Desalination 354 (2014) 181–188

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Desalination combined with hexavalent chromium reduction in a microbial desalination cell

Zhongyi An, Huichao Zhang, Qinxue Wen, Zhiqiang Chen *, Maoan Du

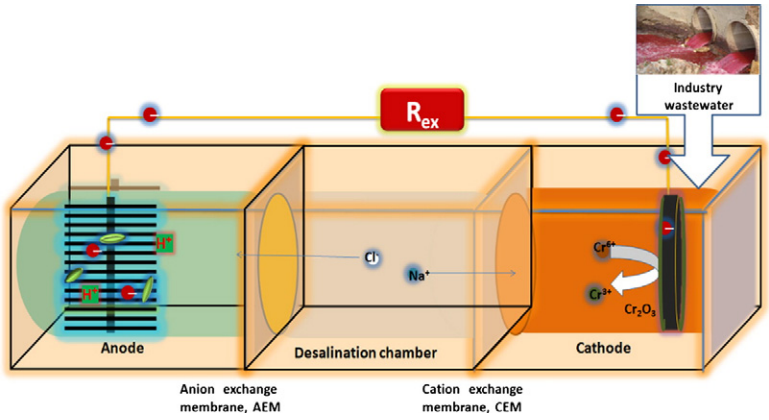
State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (SKLUWRE, HIT), Harbin 150090, PR China

HIGHLIGHTS

- Cr^{6+} removal and desalination were realized in a microbial desalination cell (MDC).
- The effects of initial pH and Cr^{6+} concentration were investigated.
- The Cr^{6+} acted as electrons accepter in MDC system and the reduction was Cr_2O_3.

GRAPHICAL ABSTRACT

The construction of a microbial desalination cell (MDC).



ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 2 October 2014
Accepted 6 October 2014
Available online 28 October 2014

Keywords:
Microbial desalination cell (MDC)
Desalination
Hexavalent chromium reduction
Electricity production

ABSTRACT

The microbial desalination cell (MDC) was a novel technology to desalinate saline water, simultaneously producing electricity and treating wastewater. In our research, an MDC using a synthetic Cr (VI)-containing wastewater as the catholyte was used to desalinate brine in the desalination chamber and simultaneously to reduce Cr (VI) in cathode chamber. Below a pH value of 2.0 with an initial Cr (VI) concentration of 100 mg/L, the hexavalent chromium removal rate was 75.1 ± 3.8% with a current density 760 mA/m^2, and the desalination rate was 2.1 mg/h. As the initial concentration of chromium increased from 200 to 1000 mg/L, the current density also increased from 884.8 mA/m^2 to 1339.8 mA/m^2, with an increase in the salt removal rate from 2.2 mg/h to 3.0 mg/h. The analyses of scanning electron microscope-energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) indicated that the Cr (VI) was reduced to Cr_2O_3 and deposited on the cathode surface. The deposition of Cr_2O_3 on the cathode surface would affect the performance of the MDCs. These results suggested that an MDC using Cr (VI) as an electron acceptor could further enlarge the application range of MDCs.

1. Introduction

Bio-electrochemical systems (BESs) use microorganisms for the catalysis of electrochemical reactions and convert the chemical energy of the organics in wastewater and lignocellulosic biomass into

* Corresponding author at: School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, PR China, 150090. Tel.: +86 451 8628 3008.
E-mail address: an_zhongyi_hit@126.com (Z. Chen).

http://dx.doi.org/10.1016/j.desal.2014.10.006
0011-9164/

electricity or hydrogen [1,2]. Furthermore, BESs can also be use to remove harmful substances from wastewater, such as nitrate [3], heavy metal ions [4] and so on. Based on the application of BESs, those systems can be further sub-divided into microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial desalination cells (MDCs) and so on [5,6]. Using BESs to remove ions from salt water is a new method of seawater desalination [7]. The microbial desalination cell (MDC) is an emerging technology based on the microbial fuel cell (MFC) as a feasible way to desalinate salt water without energy consumption [7]. In general, an MDC is composed of an anode chamber, a desalination chamber and a cathode chamber. In the anode chamber, bacteria catalyze the oxidation of organic matter, releasing some electrons produced from cell respiration to the anode, where they flow through an external circuit to the cathode [8]. In the cathode chamber, the compounds with adequately high redox potentials accept electrons and provide the other cell half-reaction, thus allowing an electric current. During this process, the ions such as Cl^- and Na^+ in the middle chamber migrate toward the anode and cathode chambers, respectively, which results in accomplishing brine desalination without any net energy consumption. Now, wastes or wastewater are usually used as the anodic substances; however, cost is still involved in the cathode reaction.

In a study by Cao et al., the researchers demonstrated that an MDC using ferricyanide as the catholyte was able to remove more than 88% of NaCl in the desalination chamber and the salt removal rate could reach 2.8 mg/h with an initial salt solution containing 5 g/L (Data calculated according to figures and profiles presented) [7]. It should be recognized that the catholyte applied in the previous research, such as the ferricyanide catholyte, is not a sustainable source despite their positive effects on power density [9]. Considering this point, Mehanna et al. introduced oxygen as the electron acceptor in a cathode chamber with a Pt/carbon (Pt/C) mixture with a Nafion solution as catalysts for the air cathode and the salt removal was only 0.22 mg/h with an initial salt concentration 5 g/L [10]. However, these MDCs that use the air cathode with Pt as catalytes are too expensive to consider for implementation on a broad scale. On the basis of the oxygen cathode, Wen et al. replaced the Pt with microorganisms as a catalyst on the cathode surface, but aeration in the cathode chamber was needed in this process which also increased the operational cost [11]. Therefore, the question of how to use certain wastes with the ability to accept electrons as an oxidant becomes an important research topic and one that would greatly enhance the environmental and economic benefit of MDCs.

