Simultaneous removal of organic matter and salt ions from saline wastewater in bioelectrochemical systems

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HIGHLIGHTS
► Microbial salinity-reduction electrolysis cells (MSCs) can treat saline wastewater.
► In MSCs, organic matter and salt ions were removed simultaneously.
► Ion-exchange membranes were not damaged for three months in MSCs.
► Exoelectrogens can generate high currents with salinities up to 36 g/L TDS.

GRAPHICAL ABSTRACT

ABSTRACT
A new bioelectrochemical system is proposed for simultaneous removal of salinity and organic matter. In this process, exoelectrogenic microorganisms oxidize organic matter and transfer electrons to the anode, hydrogen is evolved at the cathode by supplying additional voltage, and salt is removed from the wastewater due to the electric potential generated and the use of two ion-exchange membranes. Salinity removal (initial conductivity ~40 mS/cm) increased from 21 to 84% by increasing the substrate (sodium acetate) from 2 to 8 g/L. A total of 72–94% of the chemical oxygen demand was degraded in the anode and cathode chambers, with 1–4% left in the anode chamber and the balance lost through the anion-exchange membrane into the concentrate waste chamber. The maximum hydrogen production rate was 3.6 m3-H2/m3-electrolyte per day at an applied potential of 1.2 V. The Coulombic efficiency was ~100%, while the cathode recovery varied from 57 to 100%, depending on the extent of methanogenesis. Exoelectrogenic microbes generated high current densities (7.8 mA/cm2) at ≤ 36 g/L of total dissolved solids, but > 41 g/L eliminated current. These results provide a new method for achieving simultaneous removal of salinity and organic matter from a saline wastewater with H2 production.

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1. Introduction
Saline wastewaters are generated by many industries, including food processing plants, leather or tannery industries, and petroleum refineries [1]. Saline wastewater contains salt ion concentrations that are usually greater than 20 g/L and sometimes up to 150 g/L. The organic content of these wastewaters can also be very high, with up to 70 g/L of chemical...
oxygen demand (COD) [1]. The treatment of saline wastewaters usually occurs in two separate processes, with organic contaminants removed in a biological process [12], and salinities reduced in physical and chemical separation processes such as ion-exchange, electrodialysis, or reverse osmosis [1]. Both processes are energy-demanding processes, and thus are not sustainable.

Bioelectrochemical systems, such as microbial fuel cells (MFCs) or microbial electrolysis cells (MECs), can be used to remove organic contaminants in wastewater and produce valuable energy such as electrical power or hydrogen gas. At the anode in MFCs or MECs, exoelectrogenic bacteria oxidize organic matter and transfer electrons to the anode. At the cathode, different reduction reactions can occur, such as oxygen reduction in MFCs or hydrogen evolution in MECs. These coupled redox reactions create an electric field between the electrodes that can drive ionic transport. Using ion-exchange membranes (IEMs), the driven ionic transport can be manipulated to separate salt ions in the reactor. Several new bioelectrochemical systems have been proposed to separate ions using IEMs for desalination of salty water [3–11], efficient recovery of salinity-gradient energy [12–15], and chemical production [16,17]. In a microbial desalination cell (MDC), for example, water in a middle chamber between the anode and cathode chambers can be partly or fully desalinated, while the wastewater in the anode chamber gains salt ions.

A new type of IEM-based bioelectrochemical system, called a microbial saline-wastewater electrolysis cell (MSC), is proposed here for simultaneous removal of organic matter and salt ions from saline wastewater. These goals are different from that of an MDC, which is to desalinate a separate stream of water. In an MSC, exoelectrogenic microbes on the anode degrade organic contaminants in saline wastewater, and hydrogen gas is produced at the cathode as done in an MEC [18]. In addition, the electric field created by the exoelectrogens is used to remove salt ions from the saline wastewater. This allows for simultaneous wastewater treatment and salt removal in a process that can generate net energy. Wastewater desalination is accomplished by placing a cation-exchange membrane (CEM) next to the anode, and an anion-exchange membrane (AEM) next to the cathode. For the given reactor design, cations are separated from the anode chamber into the middle chamber while anions are transferred from the cathode chamber into the middle chamber, desalinating the solutions in the anode and cathode chambers, and producing more concentrated salt solutions in the middle chamber. Oxidation of organic matter releases protons into the anode solution while hydroxyl ions are discharged by hydrogen gas evolution at the cathode, creating pH imbalances between the anode and cathode chambers. To avoid these pH imbalances, water was recirculated between the anode and cathode chambers as previously described [19].

