Enhanced Performance for Treatment of Cr (VI)-Containing Wastewater by Microbial Fuel Cells with Natural Pyrrhotite-Coated Cathode

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Abstract: Here we reported the investigation of enhanced performance for the removal of hexavalent chromium (Cr (VI)) by a new microbial fuel cell (MFC) with natural pyrrhotite-coated cathode. By comparisons of the graphite-cathode, the MFCs equipped with a pyrrhotite-coated cathode generated the maximum power density of 45.4 mW·m⁻² that was 1.3 times higher than that of with bare graphite cathode (35.5 mW·m⁻²). Moreover, the Cr (VI) removal efficiency of 97.5% achieved after 4.5 h compared with only 46.1% by graphite cathode MFC. In addition, Cr (VI) removal rate with different initial Cr (VI) concentrations for 10 mg/L and 30 mg/L was investigated and a decreased removal percentage with increasing Cr (VI) concentration was observed. Batches of experiments of different pH values from 3.0 to 9.0 in catholyte were carried out to optimize system performance. The complete Cr (VI) removal was achieved at pH 3.0 and 99.59% of Cr (VI) was removed after 10.5 h, which met the requirement of the Cr (VI) National Emission Standard. When the value of pH was decreasing, the removal rate was obviously increased and Cr (VI) could be removed successfully with a broad pH range indicating pyrrhotite-coated cathode MFC had more extensive usage scope. Furthermore, cathode treatment products were studied by X-ray photoelectron spectroscopy (XPS), 

Keywords: MFCs; pyrrhotite; hexavalent chromium; wastewater treatment

1. Introduction

Hexavalent chromium (Cr (VI)) is quite widely used by various industrial production applications (Including Chrome ore processing, electroplating, and the leather-making industry) [1–4]. The problem of chromium pollution has become increasingly serious, especially in Third World countries. The removal of Cr (VI) is a major challenge in the research field of wastewater treatment. Cr (III) and Cr (VI) are most common and stable valence states of chromium in nature environment. Compared
with the high toxicity and solubility of Cr (VI), the Cr (III) is less toxic and mobile [5]. Thus, it is of
great value to reduce Cr (VI) to Cr (III) in the wastewater treatment. Over the past decades, many of
technologies have been developed to remove Cr (VI) from solutions, which include adsorption, ion
exchange, reverse osmosis, electrochemical precipitation and photoelectrochemical process, etc. [6–9].
Currently, the Microbial Fuel Cell (MFC) system has become a new technology for the disposal of
the wastewater containing heavy metals (such as copper, silver, mercury, etc.) due to promising
biotechnology that utilizes microorganisms as catalysts to decompose organic matter and harvest
electricity simultaneously [10–12]. They are used for removing of Cr (VI) as well [13–15]. Li et al. first
showed that potassium dichromate was a favorable electron acceptor in the cathode of MFC [13]. At the
meantime, 99.5% Cr (VI) was removed by the reduction of Cr (VI) in the cathode chamber. Moreover, Wang et al. reported the maximum open circuit voltage was 0.91 V with Cr (VI) concentration for
200 mg/L as electron acceptor in the MFC [14]. Biocathode MFCs, which have attracted much attention
as well. Tandukar et al. reported that Cr (VI) reduced in a biocathode MFC with graphite plate
electrodes [16]. Moreover, enhanced of Cr (VI) reduction rate and power production were achieved
using indigenous bacteria [17]. Then, Shewanella oneidensis MR-1 used as a biocatalyst and which
realized current production and Cr (VI) reduction with the help of electron shuttles. In addition, the
effect of set potentials and special structure of biocathodes were investigated as well [18–20].

