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Continuous removal of heavy metals by coupling a microbial fuel cell and a microbial electrolytic cell

Guo R. Xie[1a], Chan S. Choi[*1], Bong S. Lim[2b] and Shao X. Chu[2c]

[1]Department of Applied Chemistry, Daejeon University, 62 Daehak-ro, Dong-gu, Daejeon, 34520, Republic of Korea
[2]Department of Environmental Engineering, Daejeon University, 62 Daehak-ro, Dong-gu, Daejeon, 34520, Republic of Korea

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Abstract. This work aims at studying the feasibility of continuous removal of mixed heavy metal ions from simulated zinc plating wastewaters by coupling a microbial fuel cell and a microbial electrolysis cell in batch and continuous modes. The discharging voltage of MFC increased initially from 0.4621 ± 0.0005 V to 0.4864 ± 0.0006 V as the initial concentration of Cr^{6+} increased from 10 ppm to 60 ppm. Almost complete removal of Cr^{6+} and low removal of Cu^{2+} occurred in MFC of the MFC-MEC-coupled system after 8 hours under the batch mode; removal efficiencies (REs) of Cr^{6+} and Cu^{2+} were 99.76% and 30.49%. After the same reaction time, REs of nickel and zinc ions were 55.15% and 76.21% in its MEC. Cu^{2+}, Ni^{2+}, and Zn^{2+} removal efficiencies of 54.98%, 30.63%, 55.04%, and 75.35% were achieved in the effluent within optimum HRT of 2 hours under the continuous mode. The incomplete removal of Cu^{2+}, Ni^{2+} and Zn^{2+} ions in the effluent was due to the fact that the Cr^{6+} was almost completely consumed at the end of MFC reaction. After HRT of 12 hours, at the different sampling locations, Cr^{6+} and Cu^{2+} removal efficiencies in the cathodic chamber of MFC were 89.95% and 34.69%, respectively. 94.58%, 33.95%, 56.57%, and 75.76% were achieved for Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+} in the cathodic chamber of MEC. It can be concluded that those metal ions can be removed completely by repeatedly passing high concentration of Cr^{6+} through the cathode chamber of MFC of the MFC-MEC-coupled system.

Keywords: microbial fuel cell; microbial electrolytic cell; removal of mixed heavy metal ions; removal efficiency; hydraulic retention time; wastewater treatment

1. Introduction

Water is regarded as the most essential natural resource and of course important in daily life. The earth is largely covered with water, and gradually polluted due to human and industrial activities. The increasing contamination of water systems by the industrial and natural chemical compounds is one of the key environmental problems that human society faces. Numerous contaminants, such as heavy metal ions and some organic contaminants, are introduced into water supplies from industrialization and human activity (Schwarzenbach *et al*. 2006). Heavy metal ions, such as cadmium, lead, chromium, nickel, zinc and copper ions are naturally occurring elements, and are considered systemic toxicants that induce multiple organ damages. Hence, the development of efficient techniques for the removal of these heavy metal ions from wastewater is an important task in terms of protection of not only environment but also public health. A number of technologies have been widely employed to remove heavy metal ions from aqueous solutions: adsorption, chemical precipitation, ion exchange, electrochemical treatment, reverse osmosis, solvent extraction and membrane filtration (Mahmood *et al*. 2010). Most of these methods are not widely acceptable due to their high cost, low efficiency, disposal of sludge and inapplicability to a wide range of pollutants.

Bioelectrochemical systems (BESs) have attracted considerable attention for their innovative features and environmental benefits (Mu *et al*. 2009). BESs include the microbial fuel cell (MFC), where electrical power is harvested ($\Delta G < 0$), and the microbial electrolytic cell (MEC), where a small amount of electrical energy is supplied to drive non-spontaneous reactions in the cell ($\Delta G > 0$). In MFC, electricity can be produced spontaneously because the microorganisms (biofilm) on the anode metabolize organic matters and produce electrons and protons causing electrons to flow from the anode to the cathode with a potential gradient through an external electrical circuit. Then the electrons react at the cathode of MFC with the electron accepters in the solution. Biofilm-coated electrodes and outer cell membrane-mimicked electrodes were examined to verify an extracellular electron transfer mechanism using Marcus theory for a donor-

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[*] Corresponding author, Professor
E-mail: pchoi7@hotmail.com
[a] Post-Master
E-mail: xgr1992@hotmail.com
[b] Professor
E-mail: bslim@dju.kr
[c] Ph.D. Student
E-mail: c375383051@hotmail.com

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acceptor electron transfer. The electron transfer was believed to occur sequentially from acetate to nicotinamide adenine dinucleotide (NAD^+), c-type cytochrome, flavin mononucleotide (FMN) (or riboflavin (RBF)) and the anode substrate (Yang *et al.* 2019). The MFC system can achieve power generation and remove heavy metal ions from the wastewater. The MFC and MEC systems were applied to reduce electrochemically heavy metal ions at the cathode, such as Cu^{2+}, Hg^{2+}, Cd^{2+}, and Cr^{6+}, to metal elements or ions with lower chemical valences (Wang *et al.* 2010, Wang *et al.* 2011, Choi *et al.* 2014, Wang *et al.* 2008). The reactions for these metal ions to accept electrons at the cathode of MFC are spontaneous, when the anode is coated with biofilm. In this study, the relatively high standard reduction potentials of Cr(VI) and Cu(II) can make MFC's enable them to act as electron acceptors at the cathode of the MFC system. The metal ions may be reduced in MFC through the following processes, and their reversible half-cell reduction potential values (E) were calculated for 10 ppm concentrations:

$$\mathrm{HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O} \quad E = +1.33\ \mathrm{V\ (vs.\ SHE\ at\ 25°C)} \tag{1}$$

$$\mathrm{Cu^{2+} + 2e^- = Cu} \quad E = +0.23\ \mathrm{V\ (vs.\ SHE\ at\ 25°C)} \tag{2}$$

Many metal ions, such as Ni^{2+} and Zn^{2+}, cannot accept electrons spontaneously due to their relatively low reduction potentials, which make the voltage difference between the anodic and cathodic potentials too small to transfer the electrons from the anode to cathode, even if a bioelectrochemical system is formulated with these metal ions, i.e., a microbial electrolytic cell (MEC). Therefore, MEC without an input of external electrical energy cannot treat wastewaters containing Ni^{2+} and Zn^{2+}. The additional voltage and power should be supplied to MEC as a direct current power source or another MFC. Ni^{2+} and Zn^{2+} can be reduced in MEC with an input of external electrical energy through the following processes, and the reversible half-cell reduction electrode potential values (E) were also calculated for 10 ppm metal ions:

$$\mathrm{Ni^{2+} + 2e^- = Ni^0} \quad E = -0.37\ \mathrm{V\ (vs.\ SHE\ at\ 25°C)} \tag{3}$$

$$\mathrm{Zn^{2+} + 2e^- = Zn^0} \quad E = -0.87\ \mathrm{V\ (vs.\ SHE\ at\ 25°C)} \tag{4}$$

Therefore, it would be clear that the metals would be removed more favorably in the order of $HCrO_4^- > Cu^{2+} > Ni^{2+} > Ni^{2+}$ for the given experimental conditions, based on the half-cell reduction potentials.

