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## SIMULTANEOUS REMOVAL AND/OR RECOVERY OF Cr(VI) AND Cr(III) USING A DOUBLE MFC TECHNIQUE

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### Abstract

In order to reduce Cr(VI) and Cr(III) simultaneously, a double microbial fuel cell (MFC) system was employed to treat Cr-containing wastewater. Cr(VI)-MFC used Cr(VI) as a catholyte to supply the generated power to Cr(III)-MFC, while the latter MFC functioned as an external load resistor of the former one. Buffer characteristics of the catholyte greatly affected the reduction of chromium ions. At an initial pH of 2.0, Cr(VI) removal increased from 49.9% to 99.9% when  $\text{KH}_2\text{PO}_4$  was added. Keeping a concentration ratio of Cr(VI) and Cr(III) to 2:1 was found to guarantee Cr(III) reduction effectively. For a 10 hours reaction, the Cr(III) removal efficiency of the Cr(III)-MFC improved from 58% to 82% as the initial concentration of Cr(III) increased from 25 mg/L to 100 mg/L, indicating that a higher initial concentration could allow a higher removal efficiency of Cr(III).

**Keywords:** chromium recovery, double MFC system, electron acceptor, hydrogen peroxide

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### 1. Introduction

Chromium is one of the most widely utilized metals in nature and exists as six oxidation states, but the main important ones in the Eh–pH range of natural waters are trivalent Cr(III) and hexavalent Cr(VI) (Miretzky and Fernandez, 2010). Cr(VI) is the most toxic form among all the states, which can cause liver damage, pulmonary congestion and skin ulcer (Cieslak-Golonka, 1996). Cr(III) is 300 times less toxic than Cr(VI), which is essential to plants and animals, and plays an important role in sugar and fat metabolism. Due to its limited hydroxide solubility, Cr(III) is less mobile and less bioavailable (Krishnani and Ayyappan, 2006). However, it can cause allergic skin reactions and cancer when Cr(III) accumulates in excess (Kotas and Stasicka, 2000).

Therefore, removing Cr(III) and Cr(VI) simultaneously provides the best way to treat Cr-containing wastewater. Practical application of

physicochemical techniques, such as chemical precipitation, membrane filtration, adsorption and ion exchange, are usually applied to chromium removal from the Cr-containing wastewater. However, such techniques have limitations of a varying degree due to technical or economic constraints and production of large quantities of toxic byproducts (Lu et al., 2006; Volesky, 2001).

Microbial fuel cell (MFC) as a promising technology has advantage of treating wastewater and producing power generation at the same time (Chatterjee et al., 2018; Choi and Cui, 2012; Jadhav et al., 2014; Logan et al., 2006; Quan et al., 2012; Sevda et al., 2013). Cr(VI) removal using MFC technology has recently been widely studied (Huang et al., 2011; Li et al., 2008; Pang et al., 2013). However, Cr(III) is not suitable for applying MFC because of its low redox potential. Preliminary results, pertaining to the usage of a double MFC system, where Cr(VI)-MFC is used to supply power to Cr(III)-MFC for the

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chromium reduction. This method is novel and has not been applied to the removal and/or recovery of Cr(III) so far. Thus, in this article, the simultaneous removal of Cr(III) and Cr(VI) by a double MFC system was reported. Cr(VI)-MFC used Cr(VI) as the catholyte, which could generate power to supply the Cr(III)-MFC with, while the latter functioned as the external load resistance of the former. To verify feasibility of this double MFC system the following experiments were performed: (1) Cr(VI) removal efficiency and power generation property of Cr(VI)-MFC, (2) effects of  $\text{KH}_2\text{PO}_4$  on Cr(VI) and Cr(III) removal efficiency in a double MFC, (3) effects of initial concentration ratio of Cr(VI) to Cr(III) on Cr(VI) and Cr(III) removal efficiencies and discharge characteristics, and (4) characterization of deposits on the cathode surface.

## 2. Material and methods

### 2.1. MFC construction

Both MFCs of the double MFC system were manufactured with two acrylic rectangular chambers, each chamber can hold an effective volume of 75 mL. The two MFCs contained the same material except that a cation exchange membrane (CEM) (CMI-7000, Membrane International, Inc., USA) and an anion exchange membrane (AEM) (AMI-7001, Membrane International, Inc., USA), both with a surface area of 20 cm<sup>2</sup>, were used as separators. The membranes were pretreated by immersion in NaCl solution overnight and then washed thoroughly with distilled water before use. A carbon brush anode (length = 2.5 cm, and diameter = 2.5 cm) was prepared by twisting carbon fiber (PANEX\_35, Zoltek, USA) with titanium wire. A carbon cloth with a surface area of 2.1 cm<sup>2</sup> and gas diffusion layers (w1s1005, CeTech, USA) was used as a cathode. The back contact of the cathode surface comprised of titanium wire and silver paste (Elcoat, Type P-100, Cans, Japan), and was covered with nonconductive epoxy to allow only one

surface to expose to the solution. Before connecting the titanium wire, the carbon cloth was pretreated, as demonstrated by Wang et al. (2011). The distance between the anode and the cathode was about 2 cm for both MFCs.

