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Competitive migration behaviors of multiple ions and their impacts on ion-exchange resin packed microbial desalination cell

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HIGHLIGHTS

- Mixed resin packed MDC removed multiple anions better than multiple cations.
- Both molar conductivity and exchange selectivity affected migration of multiple ions.
- Scaling was observed on the surface of CEM when desalinating multiple cations.
- Conductivity of resin decreased when desalinating multiple cations for long time.
- Resin packed MDC is more suitable for desalination of water with lower hardness.

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ABSTRACT

Mixed ion-exchange resins packed microbial desalination cell (R-MDC) could stabilize the internal resistance, however, the impacts of multiple ions on R-MDC performance was unclear. This study investigated the desalination performance, multiple ions migration behaviors and their impacts on R-MDCs fed with salt solution containing multiple anions and cations. Results showed that R-MDC removed multiple anions better than multiple cations with desalination efficiency of 99% (effluent conductivity <0.05 ms/cm) at hydraulic retention time of 50 h. Competitive migration order was $SO_4^{2-} > NO_3^- > Cl^-$ for anions and $Ca^{2+} \approx Mg^{2+} > NH_4^+ > Na^+$ for cations, jointly affected by both their molar conductivity and exchange selectivity on resins. After long-term operation, the existence of higher concentration Ca^{2+} and Mg^{2+} caused the electric conductivity of mixed resins decrease and scaling on the surface of cation-exchange membrane adjoined with cathode chamber, suggesting that R-MDC would be more suitable for desalination of water with lower hardness.

1. Introduction

As a newly developed water desalination technology, microbial desalination cell (MDC) has been attracting great attention since it can simultaneously achieve wastewater treatment, electricity generation, and saline water desalination. It is a modified bioelectrochemical system (BES) sharing the same principle with microbial fuel cell (MFC) (Liu et al., 2004; Wang et al., 2012). A classical MDC contains three chambers: anode, desalination and cathode chambers (Cao et al., 2009). The desalination chamber is constructed by inserting a pair of anion-exchange membrane (AEM) and cation-exchange membrane (CEM) between the anode and cathode chamber. Electrochemically active bacteria in anode chamber oxidize organic matter into CO_2 and H^+, and release electron, which flows through the external electric circuit to cathode, getting established current. At cathode, hydrion is consumed with electron in the reduction of electron acceptor. Charge balance is achieved by the migration of ions in salt water held in desalination chamber through respective AEM to anode chamber and CEM to cathode chamber, leading to saline water desalination. Compared to conventional water desalination technologies such as electrodialysis, reverse osmosis and distillation, MDC offers a sustainable approach for saline water desalination without any energy input. After MDC was first invented by Cao et al. (2009), extended works have been successively reported, including air cathode MDC (Mehanna et al., 2010b), stacked MDC (Chen et al., 2012a, 2011), upflow MDC (Jacobson et al., 2011), recirculated MDC for pH control (Chen et al., 2012; Qu et al., 2012), microbial electrodialysis cell (MEDC) for simultaneously hydrogen, acid and alkali production (Chen et al., 2012b; Luo et al., 2011; Mehanna et al., 2010a), and so on.

One limitation to the MDC performance is increase in internal resistance due to the removal of ions along with desalination. Cao et al. (2009) found that ohmic resistance increased nearly 40 times from 25 to 970 Ω when salt removal efficiency achieved 88 ± 2%

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with initial concentration of 5 g/L. Luo et al. (2011) observed a 4–16 times increase in ohmic resistance from 70–250 to 850–1100 Ω with desalination efficiency of 98.8% (initial concentration of 10 g/L). Similarly Chen et al. (2011) also found the ohmic resistance increased from 21 to 312 Ω in stacked MDC with 20 g/L NaCl as saline influent. The increased ohmic resistance decreases current density and would limit its further desalination. Lowering ohmic resistance is critical to advance the performance of MDC.

One feasible approach to solve this problem is ion-exchange resin coupled MDC (R-MDC). Based on the principle of electrodeionization (EDI), mixed cation and anion exchange resins were packed in the desalination chamber of MDC. As previously reported in researches on EDI processes (Jung-Hoon et al., 2007; Yeon et al., 2004), resins have much higher conductivity than bulk solution and can work as ion conductor in low salinity water, ohmic resistance of desalination unit can be stabilized during the desalination process. Our previous study found that the ohmic resistance of R-MDC was stabilized in the range of 3.0–4.7 Ω when continuously operated at an initial salt concentration of 5–10 g/L (Morel et al., 2012), which was much lower than classic MDC of 5.5–12.7 Ω. However, dissolved solids in saline water are not only NaCl in practical application, and the existence of multiple ions may affect the performance of R-MDC. For example, cations such as Ca^{2+} and Mg^{2+} may deposit on membrane or resin surface and form scale due to pH change, which would hinder the migration of ions and increase internal resistance. Moreover, in anode anaerobic condition anions such as NO_3^- and SO_4^{2-} will be reduced into N_2 and H_2S by reducing bacteria, competing with the anode as the electron acceptors and lowering the coulombic efficiency. In addition, due to the introduction of ion-exchange resin, multiple ions in desalination chamber are subjected to two forces: ion exchange selective force and electric field force. As different ions have distinct charge and mobility they may present various migration behaviors and removal priorities. However, most studies have so far only utilized pure NaCl as saline influent, there is no reported study on transfer behaviors of multiple ions in R-MDC or characterization of resin property change and membrane fouling.