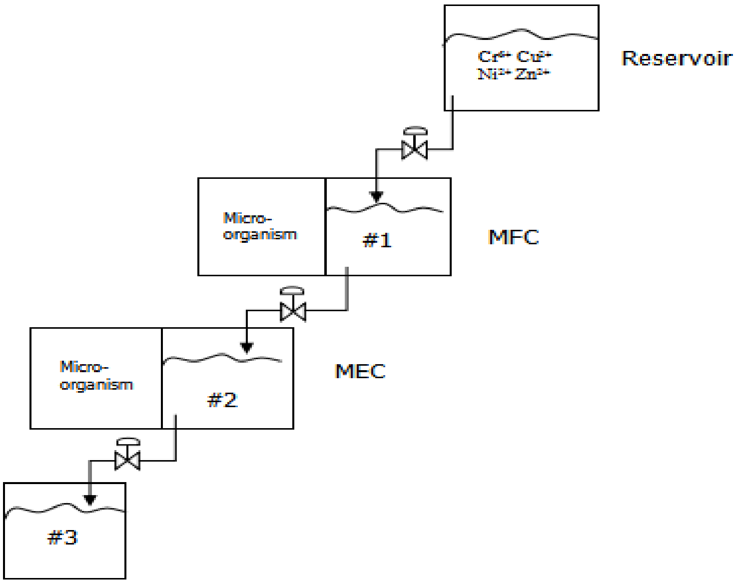
It is important to know that MEC can reduce Ni^{2+} and Zn^{2+} in its cathode chamber with additional voltages (E_{add}) lower than the applied voltage (E_{app}) of the conventional electrolytic cell because of the supply of electrons by bacteria in the bio-anode. MEC required voltage and power from an external electrical energy source to operate. The electrical energy from MFC could be applied by connection in series, and MEC functioned as an electrical load. There were no voltage reversal problems during the operation of the MFC-MEC system, while the voltage between the MEC was measured to monitor the system.

In this study, removal of heavy metal ions from synthetic wastewaters simulating zinc plating solutions was investigated using a MFC–MEC–coupled system, which was connected in series. The MFC contains a mixed solution of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} in its cathodic chamber, and can generate electrical power to supply with the following MEC which contains Ni^{2+} and Zn^{2+} wastewater in its cathode chamber. It can complement voltage required to reduce Ni^{2+} and Zn^{2+} ions to Ni and Zn metals. Cr^{6+} and Cu^{2+} in the mixed solution of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} were treated by reduction in the cathode chamber of MFC, and the treated solution was transferred to the cathodic chamber of MEC from that of MFC. The main objective of this study was to study the feasibility of removal of mixed heavy metal ions from wastewater using a MFC–MEC-coupled system both in a batch mode and in a continuous-flow mode, which was not attempted previously. In the batch mode, effects of Cr^{6+}'s initial concentration in MFC for removal efficiency of Zn^{2+} and Ni^{2+} in MEC were studied. In the continuous mode, effects of HRT were studied as well as the influence of Cr^{6+}'s initial concentration for the optimum experimental condition.

2. Experimental

2.1 Materials

Potassium dichromate (purity of > 99.5%), nickel(II) sulfate hexahydrate (purity of > 98.5%), zinc sulfate heptahydrate (purity of > 99.0%), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) (HEPES), ammonia solution (purity of 30.0%) and hydrochloric acid (purity of > 35.0%) were obtained from Dae-Jung Chemicals & Metals Co., Ltd. (Seoul, Republic of Korea). Potassium phosphate dibasic (purity of > 98.0%, ACS reagent grade), potassium phosphate monobasic (suitable for plant cell culture, purity of > 99.0%) were obtained from Sigma-Aldrich (Seoul, Republic of Korea). Sodium acetate (anhydrous, 98.5%) and sodium perchlorate monohydrate were obtained from Samchun Chemicals & Metals Co., Ltd. (Seoul, Republic of Korea). Copper(II) chloride dihydrate (purity of > 97.0%) was purchased from Right Price Chemicals & Metals Co., Ltd. (Texas, USA). Bacto yeast extract was obtained from DIFCO Laboratories (New Jersey, USA). The Bacto yeast extract is the water-soluble portion of autolyzed yeast, and it is a source of naturally-occurring B-complex vitamins and other growth-promoting substances, making this product an excellent host for a large variety of microorganisms. Anion exchange membrane (AEM, AMI-7001) were purchased from Membrane International, Inc. (New Jersey, USA). Carbon fiber (PANEX® 35) was purchased from Zoltek (Missouri, USA). Carbon felt (3.18 mm thick, 99.0%) and hard graphite plate were purchased from Alfa Aesar (Massachusetts, USA) and MTI Corporation (Shanghai, China), respectively.



Schematic 1 Diagram of MFC-MEC coupled system under the continuous mode of the cathode chamber set up in the lab. #1, cathodic chamber of MFC; #2, cathodic chamber of MEC; #3, effluent. All chamber volumes were 180 mL. MFC is electrically connected to MEC in series. Reservoir volume was 200 mL.

2.2 Preparation of MFC and MEC

A cubical dual-chamber made from acrylic rectangle was used in this study. Both anode and cathode chambers held a volume of 216 mL with an effective volume of 200 mL. The membrane, which is an anion exchange membrane, was used to separate the chambers, as shown in Schematic 1. It was sandwiched with two rubber gaskets and the two chambers were tightened with bolts and nuts to prevent the solution from leaking. The membranes used have a thickness of 0.5 mm. The function of the anion exchange membrane was stable with a catholyte at pH 2 in the present experimental time range. The carbon felt anode and the graphite cathode with a nominal surface area of 20 cm^2 (4 cm × 5 cm) were prepared.

The anaerobic inoculum was collected from anaerobic sludge, as previously published by Choi and Cui (2012). Each anodic chamber of four MFCs was inoculated by filling them with a mixture of 50 mL sludge and 150 mL artificial wastewater (AW) (pH 7). The components of AW were 2.0 g/L CH_3COONa, 1.05 g/L NH_4Cl, 1.5 g/L KH_2PO_4, 2.2 g/L K_2HPO_4, and 0.2 g/L yeast extract. The buffer, which contained solution containing 1.5 g/L KH_2PO_4 and 2.2 g/L K_2HPO_4, was poured into the cathodic chamber; and then simultaneously purged with air to utilize dissolved oxygen (DO) as an electron acceptor, growing microorganisms on the anode. For longer than three months, four MFCs were operated, producing stable voltage output cycles. When starting the experiments, the cathodic chamber of MFC was replaced with a mixture of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} as a catholyte. The cathodic chamber was purged with N_2 gas for 15 min to remove dissolved O_2. All chambers were kept air-tight, and the electrolytes were stirred continuously with magnetic stirrers. The mixture was prepared by dissolving $K_2Cr_2O_7$, $CuSO_4$, $ZnSO_4$, $NiSO_4$ with distilled water to obtain a stock solution of 10 ppm each. Then, it was divided into four parts, and three parts were chosen to obtain Cr^{6+} solutions of 20 ppm, 40 ppm,and 60 ppm by adding more $K_2Cr_2O_7$. The pH was adjusted to 2 with HCl (35%). Different Cr^{6+} concentrations of 10 ppm, 20 ppm, 40 ppm, and 60 ppm were prepared in the background solution containing the remainder of species of 10 ppm, and were used as electron acceptor solutions for MFC, and were used as electron acceptor solutions for MFC. Each heavy metal ion concentration of the catholyte was set to 10 ppm, except that Cr(VI) concentration was varied from 10 ppm to 60 ppm. Another mixture of Ni^{2+} and Zn^{2+} was prepared for MEC by dissolving $NiSO_4$ and $ZnSO_4$ with distilled water to get a stock solution of 10 ppm each. The difference between MFC and MEC was to use catholytes containing heavy metal ions having high and low reduction potentials, when the same biofilm-coated electrodes were used as anodes. Anolyte was pumped continuously into the anode chamber with a peristaltic pump. Sampling time interval for solution analysis and cell voltage was set to one hour. The experiments were repeated three times.

2.3 Continuous-flow experiments

A continuous operational mode was adopted in this experiment, infusing from the reservoir containing 200 mL solution with an infusion tube to cathodic chambers at a different flow rate. The cathodic chamber volumes were 180 mL. The experiments were conducted in the MFC-MEC coupled systems by using cathodic inlet and outlet flow rates of 1.66 mL/min, 0.83 mL/min, 0.56 mL/min, 0.42 mL/min, 0.33 mL/min, 0.16 mL/min, and the corresponding hydraulic retention times (HRT) were estimated to be approximately 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h, respectively. Each heavy metal ion concentration of the catholyte was also set to 10 ppm. Sampling intervals for the different hydraulic retention times were 2 h, 4 h, 6 h, 8 h, and 10 h. For all the experiments, the samples of the corresponding effluents were collected at different locations (#1, #2 and #3 in Schematic 1) for analyzing remaining concentrations for each metal ion. The sample size was 10 mL.

