Cooperative cathode electrode and in situ deposited copper for subsequent enhanced Cd(II) removal and hydrogen evolution in bioelectrochemical systems

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Abstract

Bioelectrochemical systems (BESs) were first operated in microbial fuel cell mode for recovering Cu(II), and then shifted to microbial electrolysis cells for Cd(II) reduction on the same cathodes of titanium sheet (TS), nickel foam (NF) or carbon cloth (CC). Cu(II) reduction was similar to all materials (4.79–4.88 mg/L h) whereas CC exhibited the best Cd(II) reduction (5.86 ± 0.25 mg/L h) and hydrogen evolution (0.35 ± 0.07 m3/m3 d), followed by TS (5.27 ± 0.43 mg/L h and 0.15 ± 0.02 m3/m3 d) and NF (4.96 ± 0.48 mg/L h and 0.80 ± 0.07 m3/m3 d). These values were higher than no copper controls by factors of 2.0 and 5.0 (TS), 4.2 and 2.0 (NF), and 1.8 and 7.0 (CC). These results demonstrated cooperative cathode electrode and in situ deposited copper for subsequent enhanced Cd(II) reduction and hydrogen production in BESs, providing an alternative approach for efficiently remediating Cu(II) and Cd(II) co-contamination with simultaneous hydrogen production.

1. Introduction

Heavy metals of Cu(II) and Cd(II) in electroplating wastewaters, if not removed, can severely contaminate surface waters, ground-waters, and soils, and thus threaten human health (Martin-Lara et al., 2014). Conventional techniques including physical, chemical/electrochemical, physicochemical, and biological methods can be used to effectively treat these wastewaters (Martin-Lara et al., 2014). However, other approaches that avoid the high costs and energy consumption are being sought to provide environmentally friendly and cost-effective strategies for wastewater treatment.
Bioelectrochemical systems (BESs) including microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) have been shown to be promising technologies for recovering metals from wastewaters in addition to diverse wastes and wastewaters treatment (Kook et al., 2015; Li et al., 2014; Nancharaih et al., 2015; Rivera et al., 2015; Wang and Ren, 2014). Cu(II) can be spontaneously removed in MFCs due to its favorable half-cell redox potential of 0.34 V (vs. standard hydrogen electrode, SHE) relative to that of organic matter (ca. −0.30 V for acetate), whereas Cd(II) reduction requires a more negative potential of −0.52 V that can only be obtained in an MEC (An et al., 2014; Cheng et al., 2013; Heijne et al., 2010; Tao et al., 2011; Zhang et al., 2015). Mixed metals of either Cu (II), Pb(II), Zn(II) and Cd(II) or Zn(II), Pb(II) and Cu(II) have all been individually recovered in MECs through the change of applied voltage (Modin et al., 2012; Tao et al., 2014) whereas Cu(II) and Ni(II) were simultaneously deposited on the same cathodes of MECs (Luo et al., 2014). MFCs operating with cathodic Cu(II) reduction were shown to be able to provide the voltage needed for Cd(II) reduction in MECs without any external energy consumption (Zhang et al., 2015), somewhat similar to Cr(VI)-reduced MFCs coupled with Cd(II)-reduced MFCs (Choi et al., 2014). However, only single Cu (II) or Cd(II) was individually fed in the cathodes of these MFCs or MECs, limiting the practical application of these systems. Therefore more approaches are needed to make BESs useful for Cu(II) and Cd(II) removal in the mixed solutions.

Considering the reduction of Cu(II) on the cathodes of single MFCs (An et al., 2014; Cheng et al., 2013; Heijne et al., 2010; Tao et al., 2011, 2014; Zhang et al., 2015) and Cd(II) on the cathodes of sole MECs (Choi et al., 2014; Zhang et al., 2015), we hypothesized that Cu(II) and Cd(II) could be sequentially reduced on the same cathode of BESs through the use of a timed relay to switch operational conditions (Fig. S1 in Supplementary Information (SI)). In this process, the BESs would first be operated in MFC mode for Cu(II) reduction, and then shifted to MEC mode for Cd(II) reduction. Considering the catalysts of copper for CO₂ and nitrate reduction (Gattrell et al., 2006; Haque and Tariq, 2010), it is expected the prior deposition of copper might also be helpful in achieving improved Cd(II) reduction in the MECs, which to our knowledge has not been systematically investigated.

