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Sequential Electrolysis and Reverse Osmosis to Improve Arsenic Removal from Water

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Abstract
Reverse osmosis (RO) typically removes >98% arsenate (As[V]) but removes arsenite (As[III]) comparatively poorly (approximately 50%–80%). Therefore, oxidizing As(III) to As(V) can improve arsenic removal using RO. In this study, electrolytic oxidation was used to oxidize As(III) in the feed water, and an extreme low-pressure RO membrane was subsequently used to remove the arsenic. Using Ti/IrO₂ electrodes under 30 mA DC current in 500 mg/L NaCl solution primarily generated free chlorine, which completely oxidized 300 μg/L As(III) to As(V). Subsequent arsenic removal by RO increased from 54.2% without oxidation to 98.2% with oxidation. Using electrolysis-RO, arsenic removal significantly increased beyond RO alone, even in the presence of ferrous iron and natural organic matter. When sulfide and As(III) are present in water, they react to produce thioarsenate ions, the formation of which increased As(III) removal to 90% without electrolytic oxidation and electrolytic oxidation did not improve arsenic removal beyond these levels.
1 INTRODUCTION

Today, more than 150 million people face arsenic contamination in their drinking water (Bhowmick et al., 2018; Mandal, 2002; Sarkar & Paul, 2016). Guidelines for drinking water quality set by the World Health Organization (WHO) recommend a maximum allowable concentration of 0.01 mg/L arsenic based on health concerns (WHO, 2008). In the US, the Environmental Protection Agency (EPA) reduced the Maximum Contaminant Level (MCL) of arsenic in drinking water from 0.05 to 0.01 mg/L in 2012 (EPA, 2012). The form of the arsenic present can substantially influence its removal during drinking water treatment. Commonly used arsenic removal technologies include ion exchange, sorption, oxidation, coagulation, and particle removal (e.g., granular filtration), and membrane filtration using nanofiltration or reverse osmosis (RO) (Duarte et al., 2009).

An RO membrane consists of a thin film with a charged surface and an average pore radius between 0.2 and 0.3 nm (typical range of 0.1–0.5 nm, as measured by positron annihilation spectroscopy) (Dolar et al., 2011; Fujioka et al., 2015; Shimazu et al., 2000). Thus, RO contaminant separation mechanisms depend on a combination of size exclusion and charge exclusion. Although “pores” can be somewhat ambiguous for RO membranes, this relatively simplistic parameter can provide one means of helping to explain the phenomenon of how solutes pass through RO membranes. Specifically, solutes larger than the pore size will be blocked by the membrane, while the removal effectiveness of solutes smaller than the pore size is influenced by the solute’s molecular size, conformation, and charge (Fujioka et al., 2015; Tu et al., 2011). Uncharged solutes are rejected by sieving or steric hindrance, whereas the rejection of charged solutes is mainly controlled by charge exclusion (Malae & Ayoub, 2011).

Accordingly, the effectiveness of arsenic removal by RO membranes depends on the species present. Specifically, arsenate (As(V)) removal by RO membranes is higher compared to arsenite (As(III)) at circumneutral pH (Geucke et al., 2009), which can result in poor arsenic removal using household RO systems (Walker et al., 2008). Arsenite is a weak acid (pKa1 = 9.1), with more than 92.6% present in a neutral form when the water pH is less than 8. Alternately, As(V) forms ions at neutral pH (pKa1 = 2.19), and is therefore rejected by negatively charged membranes due to electrostatic repulsion (Yoon et al., 2009). To increase As(III) removal, increasing the pH of the RO feed water can shift As(III) toward ionized species (Kang et al., 2000). Alternately, As(III) can be oxidized to As(V) to increase arsenic removal by RO treatment (Košutić et al., 2005; Ning, 2002).

