

An Improved Method of Arsenic (III) Removal By Reverse Osmosis Membrane

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Recommended Citation

Hou, Yizhi, "An Improved Method of Arsenic (III) Removal By Reverse Osmosis Membrane" (2017). *Master's Theses (2009 -)*. 424.
http://epublications.marquette.edu/theses_open/424

An Improved Method of Arsenic (III) Removal by Reverse Osmosis Membrane

By

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A thesis submitted to the faculty of the Graduate School,
Marquette University, in partial fulfillment of the requirements for the degree of
Master of Science and Engineering

Milwaukee, Wisconsin
August 2017

ABSTRACT
AN IMPROVED METHOD OF ARSENIC(III) REMOVAL BY
REVERSE OSMOSIS MEMBRANE

Yizhi Hou

Marquette University, 2017

Arsenic is a Group 1 carcinogen as there is abundant research to support that ingestion of arsenic in drinking water and food can lead to liver, lung, kidney, or bladder cancer in humans. The recommend World Health Organization (WHO) arsenic standard in drinking water is 10 $\mu\text{g/L}$, while the Environmental Protection Agency's (EPA) Maximum Contaminant Level (MCL) of arsenic in drinking water is 10 $\mu\text{g/L}$. Globally, at least 40 million people face more than 10 $\mu\text{g/L}$ arsenic contamination in their drinking water.

As(III) (trivalent state, such as arsenite), and As(V) (pentavalent state, such as arsenates) are the dominant arsenic forms in water. Because the pK_{a} s of arsenite and arsenate are 9.2 and 2.2, respectively, the dominant form of arsenite in natural water is as a neutral molecule, while arsenate is present in ionic form. According to previous research, removal of As(III) by RO treatment is 50 to 80%, but more than 98% As(V) is removed as the dissociated arsenate ions are amenable to removal by RO. Therefore, oxidizing As(III) to As(V) can improve arsenic removal by RO membranes.

In this study, electrolytic oxidation was used to oxidize arsenite in the feed water, and then arsenic removal using RO membrane was measured. The use of electrochemical pretreatment ahead of RO membranes has not been explored deeply, and no existing studies address the feasibility of electrolytic oxidation to improve arsenic removal by RO membranes.

The results of this study showed that electrolytic oxidation using Ti/IrO_2 electrodes under 30 mA DC current in 500 mg/L NaCl solution can completely oxidize 360 $\mu\text{g/L}$ As(III) to As(V) in 10 seconds. The subsequent arsenic removal by RO membranes increased from 54.2% (without oxidation) to 98.2%. The main oxidant generated in the electrolytic oxidation process was free chlorine. Using combined electrolysis-RO, the arsenic removal significantly increased beyond RO alone, even in the presence of ferrous and alkalinity and natural organic matter. The presence of sulfide impacted the As(III) form in water, producing ionic species, which increased the As(III) removal to close 90% without electrolytic oxidation.

ACKNOWLEDGEMENTS

Yizhi Hou

First I would like to appreciate Marquette University Civil and Environmental Engineering to accept my application to be one of the members of Marquette University and Environmental Department. Secondary, I would like to thank my employer, A.O. Smith Corporation, for the support. A.O. Smith generously provided the location, laboratory, equipment, and materials for the founding of this project. And also thanks to Dr. Fei Zhang, the testing engineer in A.O. Smith and Mr. Jeff West, a lab technician at A.O. Smith, for his help to finish some experiments. Finally, I would like to express gratitude for the instruction from my advisor, Dr. Brooke Mayer, who helped me to complete this project with her professional knowledge and serious research attitude, and spent so much time to amend my thesis.

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1. INTRODUCTION

Today, more than 40 million people are facing arsenic contamination in their drinking water, including people in India, Bangladesh, Vietnam, China, USA, Mexico, Chile, Hungary, Poland, and New Zealand (Mandal, 2002; Nordstrom, 2002). Guidelines for drinking-water quality set by the World Health Organization (WHO) recommend a maximum allowable concentration of 0.010 mg/L for arsenic based on health concerns (WHO, 2004b). In the US, the Environmental Protection Agency (EPA) reduced the Maximum Contaminant Level (MCL) of arsenic in drinking water from 0.05 mg/L to 0.01 mg/L in 2012 (EPA, 2012b). While arsenic regulations typically focus on total arsenic, arsenic can be present in a number of forms.

Arsenic can exist in many different chemical forms, including inorganic or organic, in combination with other elements. Inorganic arsenic exists in three main valence or oxidation states: As(0) (metalloid arsenic, 0 oxidation state), As(III) (trivalent state, such as arsenite), and As(V) (pentavalent state, such as arsenates). The form of arsenic present can substantially influence its removal potential during drinking water treatment.

Commonly used arsenic removal technologies include ion exchange, adsorption, oxidation, coagulation, filtration and membrane treatment (Duarte, Cardoso, & Alçada, 2009). Membrane treatment, especially reverse osmosis (RO) membrane treatment, is increasingly popular in small water treatment devices (Gholami, Mokhtari, Aameri, & Alizadeh Fard, 2006). Compared to other water treatment technology, RO membranes are the only process which can simultaneously remove organics, inorganics, bacteria, viruses, particles, and dissolved ions. However, some research has shown the arsenic removal

efficiency by RO membranes is low, especially when arsenite is the dominant form in water (Walker, Seiler, & Meinert, 2008). Other research showed that removal of arsenite by RO was significantly impacted by pH, but arsenate removal was consistently high throughout the pH range (Kang, Kawasaki, Tamada, Kamei, & Magara, 2000). Hence, increasing pH or oxidizing arsenite to arsenate might be an effective means to improve arsenic removal efficiency by RO membranes. However, to increase arsenite removal by RO membranes, the feed water pH has to increase from 7 to 11, meaning that 400 g NaOH will be added into 1,000 L water according to the theoretical calculation. Thus, with the added concern of operating cost and water quality change, pH adjustment is not necessarily an optimal choice, whereas oxidation is a promising alternative for improved arsenic removal.

Electrolytic oxidation offers some advantages in water treatment compared with traditional treatment methods. Electrolytic oxidation can be used in wastewater treatment and drinking water treatment to remove heavy metals and organics and to disinfect water (Chen, 2004; Marshall & Vol, 1945; Panizza & Cerisola, 2004). By applying an electric field between an anode and cathode in water, free chlorine, oxygen, ozone, and/or hydroxyl radicals can be generated, depending on the operating conditions and electrode material. Compared with conventional oxidation processes, such as addition of manganese dioxide or hypochlorous acid, electrolytic oxidation is a compact process, and easy to operate (Sirés, Brillas, Oturan, Rodrigo, & Panizza, 2014), making it a suitable pretreatment for RO membrane operations, especially for small RO systems.

2. RESEARCH OBJECTIVES

The primary goal of this study was to evaluate the feasibility of improving arsenic removal using reverse osmosis (RO) by pretreating the water with electrolysis to oxidize arsenite. The electrolysis-RO system was evaluated via three specific objectives, which defined the main research directions.

2.1 Use a novel nanofiltration-based approach to arsenic species differentiation to demonstrate improved As(III) removal using the electrolysis-RO membrane system

The first objective of the research was to demonstrate the feasibility of using electrolysis pretreatment to improve arsenite removal using RO membranes. Previous research has shown that As(III) removal by RO membranes is not effective, but oxidation of As(III) to As(V) can increase arsenic removal (Košutić, Furač, Sipos, & Kunst, 2005) .

The hypothesis was that electrolytic oxidation would be able to generate sufficient oxidants to oxidize As(III) to As(V) in water, and that this would increase the arsenic removal since As(V) forms larger, hydrated ions that can be better removed via RO.

Since the oxidation of As(III) to As(V) is a rapid process, an approach to immediately differentiate between the two arsenic species in the system was developed for use in this study. A nanofiltration (NF) membrane was used to identify As(III) and As(V), and this approach was validated as part of this objective.

2.2 Elucidate the extent of As(III) oxidation during electrolysis, and the primary responsible oxidant

The second objective of the research was to assess the extent of electrolytic oxidation under experimental conditions, and to identify the oxidant species primarily responsible for the process.

The hypothesis was that the Ti/IrO₂ electrodes would generate free chlorine from the chloride initially present in the water, and that this would primarily drive the oxidation of As(III), while hydroxyl radicals could contribute to the reaction.

2.3 Evaluate the impact of operational and water quality parameters on As(III) removal in the electrolysis-RO system

The final objective of the research was to evaluate the impact of water quality on arsenite removal using an RO membrane with electrolysis pretreatment. Several parameters which might impact arsenite oxidation and removal by RO membranes, including chloride ion concentration, ferrous ion concentration, sulfide concentration, pH, alkalinity and presence of organic matter were included in tests to evaluate their influence on the efficacy of arsenic removal.

Chloride ions can impact the generation of free chlorine, which could impact oxidation. Ferrous ion is a common reductant in groundwater, and ferrous ions can compete with arsenite oxidation by consuming oxidants in the electrolysis process. Sulfide is commonly present in groundwater, and sulfide and arsenic can form sulfarsenide, and change the reaction conditions of arsenite oxidation. Alkalinity, pH, and

organic matter also can impact arsenic oxidation; thus, it is important to know how these parameters impact the arsenite oxidation rate and arsenite removal by RO membranes.

3. LITERATURE REVIEW

3.1. Arsenic: its forms and prevalence in water

Arsenic is an element which has chemical and physical properties intermediate between a metal and nonmetal; it is often referred to as a semi-metal. Arsenic belongs to Group VA of the Periodic Table, and its main oxidation states are 0, +3 and +5. Arsenite (As(III)) and arsenate (As(V)) are the predominant oxidation states, (WHO, 2004a). Arsenite can be oxidized to arsenate at high pH, and arsenate can be reduced to arsenite at low pH. Generally, groundwater contains arsenite under anaerobic condition (Feenstra & Erkel, 2007).

Arsenic ranks 20th in abundance in the earth's crust, where the concentration is about 1.0 to 1.8 mg/kg (Matschullat, 2000). In soil, the arsenic concentration is about 0.1 to 40 mg/kg (Baker & Chesnin, 1975). This naturally present arsenic dissolves into water as water flows through soil and ore containing arsenic (Criaud & Fouillac, 1989).

Unlike most cations, such as Pb^{2+} , Cd^{2+} , and Hg^{2+} , arsenic forms a weak acid or anion in water. The background concentration of dissolved arsenic in natural water most often varies between 0.1 to 5 $\mu\text{g/L}$ (Matschullat, 2000), but the range of arsenic in natural water is large: from less than 0.5 to 5,000 $\mu\text{g/L}$ (Smedley & Kinniburgh, 2002). This is especially true in groundwater, where arsenic is a common contaminant found around the world. In addition to arsenic's natural occurrence in the earth's soil, it can enter water due to human activities. Historically, arsenic was widely used in agriculture, medical applications, alloy industry, etc. The toxicity of arsenic to insects, bacteria, and fungi led to its use as a wood preservative. It was also used in various agricultural insecticides and

poisons. For example, lead hydrogen arsenate was a common insecticide used on fruit trees (WHO, 2004a).

For perspective, several examples of locations with high concentrations of arsenic are listed following:

- In Calcutta India, the arsenic concentration in groundwater is 50 to 23,800 $\mu\text{g/L}$ (Chatterjee, Das, & Chakraborti, 1993).
- In Bangladesh, the arsenic level in groundwater is 10 to more than 1,000 $\mu\text{g/L}$ (Dhar, 1997).
- In Vietnam, arsenic levels in rural groundwater samples from private wells are 1 to 3,050 $\mu\text{g/L}$ (Berg et al., 2001).
- In southwest Finland, the arsenic level in groundwater is 17 to 980 $\mu\text{g/L}$ (Kurtio, Komulainen, Hakala, Kahelin, & Pekkanen, 1998).
- In Taiwan, many wells contain more than 50 $\mu\text{g/L}$ arsenic, and some samples are higher than 300 $\mu\text{g/L}$ (Chen & Lu, 2010).
- In Canada, arsenic levels in lakes near Yellowknife are 700 to 5,500 $\mu\text{g/L}$, and groundwater arsenic levels are 50 to 100,000 $\mu\text{g/L}$ (Wang & Mulligan, 2006).

Unfortunately, many people are not aware of the hazard posed by arsenic in drinking water, or they cannot afford arsenic removal equipment, especially in developing countries. In Bangladesh and West Bangla, more than 40 million people currently drink water with arsenic concentrations greater than 10 $\mu\text{g/L}$ (Harvey et al., 2006; Ng, Wang, & Shraim, 2003). People in Vietnam, China, Mexico, Chile, Hungary, Poland, and other countries are also facing threats from arsenic in drinking water (Mandal, 2002). Even in developed countries, the situation is not positive. More than 2.5 million

people in the US are served by water sources containing more than 25 $\mu\text{g/L}$ arsenic (Smith et al., 1992).

