



MICROBIAL DESALINATION CELL TECHNOLOGY FOR SIMULTANEOUS WATER DESALINATION AND REDUCTION OF CHROMIUM ION Cr⁺⁶

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ABSTRACT

Technology of microbial desalination cell (MDC) is a novel approach to produce renewable power, desalinate saline water and treat wastewater simultaneously. In this study, a reactor of MDC using wastewater involving Cr⁺⁶ as the catholyte was used simultaneously to desalinate brine and reduce Cr⁺⁶, in the desalination compartment and cathode compartment, respectively. The desalination rate was 2.1 mg/h, and the efficiency of chromium ion removal attained 83%, with values of voltage and current density, 384 mV and 823 mA/m², respectively, when the pH was below 2.0 and the initial Cr⁺⁶ concentration was 50 mg/L. By increasing the initial Cr⁺⁶ concentration to 100 and 1000 mg/L, as results the current density also increased to 963 and 1453 mA/m², respectively, as well as the salt removal rate increased to 2.16 and 3.04 mg/h, where the salt removal efficiency were 81.8 and 93.4%, respectively. Scanning electron microscope-energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) indicated that the Cr⁺⁶ was reduced to Cr₂O₃ and precipitated on the cathode surface. From the present findings, it would be suggested that further enlarge the application of MDC using Cr⁺⁶ as an electron acceptor.

Keywords: microbial desalination cell (MDC), water desalination, Cr⁺⁶reductions, electricity generation, technology.

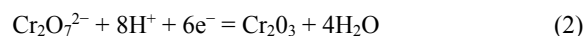
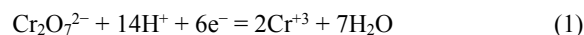
1. INTRODUCTION

Microorganisms catalyze reactions within bioelectrochemical systems (BESs) to convert the chemical energy of the organics in wastewater into renewable power [1,2]. As well harmful materials exist in wastewater (such as nitrate and heavy metal) can be eliminated by BESs [3,4]. BESs can be divided into sub-systems as microbial fuel cells (MFCs), microbial desalination cells (MDCs), microbial electrolysis cells (MECs) [5,6]. Approach of using BESs to remove ions from salt water is a new technology of seawater desalination [7]. The microbial desalination cell (MDC) is a technology based on the microbial fuel cell (MFC) as a possible method to desalinate brine without energy demand [7]. MDC is briefly composed of an anode compartment, a desalination compartment and a cathode compartment. The anode compartment includes bacteria promote the oxidation of organic substances, liberation of electrons produced from cell respiration to the anode; thereby they flow through an external circuit to the cathode electrode [8]. On the other hand the high redox compounds in the cathode compartment, accept electrons and complete the other cell half reaction, hence allowing an electric current, meanwhile this process, the ions such as Cl⁻ and Na⁺ in the middle compartment migrate toward the anode and cathode compartments, respectively, to achieve brine desalination without any net energy consumption. Anolyte in the anode are usually wastewater, although, cost is still involved as substances used in the cathode reaction. A study by Cao *et al.* [7], achieved 88% elimination of NaCl in the desalination compartment of an MDC using ferricyanide as the catholyte, the salt removal rate could reach 2.8 mg/h with an initial salt solution containing 5 g/L. Providing the ferricyanide as the catholyte in the previous work, is not a sustainable source

[9]. Mehanna *et al.* [10], used oxygen as the electron acceptor in a cathode compartment with a Pt/carbon (Pt/C) mixture with a Nafion solution as catalysts for the air cathode and the salt elimination was only 0.22 mg/h, when an initial salt concentration was 5 g/L. It is high expensive to use MDCs with Pt as catalysts on a broad scale. The Pt in a study by Wen *et al.* [11], had replaced with microorganisms as a catalyst on the cathode surface, but aeration in the cathode compartment was still needed in this process which also increased the operational cost. Thus, the question is how to use certain wastewater that has ability to accept electrons as an oxidant. and this would become an important research trend to enhance the environmental and economic benefit of MDCs. Several studies have investigated industrial wastewaters in the MFCs to use them as catholyte electron acceptors, such as Cu⁺² and Cr⁺⁶ [12]. Many industries discharge massive quantity of wastewater involving Cr into the environment in the form of Cr⁺⁶ or Cr⁺³, such as, the metal plating, paints and pigments, and leather tanning and printing ink [13]. Accumulation of Cr⁺⁶ in the environment is a great danger for organisms due to its refractory and highly toxic nature and it is well known as a highly toxic pollutant [14,15]. Many of diseases the eye, ear, skin and stomach, could be occurred due to Cr⁺⁶ [16]. With respect of, the toxicity of Cr⁺³ is a lot lower for humans and the environment [17]. Reduction of Cr⁺⁶ could be happened either directly as an electron acceptor in MFCs [18], or through the reduction of Cr⁺⁶ by microorganism in cathode compartment [19-21]. On study by Li *et al.* [22] a novel rutile-coated cathode was done, it was sensitive to visible light proposed and could improve the Cr⁺⁶ reduction rate under light irradiation than compared to dark conditions. Tandukar *et al.* [23] used microorganisms on a cathode compartment to reduce Cr⁺⁶ in an MFC, where the



Cr⁶⁺ was removed as Cr(OH)₃, which resulted in a current and power density of 123.4 mA/m² and 55.5 mW/m², respectively. Based on the literature [24,25], each Cr when using an electron acceptor as Cr⁶⁺, can receive three electrons and be reduced to Cr³⁺ following the equations below:



Cr⁶⁺ has a higher oxidation (1.33 V) than oxygen (1.23 V), which means Cr⁶⁺ is much suitable as an electron acceptor instead of O₂, and can be restored to Cr₂O₃.