Different cathode materials have been used for metals reduction in BESs, with few comparisons made of different materials under the same operational conditions. Carbon-based cathodes, such as graphite plates, graphite foil, graphite rods, graphite disks, and carbon cloth have been used as cathodes in MFCs for Cu(II) reduction (Heijne et al., 2010; Luo et al., 2014; Tao et al., 2011). For Cd(II) reduction in MECs, titanium wire, titanium sheets, carbon cloth, and carbon rods have been used (Choi et al., 2014; Modin et al., 2012; Zhang et al., 2015). In MECs, hydrogen gas production competes with metals reduction, and thus materials are desired that have a good propensity for metals reduction but not H₂ gas evolution (Kundu et al., 2013; Wang et al., 2015). The impact of the deposition of one metal on the subsequent deposition of another metal, especially in the context of its impact on hydrogen evolution, has not been previously considered.

In this study, three different materials including titanium sheet (TS), nickel foam (NF), and carbon cloth (CC) were examined as cathodes in BESs first operated as MFCs, and then switched to MECs. In the MFCs, Cu(II) was first reduced and deposited on the cathode. The reactors were then operated as MECs for Cd(II) reduction along with H₂ gas evolution. Key factors influencing the reaction rates include the concentration of Cl⁻ and SO₄²⁻ ions in solution, the impact of the deposited copper on Cd(II) reduction, and the applied voltage. The performance of the reactors was evaluated in terms of rates of Cu(II) and Cd(II) reduction, hydrogen production, coulombic efficiency, energy efficiency, overall energy recovery and cathode potential.

2. Methods

2.1. Reactor construction

In this study, three different materials including titanium sheet (TS), nickel foam (NF), and carbon cloth (CC) were examined as cathodes in BESs first operated as MFCs, and then switched to MECs. In the MFCs, Cu(II) was first reduced and deposited on the cathode. The reactors were then operated as MECs for Cd(II) reduction along with H₂ gas evolution. Key factors influencing the reaction rates include the concentration of Cl⁻ and SO₄²⁻ ions in solution, the impact of the deposited copper on Cd(II) reduction, and the applied voltage. The performance of the reactors was evaluated in terms of rates of Cu(II) and Cd(II) reduction, hydrogen production, coulombic efficiency, energy efficiency, overall energy recovery and cathode potential.

2.1. Reactor construction

Identical two-chamber BESs with cylindrical chambers 4.0 cm long by 3.0 cm in diameter were used in all experiments. The anode and cathode chambers were separated by a cation exchange membrane (CEM) (CMI-7000 Membrane International, Glen Rock, NJ), with working liquid volumes of 15 mL in the anode, and 25 mL in the cathode, due to the volume of the electrode materials. The anode was filled with graphite felt (3.0 cm × 2.0 cm × 1.0 cm, Sanye Co., Beijing, China) using a carbon rod as the current collector. Cathodes of TS, NF or CC (2.0 cm × 2.0 cm) were placed next to the CEM, and connected to the circuit using titanium wire. Chemically inert titanium wire, rather than less-expensive stainless steel or copper wire, was used to avoid any corrosion during these tests (Logan, 2012; Zhu and Logan, 2014). These electrode materials were cleaned prior to installment in the reactors (Wang et al., 2015). A reference electrode (Ag/AgCl, 195 mV vs. SHE) was installed in the cathode chamber to measure cathode potential, with all potentials reported here vs SHE. All of the reactors were wrapped with aluminum foil to exclude light to avoid the growth of algae on the anodes and side reactions on the cathodes in the presence of Cu(II) (Sun et al., 2015).