Many studies have explored the MFCs to find industrial pollutants for use as cathodic electron acceptors, such as Cu (II) [12] and Cr (VI). Many industries such as the metal plating, paints and pigments, and leather tanning and printing ink discharge large quantity waste water containing Cr into the environment in the form of Cr (VI) or Cr (III) [13]. Due to its refractory and highly toxic nature, Cr (VI) accumulation in the environment is a great danger for human beings, animals and plants [14]. Cr (VI) is well known as a highly toxic metal considered as a priority pollutant [15], and it can cause many diseases of the eye, ear, skin, stomach and so on [16]. In contrast, the toxicity of Cr (III) is much lower for humans and the environment [17].

Cr (VI) could be reduced either directly as an electron acceptor in MFCs [18], or via Cr (VI) cathodic reduction by microorganism [19–21]. Li et al. proposed a novel rutile-coated cathode that was sensitive to visible light and could improve the Cr (VI) reduction rate under light irradiation than compared to dark conditions [22]. Tandukar et al. used bio-organisms on a cathode to reduce Cr (VI) in an MFC and the Cr (VI) was removed as $Cr(OH)_3$, which resulted in a current and power density of 123.4 mA/m^2 and 55.5 mW/m^2, respectively [23] According to reports in the literature [24,25], when using Cr (VI) as an electron acceptor, each Cr can receive three electrons and be reduced to Cr (III) following the equations below:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \quad (1)$$

$$Cr_2O_7^{2-} + 8H^+ + 6e^- = Cr_2O_3 + 4H_2O. \quad (2)$$

Cr (VI) has a higher oxidation (1.33 V) than oxygen (1.23 V), which means Cr (VI) is very appropriate as an electron acceptor and can be restored to Cr_2O_3.

Thus far, the only study of using heavy metal ions in an MDC system was conducted with a synthetic copper solution in a four-chamber MDC which involved inserting a CEM next to the cathode chamber to form a concentration chamber. The salt removal rate in those MDCs was approximately 5.1 ± 0.6 mg/h. However, the construction of the four-chamber MDC was more complicated than a traditional MDC [26]. Considering the relatively high standard electrode potential of Cr (VI) compared to copper and the wide existence of Cr (VI) in industrial wastewater, synthetic wastewater containing Cr (VI) was chosen as the cathodic electron acceptor in this study. The objective of this study was to evaluate the feasibility of using Cr (VI) as the electron acceptor in a microbial desalination cell for salinity removal, generation of electricity and Cr (VI) removal. Factors such as the catholyte pH and initial Cr (VI) concentration were investigated in this paper.

2. Materials and methods

2.1. Construction of the MDC

The construction of the experimental MDC was shown in Fig. 1. It consisted of three (anode, cathode, desalination) polymethyl methacrylate chambers, including the anode and cathode chambers with dimensions of 7 × 7 × 3.5 cm (w × h × d) with an effective volume of 45 ml and the desalination chamber with dimensions of 7 × 7 × 2 cm (w × h × d) with an effective volume of 38 ml, respectively. An AEM membrane (AMI-7001, Membranes International Inc., NJ) with a cross-sectional area of 19.63 cm^2 was used to separate the anode and desalination chambers and a CEM membrane (AMI-7001, Membranes International Inc., NJ) with the same area was placed next to the cathode chamber. The electrode material in the anode consisted

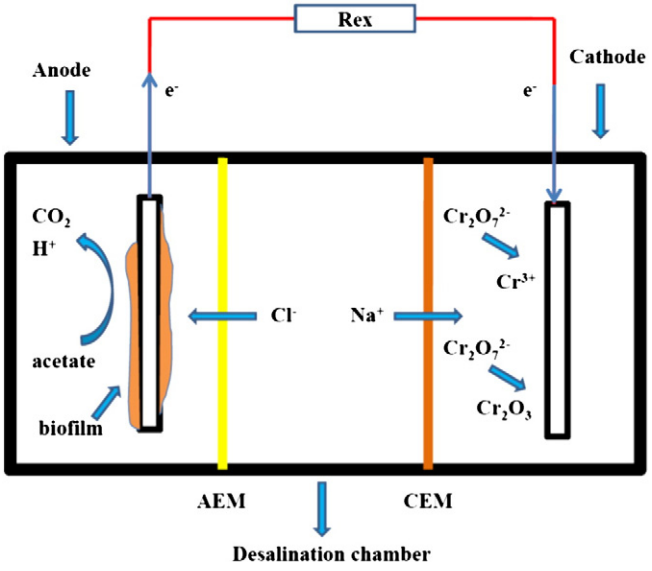


Fig. 1. Principle of the MDC with chromium reduction.