The anolyte of each cell was continuously pumped into the anode chamber at a flow rate of 1.66 mL/min (HRT of 2 h). The cell voltage was registered in one-hour interval, and all experiments were performed at 25°C±1°C under the normal atmospheric pressure.

2.4 Instruments and analysis

The voltage was recorded in one-hour interval by using a LabView system (National Instruments Models, NI-cDAQ 9219, Texas, USA). Different external resistances from 150 kΩ to 0.010 kΩ were connected to obtain a polarization curve for the determination of the maximum power generation. Additionally, electrochemical impedance spectroscopy (EIS) could also be applied to characterize the performance of microbial fuel cells. At each scheduled sampling interval, a sample of 10 mL was withdrawn from the cathodic chamber for each heavy metal ion analysis to determine the removal efficiency. The concentrations of Cr(VI) were determined by UV-visible spectrophotometry using biphenyl carbazide in acidic solution. The concentrations of Cu^{2+}, Zn^{2+} and Ni^{2+} were analyzed using an atomic absorption spectrometer (PG Instruments Ltd., Model PG-990, Leicestershire, UK).

3. Results and discussion

3.1 Effects of different initial concentration of Cr^{6+} on maximum power density

Fig. 1A shows power density vs. current density (P-J) curves with a change in the initial Cr^{6+} concentration from 10 ppm to 60 ppm. The maximum current densities (J_{max}) and maximum power densities (P_{max}) increased with an increase in Cr^{6+} concentration. P_{max} increased from 0.5347±0.0001 Wm^{-2} (5.347 kW/m^{-3}) to 0.9593±0.0110 Wm^{-2} (9.593 kWm^{-3}) (Fig. 1A and Table 1). Cr^{6+} concentration increase can be attributed to the increase in the reaction rate at the cathode, when the anodic reaction rate was ideally fast enough not to affect the cathodic reaction. To characterize the MFC, the electrochemical impedance spectroscopic (EIS) analysis of the MFCs was performed with catholytes containing different concentrations of Cr(VI) (10-60 ppm) in the cathode chamber under the open circuit potential. The parameters of Nyquist plots of MFC with respect to Cr(VI) concentrations were obtained by fitting them to the equivalence circuit. The solution resistance (R_s) was reduced from 19.33 Ω for 10 ppm to 13.37 Ω for 60 ppm; the charge transfer resistance R_{ct} also decreased from 28.14 Ω to 21.54 Ω under the same concentration change. The internal resistance (R_{int}), which is the sum of solution resistance and charge transfer resistance, decreased quickly for Cr^{6+} concentration increase from 10 ppm to 20 ppm, and decreased slowly for Cr^{6+} concentration from 20 ppm to 60 ppm. The internal resistance was significantly influenced by the Cr^{6+} concentration, leading to higher exchange current density with higher Cr^{6+} concentration involvement. Higher Cr^{6+} concentration exhibited higher MFC performance (e.g., higher P_{max}) by lowering internal resistance of the MFC cathode, compared to lower Cr^{6+} concentration, until reaching an anodic polarization quenching (Choi C. and Hu N. 2013), as shown in Fig. 1A.

3.2 Discharge curves of MFC with different concentrations of Cr^{6+}

The reversible potentials (E_{rev}) of Ni^{2+}/Ni and Zn^{2+}/Zn for 10 ppm were −0.37 V and −0.87 V vs. SHE, respectively, as calculated using the Nernst equation. If the anode is assumed to be set at a constant potential of −0.30 V, the minimum electrolysis voltage that should complement the MEC of the Ni^{2+}/Ni redox couple is 0.07 V, and that of the Zn^{2+}/Zn redox couple is 0.57 V, which is about 0.50 V lower for the former than for the latter. Nickel ion reduction is expected to be energetically easier than zinc ion reduction, when considering only the minimum voltage required for electrolysis of the ions. Fig. 1B shows voltage vs. reaction time curves of the MFC-MEC coupled system. The voltages were recorded by measuring the voltage across the MEC acting as a load resistor of MFC. By complementing the necessary voltage of MEC using the power from MFC (Fig. 1A), the recovery reactions of Ni^{2+} and Zn^{2+} were accelerated when keeping the voltage high, as shown in Fig. 1B. The discharging voltage shown in Fig. 1B is a working voltage ($E_{wk} = E_{cell} - \eta_a - \eta_c - IR$) of MFC. Recall that the available maximum powers of MFC from 0.5347±0.0001 Wm^{-2} to 0.9593±0.0110 Wm^{-2} could be utilized with the initial concentrations of Cr^{6+} changed from 10 ppm to 60 ppm in MFC (Fig. 1A and Table 1). Therefore, the discharging voltage (E_{dis}) decreases with internal resistance increase of the cell system, in particular, by reduction of metal ions in the cathodic chambers of MFC and MEC. The initial concentration was set to 10 ppm for Ni^{2+} and Zn^{2+} each in MEC. The metal ion reduction would accelerate, and the voltage of MFC dropped faster, when higher power was applied to MEC by increasing electron acceptor concentration of the cathodic chamber of MFC (Fig. 1B).

To remove nickel ions and zinc ions from wastewaters by their reduction in the cathodic chamber of MEC, least amounts of voltages of 0.07 V + η_a + η_c + IR and 0.57 V + η_a + η_c + IR were needed to be complemented to the MECs consisting of the cathode containing nickel ions and zinc ions (10 ppm), respectively, thus achieving a current of I. η_a is over-voltage for the anode, η_c is over-voltage for the cathode, and IR is over-voltage caused by Ohmic resistance. The additional voltage ($\eta_a + \eta_c + IR$) for Ohmic resistance ($R = R_{solution} + R_{separator} + R_{circuit}$) could be added to achieve nickel ion and zinc ion reduction in MEC generating power from a MFC consisting of the anode containing acetate and the cathode containing Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions of 10 ppm each. An average supply voltage of 0.4104 ± 0.02 V was obtained (Fig. 1B) under this condition. Cr^{6+} concentration was varied from 10 ppm