The main objectives of this study were (1) to demonstrate the process of simultaneous removal of organic contaminants and salt ions from a saline solution, and (2) to examine the integrity of the IEMs over an extended period of operation (three months). The long-term effects of bacterial activity in the anode chamber on the IEM integrity, such as biofilm formation or permeaselectivity changes (capability of IEMs to block the cross-over of excluded co-ions), have not been well addressed in bioelectrochemical systems with membranes. In an MSC, the anode microbes are directly impacted by the initial high salinity of wastewater. Therefore, the MSC was operated at relatively high current densities (2.8 mA/cm²) using applied voltages ≥ 1.0 V in order to enhance the rate of ionic separation here, compared to those used in previous studies with bioelectrochemical systems (< 0.6 mA/cm²) [20–22]. The specific effects of high salinities were also examined on the performance of the exoelectrogenic microbes at these high current densities.

2. Materials and methods

2.1. Reactor construction

A three-chamber MSC was built with cubic Lexan blocks with an inner cylindrical chamber (7 cm³ in cross section). The MSC consisted of the anode (27 mL), concentrate waste (18 mL), and cathode (33 mL) chambers. A cation-exchange membrane (7 cm², Selemion CMV, AGC Engineering Co., Japan) was placed between the anode and middle (concentrate waste) chambers to separate cations from the anode to the middle chamber (Fig. 1). An anion-exchange membrane (7 cm², Selemion AMV, AGC Engineering Co., Japan) was located between the middle and cathode chambers. A glass tube was glued on the top of the cathode chamber to collect H₂ [23]. The cathode was prepared with platinum as the catalyst (0.6 mg/cm²; BASF, Germany), in a mixture of carbon black (BASF, Germany) and Nafion (Sigma-Aldrich, MO), which was painted on both sides of a 7-cm² stainless steel mesh (#50) [24]. A graphite fiber brush anode (2.7 cm in diameter and 2.3 cm in length; Mill-Rose Lab Inc., OH) was inoculated with effluent from an existing MFC, which was originally started with primary effluent from a domestic wastewater treatment plant. The anode was initially enriched in a single chamber MFC before it was used in the saline wastewater treatment system [25]. During this start-up stage, the anode microbes were exposed to various NaCl concentrations of up to 20 g/L.

In separate experiments, single-chamber microbial electrolysis cells (MECs) were built without IEMs to examine the effects of various salinities on current generation by anode bacteria. The anode was prepared using preacclimated bacteria (effluents from existing MFCs) and adjusted with various NaCl concentrations of up to 20 g/L. The cathode...
was made with platinum catalysts (0.5 mg/cm²; BASF, Germany) as described above, but using a 7-cm² piece of carbon cloth [26].

2.2. Solution preparation

For the tests with the three-chamber MSC, a saline medium was prepared with 20 g/L NaCl, 50 mM phosphate buffer (4.58 g/L Na₂HPO₄; 2.45 g/L NaH₂PO₄·2H₂O; 0.31 g/L NH₄Cl; 0.13 g/L KCl), and sodium acetate (2.4, 6, or 8 g/L) with trace amounts of minerals and vitamins [27]. For a given substrate concentration, the three-chamber MSC was operated for at least two fed-batch cycles, or until the experimental results from each cycle became consistent with the previous one. To control methanogenic activities in the reactor, 2-bromoethanesulfonate with trace minerals and vitamins [27] was added to the medium (7.2 g/L as total dissolved solid, TDS), 4 g/L sodium acetate, and 10 mM brines, the medium was a mixture of NaCl, 50 mM phosphate buffer (SRI-310 C, SRI Instruments, CA) as previously described[23]. The vol of 2-bromoethanesulfonate did not appreciably change the solution conductivity. For the experiments with the single-chamber MECs without membranes, the medium was a mixture of NaCl, 50 mM phosphate buffer (7.2 g/L as total dissolved solid, TDS), 4 g/L sodium acetate, and 10 mM 2-bromoethanesulfonate with trace minerals and vitamins [27]. The NaCl concentration was increased by 5 g/L from 10 to 35 g/L (i.e., from 21.2 to 46.2 g/L as TDS). At a given TDS, the single-chamber MECs were operated over three fed-batch cycles for each salinity condition.

