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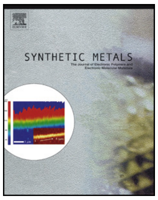

Conductive polymer-mediated Cr(VI) reduction in a dual-chamber microbial fuel cell under neutral conditions

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ABSTRACT

Microbial fuel cell (MFC) technology for Cr(VI) removal offers the advantage of simultaneous electricity generation and Cr-laden wastewater treatment, but Cr(VI) removal at neutral pH proceeds with slow kinetics. We herein report the use of conductive polymer as a mediator shuttling electron transfer from the cathode to Cr(VI), facilitating Cr(VI) reduction in MFCs under neutral conditions. It has been found that PPy films synthesized by electropolymerization on the graphite felt cathode considerably improved Cr(VI) removal from the aqueous solution. The surface morphology of PPy, which is correlated to performance of the PPy-modified cathode, was highly dependent on the type of dopants that were incorporated during electropolymerization. The PPy/AQS(9,10-anthraquinone-2-sulfonic acid sodium salt)-modified cathode with nanowire structure enabled higher Cr(VI) removal rate and exhibited larger power output than the PPy/ClO_4^--modified cathode with compact globular structure. These results are attributed to the increased surface area of electrode and the presence of AQS that is electrochemically active for reaction with Cr(VI). Cr(III) precipitates were the primary end-products of Cr(VI) reduction under neutral conditions, with no soluble Cr(III) detected.

1. Introduction

Contamination of ground water and soil due to the wide use of chromium in various industries such as electroplating, leather tanning, pigment manufacturing and wood preservatives has become a serious concern to environment scientists over the past decades [1,2]. Hexavalent chromium (Cr(VI)), highly soluble and mobile in the environment, is a well-known carcinogen and mutagen threatening public health. Chemical, electrochemical or biological reduction of Cr(VI) to trivalent chromium (Cr(III)) that is much less toxic and less mobile is the most acceptable way for the treatment of Cr(VI)-contaminated water [3]. Chemical treatment [4] and electrochemical treatment [5,6] generally proceed in an acidic solution, thus requiring pH adjustment before and after treatment. In addition, these two processes require either addition of reducing agents or energy input, leading to high costs of operation. Biological treatment [7] can occur at a neutral pH; however, it always suffers from low reaction rate and long time for the acclimation of Cr(VI)-reducing bacteria. Recently, to overcome these drawbacks, an alternative has been proposed to reduce Cr(VI) using microbial fuel cell (MFC) [8–14], in which Cr(VI) is fed to its cathode and functions as the electron acceptor due to the high redox potential of the Cr(VI)/Cr(III) couple. Although the MFC process eliminates the input of reducing agents and offers the advantage of electricity generation, low pH being thermodynamically favorable to cathodic Cr(VI) reduction suggests the need of pH adjustment to the acid condition. For example, Li et al. [11] concluded that the neutral pH in the cathode chamber resulted in negligible Cr(VI) reduction as compared to the acidic pH. However, acid environment is not desirable for running MFCs because bacteria used prefer to work at pH close to 7.0.

Here, we proposed a concept of using conductive polymer to mediate cathodic Cr(VI) reduction in an MFC under neutral conditions. Fig. 1 shows the mechanistic scheme of electron transfer in this system. The redox potential of Cr(VI)/Cr(III) couple at pH 7.0 is 0.37 V (vs. SHE), much lower than 1.33 V at pH 0. When the conductive polymer is absent from the cathode, the high cathodic activation overpotential under neutral conditions causes the slow kinetics of Cr(VI) reduction at the cathode surface. On the other hand, when the conductive polymer such as polypyrrole (PPy) is present, it can function as a mediator shuttling electron transfer from the cathode to Cr(VI) because of its reversible redox behavior and electronic conductivity, thus facilitating electron-transfer kinetics. Many previous studies [15–22] have shown that the conductive polymer has the ability to reduce Cr(VI). The PPy has a redox potential of −0.2 V (vs. SHE) [16] between those of the biological