Fig. 1 shows the arrangement of the double MFC system. The anode 1 of the Cr(VI)-MFC was connected to the cathode 2 of the Cr(III)-MFC, while the anode 2 of the Cr(III)-MFC was connected to cathode 1 of the Cr(VI)-MFC. No resistor was connected in the circuit to supply a power needed to power up the Cr(III)-MFC. Cr(III) cannot be reduced to a lower oxidation state spontaneously with a single MFC, but when using a double MFC system, the Cr(VI)-MFC can become a power source to the Cr(III)-MFC for Cr(III) reduction. The Cr(III)-MFC, which should be charged, functioned as a load resistance of the Cr(VI)-MFC. The voltage supplied to Cr(III)-MFC can be controlled with a series connection of a resistor in the circuit. This net voltage will also be affected by the discharging amount of the Cr(VI)-MFC and the reaction rate of the Cr(III)-MFC. Therefore, the concentration of Cr(VI) should be kept relatively high until the reduction of Cr(III) is complete. For example, the concentration ratio of Cr(VI) to Cr(III) higher than 2:1 is recommended.

Cr(III) forms at the cathode 1 of the Cr(VI)-MFC, but these species does not migrate to the anode 1 easily due to the fact that cations have a tendency to move toward the cathode. However, protons and Cr(III) could diffuse into the anode chamber through a CEM due to the concentration gradient, so that the adverse effect of lowering pH on the microorganism in the same chamber was avoided by circulating the anolyte from a reservoir with a peristaltic pump. On the other hand, AEM was used as the separator in Cr(III)-MFC to avoid Cr(III) and protons diffusion from the cathode to anode chamber. For accurate experiments the pH should be kept constant by using a circulation mode, but there may not be necessary to circulate the anolyte in a real mode.

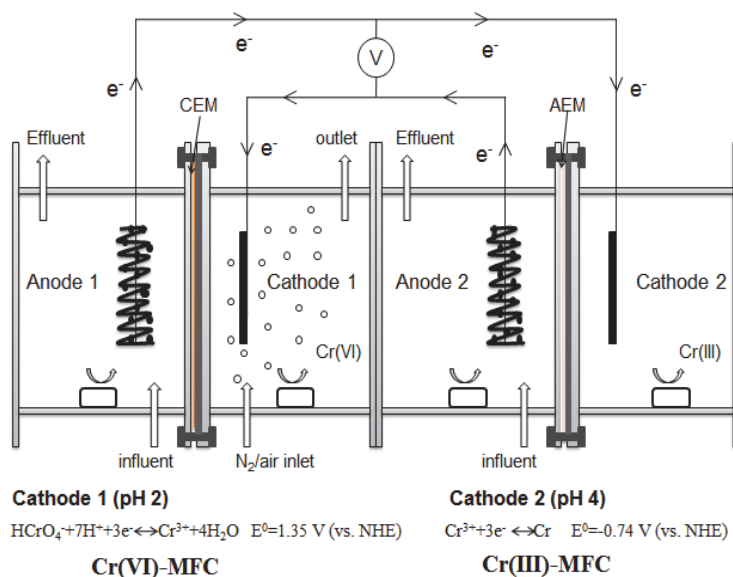


Fig. 1. Double MFC set-up for removal of Cr(VI) and Cr(III)

## 2.2. MFC set-up and operation

For inoculation, a mixture of anaerobic sludge and sodium acetate media (1:2, v/v) was injected into the anode chamber, as reported in literature (Wang et al., 2011). The acetate medium (pH=7.0) contained the following per liter: 1 g CH<sub>3</sub>COONa, 1.05 g NH<sub>4</sub>Cl, 1.86 g KCl, 0.2 g yeast extract and 50 mM PBS buffer (KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub>). The cathode chamber was filled with 50 mM PBS buffer solution. Stable voltages were obtained for three experimental trials with air bubbling in the catholyte, and the biofilm on the anode was supposed to be well established for later experiments. Both Cr(VI)-MFC and Cr(III)-MFC followed the same method for inoculation.