2.2. Start up and operation

The bioanodes were inoculated with suspended bacteria from acetate-fed MFCs reactor and an equivalent volume of nutrient solution, and acclimated in MFCs. The nutrient anode solution (pH 7.0) consisted of (g/L): acetate, 1.0; KH₂PO₄, 4.4; K₂HPO₄, 3.4; NH₄Cl, 1.3; KCl, 0.78; MgCl₂, 0.2; CaCl₂, 0.0146; NaCl, 0.5; and 1.0 mL of trace elements (Cheng et al., 2009). During the initial bioanode acclimation period, the catholyte was a 50 mM phosphate buffer solution (KH₂PO₄−K₂HPO₄). The anolyte and catholyte were periodically replaced (once every 3–5 days). The anode was considered to be fully acclimated when the anode potential was stable at −0.24 V (vs. SHE) for at least three batch cycles.

The catholyte used in metal reduction tests contained 150 mg/L Cu(II) and 50 mg/L Cd(II), based on concentrations reported for these metals in actual electroplating wastewaters (Prakash et al., 2012). After an operation period of 30 h as an MFC, which was sufficient for nearly all the Cu(II) to be deposited on the cathodes, the systems were switched to MEC mode with an applied voltage of 0.5 V (DC Power Supply PS-1502DD, Yihua, Guangzhou, China) using a timed electromagnetic relay switch (ST3PA-F, Fangfushi, Japan). A small resistor of 10 Ω was connected in series with power supply to allow calculation of the current. All potentials were collected using a data acquisition (PISO-813, Hongge Co., Taiwan).

In order to investigate the effect of amount of deposited copper on Cd(II) reduction, catholytes composed of 100–500 mg/L Cu(II) and 50 mg/L Cd(II) were used to prepare various amounts of deposited copper in MFC mode for subsequent Cd(II) reduction in MEC mode (applied voltage: 0.5 V). Considering the occurrence of hydrogen evolution and the avoidance of metal precipitants above certain pHs, a buffer was used to sustain an appropriate pH for Cd(II) reduction. It has been shown that Cd(II) in an acetate buffer can form the complex Cd(CH₃COO)₂, which has a stability constant of 2.19. This is lower than that of 2.93–7.0 for Cd(NH₃)₄²⁺ in NH₄Cl–HCl buffer, and 9.7 for Cd(OH)₄²⁻ in borate buffer (Bousher, 1995; Khallaf et al., 2008). Ions of Cd(II) were therefore less tightly held by the Cd(CH₃COO)₂ complex than they would have been in borate or NH₄Cl–HCl buffers (Chen et al., 2014; Lv et al., 2013). CH₃COONa–CH₃COOH was therefore used as a catholyte buffer as it was expected to be most beneficial for efficient Cd
(II) reduction. A pH of 4.6 was not only optimal for the buffering of CH₃C(O)ONa–CH₃COOH (Chen et al., 2014; Lv et al., 2013), it was also unfavorable for hydrogen evolution and metal precipitant formation, both of which would benefit Cd(II) reduction. The value of 4.6 was thus chosen as an initial catholyte pH. The catholyte had a solution conductivity of 5.8 mS/cm. Reactors were operated under open circuit conditions (OCC) as controls for Cd(II) adsorption on the electrodes in the absence of current generation.

The impact of applied voltage on Cd(II) reduction on the cathodes with or without deposited copper, was examined using applied voltages of 0.3, 0.5, 0.7, 0.9, 1.1 V. To examine the effect of anions on Cd(II) reduction, Cd(II) was added using two different salts (CdCl₂ and CdSO₄) at identical Cd(II) concentrations of 50 mg/L, and a fixed pH of 4.6. To examine the impact of copper oxide formation, cathodes containing copper from MFC operation were exposed in the air for 48 h, and then examined using cyclic voltammetry (CV). All catholytes in both MFC and MEC modes were bubbled with ultrapure N₂ at least 15 min before each batch cycle operation. All experiments were conducted at a room temperature of 25 ± 3 °C.