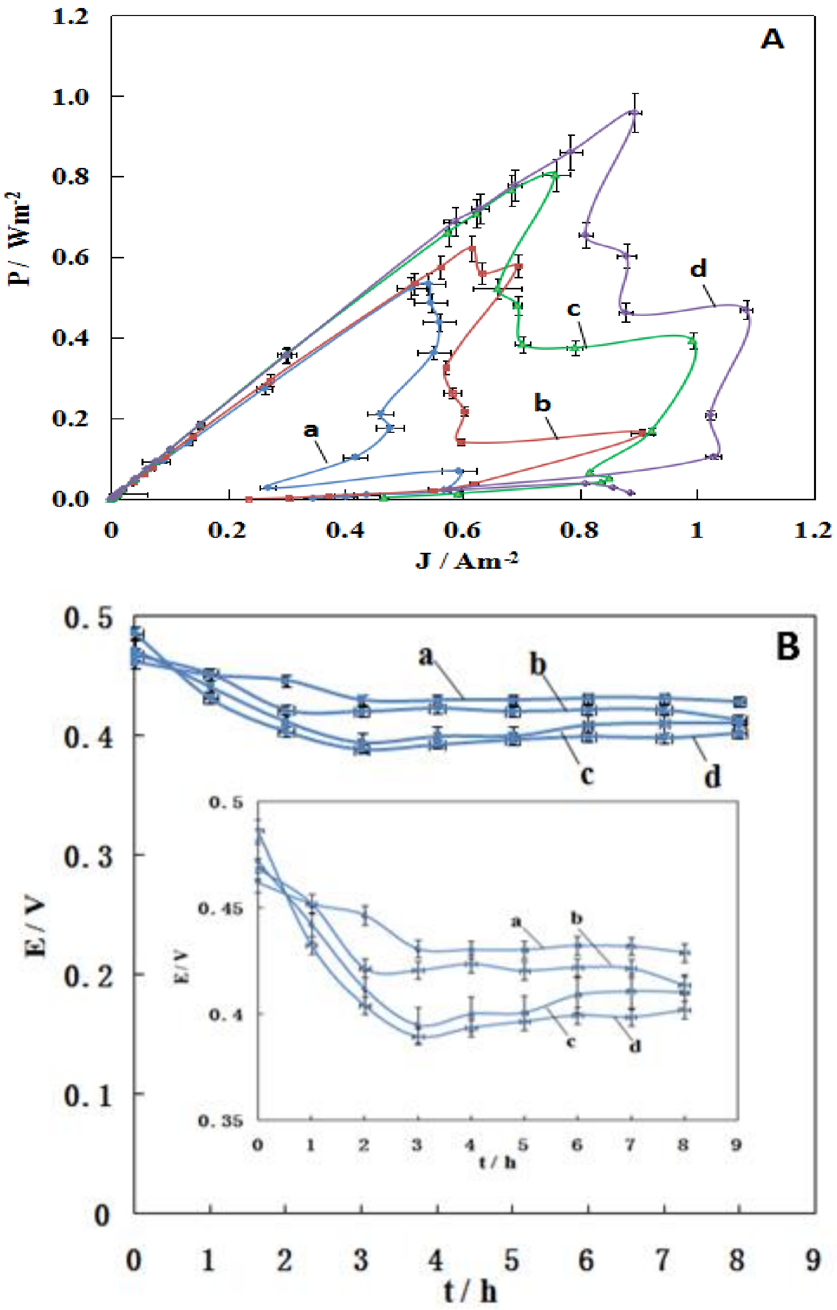


Fig. 1 (A) Effects of initial concentration of Cr(VI) on power density of the uncoupled MFC, and (B) voltage change with respect to reaction time for the MFC-MEC-coupled system. The Cr(VI) concentration was changed; (a) 10 ppm, (b) 20 ppm, (c) 40 ppm, and (d) 60 ppm in MFC. Cu(II) concentration in MFC was 10 ppm. The concentrations of Ni(II) and Zn(II) in MEC were 10 ppm each. The solution pH was 2.0. Data were measured in triplicate.

to 60 ppm in the cathodic chamber of MFC, and the cathodic chamber of MEC contained Ni^{2+} and Zn^{2+} of 10 ppm each. The discharging voltage increased initially from 0.4621 ± 0.0005 V to 0.4864 ± 0.0006 V as the initial concentration of Cr^{6+} increased from 10 ppm to 60 ppm. Consequently the discharge voltage dropped faster for higher initial concentration of Cr^{6+} than the lower ones within the first two hours. The voltage dropped slowly with further increase in time (Fig. 1B). This initial increase in discharging voltage can be attributed to the power of MFC which was increased with an increase in Cr^{6+} concentration from 10 ppm to 60 ppm. As the power of the MEC complemented by MFC was increased, Ni^{2+} and Zn^{2+} reduction rates of the MEC were increased, presumably indicating a faster resistance increasing rate due to the reduction of electron acceptors in MEC. The discharging voltage decreased faster initially, but after 2 hours the decreasing rate of the voltage became low with a slow removal rate in the cathode chamber of MEC. Prolonged high voltage for a long duration is an indicator of the stable performance of the MFC-MEC coupled system under the batch operation (Fig. 1B). Removed metals were deposited on the cathode. A quick scanning electron micrograph/energy dispersive spectroscopy (SEM/EDS)

Table 1 Electrochemical parameters for MFC with different initial Cr^{6+} concentrations*

Initial Cr(VI) Concentration	V_o/V	V_{max}/Am^{-2}	J_{peak}/Am^{-2}	J_{max}/Am^{-2}	P_{max}/Wm^{-2}
10 ppm	1.1330±0.0005	0.9870±0.0001	0.5420±0.0001	0.5935±0.0057	0.5347±0.0001
20 ppm	1.1560±0.0076	1.0100±0.0005	0.6161±0.0005	0.6943±0.0022	0.6225±0.0005
40 ppm	1.2430±0.0002	1.0620±0.0234	0.7586±0.0234	0.8505±0.0610	0.8056±0.0234
60 ppm	1.2630±0.0016	1.073±0.0110	0.8941±0.0110	1.0837±0.0108	0.9593±0.0110

*Data were measured in triplicate.

analyses would have given decent results for confirmation; these analyses were not performed. Copper, nickel, and zinc metals were assumed to be obviously deposited on the cathode because many SEM/EDS experiments performed in this laboratory showed metallic deposition on the cathodes (Wang *et al.* 2010, Hu *et al.* 2019).

$HCrO_4^-$ can cross over with the use of an anion exchange membrane, but the mixture ions in the cathode chambers of the present MFC-MEC-coupled system contained cations except $HCrO_4^-$ anion. So, the anion exchange membrane was commonly applied to separate the anode and cathode chambers, and the loss of $HCrO_4^-$ to the anode was not monitored through the membrane, even if anion exchange membranes are not ideal and thus allowing a certain degree of crossover of the metal cations.

3.3 Removal efficiency (RE) and remaining concentration (RC) of the MFC-MEC-coupled system in a batch mode

3.3.1 RE's and RC's of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}

Fig. 2 shows RE and RC occurred in heavy metal concentrations in the cathodic chambers of MFC and MEC with time. All initial concentrations of heavy metal ions were 10 ppm. MFC and MEC were operated in a batch mode by connecting them in a series mode. This figure shows that most of the metal removal reactions almost stopped in an hour, while the removal was not complete. The electron acceptors Cr^{6+} and Cu^{2+} in MFC were rapidly consumed and minimized within an hour, and then slowly reacted at a later time in the MFC-MEC-coupled system. The MFC could not function fully as a power supplier for MEC because the concentration of 10 ppm Cr^{6+} was not enough to finish the reduction of metal ions in MEC. Removal rate of Ni^{2+} and Zn^{2+} in MEC was also limited. Fig. 2A shows almost complete removal of Cr^{6+} and low removal of Cu^{2+} occurring in MFC after 8 hours. RC's of Cr^{6+} and Cu^{2+} were nearly zero ppm and 6.950 ± 0.001 ppm, and REs of Cr^{6+} and Cu^{2+} were 99.76% and 30.49%, respectively (Table 2). RE of Cu^{2+} was lower than that of Cr^{6+} by a factor of 3.3 because electrons were presumably transferred from the produced Cu metal to Cr^{6+}. On the other hand, Fig. 2B shows RCs and REs of nickel and zinc ions in MEC. After 8 hours RCs of nickel ions and zinc ions were 4.485 ± 0.011 ppm and 2.379 ± 0.002 ppm, respectively. The REs of nickel and zinc ions were 55.15%, and 76.21% (Fig. 2B and Table 2). MFC can spontaneously generate a high power with a high voltage ($\Delta G<0$), which can be complemented to insufficient voltage of MEC ($\Delta G>0$) for the electrolysis reaction to proceed, when the bio-films are applied as anodes for both MFC and MEC. The MFC cathode potential is higher (i.e. producing a Galvanic cell voltage with the bio-anode) than that of an MEC. MFC needs to provide four electrons to reduce Ni^{2+} and Zn^{2+} to metallic Ni(0) and Zn(0) in MEC. Cr^{3+} and metallic Cu(0) are created in MFC by five electrons returning from MEC. In MFC, metallic Cu(0) can react with Cr^{6+} to form Cu^{2+} and Cr^{3+} electrochemically to increase Cu^{2+} concentration and decrease Cr^{6+} concentration. Therefore, Cr^{6+} in MFC seems to be consumed faster than Ni^{2+} and Zn^{2+} in MEC for the same concentration of each ion, whereas Cu^{2+} in MFC is consumed slower than other ions. The removal efficiency of Cr^{6+} would have been greater than the rest of the ions in the MFC-MEC system arranged in series. That of Cu^{2+} could be lower than that of Cr^{6+} (Fig. 2 and Table 2).