Nowadays, with the aim to improving the performance and decreasing the cost of microbial fuel
cells, most near-term attention is focused on the alternative of cathode Pt-based catalysts by inexpensive
minerals. Some metal oxides have been used for cathode catalysts which including MnO₂, PbO₂,
Fe₂O₃ and TiO₂ [21–27]. Roche et al. investigated the performance of manganese oxide used as the
cathode catalyst [21] and the performances of MFCs was easily improved. Zhang et al. prepared three
different forms of MnO₂ (α, β and γ) by hydrothermal method. Then, pure culture tests were made
and good volumetric power densities were observed with the help of MnO₂ [22]. The performances of
cryptomelane-type octahedral molecular sieve with cerium, copper and cobalt doped catalysts were
studied as well [23] and promoted power generation was also realized by PbO₂ [24]. Moreover, even
some earth-abundant natural minerals such as hematite, pyrrhotite and rutile were employed as novel
cathode catalysts, and which were proved could be act as alternative material for MFCs [25–27].

It is worth mentioning that the MFCs equipped with a natural pyrrhotite-coated cathode was used
to treat an old-aged landfill leachate [27]. The results demonstrated that with the help of pyrrhotite,
both power generation of MFCs and oxidation rate of biorefractory pollutants was increased [27].
Notably, natural iron sulfide minerals such as pyrite and pyrrhotite shows great potential and attracts
the attention for the field of environmental mineralogy, which has been proven to be effective for
removing dissolved Cr (VI) from solutions [28–31]. However, to the best of our knowledge, reduction
of Cr (VI) by using a MFC with pyrrhotite-coated graphite cathode has not been reported at present.

In this study, a natural environmental mineralogy material-pyrrhotite and the MFC technology
was combined together for improving performance of electricity generation and removing Cr (VI) from
solution was investigated. In addition, the treatment ability with a broad pH range and different initial
Cr (VI) concentration were studied in detail. Furthermore, the final solid byproduct was investigated
by X-ray photoelectron spectroscopy (XPS) and the mechanisms of Cr (VI) removal was discussed as
well. This study demonstrated that natural pyrrhotite was well suitable for MFCs application, allowing
sufficiently high current densities, wide availability of raw materials, low cost, easy preparation as
well as friendly operating condition. This MFCs performs great prospects for research and application
for the chromium reduction and electricity production in the future.

2. Materials and Methods

2.1. Manufacture of Pyrrhotite-Coated Graphite Cathode

The mineralogical characteristics of the natural pyrrhotite were well studied and the results can be
found in a previous study [27]. Nowadays, the price of natural pyrrhotite is $0.02 per kilogram, which
is much lower than other synthetic materials. The pyrrhotite powder (Inner Mongolia dongshengmiao mining Co., Ltd., Chongqing, China) used in this work had with an average particle size of less than 44 μm. Manufacturing one piece of graphite cathode (Beijing Beiji Carbon Co., Ltd., Beijing, China) whose size is $6 \times 6$ cm$^2$ and 0.2 cm thickness went according to the following process. Firstly, the binder was made from 0.04 g Polyvinylidene Fluoride (PVDF) (Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China) dissolved in 2000 uL N-methyl-2-pyrrolidone (NMP) (Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China) and mixed for one hour with magnetic stirrers (Beijing Bailingwei Co., Ltd., Beijing, China). Secondly, a homogenous mixture was made by adding 0.9 g pyrrhotite powder into the ready binder and mixed for another 12 h. Thirdly, using a pipette drop, a small amount of the final mixture was smeared onto the surface of graphite which had already been polished by abrasive paper. The cathode was available after heating in an oven at 60 °C for 2 h.

2.2. Experimental System and Pretreatment of Materials

Self-made double chamber MFCs were applied in this experiment (Figure 1). The both volume of the anode and cathode chamber were 8 cm × 8 cm × 6 cm. Then, a commonly proton exchange membrane (PEM, Nafion 117, Dupont Co., Wilmington, DE, USA) was used to separate the two chambers. The size of graphite cathode was 6 cm × 6 cm × 0.2 cm. The graphite electrodes were cleaned by soaking in 1.0 mol/L HCl for an hour and followed by 1.0 mol/L NaOH for an hour as well. Finally, the electrodes were stored in deionized water. Before use, we drilled holes in the graphite electrode. Then, an insulated copper wire was employed to connect the cathode and the external load. A carbon felt (5 mm thickness, Beijing Sanye Carbon Co., Ltd., Beijing, China) electrode was used as the anode.