The oxidation–reduction potential (ORP) of As(III) to As(V) is 0.56 V. Thus, common disinfectants such as free chlorine, potassium permanganate, and ozone are able to oxidize As(III) (Khuntia et al., 2014; Sorlini & Gialdini, 2010). While a disinfectant could be added to improve household RO arsenic removal, most oxidation processes need special chemical dosing equipment to inject and mix the liquid oxidant into the feed water or need an extra filter containing solid MnO2 oxidizing media (Feenstra et al., 2007). Similar chemical injection/mixing would be needed for pH adjustment. These extra operations may be logistically difficult for small or remote systems. Alternately, electrolytic oxidation can be used to generate oxidants in-situ without chemical dosing, thereby avoiding the design and operation of a complicated dosing system or an extra filter (Kraft, 2008).

Compared with conventional oxidation processes, electrolytic oxidation is a compact, easy-to-operate process (Sirés et al., 2014), making it a suitable pretreatment for RO, especially for small RO systems. Electrolytic oxidation, also called anodic oxidation, is an electrochemical reaction in which an anode and cathode are placed in an electrolyte solution. When an electric current is passed through the electrodes, oxidation occurs at the anode and reduction occurs at the cathode. During electrolytic oxidation, several different oxidants may be generated, including free chlorine and reactive oxygen species (ROS). Titanium iridium oxide (Ti/Ir2O)-coated electrodes can generate free chlorine more effectively compared to other electrode materials (Bergmann et al., 2009; Bergmann & Koparal, 2005; Jeong et al., 2009; Martínez-Huitle & Brillas, 2008; Oliveira et al., 2007).
When chloride ions are present in water, electrolysis can oxidize them to diatomic chlorine, which then reacts with water to generate HOCl (Tribus & Evans, 1962). Electrolytic oxidation has not yet been applied in large-scale water treatment, but research has shown its potential in wastewater treatment (Chen, 2004; Feng et al., 2003; Seo et al., 1966) and pretreatment of RO to remove organics from feed water (Bhaskar Raju et al., 2009).

The overarching goal of this study was to evaluate the feasibility of improving arsenic, particularly As(III), removal using RO by pretreating the water with Ti/Ir2O electrolysis to oxidize As(III) to As(V). The electrolysis-RO system was evaluated to: (1) demonstrate the feasibility of using electrolysis pretreatment to improve As(III) removal using RO membranes, (2) identify the oxidant driving the process, and (3) assess performance as a function of variable water quality in the context of several typical groundwater parameters (chloride, sulfide, ferrous iron, and natural organic matter [NOM]).

2 MATERIALS AND METHODS

2.1 Experimental setup

As shown in Figure 1, the experimental system included a feed water tank, booster pump (AR-600, A.O. Smith, China), the electrolysis module (powered by adjustable power supplies [1617A, BK Precision USA]), and a cross-flow membrane testing cell. The current was monitored using a current meter (560A, EXTECH, USA).

The electrolysis module consisted of two parallel, horizontally arranged electrodes (4-cm active length, 1.5 mm diameter, MAGNETO Special Anodes B.V., Suzhou, China) spaced 5 mm apart. The electrodes were composed of a titanium base with an iridium dioxide coating, and 188 mm^2 contact area per electrode. Feed water passed through the module perpendicular to the electrodes. The complete retention time starting from the electrolysis module to the entrance of the RO membrane testing cell was 4 s. The system was operated using direct current applied at levels ranging from 0 to 40 mA (charge loading rate from 0 to 12 C/L-min). System voltage varied in response to the set current and conductivity in the water matrices tested.