Table 2 Variation of removal efficiency of heavy metal ions from MFC and MEC under the batch mode*

Reaction	MFC		MEC	
time/h	RE/%(Cr^{6+})	RE/%(Cu^{2+})	RE/%(Ni^{2+})	RE/%(Zn^{2+})
1	61.40±0.0020	28.01±0.0026	50.30±0.0021	75.00±0.0015
2	72.90±0.0132	28.76±0.0042	50.79±0.0025	75.59±0.0011
3	80.39±0.0070	28.95±0.0132	51.79±0.0010	75.64±0.0008
4	83.74±0.0116	29.25±0.0030	52.74±0.0119	75.69±0.0011
5	91.11±0.0025	29.69±0.0035	53.09±0.0173	75.76±0.0016
6	99.36±0.0015	30.36±0,0173	53.59±0.0045	75.86±0.0012
7	99.66±0.0015	30.38±0.0042	54.45±0.0159	76.09±0.0012
8	99.76±0.0012	30.50±0.0010	55.15±0.0109	76.21±0.0020

*Data were measured in triplicate.

The RE of zinc ion was higher than that of nickel ion by a factor of 1.39. This observed result differs from the result expected based on the reduction potential difference calculated from the Nernst equation. The voltage (E_{app}) required by Zn^{2+} ion reduction is higher than that of Ni^{2+}, and the removal efficiency of Zn^{2+} is expected to be lower than that of Ni^{2+}, but it is opposite (76.21% for Zn^{2+} vs. 55.15% for Ni^{2+}). This result seemed to be attributed to a faster electrochemical reduction rate of zinc ions than that of nickel ions at the cathode according to $P = \sigma Q$. P is amount of product, σ is selectivity, and Q is amount of charge consumed. P of Zn^{2+} is larger than that of Ni^{2+} due to a better σ. Over-voltage and charge transfer resistance of Ni^{2+} reduction seemed to be much larger than those of Zn^{2+} reduction. Here, the reason why both Ni^{2+} and Zn^{2+} ions were not completely removed is that the Cr^{6+} in the cathode chamber of MFC is almost completely consumed, leading to a loss of power before the completion of Ni^{2+} and Zn^{2+} reduction. Therefore, those metal ions can be removed completely by connecting MFC to MEC repeatedly. It is

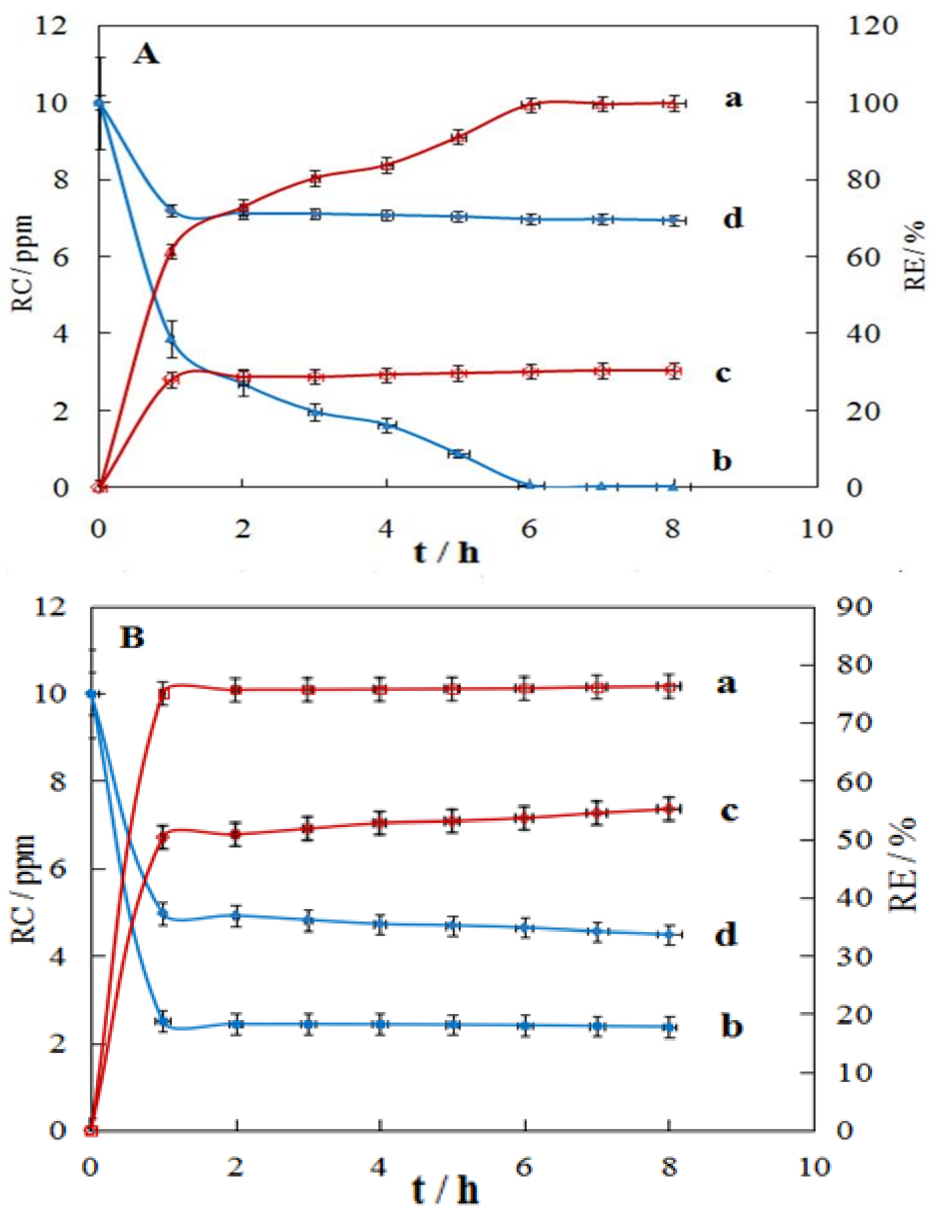
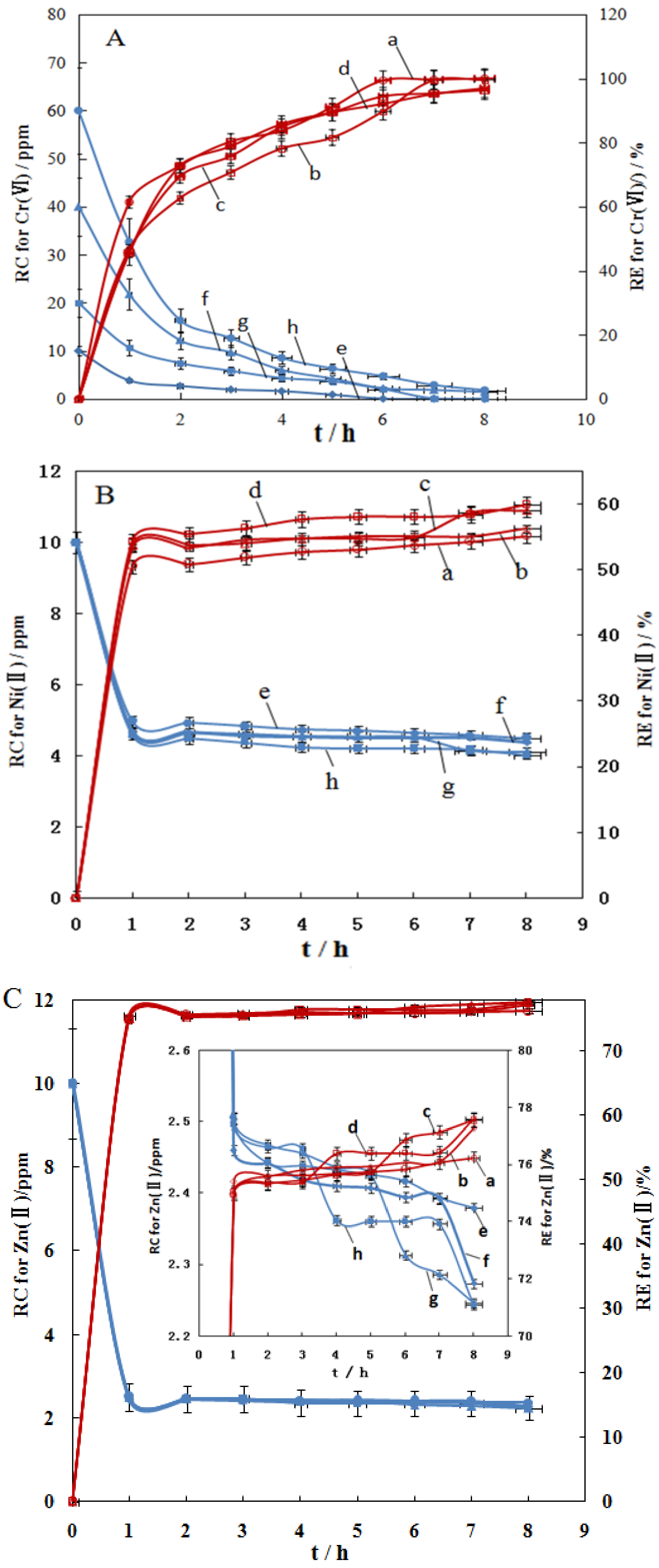