3.2. Harmfulness of arsenic in drinking water

Naturally occurring sources of human exposure to arsenic include volcanic ash, weathering of minerals and ores, and water. Arsenic is also found in food, soil, and sediment (Table, 2004). The main arsenic intake routes for humans are from consumption of food and drinking water. The daily intake of arsenic from foods and beverages is about 20 to 300 $\mu\text{g/day}$ (WHO, 2004a). The World Health Organization (WHO) arsenic guideline suggests that arsenic intake is no more than 2.1 $\mu\text{g/kg}$ body weight per day (WHO, 2010).

Normally, the average daily arsenic intake from drinking water is less than 10 μg , but in those areas where drinking water contains high concentrations of arsenic, arsenic intake from drinking water will increase significantly (WHO, 2004). Hence, controlling levels of arsenic in drinking water can make a big difference in public health protection.

In humans, the gastrointestinal tract can absorb 60 to 90% of the soluble forms of ingested arsenic. Arsenic can affect many human body systems, including cardiovascular, neurologic, dermal, hematopoietic, and reproductive. Arsenic can cause acute toxicity, chronic toxicity and carcinogenicity. Additionally, positive associations between arsenic in drinking water and spontaneous abortion, stillbirth, low birth weight, and neonatal and infant mortality have been shown (Quansah et al., 2015). Ingesting high volumes of arsenic may even lead to death in healthy adults.

Arsenic expresses its toxicity by inactivating cellular enzymes, especially those enzymes related to cellular energy pathways and DNA synthesis and repair (Ratnaike,

2003; Shi, Shi, & Liu, 2004). The 50% lethal dose (LD_{50}) of arsenite and arsenate in mice is 8 and 22 mg As /kg weight, respectively (Hughes, 2002). Acute arsenic poisoning is initially associated with nausea, vomiting, abdominal pain, and severe diarrhea. Chronic arsenic toxicity results in multisystem disease (Yoshida, Yamauchi, & Fan Sun, 2004).

Arsenic is also a carcinogenic chemical, and it can lead to skin, liver, lung, kidney, or bladder cancer (Alert, 2006; Chen, Chen, Wu, & Kuo, 1992). The International Agency for Research on Cancer (IARC) has classified arsenic and arsenic compounds as Group 1 carcinogenic matter to humans (WHO, 2010). The 10^{-4} cancer risk concentration of arsenic in water is 0.002 mg/L (EPA, 2012). For populations living at Taiwan, where arsenic levels in well water can be 170-800 $\mu\text{g/L}$, the lifetime risk of dying from the liver, lung, kidney, or bladder cancer from drinking 1 L/day of water could be as high as 13 per 11,000 persons (Smith et al., 1992).

The WHO revised the guideline for arsenic from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in 1993. In the European Union, the arsenic standard is now set at 10 $\mu\text{g/L}$ (Choong, Chuah, Robiah, Gregory Koay, & Azni, 2007). In 1975, the U.S. EPA adopted a standard of 50 $\mu\text{g/L}$ arsenic as the Maximum Contaminant Level (MCL) of arsenic in drinking water, which was set by the U.S. Public Health Service (USPHS) in 1942. At this MCL level, a risk of 1,300 cases of arsenic-related illness per 100,000 lifetimes was reported (Smith et al., 1992), while another study showed 1,650 cases per 100,000 lifetimes (Petrusevski, Sharma, Schippers, & Shordt, 2001). In the process of re-evaluating the arsenic standard in 2000, the EPA evaluated the risk posed by a MCL of arsenic in drinking water of 3, 5, 10, and 20 $\mu\text{g/L}$ (EPA, 2000), and eventually reduced the MCL for arsenic in drinking water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in 2006 (Ransom, Richland, 2013). This level accounted

for available technology and investment and operation costs in large treatment systems. However, there is still some risk associated with ingesting water even at these reduced arsenic concentrations. The estimated risk of skin cancer per 100,000 lifetimes is 3-7 skin cancer cases per 1 $\mu\text{g/L}$ of arsenic in water increase, meaning that at the 10 $\mu\text{g/L}$ MCL, there are an additional 3-7 cases of cancer per 10,000 lifetimes (Brown & Ross, 2002). To further reduce the risk from drinking water, point of use household water treatment equipment might be needed. Therefore, it is necessary to develop an affordable, highly effective, small, and lightweight device to improve arsenic removal and protect human health.

3.3. Arsenic removal methods

When treating groundwater, conventional water treatment processes can remove approximately 80-90% arsenic from raw water by using softening, coagulation and filtration (Conrad, 2013). At small water treatment systems, arsenic removals can be even lower than 80%, so even treated drinking water may still contain higher than 10 $\mu\text{g/L}$ arsenic; therefore, designing an effective arsenic removal device is important.

Generally, arsenic removal is a high cost process, especially in large water treatment facilities. In the 2000 process of re-evaluating the arsenic MCL, the EPA estimated that the costs for compliance would be \$330 million per year assuming a 20 $\mu\text{g/L}$ MCL, and \$4.1 billion per year for a 2 $\mu\text{g/L}$ MCL, making the cost of groundwater treatment higher than surface water treatment (Frey, Chowdhury, Raucher, & Edwards, Marc, 1998).

The form of the arsenic present influences removal efficiency. When present in water, As(III) and As(V) are in ionized or neutral forms, depending on the water pH. The pK_a values of arsenite and arsenate are listed in Table 3.1.

Table 3.1: Dissociation constants (pK_a) of arsenite and arsenate acids (Mohan & Pittman, 2007).

Name	Oxidation State	Formula	pK_{a1}	pK_{a2}	pK_{a3}
Arsenite	As(III)	H_3AsO_3	9.1	12.1	13.4
Arsenate	As(V)	H_3AsO_4	2.19	6.7	11.2

Based on these values, in the natural water pH range from 5.5 to 8.5, the dominant form of arsenite is the protonated neutral molecule (H_3AsO_3), while the dominant form of arsenate is the dissociated ionic form ($H_2AsO_4^-$). Figures 3.1 and 3.2 show arsenite and arsenate dissociation as a function of pH.

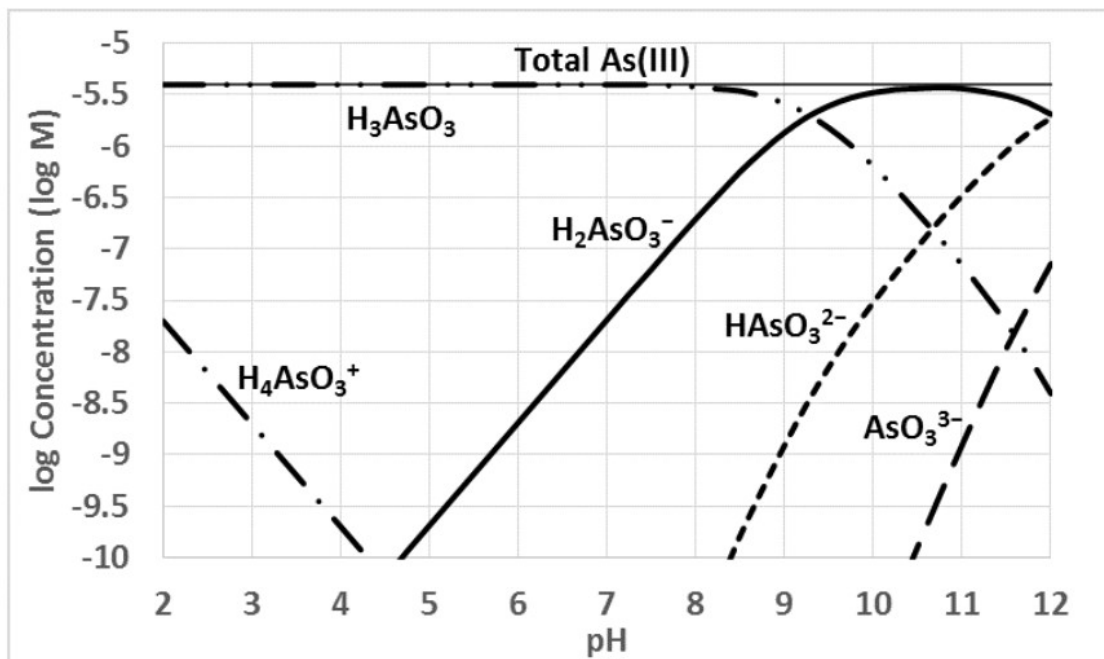


Figure 3.1: Soluble species of arsenic (III) with changes in pH. The arsenic concentration was 4×10^{-6} M. The figure was reproduced with the author's approval: (Heffron, 2015).

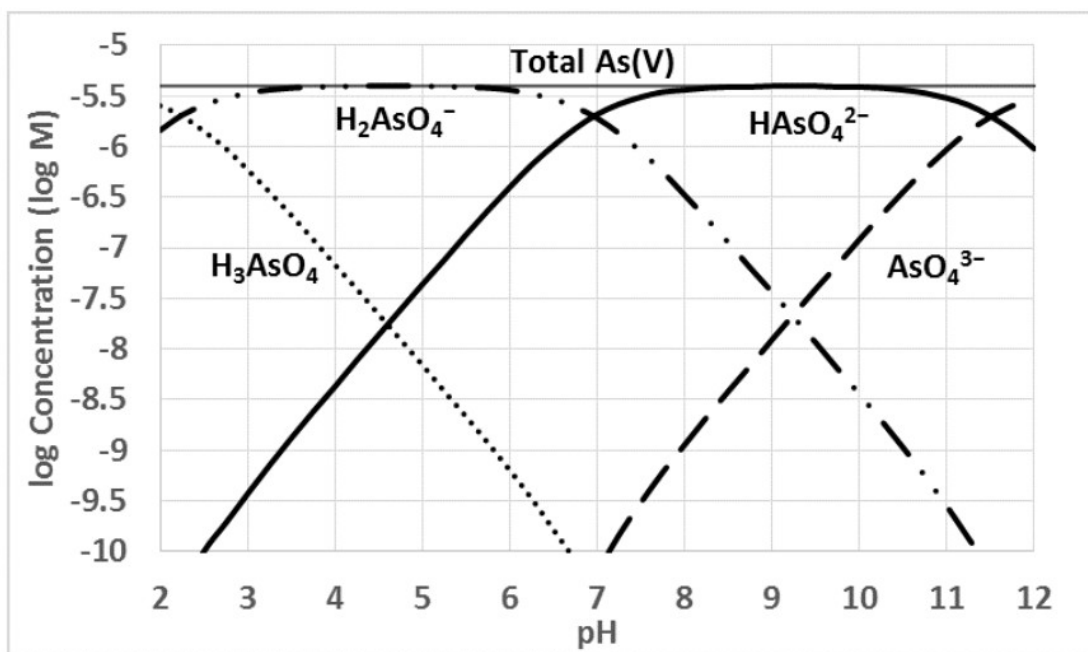


Figure 3.2: Soluble species of arsenic (V) with change in pH. The arsenic concentration was 4×10^{-6} M. The figure was reproduced with the author's approval: (Heffron, 2015).

The dissociated arsenate species present in the range of common groundwater pH values can be removed by coagulation, ion exchange, adsorption, and membrane treatment. For these technologies, typical removals are higher than 90%. For example, a coagulation-filtration process using ferric chloride can remove more than 90% arsenate from water (Song et al., 2006), anionic exchange resin can remove 80% arsenate, activated aluminum adsorption media can remove 90% arsenate, and reverse osmosis (RO) can remove more than 95% arsenate from water (Duarte et al., 2009).

Compared with As(V) removal, As(III) removal efficiency is much lower. Because most As(III) is present in a non-ionized neutral arsenite acid form at common groundwater pHs, most treatment technologies which are effective for arsenate removal provide poorer removal performance for As(III). Most As(III) removals are 30 to 60% by adsorption, ion exchange and RO.

About 20% of the population in Finland uses water from household wells as the sole source of their drinking water (Kurtio et al., 1998). In the U.S., over 15 million households rely on private water wells for drinking water, and private wells are not regulated under drinking water treatment standards. Reverse osmosis might be used in these situations because RO is simpler than conventional drinking water treatment processes in small-scale situations. However, the poor arsenite removal of RO membranes may cause the arsenite levels in treated water to be higher than the standard. In Lahontan Valley, Nevada, USA, groundwater arsenic levels are high, and many residents installed household RO systems to treat their well water for acquiring drinking water. Research showed that the RO systems removed about 80% of arsenic from well

water, but for 18 of the 59 households, arsenic levels in treated water exceeded the 10 µg/L arsenic MCL, with the highest concentration at 180 µg/L (Walker et al., 2008).