Until now, synthetic copper solution has used in a four-compartment MDC system, which involved inserting a CEM next to the cathode compartment to form a concentration compartment. The percentage of salt elimination in those MDCs was approximately 5.1 mg/h. However, the construction of the four compartment MDC was more complicated than a traditional MDC [26]. In this research, and based on the wide existence of Cr⁶⁺ in industrial wastewater and the relatively high standard electrode potential of Cr⁶⁺, industrial wastewater involving Cr⁶⁺ was chosen as the electron acceptor in cathode compartment. This study aimed evaluating of using Cr⁶⁺ as the electron acceptor in a MDC for salinity removal, generation of electricity and Cr⁶⁺ removal. Variables such as the catholyte pH and initial Cr⁶⁺ concentration were investigated in this work.

2. Materials and methods

2.1. MDC construction

Figure-1 shows construction of MDC. It consisted of anode, cathode and desalination compartments that were made of polymethyl methacrylate, with dimensions of 10 × 10 × 5 cm (w×h×d) for all. The work volume was 50ml. An anion exchange membrane (AEM) (Membranes International, USA) and a cation exchange membrane (CEM) (Membranes International, USA) were placed between the anode compartment and the desalination compartment, and the other between the desalination compartment and the cathode compartment, respectively. The anode consisted of carbon felt (3 × 3 × 2 cm) connected to a graphite rod (5-mm diameter) inserted into the felt. A graphite plate (3 × 3 × 2 cm) was used as the cathode. To remove trace metals, all of the graphite felt, rod, sheets and titanium wire were washed with 1 M HCl for 48 h, then rinsed with deionized water.

2.2. Inoculum and medium

The anode compartment was inoculated (20%, V/V) with anaerobic sludge collected from Makkah Sewage Treatment Plant (KSA), and filled with 50 mL sodium acetate medium containing (g/L): 4.4 KH₂PO₄, 3.4 K₂HPO₄·3H₂O, 1.5 NH₄Cl, 0.1 MgCl₂·6H₂O, 0.1 CaCl₂·2H₂O and 10 mL of trace elements solution [11]. The anode compartment was sparged with N₂ (80ml/min) for 30min, then sealed when the anode medium was

injected into the compartment during the inoculation. The cathode compartment was filled with 50 ml K₂PO₄ (0.05 M/L) and sparged with air (60 mL/min) till the inoculation was done. The desalination compartment was filled with 50 mL NaCl solution, the initial salt concentration was 5 g/L. The 50 mL fresh medium for the anode compartment was replaced every 48 h till the voltage of the MDC was stable at 200 mV. 10 M HCl and 1 M NaOH were used to adjust pH of the solutions.

2.3. Operation of MDC

Through operation of MDC, factors affecting the performance were investigated, including the pH of the catholyte (2, 3, 4, 5 and 6) with an initial Cr⁶⁺ concentration of 50 mg/L and different initial Cr⁶⁺ concentrations (100, 300, 700 and 1000 mg/L) under pH 2.0. The electrodes were connected through an external circuit involving a 200 Ω resistor. The electrolyte in the cathode compartment was changed using different amounts of K₂Cr₂O₇. The pH was adjusted using 1 M/L NaOH and 10 M/L HCl. The desalination compartment was injected with 50 mL of NaCl solution (5 g/L). Every experiment was conducted with triplicate samples. For investigating the effect of catholyte pH, both the anolyte and catholyte were replaced every 6 h as each batch was fed. Evaluating the effect of initial Cr⁶⁺ concentration on the efficacy of MDC, the anolyte and catholyte were changed when the voltage across the external resistance (200 Ω) fell to 50 mV, which was recognized as one batch-fed cycle. The salt solution in the middle compartment was replaced, by dropping the concentration below 1 g/L and this finished one desalination cycle.

2.4. Data analysis and calculations

The voltage of MDC was measured by a digital multimeter (Sanwa CD800a, Japan) was connected to a personal computer. Data was automatically recorded every second via Picolog software (Pico Technology Limited). The NaCl concentration was measured with a conductivity meter (SG3-ELK, Mettler Toledo, Switzerland). The pH values of samples were measured by a pH meter (HANNA HI8424, Italy). The amount of acetate was determined using a gas chromatograph (GC6890 N/FID, Agilent, United States). Cr⁶⁺ was measured by colorimetry using diphenylcarbazide as a colorimetric reagent in acidic solution. An inductively coupled plasma-optical emission spectrometer (ICP-OES; Vista-MPX, Varian, Inc.) was used to estimate the total chromium. A scanning electron microscope energy dispersive X-ray analysis (SEM, JSM-5410LV, JEOL Ltd., Japan) was used to observe microorganisms on the anode electrode. The quantity of each element and the chemical composition of the precipitation on the cathode surface were estimated using SEM-EDS (Helios Nanolab600i) and X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA System). Electrochemical impedance spectroscopy (EIS) was applied by a potentiostat (G300, Gamry Instruments Inc., NJ) to define the alteration in internal resistance of the MDC system. The cathode EIS measurements were carried out using a three-electrode configuration, with an



Ag/AgCl reference in the cathode compartment, the cathodic electrode serving as the working electrode and the anodic electrode as the counter electrode. All EIS measurements were carried out under an open-circuit voltage condition. The resistances of the cathode were acquired from Nyquist plots, where the intercept of the curve with the Zre axis was defined as the ohmic resistance. Current density C_d (mA/m²) and power density P (mW/m²) are calculated as follows:

$$C_d = U/R \times A \quad (3)$$

$$P = U^2/RA \quad (4)$$

where U is the voltage of the external resistance, R (Ω) is the external resistance, and A (m²) is the cross-sectional area of the electrode in the anode compartment.

