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Cadmium (II) removal mechanisms in microbial electrolysis cells

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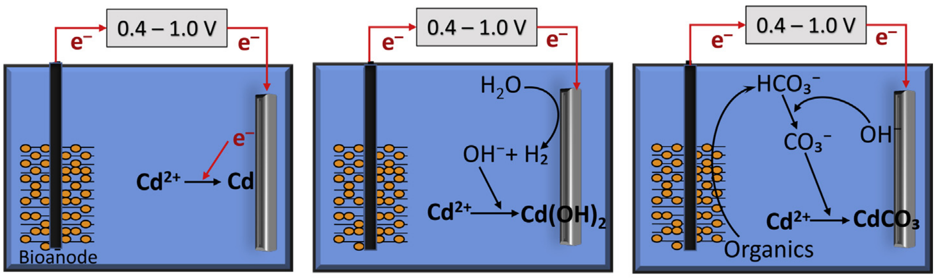
HIGHLIGHTS

- Rapid removal of Cd(II) was achieved in 24 h using microbial electrolysis cells.
- Cathodic reduction (electrodeposition) of Cd(II) cannot explain the rapid removal.
- H_2 evolution in microbial electrolysis cells increases local pH near the cathode.
- High local pH induces $Cd(OH)_2$ and $CdCO_3$ precipitation only with electric current.
- Neutral pH caused by low current and depleted substrate dissolves the precipitated Cd.

GRAPHICAL ABSTRACT



Cathode Reduction

$Cd(OH)_2$ Precipitation

$CdCO_3$ Precipitation

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ABSTRACT

Cadmium is a toxic heavy metal, causing serious environmental and human health problems. Conventional methods for removing cadmium from wastewater are expensive and inefficient for low concentrations. Microbial electrolysis cells (MECs) can simultaneously treat wastewater, produce hydrogen gas, and remove heavy metals with low energy requirements. Lab-scale MECs were operated to remove cadmium under various electric conditions: applied voltages of 0.4, 0.6, 0.8, and 1.0 V; and a fixed cathode potential of −1.0 V vs. Ag/AgCl. Regardless of the electric condition, rapid removal of cadmium was demonstrated (50–67% in 24 h); however, cadmium concentration in solution increased after the electric current dropped with depleted organic substrate under applied voltage conditions. For the fixed cathode potential, the electric current was maintained even after substrate depletion and thus cadmium concentration did not increase. These results can be explained by three different removal mechanisms: cathodic reduction; $Cd(OH)_2$ precipitation; and $CdCO_3$ precipitation. When the current decreased with depleted substrates, local pH at the cathode was no longer high due to slowed hydrogen evolution reaction ($2H^+ + 2e^- \rightarrow H_2$); thus, the precipitated $Cd(OH)_2$ and $CdCO_3$ started dissolving. To prevent their dissolution, sufficient organic substrates should be provided when MECs are used for cadmium removal.

1. Introduction

Heavy metal pollution is a serious environmental and health hazard. As many toxic heavy metals are water soluble and non-biodegradable, they are transported by water and can accumulate in soils and living organisms [1]. Cadmium, in particular, is carcinogenic and toxic, and thus it is strictly regulated in wastewater

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effluent and composted wastewater biosolids. Various industrial processes, such as electroplating, inorganic pigment, and battery manufacturing, result in cadmium contamination in wastewater streams. Conventional biological wastewater treatment (e.g., activated sludge process) is ineffective for removing heavy metals, resulting in contamination of wastewater effluent high risks in land applications of digested wastewater biosolids and treated effluent [1]. Current methods for removing heavy metals from wastewater, such as ion exchange or tight membrane filtration, are expensive. Ion exchange requires a large amount of chemicals for resin regeneration and membrane processes are prone to fouling which leads to high operation costs [1]. In addition, these advanced treatment methods are not cost effective for relatively low concentrations of heavy metals [2]. Thus, in this study, we focused on demonstrating an efficient and inexpensive method for cadmium removal from wastewater to reduce potential risks of heavy metal contamination in treated wastewater effluent and wastewater biosolids.

Microbial electrolysis cells (MECs) are an emerging technology for wastewater treatment and simultaneous energy recovery [3–7]. With a relatively low applied voltage application ($E_{ap} > 0.2$ V), exoelectrogenic bacteria oxidize organic matter at the bioanode of the cell while water is simultaneously reduced to hydrogen gas at the cathode [6]. Thus, wastewater can be treated while energy is recovered in the form of hydrogen gas. MECs and other bioelectrochemical systems (e.g., microbial fuel cells or MFCs) can also be used to remove heavy metals from aqueous solution. In addition to the hydrogen evolution reaction, the MEC cathode can reduce heavy metal ions into metallic solids. For instance, the removal of tri-valent chromium cations as metallic chromium at the MEC/MFC cathode ($Cr^{3+} + 3e^- \rightarrow Cr$), has been extensively investigated in literature papers [8–14]. Previous studies have also demonstrated removal of other heavy metals using bioelectrochemical systems. MECs were used to remove Ni^{2+}, Fe^{2+}, and Cu^{2+} from acid mine drainage [15]. Recovery of copper has been demonstrated along with electricity production using MFCs [16]. In addition, removal of Hg^{2+} has also been reported by electric reduction at the MFC cathode [17]. Recovery of cadmium has been demonstrated using multiple reactors of bioelectrochemical systems where one reactor is used to power the other reactor for the reduction of Cd^{2+} to Cd [18,19]. Modin et al. demonstrated successful removal of highly concentrated cadmium (800 mg/L) from a synthetic fly ash leachate solution [20]. In this study, we further investigated cadmium removal using MECs with the following specific research objectives: (1) demonstration of cadmium removal at a relatively low concentration (12.26 mg/L) under neutral pH conditions; (2) investigation of the effects of applied voltages (E_{ap}) on the rate of cadmium removal; (3) clarification of cadmium removal mechanisms by monitoring the cathode potential; and (4) explanation of potential dissolution of removed cadmium from the MEC cathode. By achieving the objectives, we were able to suggest optimal MEC operation conditions for cadmium removal.