To improve arsenite removal, As(III) can be oxidized to As(V), and then treated using ion exchange, adsorption, coagulation, or RO (Manning, Fendorf, Bostick, & Suarez, 2002).

3.4. Reverse osmosis: how does it remove arsenic from water?

Natural osmosis is a spontaneous phenomenon by which water molecules permeate through semi-permeable membranes from low salt concentrations toward higher salt concentrations. The driving force is the pressure generated by the salt concentration across the semi-permeable membrane. In RO, pressure is used to reverse the osmosis process, thereby passing water molecules from higher salt concentrations toward lower concentrations.

Today, advanced treatment using RO is widely used in many water treatment applications, including sea water desalination, pure water/ultra-pure water production, wastewater treatment, and drinking water treatment (Ding, Szymczyk, & Ghoufi, 2016). It can remove particles, bacteria, viruses, organics, inorganics and ions (Malaeb & Ayoub, 2011).

Typical commercial RO membranes are composed by three layers, a base polyester support layer, a middle ultrafiltration layer, and the surface is a 0.1 µm thick polyamide desalination layer. The desalination layer is the only functional layer which can reject ions and other contaminants from feed water. The pore size in the desalination layer is one parameter that impacts how fluids pass through RO membranes. The average pore radius of most commercialized RO membranes is between 0.20 and 0.29 nm in the

desalination layer. Solutes which are smaller than the pore can pass through by the force of the concentration gradient across the RO membrane. Normally, these solutes are small, neutral organic or inorganic molecules (Fujioka et al., 2015; Kurihara, 2008; Tu, et al., 2011).

For solvents and solutes bigger than the pore size of the desalination layer (for example, water molecules, ions and big organic molecules), they can permeate through the membrane in accordance with the solution-diffusion model. This model states that the solute and solvent dissolve in the desalination layer and then diffuse across the layer. The solute diffusion efficiency is unequal to the solvent diffusion efficiency due to its own chemical potential gradient across the membrane and the desalination layer material. These gradients are the concentration and pressure differences across the layer (Williams, 2003). For example, the diffusion efficiencies of water and sodium ions in polyamide are 3.86×10^{-10} and $0.018 \times 10^{-10} \text{ m}^2/\text{s}$, respectively (Fujioka et al., 2015). Thus, the diffusion efficiency of water is 214 times the diffusion efficiency of sodium ions in polyamide, which composes the RO membrane's desalination layer. Accordingly, water diffuses faster than sodium ions in the desalination layer, so more water can pass through the RO membrane from the feed water side to the permeate water side, and the sodium concentration in the permeate water is lower than the feed water.

These principles explain the difference between the permeability of arsenite and arsenate. The permeability of arsenite fits the first situation. Arsenite is a weak acid, with a pK_{a1} of 9.1, meaning more than 92.6% of arsenite in water is in the form of a neutral molecule when the pH is lower than 8. Research has shown arsenite removal to be 50% using low pressure RO membranes and 90% by seawater desalination RO membranes

(Teychene, Collet, Gallard, & Croue, 2013; Vrijenhoek & Waypa, 2000). Although arsenite removal by seawater desalination RO membranes was higher, the operating pressure of seawater RO membranes is 800 psi, so it is uneconomical to use seawater membranes for drinking water treatment.

The permeability of arsenate fits the second situation because arsenate forms ions in water, so it cannot move through the desalination layer pores; it can only diffuse through RO membranes, and the diffusion efficiency is low. Thus, arsenate removal by RO membranes is higher than arsenite removal (Geucke, Deowan, Hoinkis, & Pätzold, 2009). Therefore, to increase arsenic removal by RO membranes, the feed water pH can be increased to shift arsenite toward ionized species (Kang et al., 2000, Geucke, Deowan, Hoinkis, & Pätzold, 2009). Alternately, arsenite can be oxidized to arsenate (Ning, 2002).

To achieve 90% arsenite removal by RO membranes, the feed water pH must be higher than 11 (Kang et al., 2000). This translates to a theoretical addition of 400 mg NaOH to increase 1 liter feed water from pH 7 to 11 (assuming no alkalinity buffer). The actual base demand is even more than the theoretical demand, so the pH adjustment method is not a good option from an economic and environmental perspective. Instead, oxidation is the more reasonable choice to better protect end users from arsenic contamination in drinking water.

3.5. Pre-oxidation can improve arsenic removal using RO

The oxidation reduction potential (ORP) of arsenite to arsenate is 0.56 V. Any oxidant which has a higher ORP can oxidize arsenite, e.g., Cl_2/HClO , O_3 , KMnO_4 , MnO_2 and H_2O_2 . In actual operation, the process needs to be quick and effective. Using sodium hypochlorite dosed in excess of the stoichiometric ratio of reaction with arsenite,

complete arsenite oxidation was observed after the first minute (Sorlini & Gialdini, 2010). Potassium permanganate was an effective agent for oxidation of As(III) across a wide pH range (Na et al., 2007), with complete oxidation of arsenite within 1 minute (Sorlini & Gialdini, 2010). Additionally, MnO_2 can oxidize arsenite, but the reaction time is longer (Driehaus, Seith, & Jekel, 1995). Ozone is able to oxidize 96% arsenite in 10 minutes (Kim & Nriagu, 2000). Meanwhile, oxygen is ineffective for oxidation of arsenite (Kim & Nriagu, 2000).

Accordingly, common disinfectants such as free chlorine and ozone are able to oxidize arsenite. In some small communities, however, it is possible that there is no water treatment facility or no disinfection process in the treatment train. This may be particularly prevalent in developing countries and in cases where groundwater is used as source water in rural areas. Reverse osmosis systems may be used to treat drinking water from groundwater sources, but this would yield poor arsenite removal. While a disinfectant could be added to improve the RO arsenic removal, most oxidation processes need special dosing equipment to inject the liquid oxidant into the feed water, or need an extra filter to contain solid MnO_2 oxidant media. Alternately, electrolytic oxidation can be used to generate oxidants in-situ, thereby avoiding the design and operation of a complicated dosing system and extra filter.

3.6. Electrolytic Oxidation

Electrolytic oxidation, also called anodic oxidation, is an electrochemical reaction during which an anode and cathode are placed in an electrolyte solution, and when 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. Free chlorine includes $\text{Cl}_{2(\text{aq})}$ as well as its reaction products in water (hypochlorous acid $[\text{HOCl}]$ and hypochlorite ion $[\text{OCl}^-]$). Reactive oxygen species (ROS) include superoxide ($\text{O}_2^{\cdot-}$), hydroxyl radicals (HO^{\cdot}), ozone (O_3), peroxide (H_2O_2), and others. Production of ROS depends on the anode material; boron-doped diamond can generate HO^{\cdot} more effectively compared to other electrode materials. Ti/Ir₂O electrodes generate more chlorine species than other materials (Bergmann & Koparal, 2005; Henry Bergmann, Rollin, & Iourtchouk, 2009; Jeong, Kim, & Yoon, 2009; Martínez-Huitle & Brillas, 2008; Oliveira et al., 2007). The production rate of active chlorine using Ti/IrO₂ electrodes observed using 500 mg/L NaCl solution was $0.08 \text{ mmol min}^{-1} \text{ A}^{-1}$ (Kraft et al., 1999).

When chloride ions are present in water, electrolysis can oxidize the chloride ion to diatomic chlorine, which then reacts with water to generate HOCl (Tribus & Evans, 1962), as shown by the following reactions:

Anode reaction:



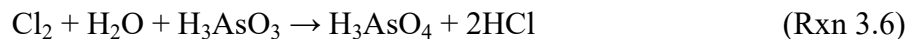
Solution reactions:



Cathode reaction:



The ORP of Cl_2 is 1.36 V, which is higher than the 0.56 V ORP of arsenite/arsenate. Thus, free chlorine can oxidize arsenite to arsenate in accordance with the equation:



Electrolytic oxidation has not yet been applied in large-scale water treatment, but research has shown its potential in wastewater treatment (Chen, 2004; Feng, Sugiura, Shimada, & Maekawa, 2003; Seo et al., 1966). The feasibility of electrolytic oxidation as a pretreatment for RO is currently unknown. Hence, the objectives of this study were to explore the feasibility of this combined process and to test the hypothesis that arsenic removal using RO membranes would improve after electrolytic oxidation pretreatment.

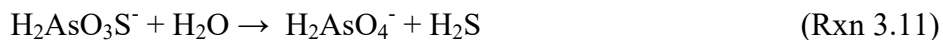
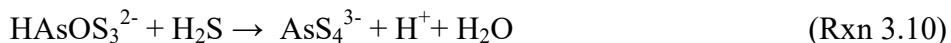
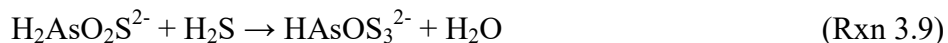
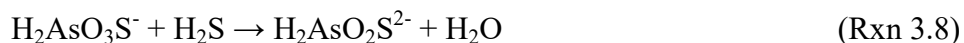
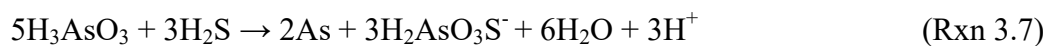
3.7. Water quality parameters with potential to affect the oxidation process

Common water quality parameters with the potential to impact the electrolytic oxidation process or other advanced oxidation processes include: chloride ions, ferrous ions, sulfide, alkalinity, hydrogen ions (pH), and natural organic matter (NOM).

Chloride ions: One important oxidant generated in electrolytic oxidation processes is free, or active, chlorine, which is generated from chloride ions. Hence, the concentration of chloride ions is an influential parameter for the electrolytic process. Chloride ion concentrations in groundwater are normally higher than 10 mg/L (Fisher & Mullican, 1997; Nas & Berkay, 2010). The production rate of active chlorine is between 0.01 to 0.02 $\text{mmol min}^{-1} \text{A}^{-1}$ when the chloride concentration is 50 to 150 mg/L (Kraft et al., 1999). However, active chlorine production is likely low when feed water chloride concentrations are low.

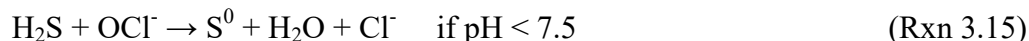
Ferrous ions: Ferric ions present in water can be reduced by bacteria under anaerobic conditions (Nyhus, Wilborn, & Jacobson, 1997); therefore, ferrous ions are common in groundwater. As the ORP of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is 0.2 V at pH 7, free chlorine can oxidize both ferrous and arsenite. The reaction rates of free chlorine with arsenite and ferrous are $4.3(\pm 0.8) \times 10^3$ and $1.7(\pm 0.1) \times 10^4 \text{ M}^{-1} \text{ S}^{-1}$, respectively (Deborde & von Gunten, 2008). Both reactions happen quickly; hence, the ferrous ions can consume part of the free chlorine generated during electrolysis, which can impact arsenite oxidation. Meanwhile, ferrous can also be oxidized to ferric by the oxygen generated during electrolysis, but oxygen oxidation of arsenite is ineffective (Kim & Nriagu, 2000). Ferric can be oxidized to Fe(IV), and Fe(IV) can subsequently oxidize As(III) to As(V) (Li et al., 2012).

Sulfide: Sulfide is common in groundwater, especially in reduced groundwater. When arsenic and sulfide are both present in water, they react to form thioarsenites, and the arsenic thioarsenites react with the remaining sulfide to form thioarsenate ions (O'Day, Vlassopoulos, Root, & Rivera, 2004). The reactions are:



The oxidation of thioarsenites to thioarsenates may take a long time using oxygen (Stauder, Raue, & Sacher, 2005); however, the oxidation process is quicker if using free chlorine because the ORP of free chlorine is higher than oxygen.

Sulfide can also be directly oxidized by hypochlorite (Cadena & Peters, 1988), and can compete with As(III) oxidation:



Arsenic removal using RO membranes is currently unknown when both arsenite and sulfide are present in the water. This study assessed arsenic removal by RO under these conditions and explored the impact of sulfide on electrolytic oxidation.

Alkalinity: Alkalinity mainly impacts ROS, because both HCO_3^- and CO_3^{2-} are radical scavengers. In Wu and Linden's research, the oxidation rate by advanced oxidation processes was reduced 50% after alkalinity increased from 25 to 500 mg/L as CaCO_3 (Wu & Linden, 2010). Other research also showed that the oxidation rate of hydroxyl radicals was suppressed after carbonate ions increased (Autin et al., 2013; Hofmann & Andrews, 2006; Li Puma & Yue, 2003). Arsenite oxidation should not be impacted if other oxidants are generated during electrolysis as research has not shown that carbonate ions impact other oxidants.