The Columbic efficiency was calculated as follows:

$$C_E = C_p/C_t \times 100\% \quad (5)$$

where C_p is the total charge in coulombs calculated by integrating the current over time. C_t is the theoretical number of coulombs produced from sodium acetate, and this can be calculated as:

$$C_t = (C_{ini} - C_{end})bVF/M \quad (6)$$

where C_{ini} (mg/L) and C_{end} (mg/L) are the concentrations of sodium acetate at the beginning and end of one batch-fed operation, respectively, b is the number of Mes of electrons produced per Me of sodium acetate, and V is the liquid volume of the anode compartment. The total desalination rate (TDR) was calculated as follows:

$$TDR = (C_{s-ini} - C_{s-end})V_{de}/t \quad (7)$$

where C_{s-ini} (mg/L) and C_{s-end} (mg/L) are the initial and final concentrations of NaCl, respectively, V_{de} (L) is the liquid volume of the desalination compartment, and t (h) is the time of one desalination cycle.

3. RESULTS AND DISCUSSIONS

3.1. Performance of desalination and power generation

3.1.1. Effect of pH

The influence of different pH levels (2.0, 3.0, 4.0, 5.0 and 6.0) on the efficacy of current density and desalination was evaluated at an initial Cr⁺⁶ concentration of 50 mg/L. Fig. 2 shows the results, according to Eq. (1), 7 M H⁺ was consumed for the reduction of 1M Cr⁺⁶. The power generated was significantly dependent on pH for this reaction that based on H⁺ concentration, therefore a lower pH might make the reaction more favorable. That the maximum current density at pH 2.0 under the initial Cr⁺⁶ concentration of 50 mg/L was 823 mA/m² with a corresponding voltage of 384 mV (Figure-2A). 7 batch-fed operations were enough, to decrease the concentration of

the salt solution in the middle compartment from 5.15 g/L to 1.98 g/L, which meant the average salt removal rate was 2.1 mg/h. When the pH increased, the current density and desalination efficiency decreased rapidly. The current density was 513 mA/m² and 409 mA/m² with a corresponding salt removal rate of 1.27 mg/h and 0.79 mg/h for pH values of 3.0 and 4.0, respectively. Increasing of the pH values to 5.0 and 6.0, led to the voltage of the MDC was reduced to approximately 73mV and 42 mV, respectively. As well, the salinity could not be eliminated at those pH values. With respect of using of MFCs for Cr⁺⁶ reduction, literature mentioned that, Li *et al.* [28] found as well, that the pH had a big effect on the power outcome of an MFC and that a low pH was more cause of a higher power outcome. For one batch-fed operation, similar to other MDCs using potassium ferricyanide or oxygen as cathode electron acceptors, the pH of the anolyte would decrease during the desalination process in the MDC. At end every batch-fed operation, the pH was measured. When initial pH conditions were 2.0, 3.0 and 4.0, the pH dropped from 6.89, 6.81, 6.75 to 5.52, 5.98 and 6.32, respectively. Decreasing of the pH in the anode compartment would inhibit the activity of exoelectrogenic microorganisms [27], and this would lower the current density through one batch-fed operation. Moreover, the initial pH values of 2.0, 3.0 and 4.0 in the cathode compartment increased to 3.35, 4.58 and 4.5 after one cycle-operation, respectively. The increase of pH was due to the decrease of H⁺ due to its consumption in the Cr⁺⁶ oxidation reduction reactions, which resulted the drop in current density through one batch-fed cycle-operation. As well, the concentration of Cr⁺⁶ too affected the current density in that the reduction of Cr⁺⁶ caused the decrease of current density shown in Figure-3. These three interpretations above could explain the decrease of current density during one batch-fed cycle-operation.

3.1.2. Effect of the initial Cr⁺⁶ concentration

The MDC technology was used to test different initial Cr⁺⁶ concentrations excite in synthetic solutions at the range of 100 - 1000 mg/L at pH 2.0. The middle compartment was filled with 5 g/L NaCl. The effect of the initial Cr⁺⁶ concentration on current density and desalination efficiency was shown in Figures 3 and 4. The increase in the initial Cr⁺⁶ concentration to 100 mg/L and 1000 mg/L caused an increase in maximum current density to 963 and 1453 mA/m², respectively, which is an increase of 17 and 76%, respectively. It have been assumed there were two reasons leading to this increase in the maximum current density. Firstly, expressing Equation (1) in the form of the Nernst equation:

$$E = 0.157 + 0.10 \log_{10} (Cr_2O_7)^2 + 0.06(H)^+ \quad (8)$$

Eq. (8) shows that the cathode open circuit potential (OCP) was clearly affected by both the initial Cr⁺⁶ concentration and the pH. At the same pH, increasing the initial Cr⁺⁶ concentration could produce a higher current density. Wang *et al.* [29] found that when the initial Cr⁺⁶ concentration increased from 25 to 200 mg/L, the cathode



potential similarly increased from 600 to 650 mV, accompanied by an increase in the OCP from 830 to 910 mV. Another cause was that the increased Cr^{+6} concentration would decrease the internal resistance of the MDC which in turn could increase the ionic strength and thereby the voltage of the external resistance increased. Li et al. [22] used potassium dichromate as the electron acceptor in a dual-compartment MFC, they found that as the Cr^{+6} concentration increased from 50 to 500 ppm, the internal resistance decreased from 300 to 100 Ω , as a result, the corresponding maximum power density increased from 602 to 2116 mW/m². From the two reasons above, it was concluded that a high initial Cr^{+6} concentration could attained a high power density. As the current density increased, the desalination rate of the MDC with different initial Cr^{+6} concentrations increased simultaneously. When using 100 mg/L Cr^{+6} solution as the catholyte, the salt removal efficiency was 81.8% after seven batch-fed operations with a total operation time of 74 h, and the corresponding salt removal rate was 2.16 mg/h. When the Cr^{+6} concentration rose to 1000 mg/L, the salt removal efficiency was 93.4% and only three batch-fed operations were needed. In addition, the corresponding salt removal rate was 3.04 mg/h, which was 29% and 56% higher than the 100 mg/L and 50 mg/L Cr^{+6} concentrations, respectively. It is clear that the desalination rate of MDC with Cr^{+6} as the catholyte in this study was higher than that of the most single desalination compartment MDCs which have been reported [7, 11]. However, the consumption of the anolyte and catholyte was the least. Therefore, it was concluded that the desalination performance of MDC with Cr^{+6} as the cathodic electron acceptor could be enhanced through optimization.