Fig. 2 Removal efficiency (RE) and remaining concentration (RC) vs. time of (A) Cr(VI) (a; RE, b; RC) and Cu(II) (c; RE, d; RC) in MFC, and (B) Zn(II) (a; RE, b; RC) and Ni(II) (c; RE, d; RC) in MEC. All initial concentrations of metal ions were 10 ppm. Data were measured in triplicate.

concluded that MFC functioned well as a complementary voltage source and a power supplier to MEC to recover nickel and zinc from the cathode chamber of MEC. However, the removal efficiencies (55.15% for Ni^{2+} and 76.21% for Zn^{2+}) in MEC of this study was lower than that of Cd^{2+} removal (~95%) in MEC previously reported in the reference (Choi *et al*. 2014) because the concentration ratio of Cr^{6+} to heavy metal ion was relatively lower, and the reaction time of this study (8 hours) was shorter than the latter (60 hours). The concentration ratio of Cr^{6+} to Cd^{2+} in the published paper was 4:1, while that of Cr^{6+} to heavy metal ion in the present study was 1:1. Modin et al. published bioelectrochemical recovery of Cu, Pb, Cd, and Zn from the dilute solution electrolyte (Modin *et al*. 2012). The electrode potentials were controlled successively to selectively deposit metals on titanium cathode by an external power source, when the bio-film was applied as an anode in the bioelectrochemical reactor. However, in the present study the MFC-MEC-coupled system was applied to remove Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. There was no input of external electrical energy to remove the metal ions from the wastewaters.

3.3.2 Effects of different initial Cr^{6+} concentrations in MFC on Cr^{6+}, Ni^{2+} and Zn^{2+} ion removal efficiencies

Fig. 3A shows RE and RC of Cr^{6+} ions in MFC of the MFC-MEC-coupled system. REs of Cr^{6+} for different initial concentrations were 100% for 10 ppm, 99.57% for 20 ppm,


A
RC for Cr(Ⅵ) / ppm
RE for Cr(Ⅵ)) / %
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
0
2
4
6
8
10
t / h
a
b
c
d
e
f
g
h
B
RC for Ni(Ⅱ) / ppm
RE for Ni(Ⅱ) / %
0
2
4
6
8
10
12
0
10
20
30
40
50
60
0
1
2
3
4
5
6
7
8
9
t / h
a
b
c
d
e
f
g
h
C
RC for Zn(Ⅱ)/ppm
RE for Zn(Ⅱ)/%
0
2
4
6
8
10
12
0
10
20
30
40
50
60
70
0
1
2
3
4
5
6
7
8
9
t / h
RC for Zn(Ⅱ)/ppm
RE for Zn(Ⅱ)/%
2.2
2.3
2.4
2.5
2.6
70
72
74
76
78
80
0
1
2
3
4
5
6
7
8
9
t / h
a
b
c
d
e
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g
h

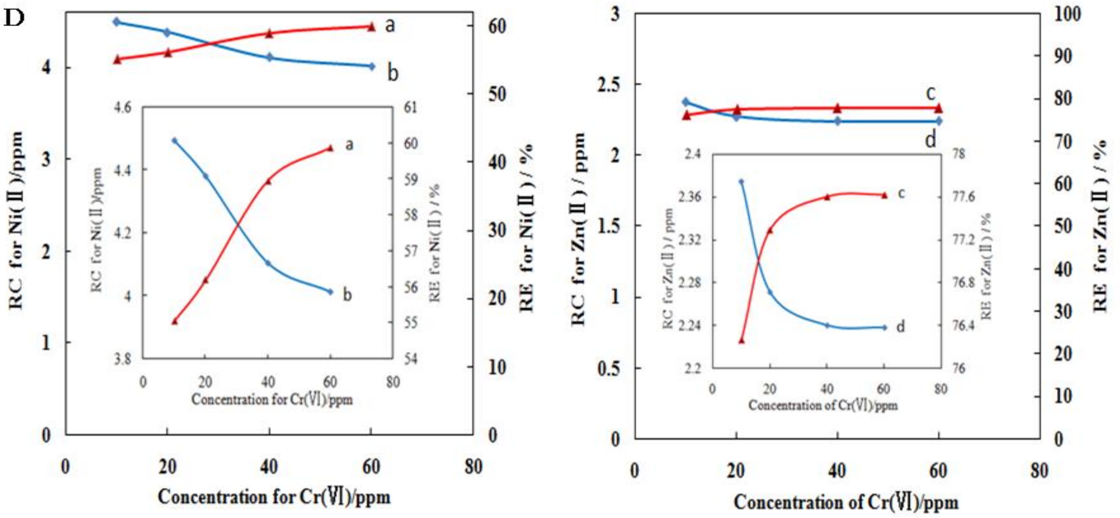

Fig. 3 Effects of different initial Cr(VI) concentrations in MFC on removal efficiency (RE) and remaining concentration (RC) of heavy metal ions: (A) Cr(VI) in MFC, (B) Ni(II) in MEC, and (C) Zn(II) in MEC. RE: a; 10 ppm, b; 20 ppm, c; 40 ppm, d; 60 ppm. RC: e; 10 ppm, f; 20 ppm, g; 40 ppm, h; 60 ppm. (D) RE's (a, c) and RC's (b, d) of Ni(II) and Zn(II) vs. different concentrations of Cr(VI) for a reaction time of 8 h.