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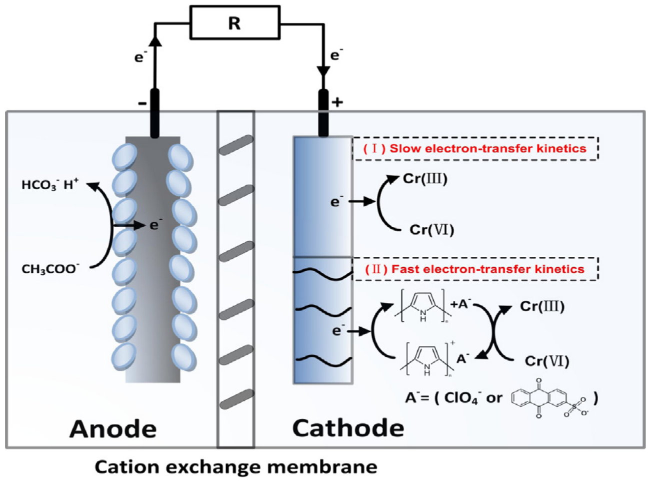

Fig. 1. Mechanistic scheme of PPy-mediated electron transfer for enhancing Cr(VI) reduction in a dual-chamber MFC under neutral conditions.

electron donor at the anode (−0.32 V vs. SHE for NADH) and the Cr(VI) electron acceptor 0.37 V (vs. SHE), satisfying the criteria as the electron shuttle. As illustrated in Fig. 1, the electrons released from anaerobic oxidation of acetate in the anode first result in the transformation of PPy from its oxidized sate (as-synthesized material) to its reduced state; at the same time, the anion is ejected from the matrix into the solution (Eq. (1)). Then spontaneous electron transfer occurs from PPy to Cr(VI), an eventual electron acceptor, causing reduction of Cr(VI) to Cr(III) and re-oxidation of PPy to its oxidized state (Eq. (2)). Upon oxidation of polymer, the anion is incorporated into the positively charged polymer matrix to obtain charge compensation, and the whole redox cycle can be initiated again. It should be noted that under neutral conditions, the resulting Cr(III) predominantly appears in its solid form, as $Cr(OH)_3$ (Eq. (3)).

$$\mathrm{PPy^+A^-(s) + e \rightarrow PPy(s) + A^-} \tag{1}$$

$$\mathrm{Cr_2O_7{}^{2-}(aq) + 6PPy(s) + 14H^+ \rightarrow 2Cr^{3+}(aq) + 6PPy^+(s) + 7H_2O} \tag{2}$$

$$\mathrm{Cr^{3+}(aq) + 3H_2O \rightarrow Cr(OH)_3(s) + 3H^+} \tag{3}$$

To demonstrate this concept, PPy-modified graphite felt cathodes were prepared and further used in a dual-chamber MFC for Cr(VI) removal. The reaction rate of Cr(VI) reduction in the MFC with the modified cathode under neutral conditions was examined and compared to that obtained in the MFC with the unmodified cathode. In addition, the influence of dopant ions incorporated in PPy on Cr(VI) reduction and electricity generation was investigated.