2.3. Experimental measurements

For the experiments with the three-chamber MSC, gas was collected in a gas bag (1-L capacity; Cali-5-Bond, Calibrated Instruments Inc., NY) and analyzed for H₂, O₂, N₂, CH₄, and CO₂ using a gas chromatograph (Fig. 1A) as previously described [23]. The volume of the collected gas was determined by the gas bag method [29]. Effluent electrolyte and concentrate waste solution were analyzed for conductivity and pH (SevenMulti, Mettler-Toledo International Inc., OH). The chemical oxygen demand (COD) was determined according to standard methods (Hach Co., CO) [30]. The COD was measured only for the fed-batch cycles performed without 2-bromoethanesulfonate, and solution samples were diluted at a relatively high ratio of 1:40 to meet the maximum chloride concentration [31].

The applied voltage (Eap) from a power supply was 1.0 V unless otherwise noted (BK Precision, CA). This relatively high voltage was used to produce high current densities to achieve rapid ion separation. High applied voltages (≥1.0 V) have previously been used in other bioelectrochemical studies to achieve high rates of chemical production [16,32]. Electric current in the reactor was determined by measuring the voltage drop across an external 10 Ω resistor using a multi-meter (Keithley Instruments, OH). Current densities were normalized using the IEM area (7 cm², equal to the cathode projected area). Anode potentials were also recorded using Ag/AgCl reference electrodes (RE-5B, BASI, IN). All experiments were performed in a constant temperature room at 30 °C.

2.4. Efficiencies and recoveries

The Coulombic efficiency (CE) is the fraction of electrons transferred to the anode among the total electron released by substrate oxidation and calculated [33] as

\[
CE = \frac{8 \int dt}{F V_{el} \Delta COD}
\]

where i is the electric current, F Faraday’s constant, Vel the electrolyte volume (60 mL), and ΔCOD the removed COD.

The cathodic H₂ recovery (rcat) represents the contribution of the mole-H₂ evolution (n_H₂) to the total cathodic charge transfer [34] as

\[
rcat = \frac{2 n_H^2 F}{\int dt}
\]

The overall H₂ recovery (r_H₂) was determined by r_H₂ = r_cath, indicating the ratio of the produced H₂ to the removed organic matter on the basis of electrons. The volumetric H₂ production rate (Q_H₂, m³-H₂/m³-Vol/day) was calculated based on the observed maximum current (i max) and cathode recovery (r_cath) at P = 1 atm and T = 298 K as [34]

\[
Q_H^2 = \frac{r_{cath} i_{max} RT}{2V_PPF}
\]

The H₂ yield (Y_H₂, mole-H₂/mole-COD) shows the molar ratio of H₂ production to COD removal as [34]

\[
Y_H^2 = \frac{32 n_H^2}{V COD}
\]

The energy recovery from supplied electricity (r_E) is the combustion energy (ΔH) of the produced H₂ normalized by the energy provided from the power supplier as shown in Eq. (5). The overall energy recovery includes the energy provided as substrate (s) as shown Eq. (6) [34].

\[
r_E = \frac{\Delta H_H^2 n_H^2}{E_{ap} \int dt}
\]

\[
r_{E,S} = \frac{\Delta H_H^2 n_H^2}{E_{ap} \int dt + \Delta H_H n_s}
\]

2.5. Ion-exchange membrane permselectivity

Fresh IEMs and used IEMs in the MSC for three months were examined for their permselectivity. With ideal cation-exchange membranes, for instance, the permselectivity equals unity and decreases as the membrane allows anionic transport. The permselectivity (Ψ) was determined by measuring the electric potential difference (ΔΨ) between 1.0 and 0.5 M KCl solutions that are separated by an IEM [35] using

\[
Ψ = \frac{ΔΨ}{15.8 \text{ mV}}
\]