The cross-flow membrane testing cell consisted of a membrane fixed between the upper and lower cell casings, with an active membrane area of 48 cm^2 (4 cm × 12 cm). An XLP (extreme low-pressure) polyamide thin-film RO membrane (Dupont, MN, USA) was selected for use as it is a high flux (average 1.8 m/d), extreme low-pressure (125 psi for 2000 mg/L NaCl feed concentration), negatively charged RO membrane suitable for drinking water treatment, particularly for household point-of-use operation. The pressure was applied at 90 psi to drive the feed water through the membrane. The feed flow was 120 mL/min, the surface velocity of the membrane was approximately 5.0 cm/s, and the membrane recovery was 3.5%. Each pristine membrane sheet was soaked in deionized (DI) water for 12 h prior to installation in the testing cell. The membranes were flushed with DI water for 2 h at 60 psi, then operated at 500 mg/L NaCl solution and 95 ± 5 psi for 60 min to precondition them prior to experimentation.
2.2 Test water formulation and reagents
All test solutions were prepared in DI water spiked with 300 µg/L of either As(III) (Na$_3$AsO$_3$, Ricca Chemical Company) or As(V) (Na$_3$AsO$_4$·7H$_2$O, Sigma Aldrich). Total dissolved solids (TDS) were added at 500 mg/L using NaCl or MgSO$_4$·7H$_2$O (Sigma Aldrich). The pH was adjusted using NaOH, HCl, or NaHCO$_3$ (Sigma Aldrich). In independent tests assessing the impact of water quality on the electrolysis-RO process, 1.0 mg/L ferrous (FeCl$_2$, Sigma Aldrich), 1.5 mg/L sulfide (Na$_2$S, Sigma Aldrich), or 2.2 mg/L total organic carbon (TOC) (humic acid, MP Biomedicals LLC) were added to the solution.

2.3 Analytical
The permeate and feed samples were analyzed using an inductively coupled plasma mass spectrometer (Agilent ICP-MS 7700) to test arsenic. TDS and pH were measured by a TDS meter (Myron L Company Handheld TDS meter 4P) and a pH meter (Thermo Scientific Star A214), respectively. Ferrous, total ferric, sulfide, and free chlorine were analyzed colorimetrically using a UV spectrophotometer (Hach RD-6000). TOC was analyzed using a Skalar CA16 TOC analyzer. Tertiary butanol, used as an oxidant quencher, was measured using a GC–MS (Agilent GC–MS 5973).

2.4 Statistics and QA/QC
All experiments were conducted in at least triplicate. Removal of arsenic was calculated as follows:

\[
\text{Removal (\%)} = \left(1 - \frac{C_p}{C_f}\right) \times 100\%,
\]

where $C_p$ and $C_f$ are the solute concentrations in the permeate and feed, respectively. Because ICP-MS can only measure total arsenic, without differentiating between As(III) and As(V), all arsenic measured in this study was total arsenic.

Comparisons of arsenic removal among tests were performed using t-test (Microsoft Excel), one-way ANOVA, or two-way ANOVA (GraphPad Prism) ($\alpha = 0.05$). For significant differences, Tukey post hoc analysis was performed following ANOVA tests (GraphPad Prism). After each experiment, the test water was drained from the system, and 10 L DI water was used to perform two flushes of the system for at least 15 min at 90 psi to clean the system and membrane sheets. Once chemicals were added to the feed water at the start of each experiment, the system was allowed to stabilize for 60 min prior to collecting samples.

3 RESULTS AND DISCUSSION
3.1 Feasibility of As(III) oxidation by electrolysis to improve arsenic removal by RO membranes
Experiments were initially performed to quantify As(III) and As(V) removal by RO membrane treatment without electrolytic oxidation pretreatment as a function of water pH. Next, the electrolysis system was operated at 0, 10, 20, 30, or 40 mA current ahead of the RO membranes.

3.1.1 Arsenic removal by RO
Figure 2a shows the removal of As(III) as a function of feed water pH, with removal increasing from 40.3% at pH 6.0 to 96.7% at pH 10.9. Arsenite removal was steady between 38.7% and 46.1% below pH 8.65. At higher pH levels, As(III) removal improved significantly ($p \leq 1.3E-5$) at each sequential pH value tested. These increases in removal coincided with the pH exceeding the acid dissociation constant ($pK_{a1} = 9.1$), when the majority of As(III) species shifted to dihydrogen arsenite ions. For these ions, charge exclusion dictates As(III) removal.
FIGURE 2 (a) Arsenite (As(III)) and (b) arsenate (As(V)) removal using an XLP RO membrane as a function of feed water pH. Values are the means of triplicate experiments with error bars showing ±1 standard deviation. Some error bars are not visible due to the small standard deviation. The theoretical fraction of dissociated As(III) or As(V) (calculated using equilibrium relationships) is shown on the secondary y-axes.