3.2. Cr^{+6} reduction performance

3.2.1. The effect of initial catholyte pH

Removal efficiency of both Cr^{+6} and total Cr were decreased rapidly as pH increased. As it clear in Figures 5 and 6, the Cr^{+6} and total Cr removal rate decreased from 83% and 26.2% to 2.8% and 2.1% when the pH rose from 2 to 6, respectively. At pH 2.0 and 3.0, the Cr^{+6} removal rate exceeded 65% while it was only 10% or even lower at pH > 3.0. The most reliable reason for low Cr^{+6} removal efficiency at higher pH conditions was that the reduction from Cr^{+6} to Cr (III) required more H^+ ions following Eq. (1). According to Figure-6, the total Cr removal rate was lower than the Cr^{+6} removal rate, and the highest total Cr removal rate 26.3% was accomplished at pH 3.0. The most credible reason for this was that when the initial pH was at 2.0, the pH of the catholyte after one batch-fed operation was increased to 3.35, which meant a large quantity of H^+ remained in the catholyte, and the Cr^{+6} that was reduced to Cr^{+3} did not precipitate in the form of Cr_2O_3 . Moreover, the high H^+ concentration was beneficial to the production of Cr^{+3} because a greater amount of H^+ was requested to reduce to Cr^{+3} than to Cr_2O_3 (according to Eq. 1). When the cathodic pH was 4, 5 and 6, there was not enough H^+ to participate in the reaction so that the Cr^{+6} removal efficiencies were only 13.8 %, 10.1 % and 2.8 %,

respectively. It could be also visually observed a yellow-greenish deposit on the cathode surface when the initial pH of the catholyte was 3.0. Thus, it could be assumed that the amount of Cr^{+3} removed was in the form of trivalent chromium oxides which precipitated on the cathode surface when the pH was 3.0.

3.2.2. Effect of Cr^{+6} concentration

Figs. 7 and 8 show the effect of the initial Cr^{+6} concentration on reduction performance. Efficacy of removal the Cr^{+6} and total Cr were 72.5% and 22.2 %, when the initial Cr^{+6} concentration was 100 mg/L, as well as , 18.9 % and 6.5 % for 1000 mg/L, respectively. In general, the relative removal rate of Cr^{+6} and total Cr decreased when more Cr^{+6} was contained in the catholyte. However, the removal efficiency did not vary a lot for different initial Cr^{+6} concentrations, with the most stable value at 130–180 mg and 45–65 mg/L for Cr^{+6} and total Cr, respectively. It could be explained, that the concentrations of H^+ in the catholyte being similar, for the initial catholytes were all kept at 2.0. Furthermore, the number of electrons transferred from the anode compartment to the cathode compartment was constant. The sole method to obtain these electrons was via the oxidation of the organic substances into sodium acetate by the microorganisms in the anode compartment. The level of sodium acetate was the similar in these experiments, thus the Cr^{+6} in the cathode acting as an electron acceptor caught the same number of electrons. Consequently, the factor of the initial Cr^{+6} concentration did not have any great effect on the Cr^{+6} and total Cr removal efficiency.

3.2.3. The analysis of the cathode surface

The yellow-greenish precipitate on the cathode surface was analyzed by the SEM-EDS and XPS techniques. This obtained from a reactor with an initial catholyte Cr concentration of 50mg/L and pH 3.0 and having operated over two whole desalination cycles (240 h). Fig. 9A shows a micrograph of a blank electrode before use. Fig. 9B clearly shows that some clumps were adhering to the graphite plate surface. These were oxides of chromium, more demonstrated by using EDS and XPS were also applied to analyze the chemical compositions of the samples and the spectrum for Cr (Fig. 9C). The binding energy of approximately 582 eV and 576.6 eV, were found to be the peaks accounting for Cr 2p_{1/2} and Cr 2p_{3/2}, respectively. Based on the analysis of SEM-EDS and XPS, the precipitate on the cathode surface was confirmed to be Cr_2O_3 which was the main product during the reaction of MDC [30].

4. CONCLUSIONS

Desalination of brine and reduction of Cr^{+6} with electricity generation were successfully achieved in an MDC with using Cr^{+6} as electron acceptor in the cathode compartment. The industrial wastewater involving Cr^{+6} in the cathode could accept electrons produced by microorganisms in the anode compartment, and the Cr^{+6} was reduced to Cr_2O_3 on the cathode. Significant effect has been attained by the pH on the current density and



desalination performance. The results accomplished from this work indicated this technology of MDC was a promising both for desalination and removal of heavy metals during wastewater treatment.

