electric field and concentration polarization; these nickel ions were then precipitated by potassium ferricyanide, resulting in green precipitation in the cathode[44]. The anodic nickel ions were precipitated by phosphates, which acted as nutrient elements,

and sulfion, which was generated by sulfate-reducing bacteria and then removed.



**Figure 4.** Distribution of  $\text{Ni}^{2+}$  in the MFCs including the anodic biofilm, solid precipitated in the anodic chamber, anodic effluent, CEM (cation exchange membrane) and catholyte.

#### 4. CONCLUSIONS

This paper studied the effect of the low standard electrode potential of nickel ions on the anode, including removal efficiency, morphology, migration and distribution. More than 98% of nickel can be removed in the anode of MFCs. The removal mechanism of nickel ions was chemical precipitation, including approximately 75.5% in the anode and approximately 15% in the cathode, while according to the EDS analyses, only 3.4% of nickel ions were absorbed in the anodic biofilm.

#### ACKNOWLEDGEMENT

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