![Figure 1. Schematic representation of microbial fuel cell (MFC) with pyrrhotite-coated graphite cathode.](image)

2.3. MFCs Start-Up and Operation

The inoculation bacteria in the anode chamber were collected from anaerobic activate sludge in a local municipal sewage treatment plant (inner Mongolia) as the biocatalyst. The anode chamber was filled by culture medium, which containing: 0.13 g/L of KCl, 0.2 g/L of MgSO$_4$, 15 mg/L of CaCl$_2$, 0.31 g/L of NH$_4$Cl, 0.56 g/L of (NH$_4$)$_2$SO$_4$, 3.13 g/L of NaHCO$_3$, and 1 g/L glucose. All the reagents used in this work were purchased from Beijing Chemical Reagent Corporation (Beijing, China) and all of them were analytical grade. The cathode chamber was filled by phosphate buffer saline (PBS) containing potassium ferricyanide (1 L of PBS consisted of K$_2$HPO$_4$, 11.4110 g; KH$_2$PO$_4$, 6.8046 g, K$_3$[Fe(CN)$_6$], 16.4620 g).
After the output power was stabilized, the cathode solution was replaced by simulation chromium-containing wastewater. Then, the output voltage across an external resistor (Huaou Industrial Co., Ltd., Beijing, China) (1000 Ω) was continuously monitored (0.5 s interval) by a data acquisition card (Pcio Log 1216, British Deco Technology Co., Ltd., Cambridgeshire, UK). The MFCs were placed in a temperature-controlled Biochemical incubator (LRH-250, Shanghai, China) and brought to a temperature of 37 °C.

2.4. Degradation Characterization of Cr (VI) and Cathode Products Analysis

Different initial Cr (VI) concentration solution for 30 and 10 mg/L Cr (VI) aqueous (pH = 3.0) were used in MFCs. Moreover, which employed for kinetic study as well. The Cr (VI) removal efficiencies under a broad pH range were investigated in MFCs. The pH values of 3.0, 5.0, 7.0 and 9.0 were selected. The initial pH of Cr (VI) solutions was adjusted by NaOH (1.0 mol/L) and H₂SO₄ (1.0 mol/L) and measured by a pH meter.

The concentration of Cr (VI) in solution was determined by the 1,5-diphenylcarbohydrazide spectrophotometric method [32]. The detection limit of this method was 0.1 μg·L⁻¹. In an acidic medium condition, chromium reagent 1,5-diphenylcarbazide was mixed with 5 mL of filtrate for 5 min, and the Cr (VI)-diphenylcarbazide product could be recognized and quantified at 540 nm by a UV-Vis spectrophotometer (Evolution 220, Thermo, Waltham, MA, USA). The efficiency of the Cr (VI) degradation was estimated by Equation (1):

\[
\text{Cr (VI) degradation(%) = (C}_0 - C_t)/C_0 \times 100%,
\]  

where \( C_0 \) and \( C_t \) (mg/L) are the initial and the equilibrium concentrations of Cr (VI) in solution respectively.

After finishing running of MFCs, the phase of products taken from the cathode chamber were analyzed by X-ray photoelectron spectroscopy (XPS Multi-functional imaging electron spectrometer, Axis Ultra, Kratos Analytical Ltd. Manchester, UK). The experimental conditions were Al kα1486.6 eV, 12 kV × 15 mA, a base pressure of 2 × 10⁻⁸ mbar, high multiple and medium resolving power. Spectral analysis was conducted by using XPS peak software package. The C1s peak (\( E_b = 286.6 \) eV) was used as a reference point with the purpose to eliminated the static charge effect.