2.3. Analytical measurements

CV (CHI 650, Chenhua, Shanghai) was carried out in a three-electrode configuration of a working electrode (bare, copper-deposited or oxidized copper-deposited electrodes), platinum plate as a counter electrode, and a Ag/AgCl reference electrode. Performance of cathodes was evaluated by linear sweep voltammetry (LSV) (CHI 650, Chenhua, Shanghai). Both CV and LSV were conducted at a scan rate of 1.0 mV/s.

Concentrations of Cu(II) and Cd(II) in the catholyte were determined by atomic absorption spectroscopy (AAAnalyst 700, PerkinElmer). Hydrogen in the headspace of cathode in the MECs was analyzed using a gas chromatograph (GC7900, Tianmei, Shanghai) and a molecular sieve column (TDX-01, 60–80, 4 mm) with nitrogen as the carrier gas.

A scanning electronic microscopy (SEM) (Nova NanoSEM450, FEI company, USA) equipped with an energy dispersive X ray spectrometer (EDS) (X-MAX 20 mm²/50 mm², Oxford Instruments, UK) was used to investigate the surface morphology of deposited copper and products as well as elemental composition. X-ray diffraction measurements (XRD-6000, Shimadzu LabX, Japan) were used to examine the morphology and crystal form of the products.

2.4. Calculations

Removal rates of Cu(II) and Cd(II) (mg/L h) were defined as the decrease of Cu(II) or Cd(II) concentration within an operation period (t). Net hydrogen production (m³ H₂/m² reactor d) based on recovery in the MEC headspace was normalized by the volume of the cathode chamber and operation time. A glass tube with an inner diameter of 8 mm was glued to the top of the reactor to create a total headspace of 12 mL. A microsyringe (200 μL, Agilent) was used to sample the headspace. Hydrogen production (m³) was then calculated based on the hydrogen concentration (m³/m³) obtained by the gas chromatograph multiplied by the gaseous phase volume of 0.0000012 m³. Energy efficiencies were calculated as the ratios of either energy consumption for Cd(II) reduction (ŋH₂, Cd- %) or energy produced by heat of combustion of hydrogen to electrical energy added (ŋH₂, Cd- %). Overall energy recoveries of cadmium reduction (ŋH₂+Cd, %) and hydrogen evolution (ŋH₂+H₂, %) were calculated based on both electrical energy added and anodic substrate consumption (Call and Logan, 2008) (Eqs. (3) and (4)). Power and current densities were normalized to the geometric surface of the cathode. One-way ANOVA in SPSS
absence of deposited copper, implying the critical roles of both circuit current and deposited copper in Cd(II) removal. More Cd(II) adsorption in the presence of deposited copper (1.77–2.30 mg/L h) than the controls with no deposited copper (0.18–1.20 mg/L h), indicated that Cu(II) deposition also enhanced Cd(II) adsorption.

Hydrogen production was competitive with metals reduction, although there was no consistent trend in these rates relative to metal reduction rates (Fig. 2B). The H2 production rate was the highest for the NF material (0.80 ± 0.07 m3/m3 d) that had the lowest rate of Cd(II) reduction. However, the next lowest H2 production rate (0.35 ± 0.07 m3/m3 d) was obtained using the CC material, which had the highest Cd(II) reduction rate, with the TS material having the lowest H2 production rate (0.15 ± 0.02 m3/m3 d). These H2 production rates were 2.0 (NF) to 7.0 (CC) times those obtained in tests without previously deposited copper.