Hydrogen ions: Hydrogen ions (pH) can impact the electrode potentials (E_H). The relationships between pH and E_H of chlorine gas, hypochlorite acid, and hypochlorite ions are:

$$E_{H(\text{Cl}_2)} = 1.36 \text{ (V)} \quad (\text{Eq 3.17})$$

$$E_{H(\text{HOCl})} = 1.50 - 0.029 \text{ pH (V)} \quad (\text{Eq 3.18})$$

$$E_{H(ClO_2)} = 1.72 - 0.058 \text{ pH (V)} \quad (\text{Eq 3.19})$$

Additionally, pH impacts the dissociation of arsenite. At low pH, arsenite forms neutral molecules, but the E_H of HOCl and OCI^- is high. At high pH, the E_H of HOCl and OCI^- drops but arsenite dissociation increases, so removal by RO membranes also increases. Common groundwater pH ranges from 5.5 to 8.5, so the E_H of Cl_2 , HOCl and OCI^- at this pH range are higher than the ORP of As(III)/As(V), which is 0.56 V. Thus, free chlorine can theoretically oxidize As(III).

NOM: 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 first order reaction rate of $0.9 \times 10^{-5} \text{ s}^{-1}$ (Westerhoff, Chao, & Mash, 2004). Alternately, the reaction between free chlorine and arsenite is extremely fast, with a second order reaction rate constant of $2.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ (Dodd et al., 2006). Thus, free chlorine should oxidize arsenite even when there is NOM present in the water.

4. METHODS AND MATERIALS

4.1. Experimental setup

As shown in Figure 4.1, the experimental system included a feed water tank, booster pump (AR-600, A.O.Smith, China), two adjustable power supplies (1617A, BK Precision USA), the electrolysis module, the membrane testing cell, a current meter (560A, EXTECH, USA), a pressure meter, and a wastewater restrictor (100cc, A.O. Smith, China).

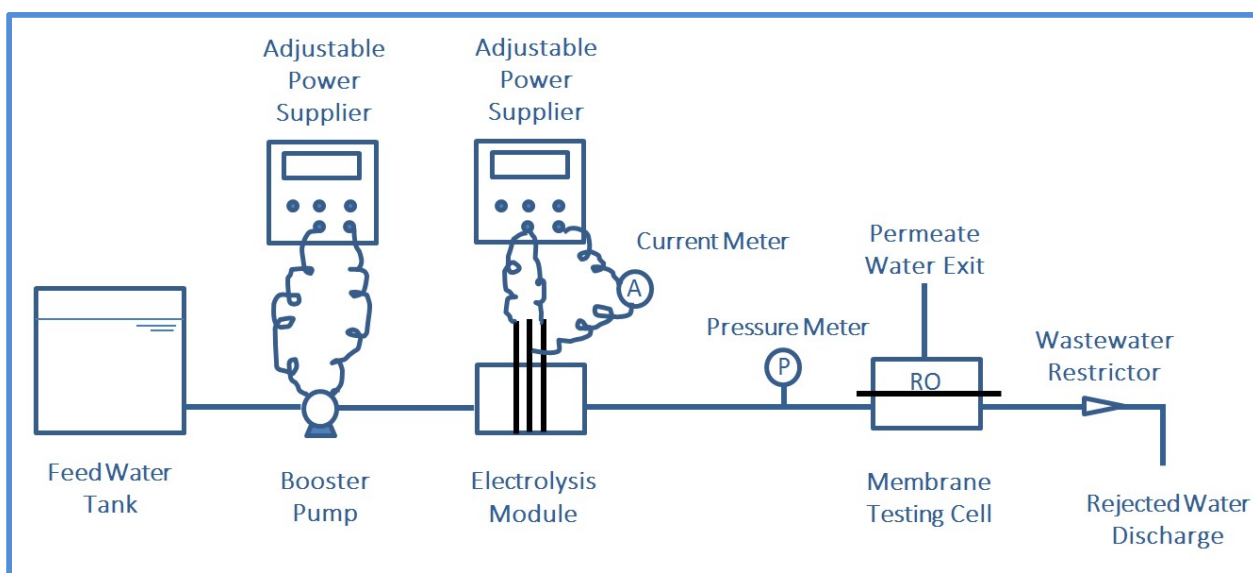


Figure 4.1 The flow chart of the experimental system

The 12 cm x 4 cm x 0.5 cm electrolysis module consisted of three electrodes and the module case. The three electrodes were arranged on a single plane in the middle of the module, with one anode between two cathodes. The distance between the two cathodes was 5 mm. The electrode material was a titanium (Ti) base with an iridium dioxide (IrO_2) coating. The electrodes (MAGNETO Special Anodes B.V. Suzhou China),

were 4 cm in length and 1 mm in diameter. The total area of electrodes in the module was 376.8 mm². Feed water was passed through the module perpendicular to the electrode plane. The retention time from the electrolysis module to the RO membrane testing cell was 10 seconds (including half of the electrolysis unit volume and the tubing connecting the electrolysis module and RO testing cell). The system was operated using direct current applied at levels ranging from 0 to 40 mA.

The 9.6 mL (12 cm × 4 cm × 0.2 cm) membrane testing cell consisted of a membrane fixed between the upper and lower cell casings. Pressure was applied at 95 ± 5 psi to drive the feed water through the membrane to the permeate water (or pure water) side. Rejected water (or wastewater) exited the system through the wastewater restrictor, which limited flow of rejected water from the membrane to prevent pressure increases. The rejected water flow was 110 ± 10 mL/min.

4.2. Membranes

The membranes used in this study included an XLP polyamide thin film RO membrane and an NF-270 piperazine thin film NF membrane (Dow Chemical, MN, USA). Beside the material difference between the XLP-RO membrane and NF-270 NF membrane, the performance of the two membranes is different. RO membranes remove most monovalent ions, while the NF membrane has low NaCl removal but can achieve high removal of multivalent ions such as magnesium, calcium and phosphate.

The NF270 membrane is a nanofiltration membrane designed primarily for organic and color removal. It has high rejection of divalent ions (99.2% MgSO₄), and organics with a molecular weight above 400. Thus, NF270 cannot removal arsenite because arsenite's molecular weight is 126 g/mole and it forms neutral molecules in

natural waters. NF270 may have high rejection of arsenate at near-neutral pH, because arsenate dissociates to H_2AsO_4^- and HAsO_4^{2-} at this pH. It was hypothesized that the removal difference of arsenite and arsenate by NF270 membranes can be used to rapidly identify arsenic species in water.

The recently developed XLP low pressure membrane has a lower operating pressure, and is designed for household RO systems. However, the rejection rate, including arsenite removal, is lower than brackish water membranes. Most previous arsenic removal research used brackish water membranes or seawater membranes (Akin, Arslan, Tor, Cengeloglu, & Ersoz, 2011; Geucke et al., 2009). Comparisons of the arsenic removal provided by these different membranes are listed in Table 4.1. Since most countries use 10 $\mu\text{g/L}$ as the drinking water MCL for arsenic, more than 97.8% removal of arsenic was the target in this study (based on initial levels of 360 $\mu\text{g/L}$).

Table 4.1 As(III) and As(V) removal by different membranes

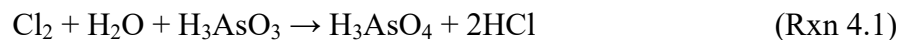
Manufacturer	Model	Type	As(III) Removal	As(V) Removal	Reference
DOW	SWHR	Seawater	78%	95%	(Akin et al., 2011)
DOW	BW30	Brackish Water	60%	94%	(Ning, 2002)
Nitto-Denko	ES-10	NF	58%	90%	(Urase, Oh, & Yamamoto, 1998)
DOW	NF-270	NF	0.1%	99%	(This study)

4.3. Testing water formulation

Arsenic removal performance was tested in synthetic feed water prepared using Type II deionized water (DI water), which met the ASTM standard (D1193-91). The

water temperature was $24 \pm 2^\circ\text{C}$. The baseline groundwater recipe used for testing was based on typical groundwater concentrations, including: Feed water pH was adjusted to $\text{pH } 7 \pm 0.5$ using Na_2CO_3 .

The water was adjusted to 500 mg/L NaCl. The production rate of active chlorine using Ti/IrO₂ electrodes in 500 mg/L NaCl solution has been shown to be 0.08 mmol min⁻¹ A⁻¹ (Kraft et al., 1999). In accordance with this production rate, 0.17 mg free chlorine can theoretically be generated in 1 min using 30 mA of DC power. This would generate 1.7 mg/L free chlorine at a process flow rate of 0.1 L/min, which, in theory, would be sufficient to oxidize 0.3 mg/L arsenite.



All water quality parameters, including the ferrous ions, alkalinity, sulfide, and total organic carbon (TOC) used to simulate groundwater in the different tests, are shown in Table 4.2.

Table 4.2 Experimental water quality parameters and measurement methods

Parameter	Chemical	Concentration	Chemical supplier/ Manufacturer	Measurement Equipment	Detection Limit
Arsenite	Na_3AsO_3	$360 \pm 20\%$ $\mu\text{g/L}$	Ricca Chemical Company	Agilent ICP-MS 7700	0.5 ppb
Arsenate	$\text{Na}_3\text{AsO}_3 \cdot 7\text{H}_2\text{O}$	$360 \pm 20\%$ $\mu\text{g/L}$	Sigma Aldrich	Agilent ICP-MS 7700	0.5 ppb
pH	$\text{NaOH}/\text{Na}_2\text{CO}_3$	$\text{pH } 7.0 \pm 1$	Sigma Aldrich	Thermo Scientific Star A214	0.01
	HCl		GFS Chemical		
TDS (total dissolved solids)	NaCl	500 mg/L	Morton	Myron L Company Handheld TDS meter 4P	0.01 ppm
	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	500 mg/L	Sigma Aldrich		
Alkalinity	NaHCO_3	250 mg/L (as CaCO_3)	Sigma Aldrich	Hach Titration Kit	0.1 ppm
Free Chlorine	Generated in- situ	N/A	N/A	DPD Method using UV Spectrophotometer Hach DR6000	0.01 ppm
Fe^{2+}	FeCl_2	1 mg/L	Sigma Aldrich	Phenanthroline Method using UV Spectrophotometer Hach DR6000	0.01 ppm
Total Iron (Fe^{3+} is difference between total iron and Fe^{2+})	N/A	N/A	N/A	FerroVer Method using UV Spectrophotometer Hach DR6000	0.01 ppm
Sulfide	Na_2S	2 mg/L	Sigma Aldrich	Methylene Blue Method using UV Spectrophotometer Hach DR6000	0.01 ppm
Tertiary Butanol (Hydroxyl radical inhibitor)	$\text{C}_4\text{H}_{10}\text{O}$	8 mg/L	Sigma Aldrich	Agilent GC-MS 5973	0.01 ppb
TOC (total organic carbon)	Humic Acid	2 mg/L	MP Biomedicals LLC.	Skalar CA16	0.1 ppm

4.4. Phase 1 Experiments: Initial arsenic removal performance using an XLP RO membrane and feasibility of improving removal using electrolytic oxidation pretreatment

Phase 1 included four experiments. The first and the second experiments were performed to quantify As(III) and As(V) removal performance by RO membrane treatment (without electrolytic oxidation pretreatment) as a function of water pH.

In addition, the theoretical arsenite and arsenate dissociation rates were calculated as a function of pH using the following equations:

$$\text{Fraction of dissociated arsenite} = \frac{[H_2AsO_3^-] + [HAsO_3^{2-}] + [AsO_3^{3-}]}{\text{Total Arsenite}} \times 100\% \quad (\text{Eq 4.1})$$

$$\text{Fraction of dissociated arsenate} = \frac{[H_2AsO_4^-] + [HAsO_4^{2-}] + [AsO_4^{3-}]}{\text{Total Arsenate}} \times 100\% \quad (\text{Eq 4.2})$$

The third experiment of Phase 1 was the electrolytic oxidation experiment. The system was operated at 0, 10, 20, 30, or 40 mA, and the TDS and total arsenic concentrations were measured to calculate percent removal of each. Free chlorine concentrations were also measured.