We particularly focused on cadmium removal in this study because removal of cadmium has not been investigated as intensively as other metals, despite its toxic effects and the serious human health risks with repeated land applications of reclaimed wastewater or wastewater biosolids [21]. Modin et al. controlled the cathode potential to demonstrate selective removal of cadmium from waste fly ash leachate in a recent study, where heavy metals were present at a relatively high concentration (800 mg/L) in a strong acid solution (2 M HCl) [20]. Cadmium removal in MECs is known to be via the cathodic reduction or electrodeposition [18–20]:

$$Cd^{2+} + 2e^- \rightarrow Cd \quad E^\circ = -0.40\,\mathrm{V\,vs.SHE} \tag{1}$$

This removal mechanism is especially dominant when the pH is substantially low in an acidic solution (e.g., 2 M HCl) or the solution contains substantially high buffering capacity (e.g., 100 mM phosphate) [18,20]. In addition to this cathodic reduction, cadmium can also be removed by precipitation as cadmium hydroxide [22,23]:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_{2,s} \quad K_{sp} = 10^{-14.3} \tag{2}$$

This removal mechanism as the hydroxide salt can be dominant in MECs when the local pH near the cathode is increased as a result of the hydrogen evolution reaction ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$). Precipitation of cadmium as $CdCO_3$ is also expected to contribute to the cadmium removal because the high local pH near MEC cathodes converts bicarbonate ions (HCO_3^-) into carbonate ions (CO_3^{2-}) and the converted carbonate ions are likely to form precipitants with cadmium ions as [23]:

$$Cd^{2+} + CO_3^{2-} \rightarrow CdCO_{3,s} \quad K_{sp} = 10^{-13.7} \tag{3}$$

Since bicarbonate is created as a byproduct of acetate oxidation at the bioanode, $CdCO_3$ precipitation can also be a dominant factor for cadmium separation.

Zhang et al. demonstrated that the removal mechanism at the cathode is dependent on substrate and pH conditions in MFCs [19]. If the formation of cadmium precipitants is the dominant pathway for cadmium removal, it is critical to maintain a high local pH near the cathode by continuously driving the hydrogen evolution reaction. Otherwise, the precipitation reactions in Eq. (2) and Eq. (3) will be reversed due to low hydroxide concentration. Thus, the amount of organic substrates can be an important factor that allows the hydrogen evolution reaction to occur at the MEC cathode. On the other hand, if the cathodic reduction of cadmium in Eq. (1) is the dominant mechanism, the cadmium removal efficiency will not be affected by the amount of organic substrate as long as the cathode potential is favorable for cadmium reduction reaction in Eq. (1). This study provides answers to these questions and suggests optimal MEC operation conditions for cadmium removal at a relatively low concentration (12.26 mg/L).

2. Materials and methods

2.1. Reactor construction

The single chamber MEC was constructed using a polypropylene block with an interior cylindrical chamber (cross sectional area of 7 cm^2) and a total volume of 45 mL as previously demonstrated. The bioanode was prepared using a graphite fiber brush (2.5 cm diameter and 2 cm in length; Mill-Rose, OH) which was pretreated in a muffle furnace at 450 °C for one hour [24]. The cathode was a piece of stainless steel mesh (5.4 cm^2 area, AISI 304, 100 mesh; McMaster-Carr, OH) without any precious metal catalyst application.

2.2. Reactor operation

The MECs were inoculated with effluent from an existing MEC reactor for digestion of waste activated sludge [25]. The feed solution was prepared using sodium acetate (0.5 g/L $NaCH_3COO$) as the substrate along with trace vitamins and minerals [26] in a 12.5 mM phosphate buffer solution (1.145 g/L Na_2HPO_4, 0.613 g/L NaH_2PO_4-H_2O, 0.078 g/L NH_4Cl, 0.033 g/L KCl). Note that alkalinity of the feed solution is approximately 313 mg/L as $CaCO_3$, which is still greater but reasonable considering the amount of alkalinity in typical domestic wastewater [27]. Cadmium was added to the prepared medium solution using $CdCl_2$. The initial cadmium concentration was 12.26 mg/L as Cd. This initial Cd(II) concentration was chosen because we found in a separate experiment that Cd(II) concentration higher than 12.5 mg/L starts inhibiting the bioanode performance in generating electric current. The MEC reactors were