Beyond charge exclusion, size exclusion also likely contributed to the increase in As(III) removal as pH increased. As noted previously, pore size/analysis of RO membranes may not be absolute. For example, Table 1 shows the Stokes radius \( r_s \) of arsenic species, where neutral As(III) is 0.21 nm, which is smaller than the average RO pores, but given the distribution of pore sizes, some pores may be smaller than the arsenite species, thus leading to some removal (Dolar et al., 2011). In comparison, the monovalent dissociated As(III) ion radius is larger, at 0.25 nm, thereby offering removal due to size exclusion as well as charge exclusion.

\[
T_S = \frac{kT}{6\pi\eta D_{i\infty}},
\]

(2)

Where \( k \) is the Boltzmann constant \( (1.38 \times 10^{-23} \text{J} \text{K}^{-1}) \), \( T \) is the temperature \( (\text{K}) \), \( \eta \) is viscosity \( (0.65 \times 10^{-3} \text{kg m}^{-1} \text{s}^{-1}) \), and \( D_{i\infty} \) \( (\text{m}^2 \text{s}^{-1}) \) is the diffusion coefficient of solute \( i \) in water.

TABLE 1. Diffusion coefficients and stokes radius of As(III) and As(V) species

<table>
<thead>
<tr>
<th>Arsenic species</th>
<th>Charge</th>
<th>Diffusion coefficient a</th>
<th>Stokes radius, ( r_s ) b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( 10^{-10} \text{ m}^2/\text{s} )</td>
<td>(nm)</td>
</tr>
<tr>
<td>As(III)</td>
<td>Neutral</td>
<td>11.6</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Monovalent</td>
<td>9.71</td>
<td>0.25</td>
</tr>
<tr>
<td>As(V)</td>
<td>Neutral</td>
<td>8.75</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>Monovalent</td>
<td>8.12</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Divalent</td>
<td>7.27</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Trivalent</td>
<td>6.40</td>
<td>0.38</td>
</tr>
</tbody>
</table>

a Diffusion coefficients were determined experimentally using a diffusion cell by Tanaka et al. (2013).

b Stokes radius was calculated from the Stokes-Einstein equation (Equation 2).

Figure 2b shows that As(V) was consistently removed to levels ≥99% between pH 6 and 11 (\( p > .546 \)). The pKa1, pKa2, and pKa3 values of arsenate are 2.19, 6.94, and 11.5, respectively, such that more than 98% of total As(V) is dissociated when the pH is higher than 4. These dissociated anions are repelled by the negatively charged RO membrane, resulting in high As(V) removal. Accordingly, one strategy to improve arsenic removal by RO is to increase solution pH to >10 to shift As(III) to As(V). An alternate strategy is to oxidize As(III) to As(V) prior to RO treatment, for example, via electrolysis.
3.1.2 Arsenic removal by electrolysis-RO
An electrolysis module was added ahead of the RO membrane testing cell to evaluate its potential to improve arsenic removal. When there was no current (0 mA), arsenic removal was low (54.2% ± 0.30%), but as current increased, arsenic removal increased significantly (Figure 3, \( p < .02 \), except \( p = .8 \) between 30 and 40 mA). Accordingly, 30 mA was considered to be the point of diminishing return to improve arsenic removal.

![Figure 3 Arsenic removal by electrolysis-RO at variable applied currents.](image)

3.2 Main mechanism of As(III) oxidation in the electrolysis system
Possible oxidants generated during electrolytic oxidation include free chlorine, oxygen, ozone, and ROS such as hydroxyl radicals. Oxygen is ineffective for oxidizing As(III) to As(V) (Kim & Nriagu, 2000), but the role of the other potential oxidants in oxidizing As(III) during electrolysis has yet to be established. Thus, a series of experiments was conducted to identify the dominant oxidant responsible for As(III) oxidation during electrolysis.