3. Results and Discussion

3.1. The Electricity Production Performance of MFCs

Two sets of MFCs equipped with both pyrrhotite-coated graphite cathodes and graphite-coated cathodes were operated simultaneously. The performance of MFCs with various cathodes was quantified by polarization and power density curves. As shown in Figure 2, the maximum power density of MFC with a pyrrhotite-coated graphite cathode was 45.4 mW·m⁻², however it was only 35.3 mW·m⁻² in control experiment with a bare graphite cathode. Although the improved power density was lower than expensive catalysts, the value of pyrrhotite cathode was close to some recent studies of MFCs with different type of catalysts. For example, the maximum power of 64.7 mW·m⁻² for Co-naphthalocyanine, 81.3 mW·m⁻² for Pt/C electrode, 29.7 mW·m⁻² for NPc/C, and 9.3 mW·m⁻² for carbon black in H-type MFCs [33]. Moreover, the value of pyrrhotite-coated cathode had similar values with hematite or manganese oxides (30–180 mW·m⁻²), carbon felt (77 mW·m⁻²) or PbO₂ (<80 mW·m⁻²) [21–25]. In addition, compared with the graphite cathode, the MFCs with cathodes modified by pyrrhotite generated the higher open circuit voltage for 528 mV and achieved a significantly lower system resistance than control group (Table 1). The value of which was comparable with previous reports [32]. Moreover, in the sterile blank experiments, the current densities were lower than 0.1 μA·cm⁻² with a load of 1000 Ω and all of them could not keep stable. The results indicated that pyrrhotite itself could not establish long-term electron transfer process. Therefore, the enhanced cell performance was mainly based on microbial extracellular electron transfer from anode.
The comparison results demonstrated that natural mineral-pyrrhotite could be considered as readily available substitute for artificial cathode catalysts without complex composites, and which was more inexpensive and easily obtained.

Table 1. The average electrical parameters in MFCs systems with different cathodes.

| Cathode          | OCV (mV) | Max. Power Density (mW/m²) | System Resistance (Ω) |
|------------------|----------|----------------------------|-----------------------|
| Graphite         | 520      | 35.5                       | 24.7                  |
| Pyrrhotite-Coated| 528      | 45.4                       | 18.1                  |
| Growth Percentage| 1.54%    | 27.89%                     | −26.72%               |

**Figure 2.** Polarization and power density curves of MFCs with pyrrhotite and graphite cathodes.

3.2. Enhanced Cr (VI) Removal Efficiency by Pyrrhotite-Coated Cathode

In order to quantitatively verify the removal efficiency of Cr (VI) in two kinds of MFCs with pyrrhotite-coated cathode and normal graphite cathode, the removal rates of Cr (VI) were compared under the experimental condition for initial Cr (VI) concentration 10 mg/L. The above two MFCs were directly used to treat the simulated chromium-bearing wastewater. As shown in Figure 3, it was clear that the removal efficiency of Cr (VI) by pyrrhotite-coated cathode MFC was 97.5% after 4.5 h, while it was only 46.1% of Cr (VI) was removed in control experiment with a general graphite cathode. It should be pointed out that the removal rate was positively correlated with time, and the MFC with pyrrhotite-coated cathode could run steadily. Previous studies showed that the Cr (VI) reduction rate with different biologic cathodes MFC was different with each other. Additionally, the performance of abiotic cathode was easily influenced by pH and temperature. Moreover, the initial concentration of Cr (VI) should be bearable by cathode bacteria [16–20]. As for abiotic cathodes with kinds of complex chemically synthesized catalysts with precious metals, which were expansive and had environmental pollution. Therefore, natural pyrrhotite-coated cathode MFCs would have more hopeful prospects for wastewater treatment applications.
3.3. Effect of Initial Cr (VI) Concentration for Cr (VI) Removal