3. Results and discussion

3.1. Ionic separation and current generation in three-chamber reactor

Ionic separation from the saline medium, based on changes in conductivities (initially ~40 mS/cm), was successfully achieved with salt removals of up to 84% (Fig. 2). The extent of salt removal was improved by 21 to 79% by increasing the initial concentration of sodium acetate from 2 to 8 g/L (Eap = 1.0 V). This trend with the substrate concentration clearly shows that the ionic separation from the anode and cathode chambers was driven by microbial activity at the anode. For a higher applied voltage of Eap = 1.2 V, the conductivity decreased from 41 to 6.8 mS/cm, which is larger than the maximum decrease to 8.6 mS/cm using an applied voltage of Eap = 1.0 V (Fig. 2).

The concentrate waste in the middle chamber of the reactor showed a substantial increase in conductivity from 37 mS/cm to 80 mS/cm (Fig. 2). The final conductivity of the concentrate waste
in the middle chamber increased with initial substrate concentrations up to 6 g/L. This lack of further increase in conductivity of the waste chamber solution was due to osmotic water transport from the adjoining anode and cathode chambers through the IEMs, as a result of the substantial ionic concentration differences across the IEMs.

The electrical currents in the three-chamber MSC ranged between 10 and 15 mA (1.4–2.1 mA/cm²) for \(E_{ap}=1.0\) V (Fig. 3A). Increasing the applied voltage from 1.0 to 1.2 V increased the maximum current to 19.5 mA (2.8 mA/cm²), which was an increase of 4.5 mA (30%). Even with the increased \(E_{ap}\), the anode potential was stable at \(-0.43 \pm 0.01\) V (vs. Ag/AgCl), after the current reached its peak at \(-1.2\) days (Fig. 3B). The 4.5-mA increase in the current increased the Ohmic losses in the solution by \(-0.06\) V (conductivity \(=41.5\) mS/cm; average distance between the electrodes \(=3.6\) cm). Thus, the rest of the 0.14 V must have been lost as cathode overpotential. This implies that the cathode overpotential can be the rate-limiting factor for higher current operation of the system. Higher current densities mean faster ionic separation, as well as more rapid degradation of organic contaminants at the anode. Therefore, improvements in the cathode catalyst or increases in the cathode area will enhance system performance.

The relatively high current densities (1.4–2.1 mA/cm² for \(E_{ap}=1.0\) V and 2.8 mA/cm² \(E_{ap}=1.2\) V) indicate rapid ionic separation in the MSC. Current densities reported in previous MDC studies have not been greater than 0.9 mA/cm² [36]. The high current generation in the MSC is partially due to the very high ionic conductivity (~40 mS/cm) of the anode and cathode solution, which minimizes resistive losses in the solution. Thus, saline wastewater can be better treated in bioelectrochemical systems than other wastewaters that have much lower ionic conductivities.

### 3.2. Water transport through ion-exchange membranes

Water volume in the middle chamber (concentrate waste) almost doubled over a fed-batch cycle, increasing from 18 to 33.4 mL (8-g/L sodium acetate and \(E_{ap}=1.2\) V), with the amount of water transport proportional to the initial amount of the substrate (Fig. 4). Water transport is inevitable in this system as ionic separation creates a concentration difference between the concentrate waste in the middle chamber and the electrolyte in the anode and cathode chambers. This concentration difference drives osmotic water transport into the middle chamber. In addition, the movement of ions in the nano-scale channels in IEMs drags water molecules in the same direction as the ion movement, transferring water into the middle chamber (electroosmosis). Thus, both osmosis and electroosmosis contributed to increasing the water volume in the middle chamber.

Water transport into the middle chamber reduces treated water recovery in the anode and cathode chambers, and increases the volume of concentrate waste in the middle chamber. Thus, the extent of water transport needs to be minimized during saline wastewater treatment. In order to try to minimize the osmotic water transport, the applied voltage was increased from \(E_{ap}=1.0\) to 1.2 V. This higher voltage reduced the fed-batch cycle time from 2.6 to 2.3 days. However, water transport was increased from 14.6 to 15.4 mL (Fig. 4). This result...
implies that the electroosmotic water transport was the dominant contributor to water transport, even though its contribution was not separately examined in this study.