Table 3 Effects of different initial Cr^{6+} concentrations in MFC on the removal efficiency (RE) and remaining concentration (RC) of heavy metal ions*

Initial concentration of Cr(VI)/ppm	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h
				A: Removal efficiency of Cr^{6+}/ %				
10	61.40±0.0021	72.79±0.0006	80.32±0.0006	83.68±0.0006	91.09±0.0006	99.370.±0.001	99.64±0.0006	100±0
20	46.74±0.0006	62.66±0.0006	70.67±0.0005	78.11±0.0005	81.56±0.0010	89.74±0.0006	99.43±0.0001	99.57±0.0002
40	45.59±0.0005	69.45±0.0006	75.77±0.0004	84.85±0.0005	89.41±0.0010	94.39±0.0005	95.33±0.0006	96.33±0.0010
60	45.52±0.0006	72.71±0.0006	78.87±0.0020	85.74±0.0012	89.41±0.0010	92.08±0.0015	95.14±0.0016	96.94±0.0006
				B: Removal efficiency of Ni^{2+}/ %				
10	50.40±0.0202	50.78±0.0025	51.84±0.0165	52.68±0.003	53.03±0.0153	53.63±0.0080	54.26±0.0192	55.07±0.0040
20	53.31±0.0040	53.32±0.0051	54.49±0.0035	54.76±0.0030	54.99±0.0192	55.01±0.0181	55.07±0.0040	56.20±0.0036
40	53.65±0.0025	53.76±0.0031	53.94±0.0042	54.65±0.0031	54.68±0.0035	54.87±0.0025	58.67±0.0252	58.96±0.0122
60	54.30±0.0020	55.33±0.0020	56.33±0.0015	57.66±0.0015	58.02±0.0010	58.03±0.0010	58.35±0.0025	59.87±0.0015
				C: Removal efficiency of Zn^{2+}/ %				
10	74.82±0.0266	75.59±0.0020	75.64±0.0025	75.7±0.0020	75.78±0.0036	75.86±0.0021	76.10±0.0036	76.26±0.0050
20	75.43±0.0026	75.60±0.0020	75.85±0.0030	75.84±0.0084	75.99±0.0204	76.09±0.0030	76.12±0.0038	77.29±0.0025
40	75.06±0.0087	75.34±0.0031	75.48±0.0040	75.68±0.0040	75.78±0.0035	76.85±0.0131	77.18±0.0040	77.59±0.0051
60	75.07±0.0035	75.38±0.0025	75.39±0.0015	76.41±0.0025	76.42±0.0025	76.43±0.0031	76.47±0.0032	77.62±0.0046

*Data were measured in triplicate.

96.33% for 40 ppm, and 96.94% for 60 ppm after 8 hours of reaction time (Table 3A). Remaining Cr^{6+} concentrations, which were nearly completely consumed in MFC after 8 hours, made the MFC lose capability to function as a complementary voltage and a power source to remove Ni^{2+} and Zn^{2+} from the cathode chamber of MEC.

The effects of Cr^{6+} initial concentration in MFC of the MFC-MEC-coupled system on nickel and zinc ion removals from its MEC were investigated (Fig. 3B and Fig. 3C). The MFC contained Cr^{6+} with different concentrations (10 ppm, 20 ppm, 40 ppm and 60 ppm) in its cathode chambers of MFC. It could generate electrical power to supply with the following MEC containing Ni^{2+} and Zn^{2+} of 10 ppm each to investigate their removal efficiencies. Data for the reaction time of 8 hours were compared. Fig. 3B shows RC and RE of Ni^{2+} ions (RE of 59.87%) (Table 3B). Fig. 3C shows RC and RE of Zn^{2+} (RE of 77.62 %) (Table 3C). RC of Fig. 3C appears to be showing one curve because there is no obvious difference of remaining concentration for Zn^{2+}. The range of remaining Zn^{2+} concentration was 2.51 ppm - 2.49

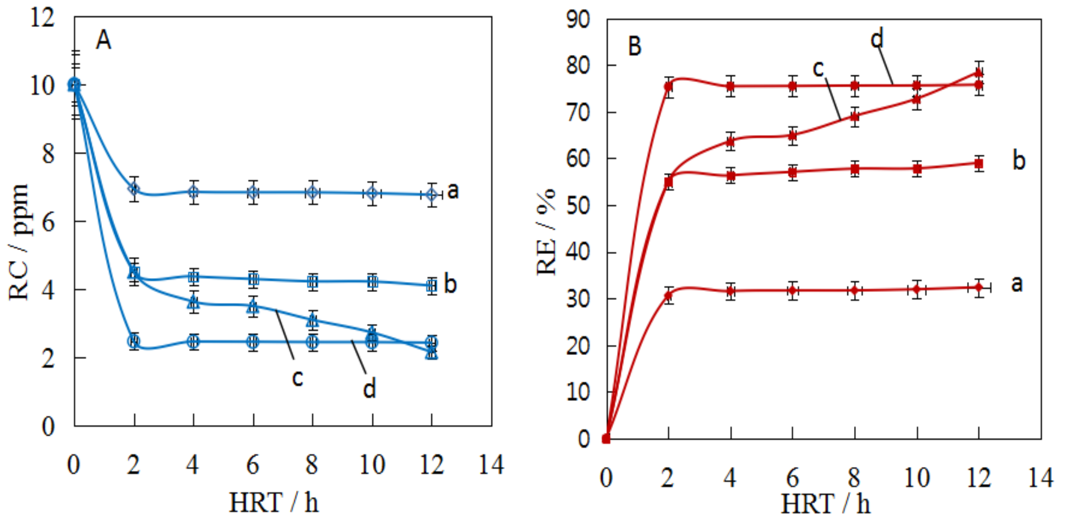

Fig. 4 (A) Remaining concentration (RC) and (B) removal efficiency (RE) of heavy metal ions in the effluent wit hdifferent HRT's. a; Cu(II), b; Ni(II), c; Cr(VI), d; Zn(II). The samples were collected from the effluent container (#3 of Schematic 1). Data were measured in triplicate

Table 4 Remaining concentration and removal efficiency of heavy metals in the effluent under the continuous operation*

			Cr(VI)		Cu(II)		Ni(II)		Zn(II)	
HRT/h	E_o/V	T_{dis}/h	RC/ ppm	RE/%	RC/ ppm	RE/%	RC/ ppm	RE/%	RC/ ppm	RE/%
2	0.5331 to 0.5116	2	4.502±0.002	54.98±0.0015	6.937±0.002	30.63±0.0021	4.495±0.001	55.04±0.001	2.465±0.002	75.35±0.0015
4	0.6017 to 0.4749	3	3.626±0.002	63.74±0.0015	6.843±0.001	31.57±0.0010	4.365±0.001	56.34±0.001	2.454±0.001	75.46±0.0010
6	0.5936 to 0.5838	3	3.499±0.001	65.01±0.001	6.831±0.001	31.69±0.0006	4.29±0.001	57.1±0.001	2.449±0.002	75.51±0.0021
8	0.6901 to 0.6721	5	3.092±0.001	69.08±0.001	6.828±0.001	31.72±0.001	4.221±0.001	57.79±0.0006	2.441±0.001	75.56±0.0010
10	0.6931 to 0.6066	8	2.720±0.002	72.80±0.0015	6.803±0.002	31.97±0.002	4.215±0.001	57.85±0.001	2.438±0.001	75.62±0.0012
12	0.6911 to 0.6043	8	2.150±0.002	78.50±0.0015	6.761±0.002	32.39±0.0015	4.095±0.003	59.02±0.0036	2.422±0.001	75.78±0.0010

*Sampling was performed in the effluent (in the container #3 of Schematic 1).

ppm for 1 hour and 2.23 ppm - 2.37 ppm for 8 hours. The data is described in Fig. 3D. RE of Zn^{2+} in MEC increased rapidly initially and then slowed down to gradual increase for concentrations higher than 20 ppm of Cr^{6+} (Fig. 3D). RE of Ni^{2+} in MEC had similar pattern of rapid initial increase then slowly increasing for concentrations higher than 40 ppm of Cr^{6+} (Fig. 3D). RE of Zn^{2+} was higher than that of Ni^{2+} by a factor of 1.3 for the concentration of 60 ppm Cr^{6+} in MFC most likely due to higher reaction rate and selectivity σ of Zn^{2+} than those of Ni^{2+}, even if relatively higher complementary voltage was required for Zn^{2+}.

3.4 Removal efficiency of the mixed heavy metal ions using the MFC-MEC coupled system under the continuous mode

3.4.1 Effects of different initial Cr^{6+} concentrations in MFC on Cr^{6+}, Ni^{2+} and Zn^{2+} ion removal efficiencies

The solution was infused from the reservoir to the cathodic chambers of MFC (#1), cathodic chamber of MEC (#2), and effluent (#3), as given in Schematic 1. All concentrations of heavy metal ions in this experiment were 10 ppm in the reservoir. Voltage change with respect to hydraulic retention time (HRT) was recorded by measuring the voltage across MEC, which functioned as a load resistor of MFC. The voltage initially increased, then gradually decreased and further increased in time. The gradual decreasing voltage indicated a stable performance of the MFC-MEC coupled system under the continuous operation mode. The average voltage was found to be 0.523±0.013 V for HRT of 2 h, 0.527±0.048 V for HRT of 4 h, 0.585±0.019 V for HRT of 6 h, 0.655±0.012 V for HRT of 8 h, 0.606±0.020 V for HRT of 10 h and 0.598±0.020 V for HRT of 12 h.