The ratio of charge consumed for Cd(II) reduction to hydrogen evolution (shown as Cd/H2 in Table S2) was further used to clarify the relationship between Cd(II) reduction and hydrogen evolution on the various cathode materials in the absence or presence of copper. Despite the consistent increase in net charge for both Cd(II) reduction and hydrogen evolution on all the material cathodes in the presence of copper, more charge was diverted for Cd(II) reduction as shown by a higher Cd/H2 ratio of 0.02 ± 0.00–0.03 ± 0.00, compared to 0.01 ± 0.00 in the absence of copper (Table S2 and Fig. S2). Conversely, lower Cd/H2 ratios of 0.18 ± 0.02–0.33 ± 0.03 (TS) and 0.08 ± 0.00–0.16 ± 0.01 (CC) were obtained in the presence of deposited copper, compared to 0.56 ± 0.00 (TS) and 0.35 ± 0.03 (CC) in the absence of copper. These results clearly demonstrated the competitive relationship between Cd(II) reduction and hydrogen evolution on all cathode materials, and that NF was better than TS or CC for Cd(II) reduction compared to hydrogen evolution due to the presence of deposited copper.

While the intrinsic NF material was superior for higher exchange current densities and lower overpotentials for hydrogen evolution than TS and CC in the absence of copper (Kundu et al., 2013), a better resulting morphology of the copper deposited on the NF cathodes may have provided a more effective catalytic surface area, and thus better system performance in the present system as shown in the later Fig. S4B. The morphology of the metallic deposits has previously been shown to play a critical role in the effective catalytic surface area, and thus system performance by others (Habibi et al., 2008; Liu et al., 2014).

Increasing the amount of copper in solution in the MFC tests, and thus the amount of copper deposited on the cathode, did not necessarily improve Cd(II) deposition rates or H2 production. Higher initial Cu(II) concentrations of 300 mg/L or 500 mg/L diminished subsequent Cd(II) reduction rates on all cathodes (Fig. 3A), presumably due to the aggregation of large metallic Cu(0) particles that would decrease the active surface area (Habibi et al., 2008). Higher Cd(II) reduction rates were consistently obtained using the CC cathodes in both the absence and the presence of copper (Fig. 3A), and deposition rates were substantially lower in the OCC controls (Fig. 3B). Hydrogen production (Fig. 3C) and current densities (Fig. 3D) were similarly decreased using the two highest initial copper concentrations. These results show improvements in Cd(II) reduction rate and hydrogen production in MEC mode that changed with the amount of copper deposited in MFC mode. Considering the fluctuation of these ratios in actual wastewaters, more controlled ratios of deposited copper and reduced Cd(II) would be
needed for the subsequent efficient Cd(II) reduction in MEC mode. Further investigations in this direction are warranted.

3.3. Energy recovery in MECs

Energy produced in the MFC was \( \pm 0.8 \text{ kWh/kg Cu} \) for all three electrode materials (Table S1). The deposition of copper on the cathode in the MFC improved both Cd(II) reduction and hydrogen evolution in the MEC (Table S2). This finding is in agreement with other reports which have shown that copper reduction facilitates hydrogen evolution or oxygen reduction (Heijne et al., 2010; Modin et al., 2012; Luo et al., 2014). The reduced overpotentials in the presence of copper resulted in good energy recoveries, with \( \eta_{\text{E},\text{H}_2} > 100\% \) in most cases (Table S2). The energy production required for Cd(II) reduction in MEC mode ranged from 4.1 kWh/kg Cd (CC) to 8.5 kWh/kg Cd (NF) (Table S1). The energy production in the MFC, combined with energy in the hydrogen gas that was produced (0.5–14.8 kWh/kg Cd), resulted in a net energy input of 0.3 kWh for the TS cathode, whereas the use of the other material cathodes produced net energies of 7.7 kWh (NF) and 0.5 kWh (CC) based on per kilogram copper and cadmium. On the basis of this energy demand, the TS material cathode was the least suitable for use in these reactors and the NF cathodes provided a good compromise in terms of performance and energy recovery.