3.2.1 The role of free chlorine concentration in the electrolysis-RO system
Concentrations of free chlorine in the solution rejected by the membrane without As(III) present (500 mg/L NaCl initially) were 0.29, 0.82, 1.42, and 1.91 mg/L using 10, 20, 30, and 40 mA current input, respectively. According to the stoichiometric reaction of As(III) oxidized by free chlorine (Equation (3)), 0.28 mg/L Cl\(_2\) can oxidize 300 \( \mu \)g/L As(III) to As(V). Thus, the concentration of free chlorine generated in the electrolysis process with 10 mA current or higher was more than adequate to oxidize the 300 \( \mu \)g/L As(III) in the feed water.

\[
H_3AsO_3 + H_2O + Cl_2 = 3H^+ + H_2AsO_4^- + 2Cl^- 
\]

(3)

To illustrate the relationship between free chlorine and arsenic removal as a function of current, another experiment was conducted at lower current levels (0, 2, 4, 6, 8, and 10 mA). Arsenic removal and free chlorine concentration showed similar tendencies as a function of current, with arsenic removal increasing in step with increases in current and the resulting increases in free chlorine generation (Figure 4). There was no significant difference between arsenic removals at 0 and 2.12 mA (\( p = 1 \)), but removal significantly improved for all currents above 2.12 mA (\( p \leq 6.1E-6 \)).
Predicted concentrations of arsenic in the permeate water were estimated stoichiometrically based on free chlorine generation (taken from Figure 4) and the assumption that 98% As(V) was removed while 40.1% As(III) was removed (based on Figure 2). The predicted and experimental values are shown in Figure 5. Measured arsenic concentrations dropped from 176 to 20.6 μg/L (removal increased from 40.1% to 93.3%) when current increased from 0 to 9.96 mA. The experimentally measured arsenic concentrations were similar to the stoichiometrically predicted arsenic concentrations in the permeate, suggesting that free chlorine was the dominant oxidant responsible for arsenic oxidation in the electrolysis system.

3.2.2 The role of ROS in As(III) oxidation
To isolate the impact of ROS relative to free chlorine during electrolysis, the NaCl electrolyte was replaced with 500 mg/L MgSO₄ in DI water at a pH of 7.0. As shown in Figure 6, when current was applied, arsenic removal was significantly higher using NaCl versus MgSO₄ (p ≤ .0001). Further, there was no significant difference between the current-free NaCl test and any of the MgSO₄ tests (p ≥ .12), indicating that MgSO₄ offered no ROS production. As the Ti/IrO₂ electrodes used in the electrolysis module are known to efficiently generate free chlorine in NaCl solution, it makes sense that chloride (and therefore free chlorine) was closely related to As(III) oxidation.
An additional test was performed to confirm that no ROS, such as hydroxyl radicals, were generated during the electrolysis-RO process. In this test, the radical scavenger tertiary butanol (TBA) was added into arsenic-free water with 500 mg/L NaCl. While TBA does not react with free chlorine (Lee et al., 2020), its reaction rate with hydroxyl radicals is $5 \times 10^8 \text{L mol}^{-1} \text{s}^{-1}$ (Ma et al., 2006), so any ROS generated during electrolysis would be consumed by reactions with TBA. There was no statistical difference in TBA concentrations between the feed water and the 30-mA electrolysis-RO treated water ($p = .83$). Accordingly, there was no evidence that ROS was generated during electrolysis.

### 3.3 The influence of water quality on As(III) removal using electrolysis-RO

To assess how feed water quality impacted electrolysis of As(III), and subsequent arsenic removal using the RO membrane, experiments were performed at the optimal current identified previously (30 mA) using varying concentrations of chloride, sulfide, ferrous iron, and NOM.