Validation using the NF-270 membrane to evaluate the extent of As(III) oxidation was performed. The oxidation of As(III) to As(V) is fast, with complete oxidation occurring within one minute. Thus, the use of conventional analytical techniques to quantify As(III) and As(V) immediately after the reaction occurred presented a difficulty in that the analysis would be too slow to accurately differentiate between the species resulting from treatment. For example, ion chromatography can identify both As(III) and As(V), but the time to prepare the sample is more than 1 min, so changes in speciation could occur between testing and analysis. Thus, a novel approach to differentiate between arsenic species during analysis was employed in this study. A NF membrane was used to

identify As(III) and As(V) immediately after the water exited the membrane testing cell. In this experiment, a second membrane testing cell containing the NF membrane was connected after the RO membrane testing cell. The retention time from the RO membrane testing cell to NF membrane testing cell was 5 seconds. Water samples were collected from both membranes, and analyzed for arsenic concentrations. By comparing the arsenic removals through the NF membrane, the extent of As(III) oxidation was quantified, as described in the Results and Discussion section.

4.5. Phase 2: Identifying the main oxidant responsible for oxidizing As(III) during the electrolytic oxidation process

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 has yet to be established. Thus, phase 2 of the study included three experiments focused on identifying the main oxidant responsible for As(III) oxidation during electrolytic oxidation.

One experiment was designed to explore the potential for ROS generation in the system. Tertiary butanol was added as a radical scavenger. The reaction rate of tertiary butanol and hydroxyl radicals is $5 \times 10^8 \text{ L mol}^{-1} \text{ S}^{-1}$ (Jun, Li, Cheng, 2006), so any ROS generated during electrolysis would be consumed by reactions with tertiary butanol, and would be unable to participate in the oxidation of As(III).

The second experiment replaced the 500 mg/L NaCl electrolyte solution with 500 mg/L MgSO₄. This prevented the formation of free chlorine as no precursor chloride was present in the system. Thus, this experiment was used to assess the role of free chlorine in

As(III) oxidation as well as the influence of any other oxidants generated in the system. As the theoretical conductivity of 500 mg/L NaCl and MgSO₄ is 2.16 and 2.18 $\mu\text{s}/\text{cm}$, respectively, minimal impact from using different electrolytes in water was expected.

The final experiment assessed the influence of current by adjusting the electrolysis module to 0, 2, 4, 6, 8 and 10 mA current. Both arsenic and free chlorine were measured in the treated water to assess the relationship between free chlorine and arsenic removal as a function of current. By comparing arsenic removal across the three experiments, the main oxidants could be identified.

4.6. Phase 3: The influence of water quality on As(III) removal using electrolytic oxidation-RO treatment

Six independent experiments were performed in Phase 3 to assess how feed water quality impacted the electrolytic oxidation of As(III), and subsequent arsenic removal using the RO membrane. Experiments were performed at the optimal current identified in Phase 1 using varying the concentrations of chloride, ferrous, pH, sulfide, alkalinity and NOM, as described in Table 4.1.

Chloride concentrations were 15, 30 and 60 mg/L. The chlorine generation efficiency was calculated in accordance with the following equations:

$$\text{Chloride Generation Efficiency} = \frac{\text{Free Chlorine Concentration}}{\text{Power}} \quad (\text{Eq 4.5})$$

$$\text{Power} = \text{Current} \times \text{Voltage} \quad (\text{Eq 4.6})$$

4.7. Statistics

Comparisons of As(III) removal (means of at least three experiments) among the tests were performed by using the t-test or ANOVA single factor analysis ($\alpha = 0.05$). For significant differences, the Tukey post hoc analysis was performed. The t-test was performed using Microsoft Excel to compare the means of two tests, while ANOVA was performed using OriginPro 8 to assess for statistical differences among multiple tests.

4.8. Quality control

After each experiment, the water was drained from the testing equipment, and Type II DI water was used to flush the system for at least 5 minutes. Once chemicals were added to the feed water at the start of each experiment, the system was allowed to stabilize for 15 min prior to collecting samples.

Each new membrane sheet was flushed using Type II DI water for 30 minutes, and then run under 500 mg/L NaCl solution and 95 ± 5 psi for 30 minutes to precondition it prior to experimentation. To avoid membrane fouling, the membrane was cleaned using pH 3 citric acid solution and pH 10 NaOH solution for 30 minutes after the experiment when ferrous and NOM were involved. The membrane sheets were assumed to have degraded (due to oxidant generation in the system) once the permeate water flow dropped to less than 80% of the initial flow or the TDS rejection rate dropped more than 5%. At this point, the membrane sheet was replaced.

5. RESULTS AND DISCUSSION

5.1. The feasibility of As(III) oxidation by electrolysis to improve arsenic removal by RO membranes

5.1.1. As(III) removal using an XLP RO membrane as a function of pH

Figure 5.1 shows removal of arsenite and Total Dissolved Solid (TDS) as a function of feed water pH. TDS was included in all experiments to provide an indicator of effective membrane operation. Arsenite removal increased from $40.3\% \pm 1.3\%$ at pH 6.0 to $96.7\% \pm 0.1\%$ at pH 10.94. Below pH 8.65, arsenite removals remained statistically unchanged, whereas at higher pH levels, arsenite removal improved significantly at each consecutive pH value tested.

The increase in arsenite removal shown in Figure 5.1 is observed once the water pH exceeds the acid dissociation constant ($pK_{a1} = 9.1$), when the majority of the arsenite species shift to hydrated dihydrogen arsenite ions, as governed by chemical equilibrium. For example, 92.6% of dissolved arsenite is in the protonated arsenite acid form when the pH is 8.0, and arsenite acid can easily pass through RO membranes. As pH increases, arsenite acid begins to dissociate to dihydrogen arsenite ions, which combine with water molecules through hydrogen bonding to form hydrated dihydrogen arsenite ions. These hydrated ions are larger than the RO membrane's pore size; thus, the ions cannot pass through the membranes, thereby increasing arsenite removal.

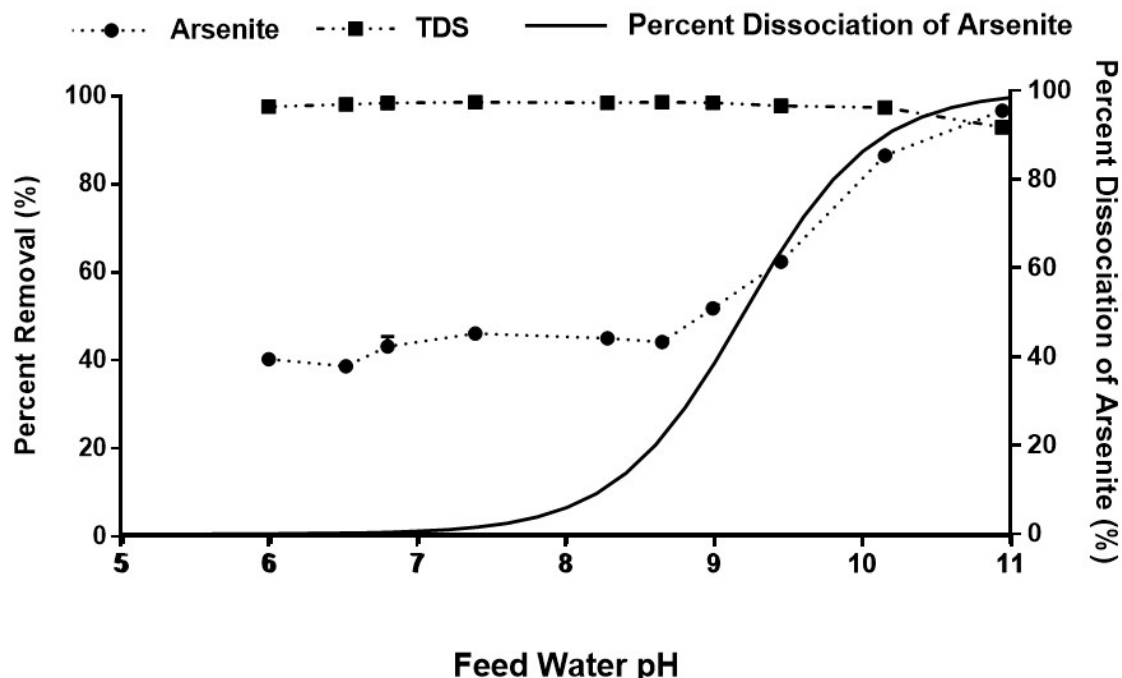


Figure 5.1: Arsenite and TDS removal using a XLP RO membrane at different feed water pHs. The theoretical fraction of dissociated arsenite as a function of feed water pH (calculated using equilibrium relationships) is shown on the secondary y axis. The arsenite removals are the means of triplicate experiments ± 1 standard deviation. Some error bars not visible due to the small standard deviation.

5.1.2. As(V) removal using a XLP RO membrane as a function of pH

Arsenate removal tests as a function of pH indicated that the average As(V) removals by RO membranes were consistently higher than 99% from pH 6 to 11. The pK_{a1} , pK_{a2} and pK_{a3} values of arsenate are 2.19, 6.94 and 11.5, respectively. This means that more than 98% of total arsenate is [at least partially] dissociated when the pH is higher than 4. Since the dissociated species are ions, they hydrate with water molecules to form bigger hydrated ions, which are blocked by RO membranes, so arsenate removal is high. As all of the pH values tested here were much greater than pK_{a1} of 2.19, statistically consistent removals greater than 99.9% were observed at all pHs tested (ANOVA P-value = 0.546), as shown in Figure 5.2. Removal of As(V) was higher and more consistent

than As(III) across the pH range tested. Thus, one strategy to improve arsenic removal during RO is to oxidize the As(III) to As(V).

The TDS removal increased slightly from pH 6.0 to pH 9.50, and then started to decline when the pH exceeded 9.5. The lowest removal was at pH 11.0, at 95.8%. One possible cause of the decline in TDS removal was the membrane surface charge changed after the pH increased, and the hydrated ion radius can change when pH increases.

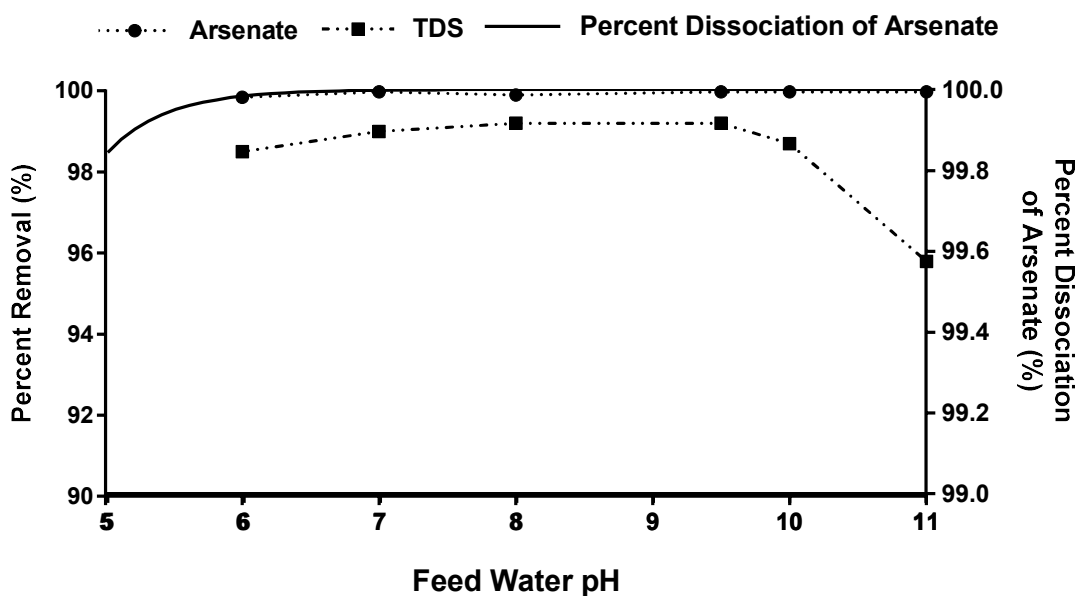


Figure 5.2: Arsenate and TDS removal using a XLP RO membrane at different feed water pHs. The theoretical fraction of dissociated arsenate as a function of feed water pH (calculated using equilibrium relationships) is shown on the secondary y axis. The arsenate removals are the means of triplicate experiments ± 1 standard deviation. Error bars were not visible due to the small standard deviation.

5.1.3. Arsenic removal by RO when using electrolysis to pretreat the water

An electrolysis module was added before the RO membrane testing cell in an attempt to oxidize As(III) to As(V), and thus improve the arsenic removal by RO. The arsenic removals using 0, 10, 20, 30, or 40 mA current during electrolytic oxidation were measured.