3.3. Hydrogen production

Hydrogen production increased from 61 to 338 mL per cycle, in proportion to the increase in sodium acetate concentration from 2 to 8 g/L (Fig. 5A). Carbon dioxide or oxygen was not detected in the gas, indicating that there were no leaks into the reactor. As 2-bromoethanesulfonate was occasionally added in the medium for sodium acetate concentrations 6 g/L and higher, methane contributed less than 4% of the total gas generated in the reactor for these conditions, resulting in very high cathode recoveries ($r_{\text{cat}}$ of 95–100%, Fig. 5B). The Coulombic efficiency was also high (~100%) and thus the overall H$_2$ recovery ($r_E$) was identical to the cathode recovery ($r_{\text{cat}}$). However, for cycles where 2- or 4-g/L sodium acetate was added without 2-bromoethanesulfonate, there was substantial methanogenic activity which reduced the cathodic recovery ($r_{\text{cat}}$ of 60–70%, Fig. 5B). Even with substantial methanogenesis (2- and 4-g/L sodium acetate), Coulombic efficiencies were very high (~100%), implying that the methanogenic activities were mainly hydrogenotrophic and not acetoclastic. If acetoclastic methanogenesis had been dominant, the Coulombic efficiency would have been lower. In batch cycles with 6- and 8-g/L sodium acetate, hydrogen yields were very high (>1.95 mole-H$_2$/mole-COD) as methanogenesis was inhibited by 2-bromoethanesulfonate (not shown). The maximum hydrogen production rate ranged from $Q_H = 2.7$ to $3.6$ m$^3$-H$_2$/m$^3$-electrolyte/day for the batch cycles with 6- and 8-g/L sodium acetate ($r_{\text{cat}} = 97.6$; $i_{\text{lim}} = 15–20$ mA). The energy recovery from the applied electric energy ($r_E$) was 140–171%, and the overall energy recovery from the supplied electricity and substrate ($r_{E+S}$) ranged 52 to 60% (Fig. 5B). However, these parameters decreased by up to 50% for the fed-batch cycles with 4-g/L sodium acetate due to methanogenesis in the absence of 2-bromoethanesulfonate.

3.4. COD removal

COD removals decreased from 94 to 72% with increasing substrate concentration (Fig. 5B). Since the influents and effluents were always neutral with a pH = 6.8 ± 0.1, the substrate was present primarily as anionic acetate (pKa of acetic acid = 4.8). The anionic acetate in the cathode chamber can pass through the AEM into the middle chamber. This substrate loss through the AEM can explain the decrease in COD removal with increased substrate concentrations. At the end of the fed-batch cycles with the high sodium acetate concentrations (6 and 8 g/L), most of the residual COD (18 to 24% of the initial COD) was observed in the concentrate waste, while only 1–4% of the initial COD was measured as residual in the anode and cathode chambers.

The periodic recirculation of solutions between the anode and cathode chambers successfully limited changes in electrolyte pH, as previously described [19]. The low COD residuals in the anode and cathode chambers (i.e., 1–4% of the initial COD) indicated that the MEC performance was not limited by pH imbalances, as incomplete COD removals were previously reported with low anolyte pH [10]. The successful control of pH in this study implies that the periodic recirculation will be especially useful for treating wastewaters with low pH buffering capacities.

3.5. IEM integrity after three-month operation

New IEMs had permselectivities of $\Psi = 0.97 ± 0.04$, which agrees well with the permselectivity given by the manufacturer of $\Psi > 0.96$ [37]. The permselectivities of the IEMs after three months of operation were $0.96 ± 0.06$. This comparison indicates that three months of operation did not impair the permselectivities of either CEMs or AEMs. During this three-month period of operation, the membranes were not either physically or chemically cleaned. When the IEMs were taken out from the reactor after three months, the AEM appeared clean based on the absence of visible biofilms. Thin biofilms (~1 mm) were observed on the both sides of the CEM, but they readily detached from the membrane surface when the membrane was rinsed with a NaCl solution. These findings demonstrate the biological reactor does not impose an aggressive environment for the IEM integrity even with high organic concentrations and microbial activity by exoelectrogens and other anaerobic microbes such as methanogens.