To gain a better understanding of the performance of Cr (VI) removal by MFC with pyrrhotite-coated cathode. Two different initial Cr (VI) concentration solution were treated by MFCs (Figure 4). As shown in Figure 4, 99% of Cr (VI) could be removed in 4.75 h from solutions with an initial Cr (VI) concentration of 10 mg/L. However, 54% of Cr (VI) was removed successfully from solutions with an initial Cr (VI) concentration of 30 mg/L after 4.5 h. It was obvious that 10 mg/L of Cr (VI) could be completely removed in 5 h but the removal percentage was decreased with a higher Cr (VI) concentration. When treating the Cr (VI) containing wastewater in system, Cr (VI) adsorbed firstly by electrode. Cr (VI) adsorption and removal process should be fitted by Langmuir–Hinshelwood model [1], therefore the initial Cr (VI) concentration will influence the removal progress. At determinate Cr (VI) concentration solution, a linear relationship between ln(C/C_0) and time can be found (Figure 4, insert). With increased Cr (VI) concentration, removal rate was decreased, which was mainly due to the limitation of active adsorption sites on the surface of pyrrhotite [1,31].
3.4. Removal Efficiencies of Cr (VI) under Different pH Values

With the aim to achieve a better understanding of the performance for the MFCs, the feasibility of the MFCs with pyrrhotite-coated cathode dealing with high concentration Cr (VI) wastewater under different initial pH values (3.0, 5.0, 7.0, 9.0) were further investigated. The Cr (VI) removal efficiencies under different pH values with an initial Cr (VI) concentration of 30 mg/L was shown in Figure 5. Under same pH value condition, the removal efficiency of Cr (VI) was significant increased with the running time of MFC.

With the decreased value of pH, the removal rate was obviously increased. The complete Cr (VI) removal was achieved at pH 3.0 and 99.59% of Cr (VI) was removed after 10.5 h. At this state, the residual concentration of Cr (VI) in solution was only 0.12 mg/L, which was far lower than the Cr (VI) National Emission Standard (0.5 mg/L).

Although a little decreased removal efficiency was obtained under higher pH conditions, 59.43% of Cr (VI) still could be removed with a pH value of 9.0. These indicate that this MFCs equipped with pyrrhotite-coated cathode had more extensive usage scope. With a broad pH range, Cr (VI) could be removed successfully. Therefore, the new MFC possessed the merits of cost-effectiveness, which exhibited promising potential for practical application of wastewater treatment.

![Figure 5. Cr (VI) removal efficiencies under different pH values by MFCs equipped with pyrrhotite-coated cathode.](image)

3.5. XPS Analysis of Reduced Production of Cr (VI) on Cathode

The valence state of the Cr and reduced production were characterized using XPS. As documented before, for Cr2p spectrum results, the peaks at 580.0–580.5 eV and 589.0–590.0 eV are contributed by Cr (VI), and the characteristic binding energy peaks at 577.0–580.0 eV and 586.0–588.0 eV correspond to Cr (III) [34–37]. Figure 6 showed the XPS Cr2p spectra results of the educed production on pyrrhotite-coated cathode MFCs. It was obvious that the binding energy peaks of Cr2p were observed at 577.1 and 578.7 eV, which were attributed Cr2O3. For Cr2O3, significant bands appeared at binding energies of 576.0–579.0 eV which including 576.11, 577.10, 577.90, 578.90 and 579.72 eV [34,35].

Moreover, another two binding energy peaks of Cr2p were observed at 586.9 and 588.3 eV, which were due to Cr (III)-acetate with significant bands appeared at 586.0–588.0 eV [34]. In addition, no Cr (VI) was detected on the cathode by production XPS Cr2p spectra. Previous study found that Cr2S3 (574.80 eV) was positively identified when removing Cr (VI) from aqueous solutions by natural clino-pyrrhotite [31], but it did not appear in our system. All above results indicating that the Cr on the cathode surface was reduced to Cr (III) by MFCs equipped with pyrrhotite-coated cathode.
3.6. Mechanisms of Enhanced Cr (VI) Removal by Pyrrhotite-Cathode MFC