As shown in Figure 5.3, the results indicated that when there was no current (0 mA), arsenic removal was low ($54.2\% \pm 0.30\%$). As current increased, arsenic removal increased (exceeding 90% removal in all cases). ANOVA analysis indicated significant improvements in arsenic removal were achieved as the current increased incrementally from 0 to 30 mA ($P=0.067$). There was no significant improvement between 30 and 40 mA (t-Test $P=0.22$). This demonstrates that electrolysis pretreatment can significantly improve arsenic removal using an RO membrane, and 30 mA appears to be the minimum (or optimal) current to achieve the 98% arsenic removal target. Moreover, the addition of electrolysis did not detract from TDS removal, as shown in Figure 5.3.

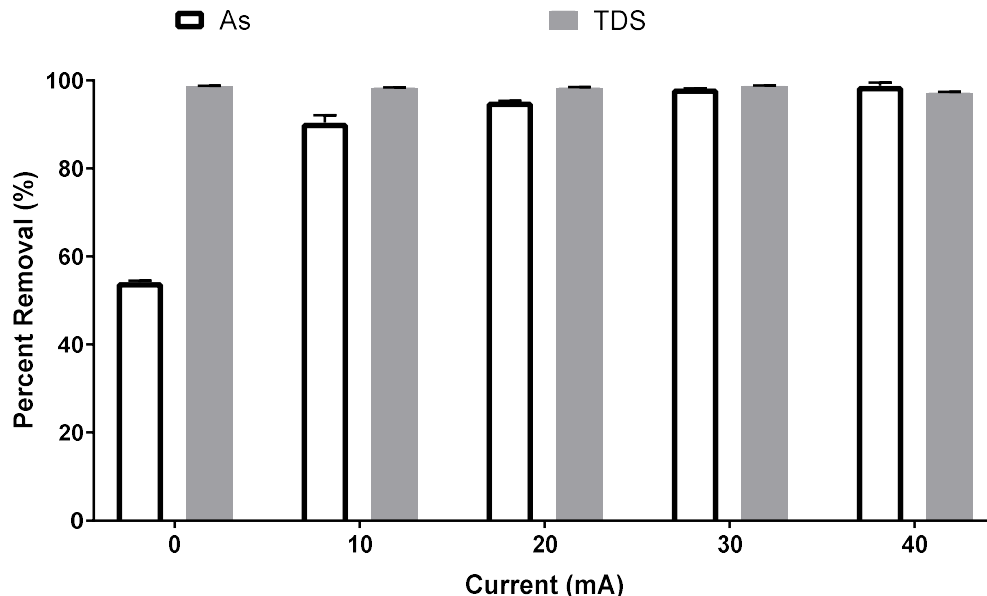


Figure 5.3: Arsenic (As) and TDS removal by RO using electrolytic oxidation pretreatment at variable applied currents. Values shown are the means of four tests ± 1 standard deviation. Some error bars were not visible due to the small standard deviation.

5.1.4. Using NF membrane to identify As(III) and As(V) distribution following electrolysis

In this study, an NF (NF-270, Dow, Minnesota USA) membrane was used to differentiate between As(III) and As(V) species on the basis of the difference in removals of the two arsenic species using the membrane. The NF membrane was added to the system immediately after the RO membrane.

As shown in Table 5.1, removal of As(III) using the NF membrane was very low, while removal of As(V) was very high. Thus, this study demonstrated a novel approach to differentiating between arsenite and arsenate concentrations using NF membranes. Accordingly, NF membranes were employed to quantify arsenic concentrations after electrolysis in this study.

Table 5.1 Arsenic removal using XLP RO and NF-270 membranes with and without electrolysis pretreatment. Spiking concentrations were 500 mg/L NaCl and 300 µg/L arsenic. SD = 1 standard deviation.

Membrane	As(III) + 0 mA			As(V) + 0 mA			As(III) + 30 mA		
	Mean	SD	n	Mean	SD	n	Mean	SD	n
RO	52.9%	0.1%	3	99.9%	0.0%	3	99.9%	0.0%	3
NF	0.1%	1.7%	3	98.3%	0.3%	3	98.2%	0.1%	3

The experimental results showed that there was no significant difference between the arsenic removal using an RO membrane with 30 mA electrolysis pretreatment and the As(V) removal using an RO membrane with 0 mA electrolysis treatment (t-test, $P=0.18$). There was no significant difference between the arsenic removals by the NF membrane with 30 mA electrolysis pretreatment and the As(V) removal by the NF membrane with 0 mA electrolysis treatment (t-test, $P=0.50$). Together, these results indicated that As(III) was oxidized to As(V) via electrolytic oxidation, and that the NF membrane could be employed to rapidly differentiate between the two species.

5.2. Main mechanism of As(III) oxidation in the electrolysis system

5.2.1. The role of ROS in As(III) oxidation

To isolate the impact of ROS relative to free chlorine during electrolysis, the NaCl was replaced with 500 mg/L MgSO_4 in DI water at a pH of 7.0. Arsenite was spiked at an average concentration of 285 µg/L. As shown in Figure 5.7, no significant difference in the arsenic removal using the RO membrane was observed for electrolysis currents of 0, 20, 30 and 40 mA (ANOVA $P=0.18$). However, these removals were significantly different from the arsenic removals with electrolysis treatment in 500 mg/L

NaCl solution (ANOVA $P=8E-21$). This result indicates that no ROS were generated during electrolysis as no difference in removal was achieved with the addition of current in the absence of chloride. It also further validates the importance of the free chlorine generated from chloride ions for the oxidation and subsequent removal of arsenic.

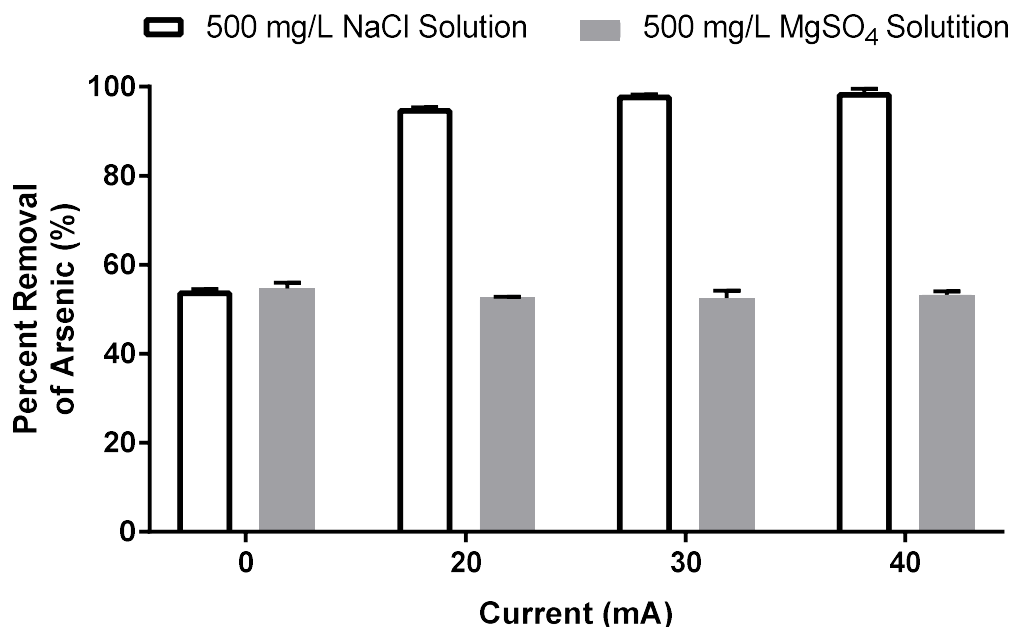


Figure 5.4: Arsenic removal using electrolysis-RO with 500 mg/L NaCl or MgSO₄ solutions. Values shown are the means of three tests \pm 1 standard deviation.

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 arsenic oxidation. However, one additional test was performed to confirm that no ROS were generated during the process. In this test, tertiary butanol (TBA) was added to 500 mg/L NaCl or MgSO₄ solution. TBA is commonly used as a hydroxyl radical scavenger, and its removal would indicate the presence of ROS. No statistical difference in TBA concentration was found for the feed water compared to 30 mA electrolysis-RO treated water (t-test, $P=0.83$ for NaCl solution and 0.77 for MgSO₄

solution). Accordingly, there was no evidence that ROS were generated during the electrolytic oxidation process.

5.2.2. Role of free chlorine in As(III) oxidation

Concentrations of free chlorine in the water rejected by the membrane testing cell are shown in Figure 5.4. The increase in free chlorine concentrations in response to increased current parallels the trend observed for arsenic removal. Accordingly, the influence of the free chlorine generated in the electrolysis system on arsenic oxidation and removal was explored to determine the species responsible for arsenic oxidation in the electrolysis system.

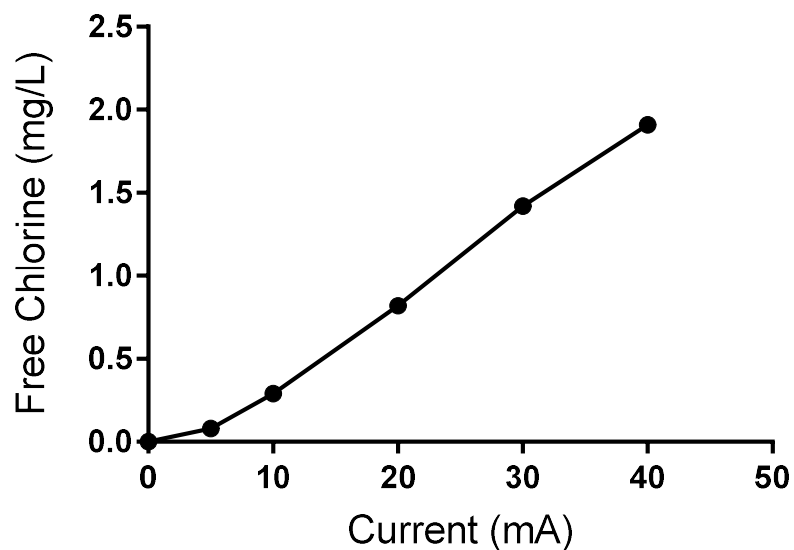


Figure 5.5: Free chlorine generated during electrolytic oxidation using 500 mg/L NaCl solution. Values were measured in the membrane reject water.

Because the ORP of free chlorine is 1.36 V, which is higher than the ORP of As(III) /As(V) at 0.56 V, free chlorine can oxidize As(III) to As(V). This is shown stoichiometrically in Rxn 3.7, which indicates that 0.95 mg/L Cl_2 can oxidize 1.0 mg/L

As(III) to As(V). The concentration of free chlorine generated in the electrolysis module was 1.5 mg/L using 500 mg/L NaCl solution and 30 mA current. Thus, the concentration of free chlorine generated in the electrolysis process was higher than the amount required to oxidize the 300 µg/L arsenite in the feed water. This suggests that all of the arsenite was oxidized to arsenate, which demonstrates superior removal during RO, as supported by the study results (98.2% vs. 54.2%, respectively, as shown in Figure 5.5).

To test the role of free chlorine in arsenic removal (via oxidation to arsenate and subsequent removal by RO treatment), the electrolysis current was varied and the resulting free chlorine concentrations and arsenic removal were quantified. The results are shown in Figure 5.5. There was no significant difference between the arsenic removals at 0 and 2.12 mA (t-test, $P=1$), but significant improvements in removal were observed for all currents above 2.12 mA (ANOVA, $P = 2.7E-16$). The arsenic removal and free chlorine concentration show similar tendencies as a function of current, with the arsenic removal increasing in step with increases in the free chlorine concentration.

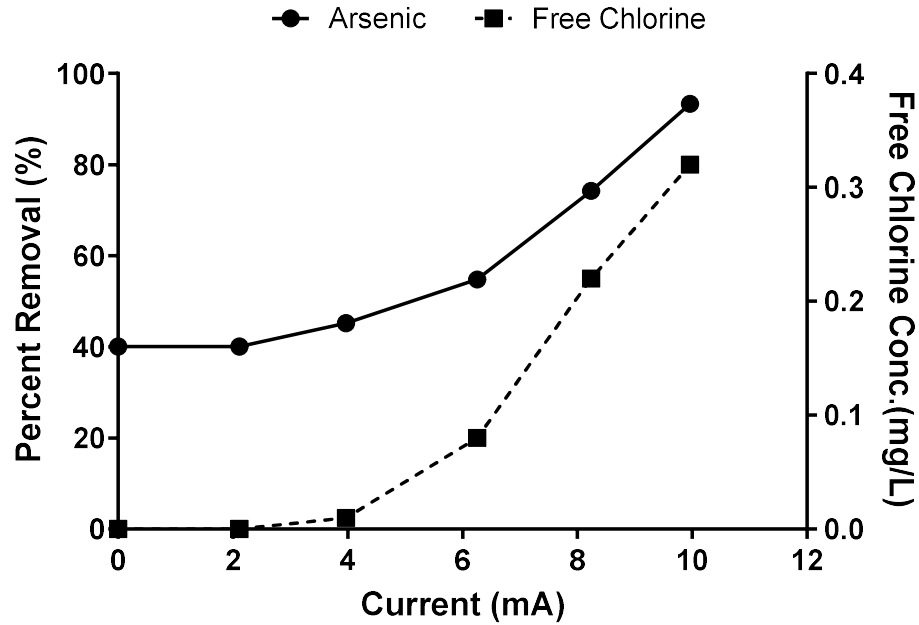


Figure 5.6: Arsenic removal using a XLP RO membrane with electrolysis pretreatment operated at variable current. The free chlorine concentration was measured in an independent arsenite-free test. Values shown are the means of three tests \pm 1 standard deviation. The feed water NaCl concentration was 500 mg/L. Error bars were not visible due to the small standard deviation.