Fig. 4 shows remaining concentration vs. HRT (Fig. 4A) and removal efficiency vs. HRT (Fig. 4B) of the mixed heavy metals in the effluent sampled at #3, as shown in Schematic 1, under the continuous operational mode. The data is summarized in Table 4. A longer HRT was expected to result in the effluent containing low levels of heavy metal ions but needs a large reactor size. A wide range of HRT of 2, 4, 6, 8, 10 and 12 hours was studied in order to compare

Table 5 Remaining concentration (RC) and removal efficiency (RE) of heavy metal ions from different sampling locations in a continuous mode after 12 h*

Sampling locations	Cr(VI)		Cu(II)		Ni(II)		Zn(II)	
	RC/ppm	RE/%	RC/ppm	RE/%	RC/ppm	RE/%	RC/ppm	RE/%
MFC (#1)	1.005±0.001	89.95±0.0013	6.531±0.001	34.69±0.0013	3.662±0.003	63.38±0.0029	2.426±0.002	75.74±0.0015
MEC (#2)	0.542±0.002	94.58±0.0017	6.605±0.002	33.95±0.0016	4.343±0.003	56.57±0.0034	2.424±0.001	75.76±0.0012
Effluent (#3)	2.150±0.002	78.50±0.0015	6.761±0.002	32.39±0.0015	4.095±0.004	59.02±0.0036	2.422±0.001	75.78±0.001

*#1, cathode of MFC; #2, cathode of MEC; #3, effluent. Data were measured in triplicate.

the removal efficiencies of the heavy metals at different HRTs. Almost constant open circuit voltage (E_o) was applied to MEC because the voltage applied to MEC did not significantly change during the experiments (Table 4). From 0 hours HRT to 2 hours HRT, Cr^{6+}, Zn^{2+}, and Ni^{2+} were rapidly removed from the catholyte, compared with Cu^{2+}. The removal efficiency (RE) of Cr^{6+} was increased from 54.98% (RC of 4.502±0.002 ppm) to 78.50% (RC of 2.150±0.002 ppm) for an increase of HRT from 2 h to 12 h (Fig. 4B and Table 4). A minimal change in RE of Cu(II) from 30.63% (RC of 6.937±0.002 ppm) to 32.39% (RC of 6.761±0.002 ppm) was observed during the same range of HRT change. These phenomena were caused by transferring electrons from Cu metal to Cr^{6+} electrochemically. As illustrated in Table 4, RE's of Ni^{2+} were increased from 55.04% (RC of 4.495±0.001 ppm) for HRT of 2 hours to 59.02% (RC of 4.095±0.003 ppm) for HRT of 12 hours (Fig. 4 and Table 4). The RE's of Zn^{2+} nearly had no significant change with HRT from 2 hrs to 12 hrs, indicating that it reached maximization up to 75.35% (RC of 2.465 ppm) within HRT of 2 hours. This quick maximization may be attributed to a decrease of voltage and power density of MFC with consumption of Cr^{6+} and Cu^{2+}. The Cr^{6+} reduction was nearly completed before the completion of heavy metal ions reduction. Cu^{2+} reduction reaction was slow and power contribution to MEC was low. In conclusion, HRT of 2 hours would be the optimum HRT needed to ensure mixed heavy metal ion removal. The removal efficiencies of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} were 54.98%, 30.63%, 55.04%, and 75.35%, respectively. The reason why the removal efficiencies did not reach 100% is that the current flowing through the entire system was insufficient due to the low concentration level of Cr^{6+} (RE of Cr^{6+} of 78.50±0.0015% for HRT of 12 h, Table 4) in MFC, regardless of voltage being nearly constant during the operation. The complete removal of heavy metal ions in MEC can be achieved by connecting fresh MFC's repeatedly or using higher concentration levels of heavy metal ions with high reduction potentials in MFC.

3.4.2 Different sampling locations

Table 5 shows remaining concentration and removal efficiency of the heavy metal ions at the different sampling locations under the continuous mode. After HRT of 12 hours, Cr^{6+} and Cu^{2+} removal efficiencies in the cathodic chamber of MFC (#1) were 89.95% and 34.69%, respectively. 94.58%, 33.95%, 56.57%, and 75.76% were achieved for Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} in the cathodic chamber of MEC (#2). Removal efficiencies in the effluent (#3) represented 78.50%, 32.39%, 59.02%, and 75.78%, respectively, as also showed in Table 4. The Cr^{6+} removal efficiency was 94.58% in the cathodic chamber of MEC (#2), and then decreased to 78.50% in the effluent (#3), probably because the initial un-reacted high concentration of Cr^{6+} was transferred from the reservoir. The Cu^{2+} removal efficiencies started at 33.95% for MEC (#2), and then decreased to 32.39% in effluent (#3). The Ni^{2+} removal efficiencies started at 56.57% for the MEC (#2), and increased to 59.02% in effluent (#3). Zn^{2+} removal efficiencies started at 75.76% for the MEC (#2), and increased to 75.78% in effluent (#3). The low removal efficiency incurred for Cu^{2+} and Ni^{2+} seems to be attributed to the un-reacted Cr^{6+} flowing into the MEC (#2) and the Cr^{6+} reduction by reduced Cu(0) or Ni(0) can occur in MEC (#2). The power supplied to MEC was not enough due to the low level of Cr^{6+} at the end of MFC reaction.

4. Conclusions

This study successfully demonstrated the feasibility of removing Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} from simulated zinc plating wastewaters containing the mixed heavy metal ions using a MFC-MEC-coupled system in batch and continuous modes, where MFC functioned as a power source to operate MEC. The discharging voltage of MFC increased initially from 0.4621 ± 0.0005 V to 0.4864 ± 0.0006 V as the initial concentration of Cr^{6+} increased from 10 ppm to 60 ppm. Almost complete removal of Cr^{6+} and low removal of Cu^{2+} occurred in MFC of the MFC-MEC-coupled system after 8 hours under the batch mode. REs of Cr^{6+} and Cu^{2+} were 99.76% and 30.49%, respectively. RE of Cu^{2+} was lower than that of Cr^{6+} by a factor of 3.3 because electrons were presumably transferred from the produced Cu metal to Cr^{6+}. After the same reaction time, the REs of nickel and zinc ions were 55.15%, and 76.21%. Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} removal efficiencies of 54.98%, 30.63%, 55.04%, and 75.35% were achieved in the effluent within optimum HRT of 2 hours under the continuous mode. The incomplete removal of Cu^{2+}, Ni^{2+} and Zn^{2+} ions in the effluent was due to the fact that Cr^{6+} was remained low at the end of MFC reaction. As the power of the MEC complemented by MFC was increased, Ni^{2+} and Zn^{2+} reduction rates of the MEC were increased. RE of Zn^{2+} was higher than that of Ni^{2+} by a factor of 1.3 for the concentration of 60 ppm Cr^{6+} in MFC most likely due to higher reaction rate and selectivity σ of Zn^{2+} than those of Ni^{2+}, even if relatively higher complementary voltage was energetically required for Zn^{2+}. After HRT of 12 hours, at the different sampling locations, Cr^{6+} and Cu^{2+} removal efficiencies in the cathodic chamber of MFC were 89.95% and 34.69%, respectively. 94.58%, 33.95%, 56.57%, and 75.76% were achieved for Cr^{6+}, Cu^{2+}, Ni^{2+} and Zn^{2+} in the cathodic chamber of MEC. It can be concluded that those metal ions can be removed completely by repeatedly passing high concentration of Cr^{6+} through the cathode chamber of MFC of the MFC-MEC-coupled system.

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