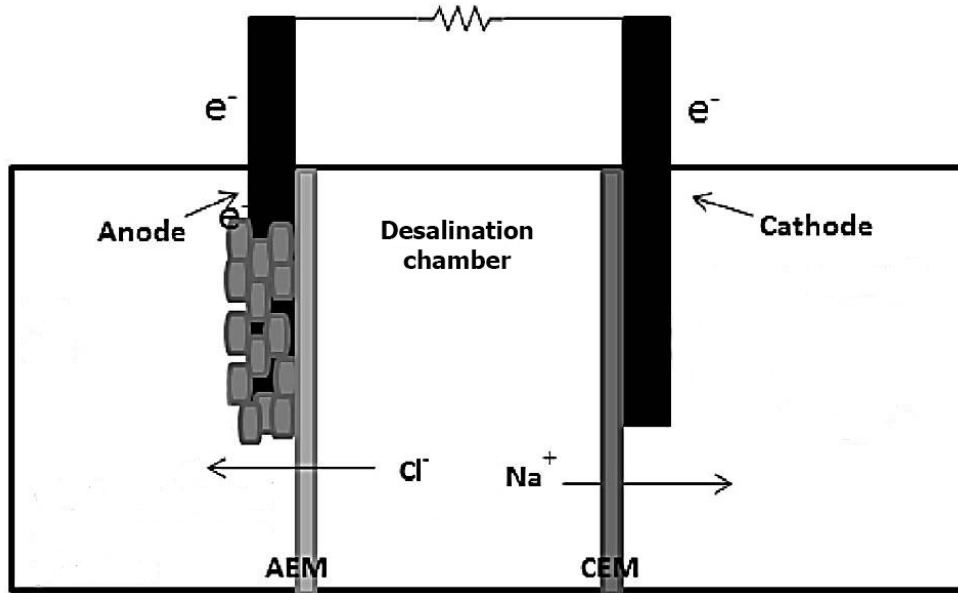
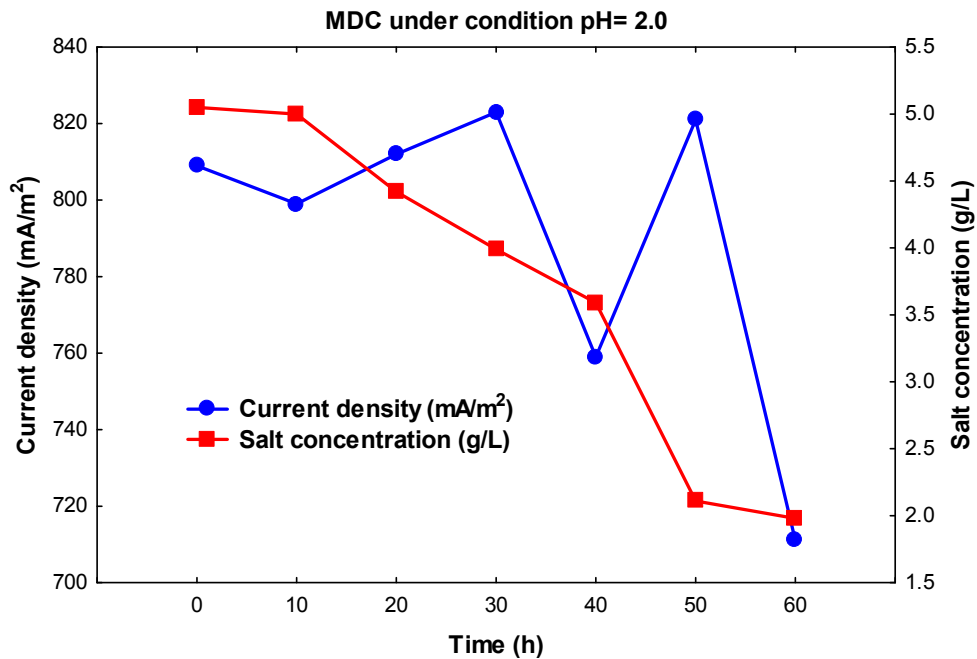


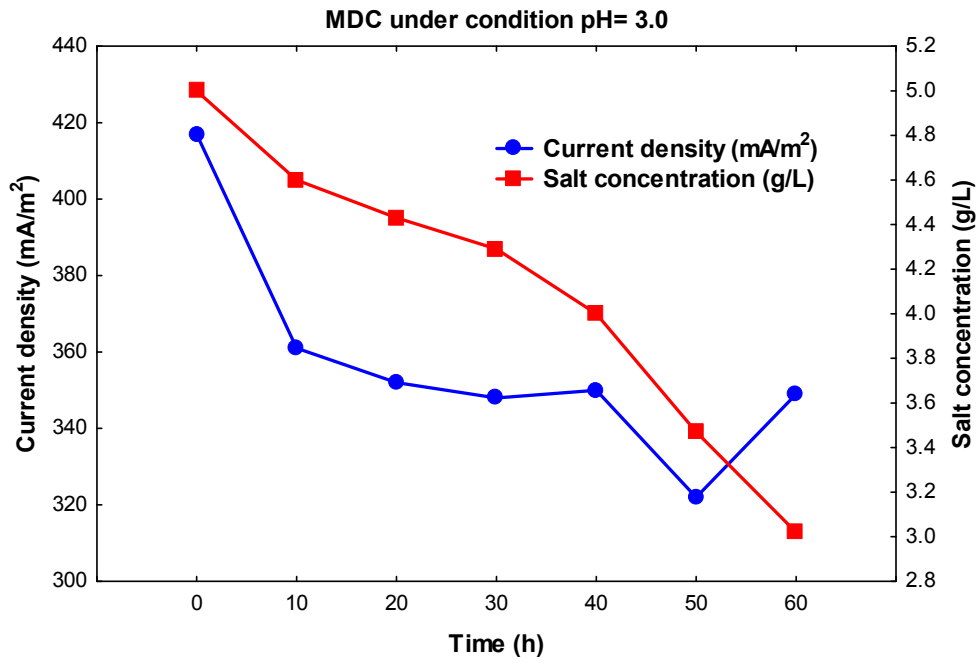
Figure-1. Schematic diagram of microbial desalination cell.