The primary mechanisms for the enhanced removal efficiency of Cr (VI) in the pyrrhotite-cathode MFC may be depicted as follows (Figure 7). At anode, electrochemically active biofilm was developed on carbon felt, which oxidizing acetate and producing bio-electrons and protons. Then, the protons through the PEM and permeated to the cathode chamber. Moreover, the electrons were transferred from the anode to the cathode through the external circuit. As a positive electron acceptor in cathode, hexavalent chromium could capture electrons, and directly realized for the reduction of Cr (VI) to Cr (III) (Equation (2)). With the presence of pyrrhotite catalyst on cathode, which was demonstrated that could enhance the electricity production performance of MFCs. In this case, much more electron pumped out from anode and enhance the reaction rate of removing Cr (VI).

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- & \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}, \\
2\text{HCrO}_4^- + 8\text{H}^+ & \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 8\text{H}_2\text{O}, \\
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 8\text{H}^+ & \rightarrow \text{Cr}_2\text{O}_3(\text{s}) + 6\text{Fe}^{3+} + 4\text{H}_2\text{O}
\end{align*}
\]  

Figure 6. XPS Cr2p spectra of cathode treatment products by MFCs equipped with pyrrhotite-coated cathode (Cr (VI) initial concentration of 30 mg/L and pH of 3.0).

It should be mentioned that the nonstoichiometry of pyrrhotite was Fe\(_{(1-x)}\)S (\(x = 0\)–0.17). The nonstoichiometry character was attributed to the existence of vacancies of the Fe sites, instead of an excess of sulfur ions. Moreover, charge balance was maintained mainly by the existence of Fe\(^{3+}\) in the crystal structure as proposed by Vaughan and Craig [37] and the interaction mainly occurred at the surface of pyrrhotite [38,39]. Under the mildly acidic condition, Fe\(^{3+}\) and Fe\(^{2+}\) would be generated via the dissolving reaction of pyrrhotite. Simultaneously, the Fenton’s reaction took place as well and lead to the production of H\(_2\)O\(_2\) [27]. Thus, the oxidation-reduction reaction between hexavalent chromium and hydrogen peroxide could take place (Equation (3)). Moreover, as an environmental mineralogy material, Cr (VI) reduction could take place at surface reactive sites of pyrrhotite owing to the vacant Fe sites (Equation (4)) [31]. Therefore, the efficiency of Cr (VI) removing was further enhanced based on Equations (3) and (4). Based on the results above mentioned, we could draw a conclusion that pyrrhotite not only played a significant role for cathode catalyst of MFCs, but also acted as surface reactive sites for Cr (VI) reduction. Finally, an enhanced Cr (VI) realized in our system.
4. Conclusions

Results from this study demonstrated that using natural pyrrhotite-coated cathode in MFCs treating wastewater was better than a bare graphite electrode. Polarization and power density curves showed that the modified MFCs generated higher maximum power density of 45.4 mW·m$^{-2}$ and lower resistance of 18.1 $\Omega$ compared with 35.5 mW·m$^{-2}$ and 24.7 $\Omega$ for graphite cathode MFC. It was suggested that pyrrhotite was an ideal cathode catalyst. The enhanced performance for Cr (VI) removal was realized in MFC with natural pyrrhotite-coated cathode. A more thoroughly Cr (VI) removal was acquired at pH 3.0 and 99.59% of Cr (VI) was removed after 10.5 h. Furthermore, Cr (VI) could be removed successfully with a broad pH range from 3.0 to 9.0. Even though under the pH value of 9.0, 59.43% of Cr (VI) removed after 630 min indicating a broad usage scope potential. Finally, XPS was used to study the valence state of Cr in reduced production. The binding energy peaks of Cr2p were observed at 577.1, 578.7, 586.9 and 588.3 eV, which were attributed Cr$_2$O$_3$ and Cr (III)-acetate. The system in our study with no commercial reagent was needed and this new MFCs not only could make use of tailings as resource, but also could achieve degradation of Cr (VI) and electricity production. The future looks bright for reduction of wastewater containing heavy metals.

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