2. Experimental

2.1. Synthesis of PPy films on the graphite felt cathode by electropolymerization

Cathode modifications with PPy were performed according to the procedures described in our previous work [23,24]. The starting cathode substrate was a piece of graphite felt (5.5 cm in diameter and 0.5 cm in thickness) that was cleaned in a hot H_2O_2 (10%, 90 °C) solution for 3 h, followed by thorough rinse with deionized water and dry at 60 °C. A Ti wire (0.6 mm in diameter) was inserted inside the graphite felt to allow the external circuit connection. The PPy films were electrochemically deposited onto the cathode surface using a three-electrode, single-chamber electrochemical cell that was controlled by a CHI 660 C potentiostat (Shanghai CH Instrument Company, China). A saturated calomel electrode (SCE) electrode and a Pt mesh electrode were inserted into the cell as reference electrode and counter electrode, respectively. It should be noted that all the potentials reported throughout this paper were referred to SCE, if not otherwise stated. The pyrrole monomer was purified using distillation prior to use. A constant potential of 0.8 V was applied for the anodic electropolymerization in a non-stirred N_2-saturated solution that contained 0.1 M pyrrole monomer and 10 mM AQS (9,10-anthraquinone-2-sulfonic acid sodium salt) or 10 mM $NaClO_4$, resulting in the formation of PPy/AQS or PPy/$ClO_4{}^-$ films, respectively. The freshly prepared PPy/AQS-modified and PPy/$ClO_4{}^-$-modified graphite felt cathodes were then thoroughly rinsed with distilled water and air-dried at room temperature.

2.2. MFC construction, operation and calculation

The two-chamber MFC made of Perspex flames was fabricated as described previously [23–25]. It consists of the modified graphite felt cathode and a bare graphite felt anode (5.5 cm in diameter and 0.5 cm in thickness) in each chamber. The two chambers were separated by a cation exchange membrane (Zhejiang Qianqiu Group Co., Ltd., China), with each having an effective volume of 100 mL. For MFC operation, the anode chamber was inoculated with *Shewanella oneidensis* MR-1 purchased from ATCC (700550). The anolyte contained the lactate-growth medium including 20 mM lactate and 0.1 M phosphate buffer solution (PBS)-based nutrient solution (pH 7.0) consisting of 5.84 $g\,L^{-1}$ NaCl, 0.10 $g\,L^{-1}$ KCl, 0.25 $g\,L^{-1}$ NH_4Cl, 10 mL of vitamin solution and 10 mL of mineral solution. The cathode chamber was fed with a PBS solution (0.1 M, pH 7.0) containing 20 $mg\,L^{-1}$ Cr(VI). Cr(VI) stock solution was prepared by dissolving 2.83 g of $K_2Cr_2O_7$ in 100 mL of deionized water. Cell voltages were recorded by a 32-channel voltage collection instrument (AD8223, China) under the conditions of a 300 Ω external resistance and a controlled temperature of 30 °C. The anode and cathode polarization curves and the cell power density curves were obtained by recording the cell voltages at various external resistors over the range from 4000 to 10 Ω, followed by the calculation of current (I) as $I = V$ (cell voltage)/R (external resistance), and power (P) as $P = V \times I$. Both I and P were normalized to the projected area of cathode surface. It should be noted the cell voltage was recorded at the time interval of 20 min for each resistor. The cathodic Coulombic efficiency (CCE) of Cr removal in the cathode chamber of an MFC was calculated as $\eta = Q_{Cr}/Q_t$, where Q_t is the total Coulombs obtained by integrating the current over time, and Q_{Cr} is the Coulombs calculated from the amount of Cr(VI) transferred to Cr(III) by applying the Faraday's Law.

2.3. Physical and chemical characterizations

The surface morphologies of the unmodified, PPy/AQDS-modified, and PPy/$ClO_4{}^-$-modified graphite felt cathodes before and after treatment were examined using an S-3700N (Hitachi, Japan) scanning electron microscope (SEM). The X-ray photoelectron spectroscopy (XPS) technique was further used to analyze the elemental composition and oxidation state of Cr species that exists on the cathode surface after treatment. XPS spectra were measured with an Axis Ultra DLD spectrometer (Kratos Analytical Ltd.) by employing AlKα ($h\nu$ = 1486.6 eV) irradiation as the photosource, with a primary voltage of 15 kV and an emission current 10 mA. The analysis chamber pressure during scans was 5×10^{-9} Torr.

The concentration of Cr(VI) taken from the cathode solution was determined via the colorimetric 1,5-diphenylcarbazide method following the procedures elsewhere [13,14]. For the analysis of total