A





B



C

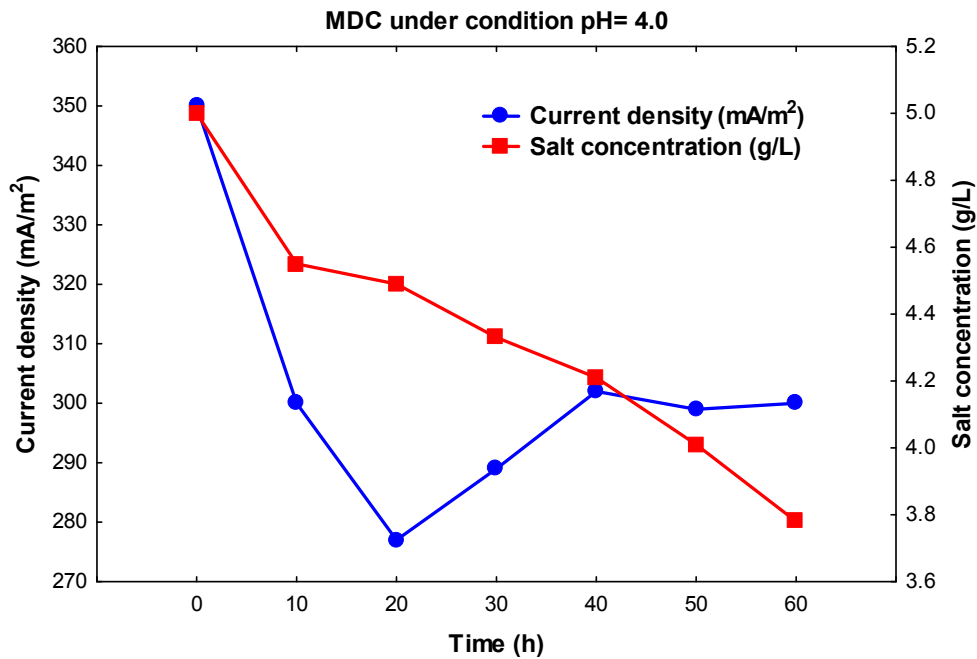


Figure-2. The current density and desalination performance of MDC under different pH conditions, A: pH= 2.0; B: pH= 3.0; C: pH= 4.0.

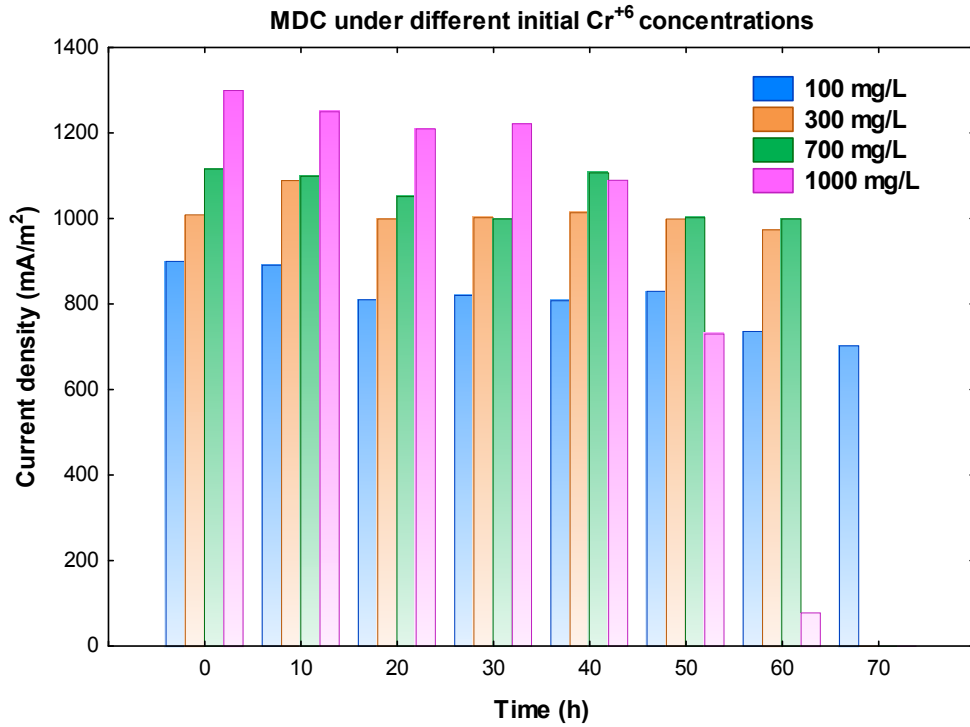


Figure-3. The current density of the experimental MDC under different initial Cr⁺⁶ concentrations, 200 mg/L, 400 mg/L, 800 mg/L and 1000 mg/L.

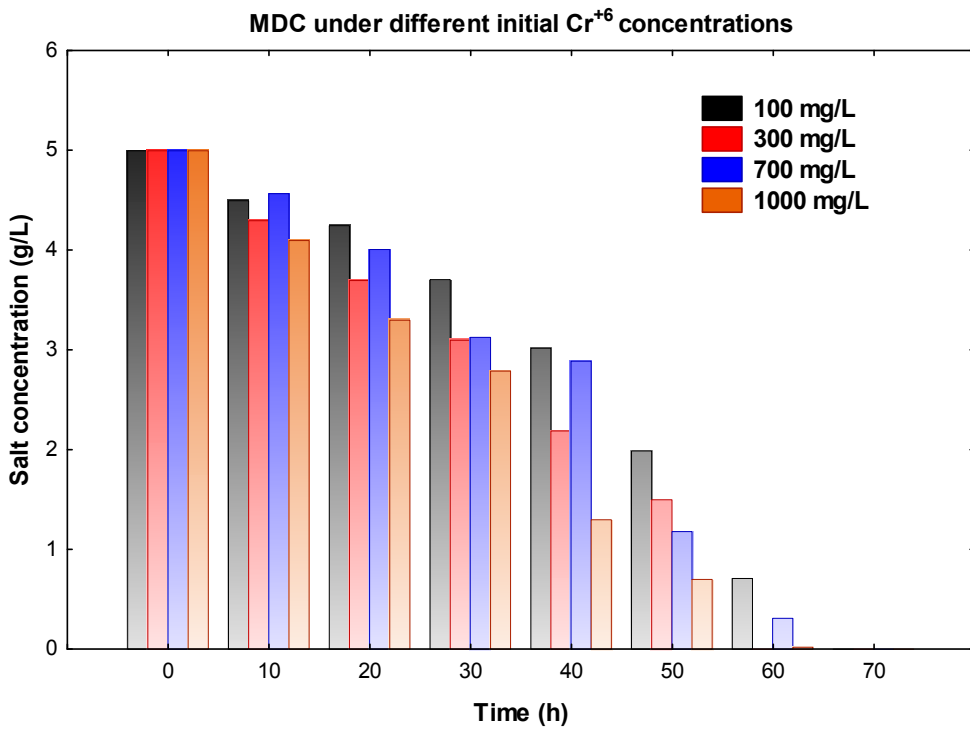


Figure-4. The desalination performance of the experimental MDC under different initial Cr⁺⁶ concentrations, 200 mg/L, 400 mg/L, 800 mg/L and 1000 mg/L.