3.4. Electrode morphologies and product characterization

Compared to the bare cathodes of TS (Fig. S3A), NF (Fig. S3E) and CC (Fig. S3I), a layer of typical reddish-brown color was observed on the electrodes with deposited copper (Fig. S3B, F and J), implying the successful occurrence of Cu(II) reduction on these various electrodes (An et al., 2014; Tao et al., 2011; Wu et al., 2015b). With subsequent Cd(II) reduction, the color was reddish-brown, resulting in the blend as shown in Fig. S3C, G and K. Compared to the reddish-brown color of freshly deposited copper, dark black was observed on the various material cathodes after exposed in the air for 48 h (Fig. S3D, H and L), implying the oxidation of pure copper and the transformation of pure copper to cuprous and cupric oxides.

The copper-deposited cathodes were observed by SEM (Fig. S4A–C), EDS (Fig. S4D–F) and XRD (Fig. S4G–I) after Cd(II) reduction with 3 batch cycles operation. The three different materials showed distinctive morphologies, with comparatively larger cluster crystals observed on the NF cathodes (Fig. S4B) compared to the TS (Fig. S4A) and CC (Fig. S4C) cathodes. This result may explain the better performance of NF than the others (Fig. 2). Using EDS to examine the composition of the precipitates, Cu and Cd signals were detected on all the precipitates of TS (Fig. S4D), NF (Fig. S4E) and CC (Fig. S4F) cathodes. Similarly, peaks of copper matched those of Cu\(^0\) at 43.3, 50.4, and 74.1 in 2\(\theta\) (Fig. S4G–I), consistent with other reports on electrodeposited copper (Luo et al., 2014; Wu et al., 2015a,b; Zhang et al., 2015). This result demonstrates the independency of copper crystal form on these cathode materials. The absence of Cd signals in XRD (Fig. S4G–I), but appearance in the EDS analysis (Fig. S4D–F), implies an amorphous state of the reduced cadmium on these materials. The intensity of copper peak declined after Cd(II) reduction (Fig. S4G–I), which is expected due to the deposition of the cadmium.

3.5. Cyclic voltammetry analysis

Cd(II) reduction peaks were observed at potentials of \(-0.592 \text{ V (TS)} \) (Fig. 4A) and \(-0.576 \text{ V (CC)} \) (Fig. 4C) with deposited copper, which were more positive than those of the controls in the absence of copper (\(-0.621 \text{ V (TS)} \) and \(-0.613 \text{ V (CC)} \) (Fig. 4A and C), demonstrating the similar catalysis role of deposited copper in Cd(II) reduction on these electrodes. The different Cd(II) reduction peak potentials for TS and CC without the presence of deposited copper was mainly ascribed to the intrinsic characters of these materials. No apparent Cd(II) reduction peaks appeared on the NF cathodes.
were always higher than the controls with no copper. Higher reductive peak currents were observed on the CC electrodes than NF, followed by TS with deposited copper on the surface. The different reductive peak currents and reductive peak potentials on these materials can be also explained by the diverse morphologies of deposited copper (Fig. S4A–C), which may have resulted in the different effective catalysis surface area, and thus affected system performance (Habibi et al., 2008; Liu et al., 2014). All three materials with oxidative copper-deposited on the surface exhibited similar abatements in reductive peak currents (Fig. 4A–C), demonstrating the adverse effects of oxidative copper on Cd(II) reduction and reflecting the role of pure copper instead of oxidative copper in high reductive peak currents. Hydrogen evolution was observed based on the formation of gas bubbles on the surface of all material electrodes with deposited copper at a potential more negative than $-0.6 \text{ V}$ for NF, compared to $-0.7 \text{ V}$ for TS and CC, illustrating that NF had more superior catalytic properties for hydrogen evolution, consistent with higher hydrogen production rates in MEC tests (Fig. 2B) and the lowest ratio of charges consumed for Cd(II) reduction and hydrogen evolution (Table S2).