After successful inoculation, the media of the anode chambers were both replaced with fresh acetate media solutions, which were sparged with N<sub>2</sub> for 20 minutes to remove dissolved oxygen. The medium of the cathode chamber of the Cr(VI)-MFC was replaced with a synthetic wastewater containing K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (initial Cr(VI) concentration of 100 mg/L) and 300 mM KCl incorporated as an ionic conductivity supporter at pH 2.0. The medium of the cathode chamber of the Cr(III)-MFC was replaced with a synthetic wastewater containing CrCl<sub>3</sub>·6H<sub>2</sub>O at pH 4.0 (initial Cr(III) concentration of 50 mg/L) and 200 mM KCl was added to the cathode 2. The pH was adjusted with diluted HCl and NaOH solutions (0.1 M). Particularly in consideration of Cr(VI)-H<sub>2</sub>O<sub>2</sub> interaction in acidic solution, Cr(VI) behaves as an electro-catalyst for the dismutation of H<sub>2</sub>O<sub>2</sub> (2H<sub>2</sub>O<sub>2</sub> = O<sub>2</sub> + 2H<sub>2</sub>O) with Cr(VI) reduced to Cr(III) (van Niekerk et al., 2007). The cathode 1 was continuously purged with air or N<sub>2</sub> (both 70 mL/min) for a power generation experiment. In order to determine the effects of various parameters on Cr(VI) and Cr(III) removal efficiencies, the buffer effects of catholytes (by adding 0.1 M KH<sub>2</sub>PO<sub>4</sub>) in both cells and initial concentrations of Cr(VI) (50-200 mg/L) and Cr(III) (25-100 mg/L) were investigated. All the experiments were performed at room temperature under atmospheric pressure.

## 2.3. Calculation and analysis

Voltages were measured with a LabView (National Instruments, USA) in one-minute intervals. Voltage vs. current density (V-J), power density vs. current density (P-J), and internal resistance were obtained, as published by Wang et al. (2011). The surface area of the cathode was used to calculate current densities. The concentration of Cr(VI) was determined by applying a colorimetric method with 1,5-diphenylcarbazide in acidic solution. In the present system there exist soluble HCrO<sub>4</sub><sup>-</sup> and Cr(III) at pH 2 and soluble Cr(OH)<sub>2</sub><sup>+</sup> at pH 4. The concentration of Cr(III) was analyzed by flame atomic absorption spectrophotometry (Clesceri et al., 1998). The chemical forms of the chromium compounds deposited on the carbon cloth were identified with a

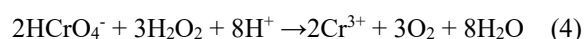
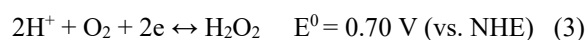
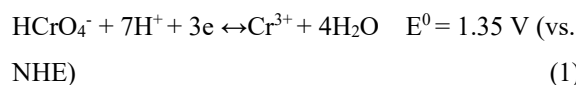
scanning electron microscopy (SEM) (LEO 1455 VP, Hitachi, Japan: S-4700, China) and an energy dispersive X-ray spectrometer (EDS) (Horiba 7200-H, China). All the experiments were repeated twice and the mean values were used for analysis.

## 3. Results and discussion

### 3.1. Cr(VI) removal efficiency and power generation property of Cr(VI)-MFC

Initially, Cr(VI)-MFC including Cr(VI) was studied, of which the catholyte was replaced with a synthetic wastewater containing 100 mg/L Cr(VI), and a load resistor of 1000 Ω was connected in the circuit. KH<sub>2</sub>PO<sub>4</sub> was added to form a buffer solution. Fig. 2a shows buffering effects of the catholyte on Cr(VI) removal efficiency. After adding KH<sub>2</sub>PO<sub>4</sub>, the pH of the catholyte remained at around 2.0 even after 60 hrs, while the pH rose up to about 5.0 without adding KH<sub>2</sub>PO<sub>4</sub> after the same period of time. Under the former condition, Cr(VI) removal efficiency of 99.9% was achieved, but a removal efficiency of only 49.9% could be achieved under the latter one. According to the Eh-pH diagram (Fig. 2b), Cr(III) was found to predominate at pH's < 3.0 because it was the most thermodynamically stable oxidation state under the reducing condition (Mohan and Pittman, 2006). When pH was increased to 3.0, the reduction reaction of Cr(VI) at Cathode 1 was observed to decrease and result in its low removal efficiency in this research. Precipitate formed as pH increased and attached on the cathode surface, causing the rate of additional reduction reaction to be decreased. It could be concluded that keeping the pH constant using the buffer condition of the catholyte affected the MFC performance significantly.