In the present study, two R-MDCs were constructed and continuously operated with saline influent containing multiple anions and cations. The desalination performance and power generation of R-MDCs were evaluated at different hydraulic retention times (HRTs). The competitive migration behaviors of multiple ions were elucidated. In addition, the electric conductivity change of mixed resin after used in R-MDCs, and membrane fouling after long-term operation were investigated to reveal the impacts of multiple ions on R-MDC performance.

2. Methods

2.1. Construction of MDC reactors

Two liter-scale biocathode MDCs were constructed, the detailed configuration and size of which can be found in the previous study (Morel et al., 2012). The anode and cathode chambers were filled with activated carbon granules with a size of 2 mm in diameter and approximately 5 mm in length. Graphite rods with a diameter of 6 mm were inserted in two electrode chambers to collect electrons. Prior to use, graphite rods were treated with 1 M HCl to remove inorganic impurities, and activated carbon granules were rinsed with potable water to wipe off carbon dusts. An AEM (AMI-7001, Membrane International, Inc.) and a CEM (CMI-7000, Membrane International, Inc.) were placed between anode, desalination and cathode chambers. The working surface of each membrane was 150 cm^2. A saturated calomel electrode (SCE, 0.242 V vs. standard hydrogen electrode (SHE), Leici, China) was inserted into anode chamber to serve as the reference electrode.

To decrease internal resistance mixed ion-exchange resins were packed in desalination chamber to serve as ion conductor. As water-splitting and electro-regeneration are carried out at places where there is cationic material in contact with anionic material, the strong base anion resin (Amberlite® IRA-402, Cl form, Acros Organics, Belgium) and strong acid cation resin (Amberlite® IR-120, Na form, Acros Organics, Belgium) were mixed at a ratio of 1:1 (v/v) to obtain comparable surface area, despite that the exchange capacities of anion resin (1.2 eq/L) and cation resins (2.0 eq/L) were different. Both resins have the same diameter of 0.60–0.75 mm.

2.2. Microorganisms and solutions

The anode and cathode chambers of R-MDCs were inoculated with microbial consortium previously enriched in a biocathode MFC for a long time in our laboratory. The anode chamber was fed with phosphate buffered sodium acetate solution, which contains (per liter of deionized water) 1.64 g CH_3COONa, 1.0 g NH_4Cl, 2.2 g KH_2PO_4 and 1.7 g K_2HPO_4 $3H_2O$. The conductivity was 6.71 ms/cm and pH was 6.93. The cathode chamber was fed with a similar solution as the anode, except that CH_3COONa was replaced by 1.92 g $NaHCO_3$. The conductivity of catholyte was 6.94 ms/cm and pH was about 7.00. In the desalination chamber, 10 mmol/L NaCl was fed as salt solution to represent municipal wastewater. To explore the migration behaviors of multiple ions, additional 10 mmol NO_3^- and SO_4^{2-} with Na^+ as counter ion was added in per liter of NaCl solution (conductivity of the mixture was 4.72 ms/cm) of one R-MDC, called as anion R-MDC (AR-MDC), another R-MDC fed with salt solution containing 10 mmol/L Na^+, NH_4^+, Ca^{2+} and Mg^{2+} (Cl^- as counter ion) (conductivity of 6.49 ms/cm) was called as cation R-MDC (CR-MDC).

2.3. MDC start-up and operation

The two reactors were initially operated in parallel in MFC mode with CEM as separation material to achieve rapid micropropagation and shorten start-up time. Anolyte and catholyte were recirculated separately from two 1 L reservoirs using peristaltic pumps (BT00-300T, Longer Pump, USA). The anode pipe system was completely sealed to achieve anaerobic circumstance, while air was continuously supplied to cathode reservoir with an air pump (ACO-208, HAILEA, China). The external resistance was set at 1000 Ω by a resistance box (0.1–99,999 Ω; ZX21, Tianshui, China), and then gradually decreased to 20 Ω to achieve higher current density.

After start-up, the MFC reactor was changed to MDC reactor where a desalination chamber was inserted and separated with two new ion-exchange membranes (AEM and CEM) between anode and cathode. Mixed anion-exchange and cation-exchange resins were injected into the desalination chamber using a 50 mL syringe. Salt solutions with multiple anions and multiple cations were continuously fed to AR-MDC and CR-MDC, respectively from bottom to top with different flow rates (different HRTs of saline water in desalination chamber) using two peristaltic pumps (LSP01-1C, Longer Pump, USA). Before pumped into the desalination chamber the salt solutions stored in two 5 L tanks were degased to avoid air entering, which would occupy a part of space and increase internal resistance. The anolyte and catholyte were replaced every 70 h to ensure enough nutrient and avoid sharp pH changes. After a stable effluent conductivity was reached, both AR-MDC and CR-MDC were further operated for two cycles (140 h) at each flow rate of salt solution to compare desalination performance, and then another two months operation at flow rate of