The theoretical and experimental arsenic concentrations in the permeate water are shown in Figure 5.6. The theoretical concentration was calculated using the following equation based on the stoichiometry of reaction with free chlorine.

$$\begin{aligned}
 \text{Theoretical As(III) Conc.} = & \left(\text{Feed As(III) Conc.} - \frac{\text{Generated Free Chlorine conc.} \times 75}{71} \right) \\
 & \times (1 - \text{Percent Removal}_{\text{As(III)}}) \quad (\text{Eq 5.1})
 \end{aligned}$$

The experimentally-measured arsenic concentrations were similar to the theoretical As(III) concentrations (no statistical difference at three of the currents tested, small difference for the other three: ANOVA $P=0.008$, $1.1\text{E-}5$, 0.002 at 3.97, 8.24 and 9.96 mA, respectively. As the experimental results agreed with the stoichiometrically-

derived values based on reactions of free chlorine and arsenic, these results indicate that free chlorine was the main oxidant responsible for arsenic oxidation in the electrolysis system.

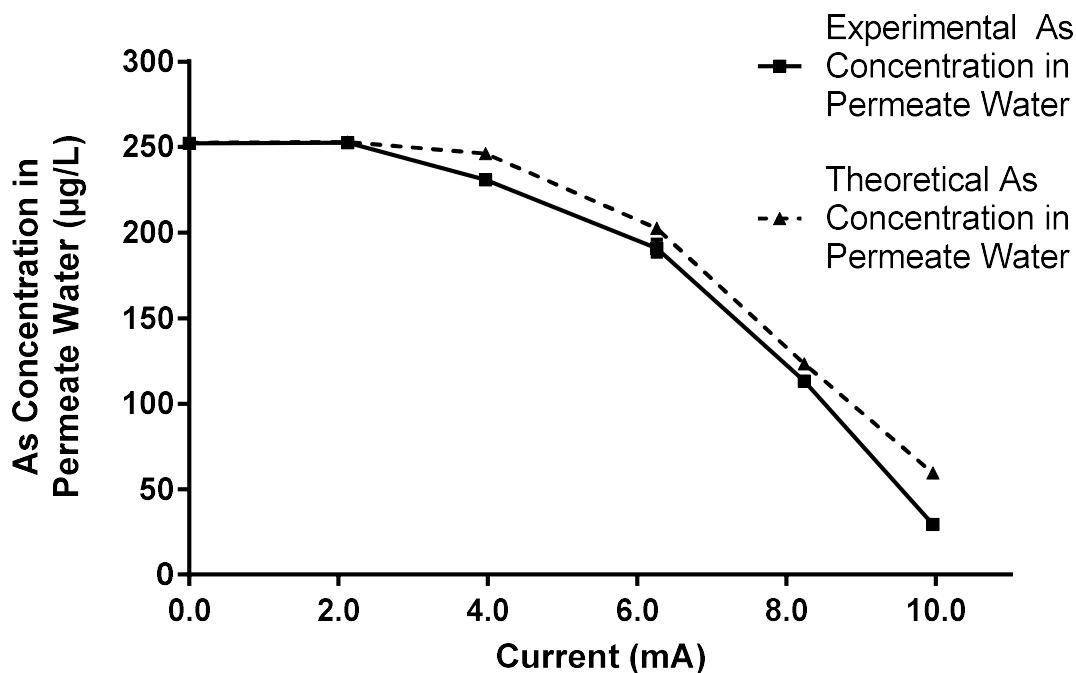


Figure 5.7: Experimental arsenic (As) concentrations and theoretical arsenic concentrations (based on chlorine-based stoichiometry) in permeate water as a function of electrolysis current. Experimental values shown are the means of three tests ± 1 standard deviation. Error bars were not visible due to the small standard deviation. The feed water NaCl concentration was 500 mg/L.

5.2.3. Arsenic removal by HOCl oxidation

To provide additional evidence that free chlorine was primarily responsible for arsenic oxidation in the electrolysis-RO system, a dosing pump was installed between the feed water tank and membrane testing cell (reaction time of 10 seconds). A HOCl solution was added directly to the testing system. The results showed that when HOCl concentrations were 0, arsenic removal was 38%, but removal efficiency significantly

increased when HOCl was added to the system (ANOVA $P=2.7E-15$). When HOCl concentrations were higher than 0.38 mg/L, arsenic removals by RO membranes were equivalent to As(V) removal (ANOVA $P=0.07$), and also equivalent to removal using 30 mA electrolytic oxidation pretreatment (ANOVA $P=0.10$). These results suggested that free chlorine can oxidize arsenite and significantly improve arsenic removal by RO membranes.

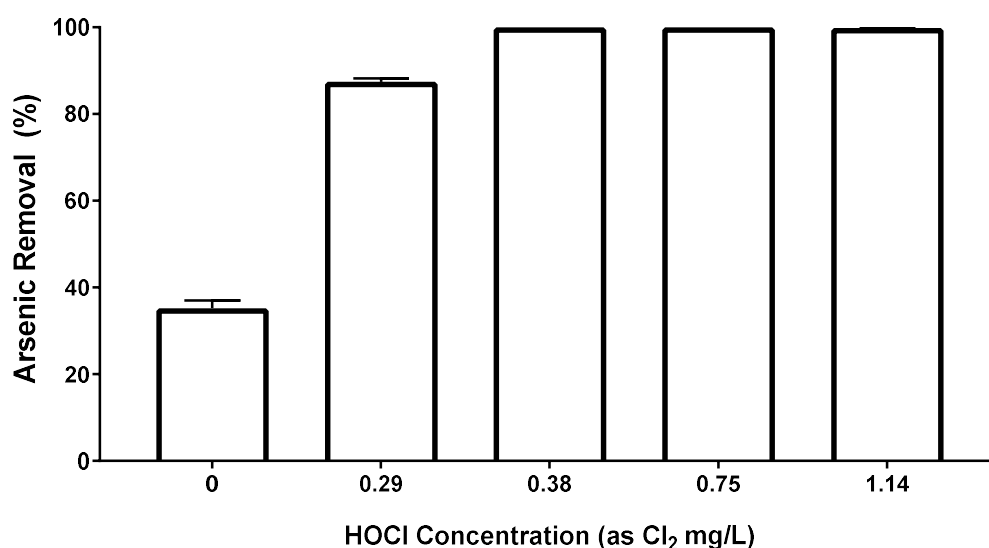


Figure 5.8: Arsenic removal using a XLP RO membrane with HOCl pre-oxidization at different oxidant concentration. Values shown are the means of three tests \pm 1 standard deviation. Some error bars are not visible due to the small standard deviation.

5.3. The influence of water quality parameters on arsenic removal

Objective 3 of the study was to explore the impact of feed water quality parameters on As(III) oxidation by the electrolysis process. Those parameters included chloride, ferrous, pH, sulfide, alkalinity and NOM, as described in the following sections.

5.3.1. Chloride concentration

The removal of As(III) using 30 mA electrolysis treatment followed by an RO membrane was measured in 25, 50 and 100 mg/L NaCl solution (15, 30 and 60 mg/L chloride, respectively). As shown in Figure 5.8, the arsenic concentrations in the permeate water after treatment by electrolysis-RO were lower than the minimum detection limit of the ICP-MS (reported here as 100% removal at each of the chloride concentrations tested). Electrolysis treatment significantly increased the arsenic removals (t-test, $P = 0.0002$, 0.0005 and 0.0002 for 15, 30 and 60 mg/L chloride, respectively).

The difference in the free chlorine concentration with and without As(III), shown in Figure 5.8, closely matched the theoretical concentration of free chlorine consumed by the oxidization of arsenite based on stoichiometry. The chlorine generation efficiency using 15, 30, 60 and 300 mg/L chloride solutions was calculated and is listed in Table 5.2. The results showed that the chlorine generation efficiency increased as chloride concentration increased. This indicates that electrolytic oxidation consumes more power as chloride concentrations decline.

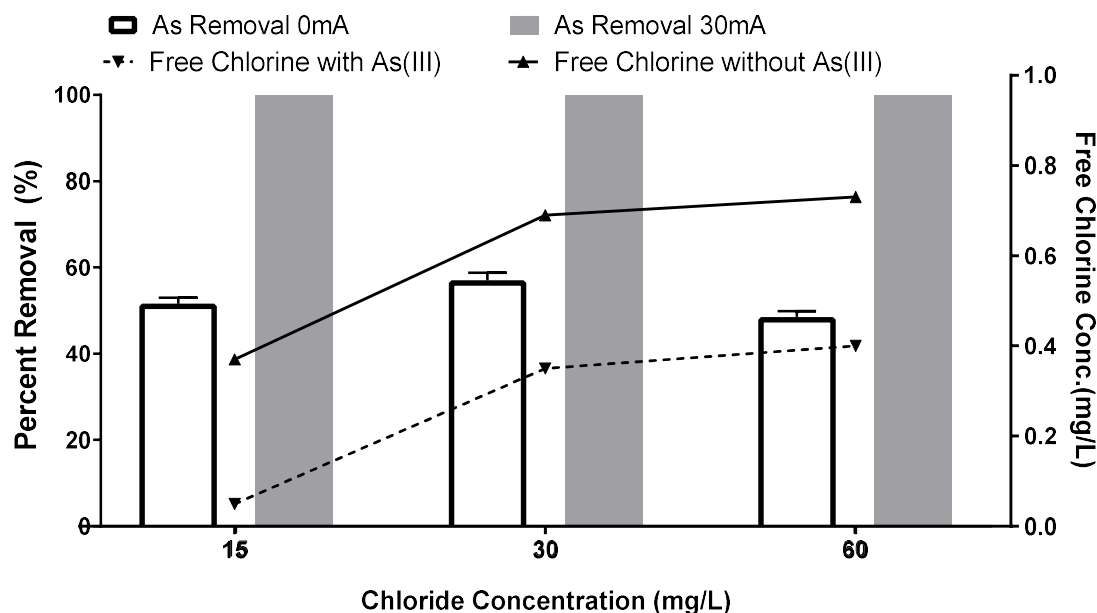


Figure 5.9: Arsenic (As) removal using RO with 0 and 30 mA electrolysis pretreatment with varying chloride concentration solution. The corresponding concentrations of free chlorine with and without As(III) are shown on the secondary y axis. Values shown are the means of three tests \pm 1 standard deviation. Some error bars are not visible due to the small standard deviation.

Table 5.2 Chlorine generation efficiency in different NaCl concentration solutions

NaCl (mg/L)	Cl ⁻ (mg/L)	Current (mA)	Voltage (V)	Free Chlorine (mg/L)	Power (W)	Chlorine Generation Efficiency (mg L ⁻¹ W ⁻¹)
25	15	30	29.5	0.37	0.89	0.42
50	30	30	18	0.69	0.54	1.28
100	60	30	11.2	0.73	0.34	2.17
500	300	30	4.5	1.42	0.14	10.52

5.3.2. Ferrous ion (Fe²⁺)

Ferrous ions were added to pH 6.78 feed water at a concentration of 1.04 mg/L (total iron concentration of 1.16 mg/L). Arsenite was added to the water at a concentration of approximately 300 μ g/L. As shown in Figure 5.9, the arsenic removal did not change with ferrous addition (t-test, $P=0.15$ for 0 mA and 0.13 for 30 mA). While

ferrous did not impact As(III) oxidation, the test indicated that ferrous was oxidized to ferric as the concentration of ferrous in the membrane reject stream was 0.02 mg/L compared to the feed water concentration of 1.04 mg/L (total iron concentration of 1.14 mg/L vs. 1.16 mg/L in the feed).