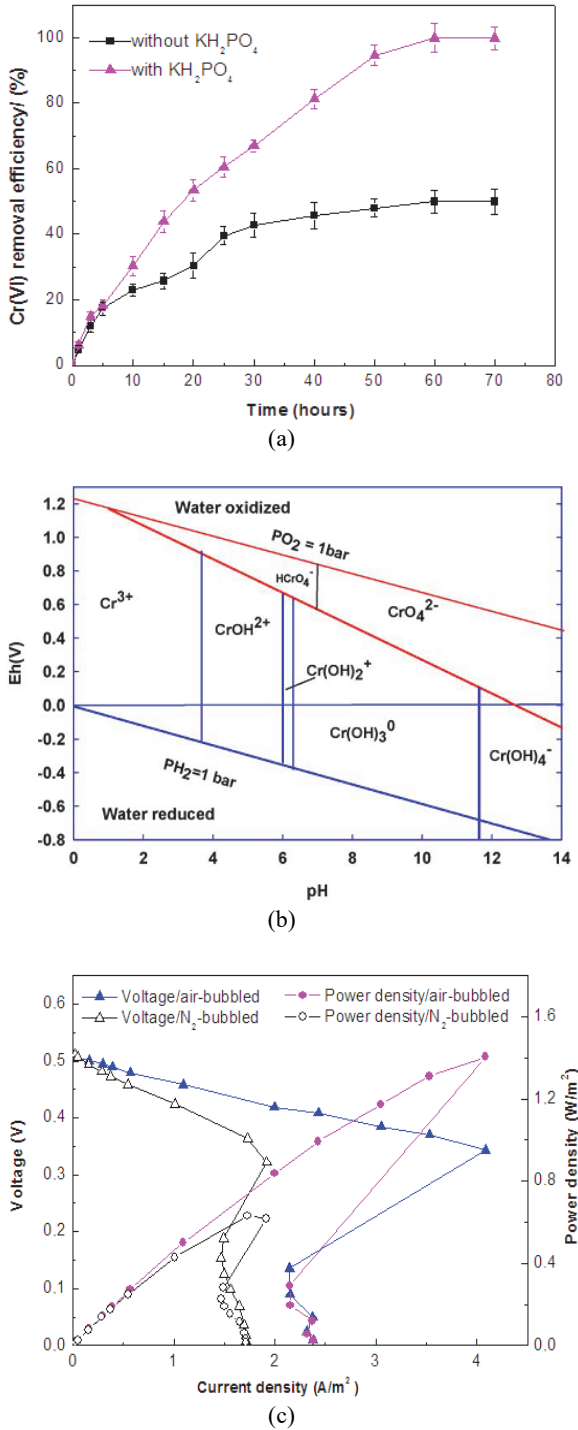
The fact that H<sub>2</sub>O<sub>2</sub> played an important role in power generation in a Cr(VI)-MFC was reported in literature (Liu et al., 2011). In this study, air-bubbling and N<sub>2</sub>-bubbling cathodes were studied to investigate the electrochemical properties under a gas flow rate of 70 mL/min. Different load resistors (20-100,000 Ω) were connected to obtain polarization curves (Fig. 2c). All of the electrochemical parameters are summarized in Table 1, where the maximum voltage ( $V_{max}$ ) and maximum current density ( $J_{max}$ ) are defined as voltage and current density at the maximum power point ( $P_{max}$ ), respectively. A  $P_{max}$  of 1.40 W/m<sup>2</sup> was achieved under the air bubbling condition, while that of 0.630 W/m<sup>2</sup> could only be achieved under the N<sub>2</sub> bubbling condition. When O<sub>2</sub> co-existed in the cathode, the reactions occurring at the cathode were:



**Table 1.** Electrochemical parameters of MFC with the same concentration of Cr(VI) with N<sub>2</sub>-bubbled cathode -and air-bubbled cathode, based on Fig. 2c

Cathode	$V_{oc}/V$	$V_{max}/V$	$J_{max}/A/m^2$	$P_{max}/W/m^2$	$R_{int}/\Omega$
N <sub>2</sub> -bubbled cathode	0.518	0.322	1.92	0.630	348
Air-bubbled cathode	0.509	0.343	4.09	1.40	158

Note:  $V_{oc}$ , open circuit voltage;  $V_{max}$ , maximum voltage;  $J_{max}$ , maximum current density,  $P_{max}$ , maximum power density,  $R_{int}$ , internal resistance; Cr(VI): 100 mg/L



**Fig. 2.** Cr(VI) removal efficiency and power generation property of Cr(VI)-MFC; (a) Buffer effect on Cr(VI) removal efficiency, (b) Potential (Eh)–pH diagram for chromium (Mohan and Pittman (2006)), and (c) Effects of air-bubbling and N<sub>2</sub>-bubbling of the catholyte on the polarization behavior

O<sub>2</sub> was reduced heterogeneously at the cathode as well as HCrO<sub>4</sub><sup>-</sup>, resulting in an additional current density increase in the V-J curve, as shown for the air bubbling in Fig. 2c, compared to the N<sub>2</sub> bubbling condition. The reactions, as represented by Eq. (1), Eq. (2) and Eq. (3), are competing with each other, and increase the current density. A part of HCrO<sub>4</sub><sup>-</sup> could be reduced to Cr<sup>3+</sup> by Eq. (4) through Eq. (3), which is a typical electrochemical-chemical (EC) mechanism. By observing the current density increase by an addition of H<sub>2</sub>O<sub>2</sub>, Eq. (3) was known to contribute to the current density increase in the V-J curve. On the other hand, it was hard to find the Coulombic efficiency originated from Cr(VI) only under the air bubbling condition because the current density consists of contributions from Eq. (1), Eq. (2) and Eq. (3). It could be expected to be lower or equal to that under the N<sub>2</sub> bubbling condition due to the slow O<sub>2</sub> reduction reaction involvements, as shown in Eq. (2) and Eq. (3), even if the total current density was increased in the V-J curve. However, the aeration played an important role in improving the power generation.