#### 3.3.1 Chloride concentration

As shown in Figure 7, arsenic removal increased from around 45% (no current) to more than 99% with 15, 30, or 60 mg/L chloride at 30 mA electrolysis current. Electrolysis treatment significantly increased arsenic removal ($p \leq .0001$ at each chloride concentration), and there was no difference in arsenic removal using electrolysis-RO among the three chloride concentrations tested ($p \geq .32$).

The differences in the free chlorine concentrations with and without As(III) at 15, 30, and 60 mg/L chloride concentration were around 0.3 mg/L, as shown in Figure 7, which closely matched the predicted concentration of free chlorine consumed by the oxidization of As(III) based on stoichiometry. Meanwhile, the chlorine...
generation efficiency increased as chloride concentration increased (Table 2), indicating that electrolysis consumed less power with increasing chloride concentrations.

**TABLE 2. Chlorine generation efficiency during electrolysis (30 mA) for different NaCl concentrations**

<table>
<thead>
<tr>
<th>NaCl (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>Voltage (V)</th>
<th>Free chlorine (mg/L)</th>
<th>Power (W)</th>
<th>Chlorine generation efficiency (mg/min*W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>15</td>
<td>29.5</td>
<td>0.37</td>
<td>0.89</td>
<td>0.05</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
<td>18</td>
<td>0.69</td>
<td>0.54</td>
<td>0.15</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>11.2</td>
<td>0.73</td>
<td>0.34</td>
<td>0.26</td>
</tr>
<tr>
<td>500</td>
<td>300</td>
<td>4.5</td>
<td>1.42</td>
<td>0.14</td>
<td>1.26</td>
</tr>
</tbody>
</table>

3.3.2 Ratio of chloride to TDS

Figure 7 shows arsenic removal in NaCl-only solution; however, in actual application, it is rare to see feed water containing only chloride. Chloride concentrations in tap water and groundwater often account for about 10%–20% of total dissolved solids (TDS). Thus, to better understand the impact of chloride on As(III) removal using electrolysis-RO, feed waters with 500 mg/L TDS composed of NaCl and MgSO₄ with NaCl comprising 10%, 20%, or 100% of the TDS were tested. As the NaCl ratio decreased, the current input required to improve arsenic removal increased (Figure 8). To achieve ≥99% arsenic removal, 40, 100, and 300 mA were needed using 100%, 20%, and 10% NaCl, respectively.

![ArSENIC REMOVAL USING ELECTROLYSIS-RO WITH NaCl COMPRISING VARYING PERCENTAGES OF TDS](image)

**FIGURE 8** Arsenic removal using electrolysis-RO with NaCl comprising varying percentages of TDS. The feed water contained 300 μg/L As(III) and 500 mg/L TDS made with NaCl and MgSO₄, pH = 7. The values shown are the means of triplicate experiments ±1 standard deviation. Error bars are not visible due to the small standard deviations.

3.3.3 Other water quality parameters: Sulfide, ferrous, and NOM

To explore the impact of important groundwater constituents that could potentially impact electrolysis-RO, sulfide, ferrous iron, and NOM were added to the test matrix in separate tests (Figure 9).
Arsenic removal increased significantly from 38.7% to 87.7% after sulfide was added, even without electrolysis ($p \leq .001$ except $p = .44$ for the 0 and 30 mA samples with 1.4 mg/L sulfide). Thus, the presence of sulfide significantly increased As(III) removal, and electrolysis did not further improve removal. When arsenic and sulfide co-occur in water, they react to form multiple species, ranging from neutral to −3 valence species (Battaglia-Brunet et al., 2012), including thioarsenites. Thioarsenites can further react with remaining sulfide to form thioarsenate ions (O’Day et al., 2004), which are rejected by negatively charged membranes, thereby increasing arsenic removal.