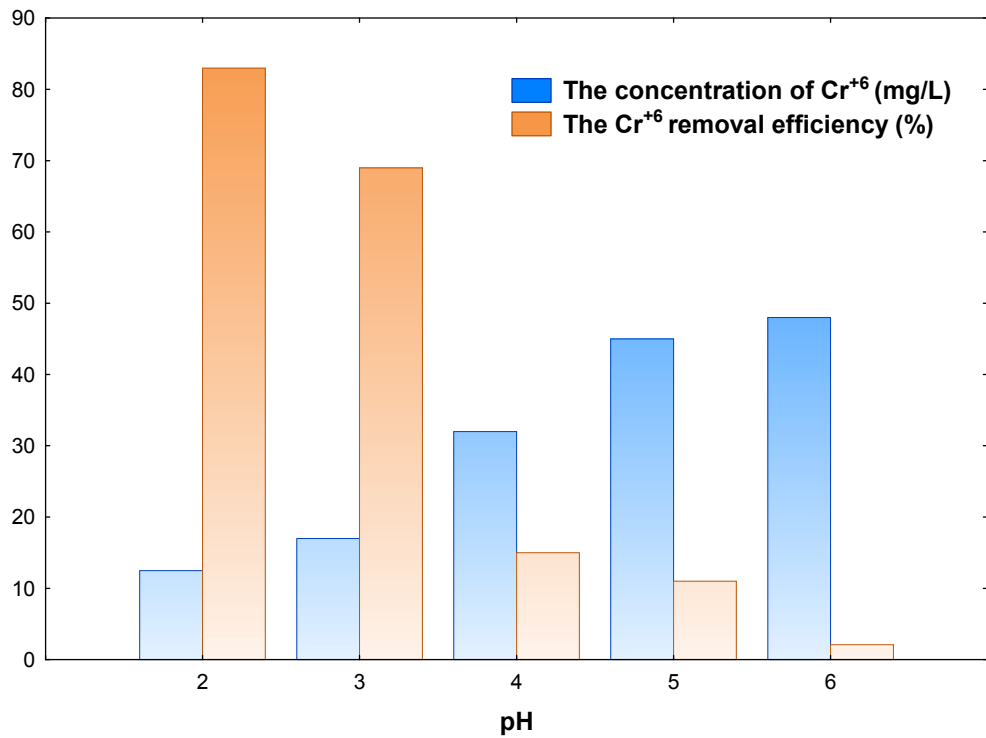


Figure-5. The Cr⁺⁶removal performance at different pH condition.

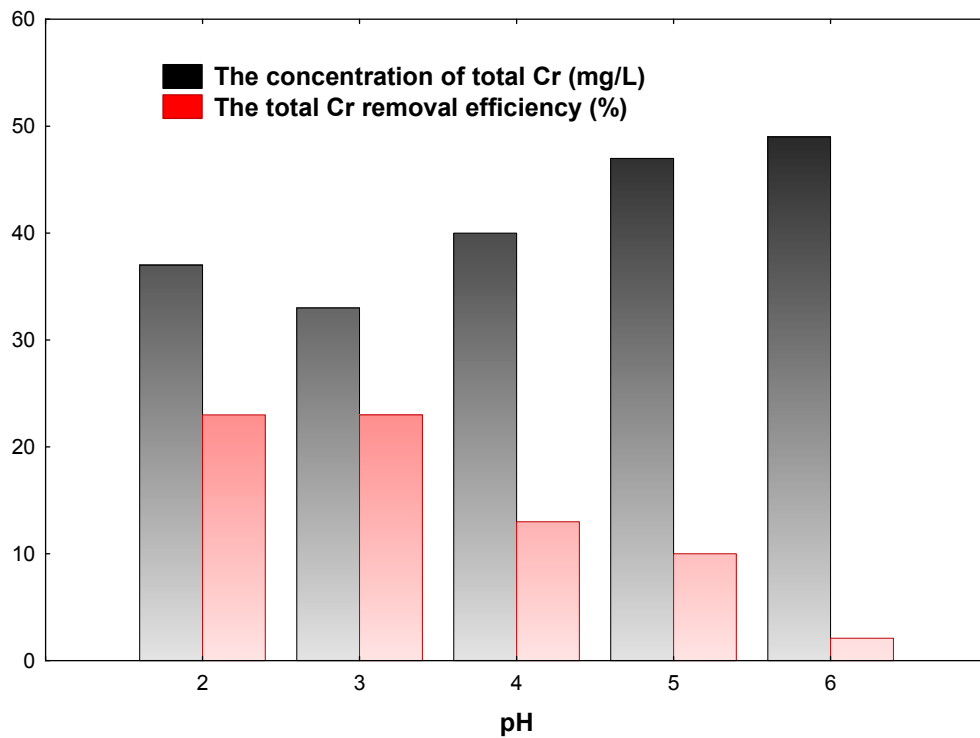


Figure-6. The total Cr removal performance at different pH condition.