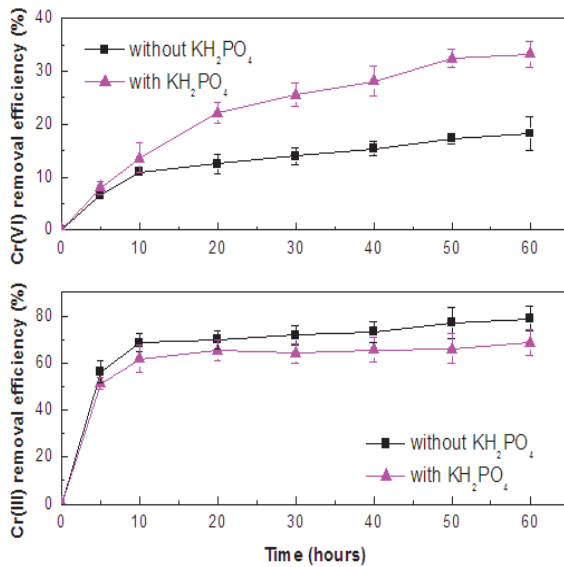
This result coincides well with the previous research (Liu et al., 2011). On the other hand, although a smaller ratio of solution volume to electrode area was used in the present study compared to the ratio data published in literature (Li et al., 2008), a higher  $P_{max}$  was achieved. Thus, the Cr(VI)-MFC used in this study represented a more effective electrical energy generation because a higher  $P_{max}$  can usually be achieved for a higher ratio of the solution volume to electrode area. For later experiments operating with double MFCs, the catholyte of the Cr(VI)-MFC was bubbled with air.

The internal resistance ( $R_{int}$ ) of Cr(VI)-MFC obtained by the slope method of polarization curves with the air-bubbled cathode shows a value lower than that with the N<sub>2</sub>-bubbled cathode. Because ohmic resistance of the solution is expected to be the same under the two conditions, the difference should originate from the differences in charge transfer resistances ( $R_{ct}$ ) of the cathode reactions. It is concluded that the air-bubbled cathode can include factors decreasing a  $R_{int}$ , compared to the N<sub>2</sub>-bubbled cathode, and the factors can be other cathode reactions, such as Eqs. (1)-(3).

### 3.2. Effect of KH<sub>2</sub>PO<sub>4</sub> on Cr(VI) and Cr(III) removal efficiency in double MFC

In the double MFC system, KH<sub>2</sub>PO<sub>4</sub> was added into both catholytes. H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is a weak acid, which can

produce a conjugate base  $\text{HPO}_4^{2-}$ . The conjugate base can hydrolyze simultaneously in aqueous solution, so it can function as a buffer. In this research, hydrolysis of  $\text{HPO}_4^{2-}$  is the main reaction, forming  $\text{H}_2\text{PO}_4^-$ , and the ratio of these species will form a buffer system to absorb pH change. It is interesting to know that the buffer condition still favored Cr(VI) reduction (Fig. 3a), but much benefit was not shown for Cr(III) removal (Fig. 3b). When 0.1 M  $\text{KH}_2\text{PO}_4$  was added to the catholyte of Cr(III)-MFC, its pH could be kept at around 4.0 to avoid  $\text{Cr}(\text{OH})_3$  precipitate formation (Fig. 2b), but without the buffer, the pH could increase to the  $\text{Cr}(\text{OH})_3$  precipitate formation range, resulting in a chemical loss of Cr(III). This is the reason why Cr(III) removal was calculated to be a 20% improvement without buffer, compared to with buffer. However, in this research, precipitation was supposed to be prevented from forming because it consumes a lot of Cr(III) and decreases the efficiency of Cr(III) removal by electrical power received from Cr(VI)-MFC. The possible formation of precipitation would make the Cr(III) removal mechanism complicated. Therefore, utilization of the buffer solutions was suitable for this study, and later related experiments adopted  $\text{KH}_2\text{PO}_4$  addition in both catholytes.