Ferrous iron is a common reductant in groundwater, and Fe$^{2+}$ can compete with As(III) oxidation by consuming oxidants in the electrolysis process. As the ORP of Fe$^{2+}$/Fe$^{3+}$ is 0.2 V at pH 7, free chlorine can oxidize both Fe$^{2+}$ and As(III). The reaction rates of free chlorine with As(III) and Fe$^{2+}$ are $4.3(\pm 0.8) \times 10^3$ and $1.7(\pm 0.1) \times 10^4$ M$^{-1}$ s$^{-1}$, respectively (Deborde & von Gunten, 2008). As both reactions happen quickly, the Fe$^{2+}$ can consume part of the oxidant generated during electrolysis. As shown in Figure 9, arsenic removal was not impacted by the addition of Fe$^{2+}$ ($p = .99$), although removal increased from 38.4% to 98.2% with the addition of 30 mA electrolysis-RO ($p \leq .0015$). With the addition of current, Fe$^{2+}$ was oxidized to Fe$^{3+}$ as the concentration of Fe$^{2+}$ in the membrane reject stream dropped to 0.02 mg/L compared to the feed water concentration of 1.04 mg/L. The resulting Fe$^{3+}$ precipitates out of the solution as ferric hydroxide, which can effectively bind arsenic ions, thus decreasing arsenic in the permeate.

Both conventional oxidation, using free chlorine, and advanced oxidation processes can oxidize NOM. The reaction between NOM and free chlorine is relatively slow, with a second-order reaction rate of $0.9 \times 10^{-5}$ M$^{-1}$ s$^{-1}$ (Westerhoff et al., 2004). Alternately, the reaction between free chlorine and As(III) is extremely fast ($4.3(\pm 0.8) \times 10^3$ M$^{-1}$ s$^{-1}$) (Deborde & von Gunten, 2008); thus, free chlorine should oxidize As(III) even when NOM is present. In this study, humic acid was added to the feed water at a concentration of 2.2 mg/L TOC. With the application of 30 mA electrolytic oxidation, the average arsenic removal significantly increased from 46.8% to 93.7% ($p \leq .0034$, Figure 9). Meanwhile, arsenic removal using RO only (0 mA) was higher than removal without TOC present (46.8% vs. 40.3%, $p = .003$), potentially because the arsenic bound with the NOM to increase molecular size (Buschmann et al., 2006), and therefore As(III) removal. The feed water and the reject water had 2.2 mg/L TOC, indicating that NOM did not completely oxidize by free chlorine. Instead, NOM was blocked by the RO membrane as no TOC was present in the permeate.
4 CONCLUSIONS
Arsenite removal using an XLP RO membrane (Dupont, USA) alone was approximately 40%–54%. Using electrolysis-RO significantly improved arsenic removal, to more than 98% using 30 mA DC current in 500 mg/L NaCl solution. The improvement was associated with the electrolysis of As(III) to As(V), which is much more effectively removed using RO treatment. The main oxidant responsible for the electrolysis of As(III) was free chlorine, while no evidence was found to support the presence of other oxidants using Ti/IrO2 electrodes.

High chloride concentration increased free chlorine generation efficiency and required less power consumption to achieve the same arsenic removal using electrolysis-RO. The impact of several water quality parameters on the electrolysis-RO process was assessed. Feed water ferrous iron and NOM concentrations did not significantly impact arsenic removal in the electrolysis-RO system. However, the reaction of sulfide and arsenic can generate ionized species, which significantly improved arsenic removal using RO membranes, even without electrolysis (and application of current did not provide any additional benefit in this case).

Future research should focus on the use of different electrode materials to evaluate the role of other oxidant species and operational conditions. Additionally, arsenic removal using electrolysis-RO in complex and more realistic water matrices should be evaluated; of particular interest is high hardness feed water, wherein the risk of electrode scaling (and subsequently diminished electrode life) is higher.

AUTHOR CONTRIBUTIONS
Yizhi Hou: Conceptualization; resources; data curation; formal analysis; funding acquisition; investigation; visualization; methodology; writing – original draft; writing – review and editing. Brooke K. Mayer: Supervision; project administration; writing – review and editing.

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CONFLICT OF INTEREST
The authors declare no conflicts of interest that would otherwise impact or otherwise influence the production of this work.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES