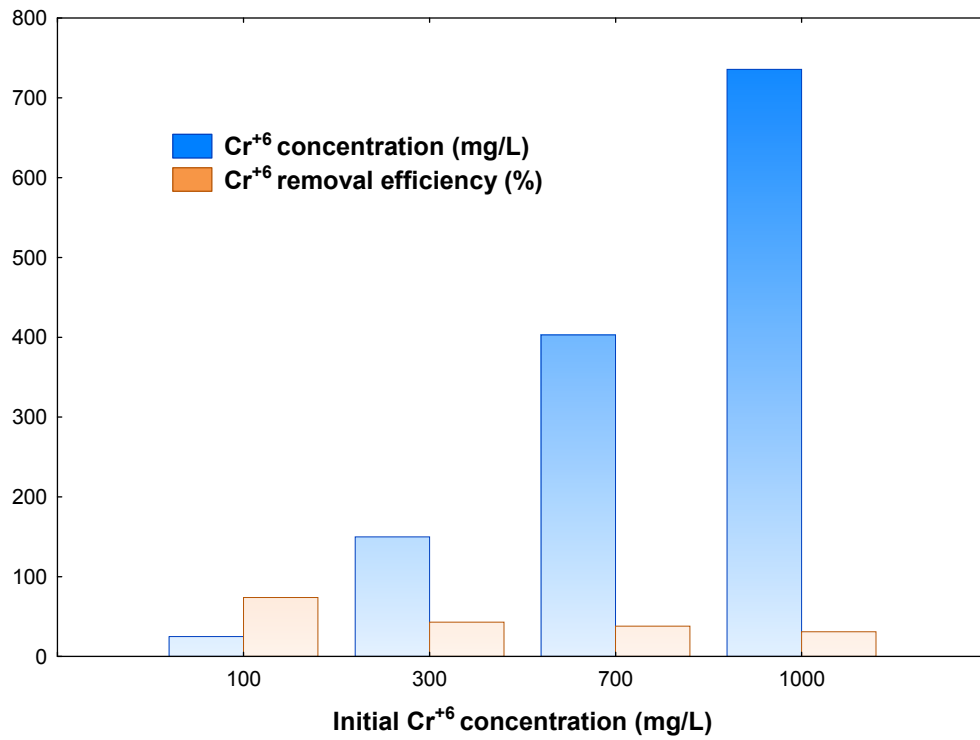


Figure-7. The Cr⁺⁶ removal performance at different initial Cr⁺⁶ concentration.

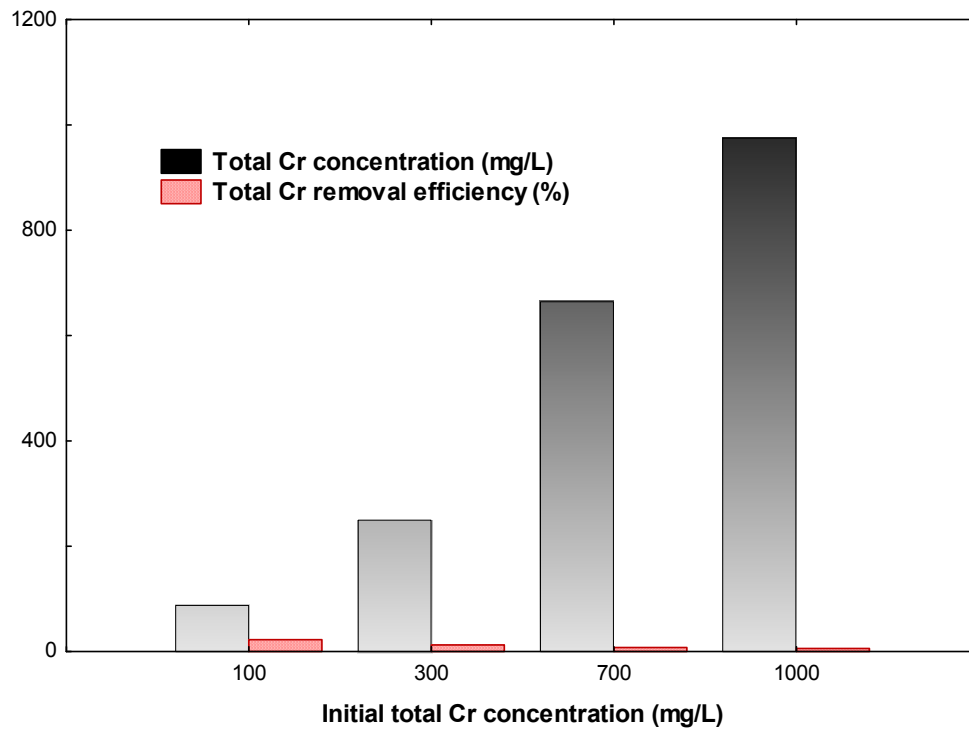


Figure-8. The total Cr removal performance at different initial Cr⁺⁶ concentration.

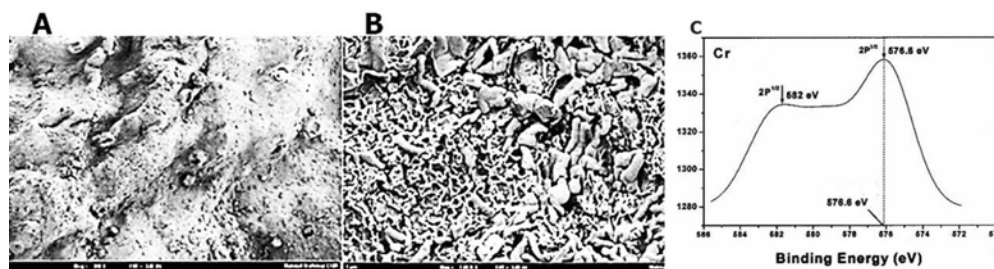


Figure-9. (A) SEM photomicrographs of the surface of the graphite plate before operation, (B) SEM photomicrographs of the surface of the graphite plate after operation, (C) EDS and XPS analysis of the crystals precipitated on the cathode surface of graphite plate.

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