3.6. Effects of salinity on anode bacteria

During a single-chamber MEC experiment, exoelectroactive microorganisms generated current with saline solutions of up to 36 g/L of TDS (25 g/L NaCl; 7.2 g/L phosphate buffer medium; 4 g/L sodium acetate) (Fig. 6). This result indicates that the exoelectrogens were capable of generating current at the maximum capacity possible in this system at salinities typical of seawater (~35 g/L TDS). However, at 41 g/L TDS, exoelectroactive activity was impaired, as there was a gradual decrease in current, and at 46 g/L TDS, the maximum current decreased to less than 4.1 mA (Fig. 6). This high salinity condition for 9 days permanently damaged the exoelectrogenic bacteria at the anode as the current remained low in subsequent fed-batch cycles with only 21 g/L TDS (Fig. 6).

The two MECs operated as duplicates showed slightly different responses to the increasing salinity. The current in MEC-1 was always higher than that in MEC-2 (Fig. 6). At TDS = 36 g/L, the maximum current in MEC-1 was constant (19.8 to 19.9 mA) over three consecutive cycles. However, MEC-2 showed a gradual decrease in the maximum current from 16.2 to 14.7 mA under the same conditions. This difference between the MECs was more pronounced in the cycles that followed at TDS = 41 g/L: the current was 15.4–17.9 mA in MEC-1, and 8.5–11.4 mA in MEC-2. In addition, when the salinity was reduced from 46 to 21 g/L TDS, the maximum current in MEC-1

![Fig. 5.](image-url)
was 6.5 mA which was 33% of the maximum current (19.9 mA) before the anode was damaged by the high salinity. However, the recovered maximum current in MEC-2 was 4.4 mA, which was only 25% of the maximum current (17.3 mA) before the anode was damaged (Fig. 6). The lack of replication on the effects of salinities shows that there were slight differences in the performance of the biofilms that developed in the reactors in response to increases in salinity. This finding suggests that it might be possible in the future to develop exoelectrogenic biofilms more resistant to the higher salinities through extensive pre-acclimation to high salinities.

4. Conclusions

The microbial salinity-reduction electrolysis cell (MSC) developed here can be used to simultaneously remove organic matter and salt from saline wastewaters. Exoelectrogenic bacteria at the anode degraded 72–94% of the COD. The conductivity of the anode solution was decreased by up to 84% with the middle waste chamber doubling in conductivity by the end of the fed-batch cycles. The Coulombic efficiencies were very high (~100%) indicating a lack of substrate losses to aerobic microbes due to oxygen leaks. Hydrogen gas was produced at a rate of \( Q_{\text{H}_2} = 3.6 \text{ m}^3\text{H}_2/\text{m}^3/\text{d} \) (sodium acetate = 8 g/L; \( E_{\text{flm}} = 1.2 \text{ V} \)), although this was reduced in the absence of 2-bromoethanesulfonate due to methanogenesis. High Coulombic efficiencies in the absence of 2-bromoethanesulfonate indicated that hydrotrophic methanogens were the predominant source of methane.

Water transport through IEMs was found to decrease not only the rate ofionic separation but also the volume of treated water that was recovered. Water recovery decreased from 71 to 57% when conductivity removals increased, creating greater water losses by both osmosis and electroosmosis.

The IEM integrity was investigated under high microbial activities and organic contents because high IEM costs can be a limiting factor for practical applications of the suggested system [35]. Over the three-month operation, there was no noticeable reduction in the permeability of either the AEM or CEM. Also, there was no physical deterioration on the membrane surface, and biofilms developed on the CEM surface were easily removed by rinsing the membrane. Even though further tests are necessary, our results indicate that the microbes, including the exoelectrogens in this system, do not create an environment that adversely affects IEM integrities.

The key to successful treatment and salinity removal in this system is good performance of the microbial communities at different wastewater salinities. Exoelectrogens were found to be versatile at salinities as high as those of typical seawater. However, salinities above 41 g/L TDS reduced current generation, and very high salinities (46 g/L TDS) permanently damaged the exoelectrogenic activities of the anodes as reducing the salinities could not restore current generation to the previous levels. However, the different responses of the replicate reactors to higher salt concentrations suggest that greater tolerance to high salinities might be possible through extended acclimation of the biofilms.

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**References**