### 3.6. Effect of anions of Cl$^-$ and SO$_4^{2-}$

For all the three material cathodes with copper deposited on the surface, Cd(II) reduction (Fig. S5A), hydrogen production rates (Fig. S5B) and current densities (Fig. S5C) were higher using the Cl$^-$ catholyte compared to catholytes with SO$_4^{2-}$. The improvements of 5–9% in Cd(II) reduction, 74–650% in hydrogen production, and 28–195% in current density were achieved. In the absence of copper on the cathodes, there was very little difference in Cd(II) reduction (Fig. S5A) or hydrogen production (Fig. S5B) due to the use of Cl$^-$ or SO$_4^{2-}$ in the catholyte. However, Cl$^-$ ions in the catholyte resulted in copper corrosion during Cd(II) reduction, with the release of 0.2% (CC), 0.8% (TS) and 5.3% (NF) of the deposited copper into the catholyte, compared to 0.0% (CC), 0.3% (TS) and 0.3% (NF) using the CdSO$_4$ catholyte. These results were consistent with previous reports using conventional electrochemical processes (Tansuğ et al., 2014), where a copper electrode corroded in chloride media.

### 3.7. Effect of applied voltage

Cd(II) reduction on all the three material cathodes increased with the applied voltages up to 0.7 V, approaching the maximal rates of 5.65 (NF)–6.59 (CC) mg/L h, and decreased thereafter (Fig. S6A). Hydrogen evolution on all the cathodes, however, always increased with the increase in applied voltage (Fig. S6B). Although the NF cathodes had the highest current densities at the different applied voltages (Fig. S6C), more electrons were diverted to hydrogen evolution (Fig. S6B) than Cd(II) reduction at higher applied voltages (Fig. S6A and Table S3). CC cathodes were more favorable for Cd(II) reduction (Fig. S6A) than hydrogen evolution (Fig. S6B and Table S3) despite a low current density (Fig. S6C). These results demonstrate the dependency of both Cd(II) reduction and hydrogen evolution on cathode material with deposited copper.

Anode potentials stabilized at $-0.250 \text{ V}$ at applied voltages below 0.7 V, whereas cathode potentials always decreased inversely with the applied voltage (Fig. S6D), showing the importance of cathode rather than anode potential. The lowest energy consumption for Cd(II) reduction was obtained at 0.5 V, reaching 1.6 ± 0.1 kWh/kg Cd (TS), 2.1 ± 0.0 kWh/kg Cd (CC) and 7.8 ± 0.2 kWh/kg Cd (NF) (Table S3). Net energy production was only obtained at 0.3 and 0.5 V for the TS and CC materials.
3.8. Long-term stability of copper deposited cathodes

In order to assess the stability of Cu-deposited cathodes, the cathodes with deposited copper of 150 mg/L were subsequently used in multiple batch cycles for Cd(II) reduction. A similar decreased trend in Cd(II) reduction rates were observed for all three materials over the 20 cycles, where there was a decrease in the rate of 31% (NF) to 37% (CC) compared to cycle 1 (Fig. 57A). These results show the instability of the copper on the surface over repeated cycles. Hydrogen production showed a steeper sharper decline over time, with a reduction of 100% (TS), 59% (NF) and 91% (CC) after 20 cycles (Fig. 57B). This indicates that hydrogen evolution was affected to a greater extent than Cd(II) reduction over time. Current density was decreased over time in all cases (Fig. 57C). LSVs on all material cathodes were consistent with the performances (Fig. 57D–F), where the conductive and catalysis deposited copper resulted in higher current densities and lower voltages needed to initiate substantial currents while the un-conductive cadmium deposited within an 8 cycles operation adversely affected current densities and voltages needed to initiate substantial currents.

4. Conclusions

Cathodes with in situ deposited copper from MFC operation successfully enhanced subsequent Cd(II) removal and hydrogen evolution in MEC mode using the cathode materials TS, NF and CC. Despite similar Cu(II) reduction rates in MFC mode, reduction of Cd(II) competed with hydrogen evolution in the MEC mode for the produced cadmium charge. This competitive relationship was always found on all the material cathodes, but it changed with cathode material, anions of Cl⁻ versus SO₄²⁻, and applied voltage. These results show this BES can be used for efficient remediation of Cu(II) and Cd(II)) contaminated waters with simultaneous energy recovery.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.10.084.

References