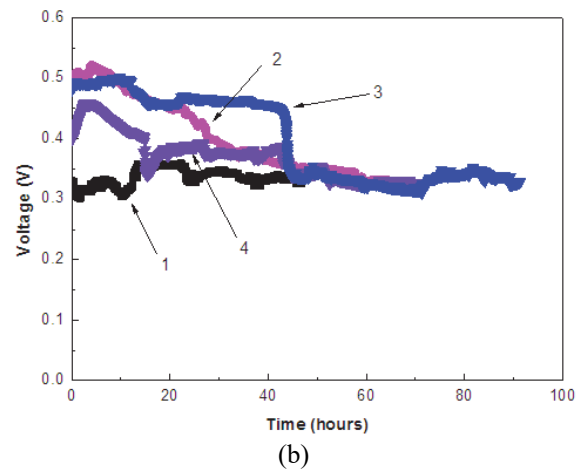
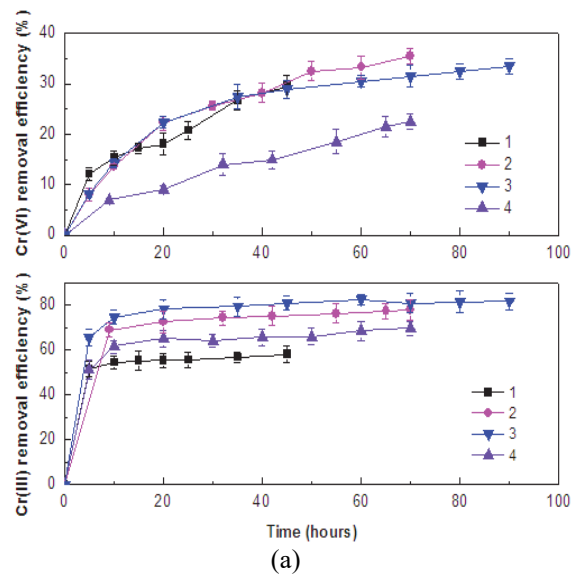


**Fig. 3.** Buffer effects on Cr(VI) and Cr(III) removal efficiencies; (a) Cr(VI) removal efficiency, and (b) Cr(III) removal efficiency. Initial concentrations of Cr(VI) and Cr(III) were 100 mg/L and 50 mg/L

### 3.3. Effects of the initial concentration ratio on Cr(VI) and Cr(III) removal and/or recovery efficiencies and discharge characteristics

To determine the effects of initial concentration on Cr(VI) and Cr(III) removal, Cr(VI) and Cr(III) concentrations varied in the range of 50-200 mg/L and 25-100 mg/L, respectively (Fig. 4a). Under the acidic condition, Cr(VI) can easily be reduced to Cr(III) in the Cr(VI)-MFC, while generating high power to allow enough power to be supplied in order to reduce Cr(III) to Cr metal in the

Cr(III)-MFC. There were low Cr(VI) removal efficiencies for different concentration combinations with the highest maximum removal efficiency of only 35% (upper, Fig. 4a). The maximum removal efficiency of Cr(III) increased from 58% to 82% as the initial concentration increased, and all concentrations reached a fast maximization of removal efficiency within 10 hrs (below, Fig. 4a). This means that the Cr(VI) concentration remained high until the removal efficiency of Cr(III) reached a maximum value. As the concentration of Cr(III) increased, its removal efficiency of Cr(III) also increased due to the lowered internal resistance, which is the sum of ohmic resistance and charge transfer resistance, as defined in literature (Choi and Hu, 2013).



**Fig. 4.** (a) Effects of different initial concentrations on Cr(VI) and Cr(III) removal efficiencies. (b) Discharge characteristics of the MFCs with different initial concentrations of Cr(VI) and Cr(III). (1) 50 mg/L Cr(VI) and 25 mg/L Cr(III), (2) 100 mg/L Cr(VI) and 50 mg/L Cr(III), (3) 200 mg/L Cr(VI) and 100 mg/L Cr(III), and (4) 100 mg/L Cr(VI) and 100 mg/L Cr(III)

The high power supply of the Cr(VI)-MFC with a high concentration of Cr(VI) also caused an increase in the removal efficiency of Cr(III). However,

the concentration combination of 100 g/L Cr(VI) and 100 g/L Cr(III) showed lower removal efficiencies for both Cr(VI) and Cr(III) than the combination of 200 g/L Cr(VI) and 100 g/L Cr(III). This low Cr(III) removal efficiency can be explained by Cr(VI) concentration insufficient to supply the amount of electrons needed for the reduction of Cr(III). A higher initial Cr(VI) concentration leads to a higher power generation available for more energy supply for Cr(III) removal.

On the other hand, the ionic conductivity and charge transfer also improved functionality of the Cr(III)-MFC with the increased Cr(III) concentration, and thus a higher removal efficiency of Cr(III) could be achieved. But because the Cr(VI)-MFC was used as a power supply, the same ratios of Cr(VI) and Cr(III) resulted in a comparative ability to remove Cr(VI). It is obvious that different ratios of Cr(VI) to Cr(III) may result in different removal efficiencies. This can be demonstrated by comparing these three ratios; (1) 50 mg/L Cr(VI) to 25 mg/L Cr(III), (2) 100 mg/L Cr(VI) to 50 mg/L Cr(III), (3) 200 mg/L Cr(VI) to 100 mg/L Cr(III), and (4) 100 mg/L Cr(VI) to 100 mg/L Cr(III). This study showed that maintaining the ratio of Cr(VI) to Cr(III) higher than 2:1 would lead to a well-functioning double MFC system for Cr(VI) and Cr(III) removal and recovery.

Discharge characteristics of the double MFC system were shown in Fig. 4b, and the discharging voltage decreased as the remaining Cr(VI) concentration was decreased. This experiment confirmed that a lower voltage was obtained from experiment (4) than other experiments (2) and (3), which is supported by the Cr(III) removal efficiency trend shown in Fig. 4a. Therefore, it can be concluded that a complete removal of Cr(III) can be achieved when enough power is provided by Cr(VI)-MFC of a double MFC system.

### 3.4. Characterization of the cathode surface

SEM images clearly revealed deposits formed on the cathode surface (Fig. 5). To identify chemical forms of the deposits, EDS analysis was applied. Table 2 shows the quantitative composition of elements. On a plain cathode cloth, carbon was the main element, but after 90 hours reaction, Cr appeared on cathodes. According to Fig. 2b and Fig. 5b, Cr existed as soluble Cr(III) in a great amount, continuous aeration led to plenty of O in the cathode chamber of Cr(VI)-MFC, it could be supposed that

Cr<sub>2</sub>O<sub>3</sub> was the main product in Cathode 1, this conjecture was agreed with previous study (Li et al., 2008). Meanwhile, P was partly existed in Cr(VI)-MFC, that might have some CrPO<sub>4</sub> formed since green colour was in the electrode. According to Fig. 5c, small quantity of Cr was detected in cathode 2. Based on the mechanism of Cr(III) reduction, 0.74 V were needed to reduce Cr(III) to Cr metal, and then integrated with the anode potential of -0.20 V (which was tested by Cyclic voltammetry, with the microbial anode and Ag-AgCl electrode as the working electrode and reference electrode, respectively), about 0.54 V was required for the application of Cr(III)-MFC. In Fig. 4b, 0.5 V-0.6 V could be provided by Cr(VI)-MFC, hence there's reason to think that Cr(III) could be reduced to Cr in cathode 2. For identification of oxidation states of the chromium, X-ray photon spectroscopy (XPS) can be applied. For the following experiments, this instrument will be applied to identify it. In this study, small volumes and low concentrations were employed when large volumes and high concentrations of Cr(VI) could lead to an efficient metallization of Cr(III) by Cr(VI)-MFC, and Cr(III) in Cr(III)-MFC could be efficiently reduced to Cr metal. It was proved that the double MFC system not only disposed Cr(VI) and Cr(III) at the same time, but also recycled Cr metal effectively. Thus, this technique would be applied very usefully in disposing Cr-contaminated wastewaters.

## 4. Conclusions

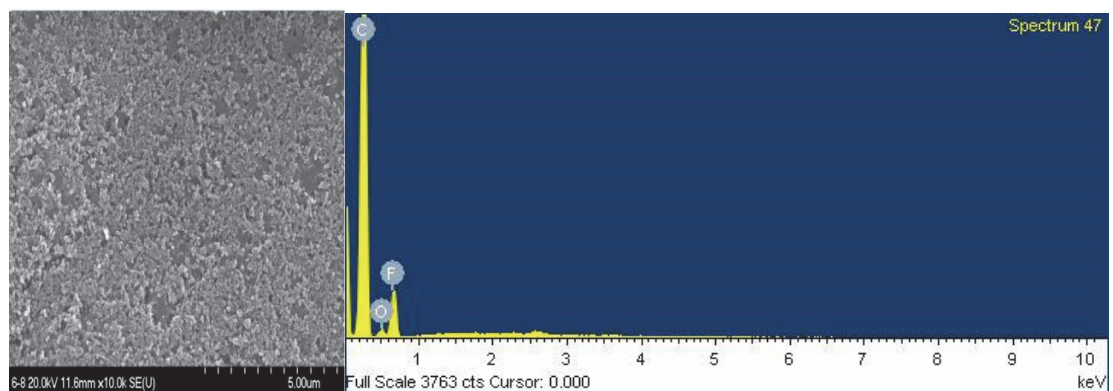
This study successfully verified that a double MFC technique could be applied to effectively remove and/or recover Cr(VI) and Cr(III) simultaneously. With this technique, the removal and/or recovery of Cr(III) results in an efficiency higher than that of Cr(VI).

Using buffer solutions to maintain the pH of catholytes in a certain range was needed for removal of Cr ions. Cr(III) removal increased with increased initial concentration, and all reactions were finished within 10 hrs. Keeping a concentration ratio of Cr(VI) and Cr(III) to 2:1 guaranteed an effective removal efficiency of Cr(III). A higher initial concentration of Cr(III) allows a higher removal efficiency of Cr(III). The Cr metal, that can exist on the cathode surface of Cr(III)-MFC, confirmed that using a double MFC system can remove Cr pollutants thoroughly and recover as metal.

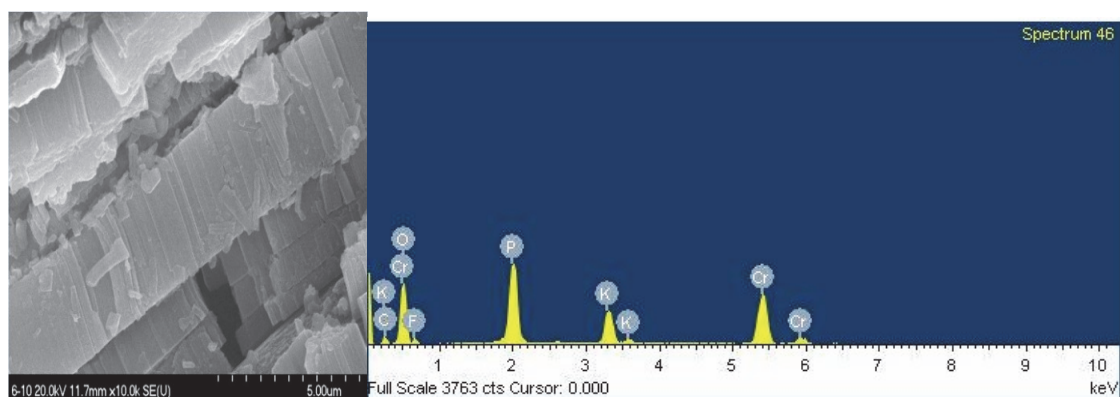
**Table 2.** Main elements on the carbon cloth, based on EDS data

	<i>Element</i>	<i>C</i>	<i>O</i>	<i>F</i>	<i>P</i>	<i>K</i>	<i>Cr</i>
a	weight%	77.22	4.67	18.10			
	atomic%	83.78	3.81	12.42			
b	weight%	12.77	36.83	9.25	13.29	6.77	21.08
	atomic%	21.88	47.37	10.02	8.83	3.56	8.34
c	weight%	69.05	15.86	12.29	0.91	0.97	0.92
	atomic%	77.04	13.29	8.67	0.39	0.33	0.28

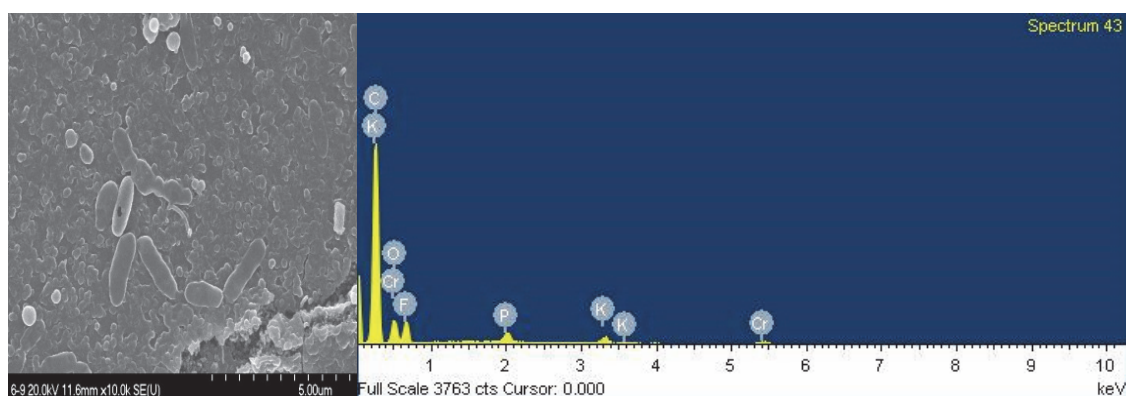
Note: a) plain carbon cloth; b) surface of carbon cloth in Cr(VI)-MFC; c) surface of carbon cloth in Cr(III)-MFC



(a) Fresh carbon cloth



(b) The surface of Cathode 1 after 90 hours experiment



(c) The surface of Cathode 2 after 90 hours experiment

**Fig. 5.** SEM and EDS analysis of the cathode; (a) plain carbon cloth, (b) surface of carbon cloth in Cr(VI)-MFC, (c) surface of carbon cloth in Cr(III)-MFC. Catholytes were 200 mg/L Cr(VI) in Cr(VI)-MFC and 100 mg/L Cr(III) in Cr(III)-MFC. The reaction time was 90 hrs

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