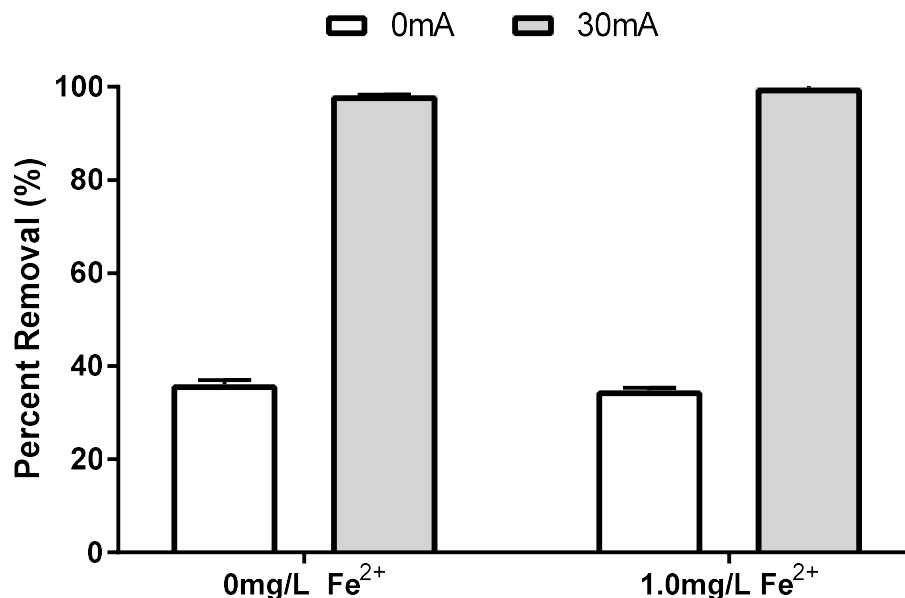


Figure 5.10: Arsenic (As) removal using 0 or 30 mA electrolytic treatment with 1 mg/L ferrous ion present in the feed water. The values shown are the means of three tests \pm 1 standard deviation. Some error bars are not visible due to the small standard deviation. The NaCl concentration in the feed water was 500 mg/L and the pH was 6.78.

As the ORP of the three main free chlorine compounds is higher than the ORP of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{As}^{3+}/\text{As}^{5+}$ (as shown in Table 5.3), the electrolysis process can oxidize ferrous to ferric and arsenite to arsenate if stoichiometrically-sufficient free chlorine concentrations are present.

Table 5.3 ORP of the chemicals involved in the oxidation process

Redox Pair	ORP (V)
$\text{Fe}^{2+}/\text{Fe}^{3+}$	0.2
$\text{As}^{3+}/\text{As}^{5+}$	0.56
Cl_2/Cl^-	1.36
HOCl/Cl^-	1.29
OCl^-/Cl^-	1.31

The concentration of free chlorine in the membrane testing cell effluent was 2.08 mg/L when arsenite and ferrous were not present, but decreased by 0.41 mg/L when 400 $\mu\text{g/L}$ arsenite (excess stoichiometric dose) was added to the feed water. According to the stoichiometric ratio, 400 $\mu\text{g/L}$ arsenite consumes 0.39 mg/L of free chlorine, which agrees with the experimental results. Additionally, ferrous consumes 0.79 mg/L free chlorine according to the stoichiometric ratio, which was the exact decrease observed for tests with and without ferrous. The results demonstrate that free chlorine was able to oxidize both the arsenite and ferrous present in the solution.

5.3.3. pH

The previous results suggested that free chlorine was the main As(III) oxidizer in the electrolysis module. Chloride ions lose electrons to generate Cl_2 , and Cl_2 reacts with water to form HOCl and OCl^- . The electrode potentials of HOCl and OCl^- decline as pH increases (Eq 3.17 to 3.19), but in the typical ground and surface water pH range (5 to 9), their E_H are higher than the ORP of $\text{As}^{3+}/\text{As}^{5+}$. Tests of As(III) removal at pH 7, 8, 9 and 10 using 30 mA electrolysis treatment demonstrated statistically consistent removal (Figure 5.10, ANOVA, $P=1$). With current, removals were much greater than the removals without electrolysis. According to the results shown here, the range of pH

values encountered in natural waters have negligible impact on arsenic removal when RO-electrolysis was used.

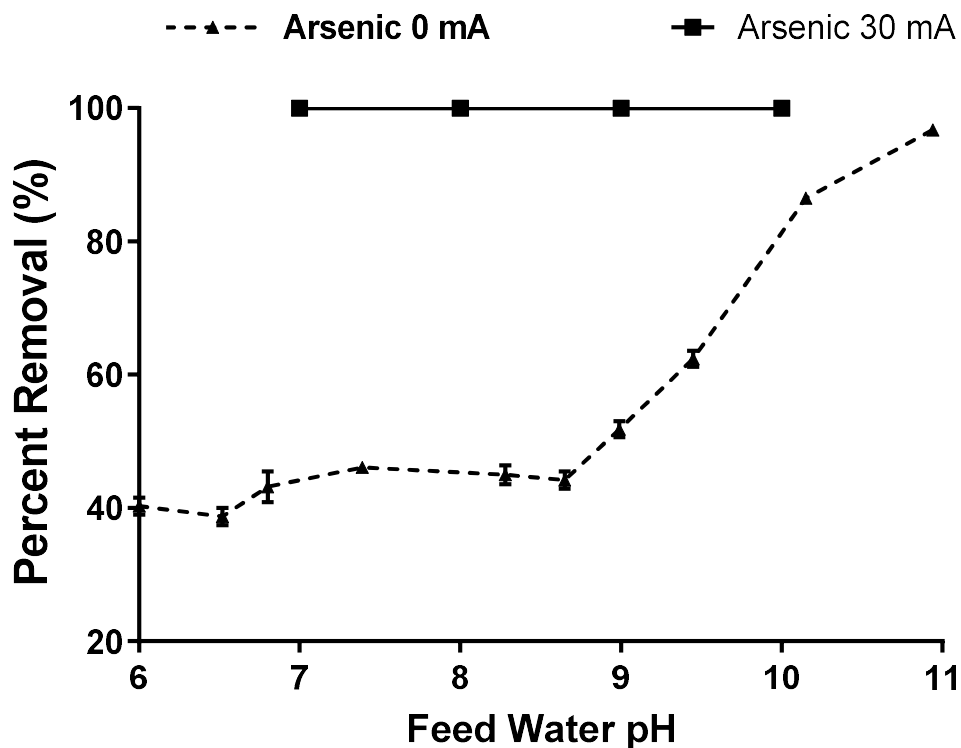


Figure 5.11: Arsenic removal using XLP RO membrane and 0 or 30 mA electrolysis treatment at different feed water pH. Values shown are the means of three tests \pm 1 standard deviation. Some error bars are not visible due to the small standard deviation. The NaCl concentration in the feed water was 500 mg/L.

5.3.4. Sulfide

Sodium sulfide was added to the feed water at a concentration of 1.4 mg/L. The resulting influence on arsenic removal using the RO membrane is shown in Figure 5.11. Arsenic removal increased significantly after sulfide was added, even without electrolytic oxidation (t-test $P=2.6E-4$). However, arsenic removal did not significantly change with the addition of electrolysis treatment when sulfide was present in feed water (t-test $P=0.38$). According to Rxns 3.8 through 3.17, sulfide and arsenite can react to generate

thioarsenite and thioarsenate, both of which are dissociated in water and form ions. Removal of ions by RO membranes is higher than neutral arsenite molecules; therefore, arsenic removal by RO membranes increased in the presence of sulfide even when there was no electrolytic oxidation.

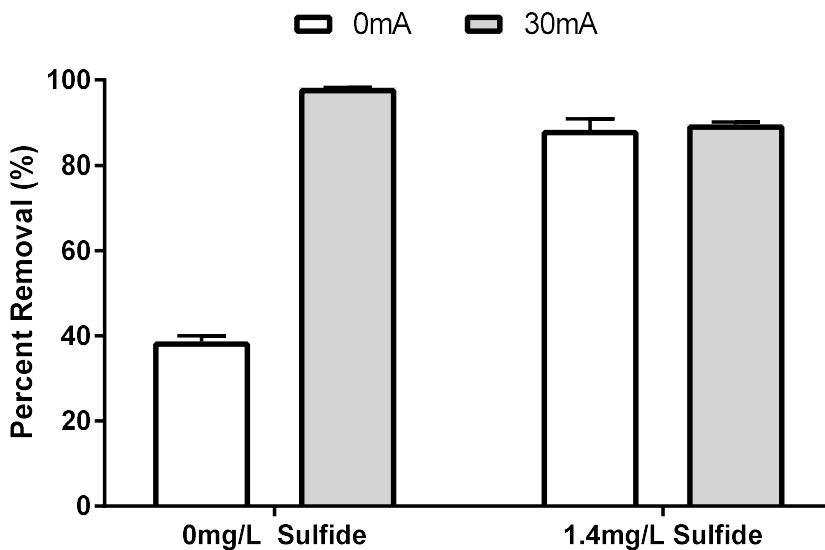


Figure 5.12: Arsenic removal using electrolysis-RO with and without sulfide present in the feed water. Values shown are the means of four tests \pm 1 standard deviation. The NaCl concentration in the feed water was 500 mg/L and the pH was 6.58.

5.3.5. Alkalinity

Sodium bicarbonate was added to the feed water at a concentration of 248 mg/L as CaCO_3 . The results shown in Figure 5.12 indicated that the arsenic removal using the RO membrane did not change with the addition of alkalinity (t-test, $P=0.08$), but the average arsenic removal using the RO membrane increased significantly after applying 30 mA current (t-test, $P=0.001$). The alkalinity of the RO testing cell effluent did not differ significantly from the feed water. The results showed that alkalinity did not impact

the oxidation of arsenite by free chlorine, although alkalinity can impact advanced oxidation processes (Autin et al., 2013).

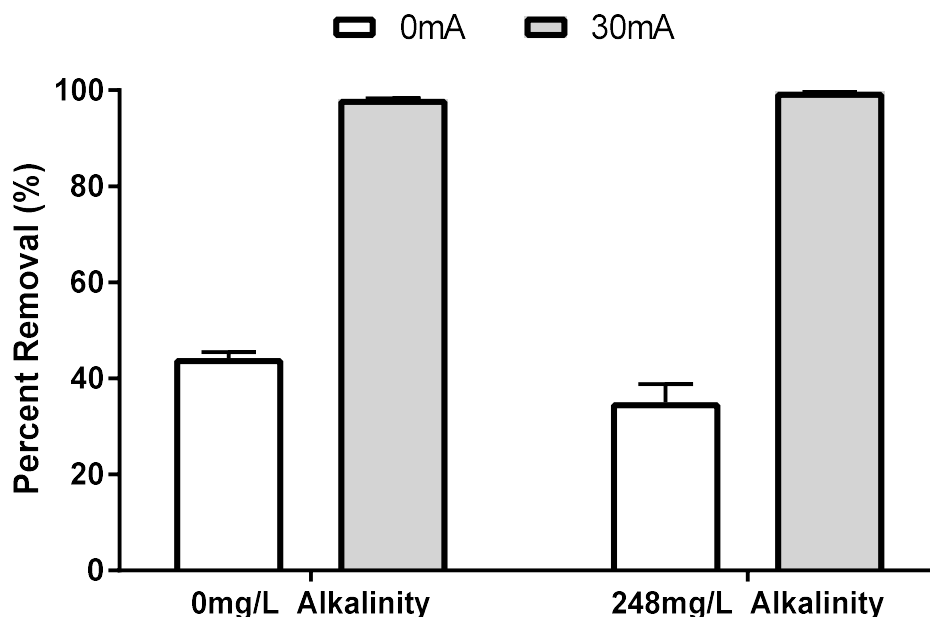


Figure 5.13: Arsenic removal using electrolysis-RO at 0 or 30 mA with and without alkalinity. The values shown are the means of three tests \pm 1 standard deviation. The NaCl concentration in feed water was 500 mg/L and the pH was 8.49.

5.3.6. NOM

Humic acid was added to the feed water at a concentration of 2.2 mg/L TOC. Figure 5.13 shows the arsenic removal using the RO membrane increased slightly from $53.8\% \pm 0.8\%$ to $54.6\% \pm 0.9\%$ after humic acid was added (t-test, $P=0.03$). With the application of 30 mA electrolytic oxidation, the average arsenic removal significantly increased to $99.9\% \pm 0.1\%$ (t test, $P=0.13$). The TOC concentration of the membrane reject water and feed water were both 2.2 mg/L This indicated that free chlorine cannot completely oxidize humic acid, at least during the retention time of the experiment.

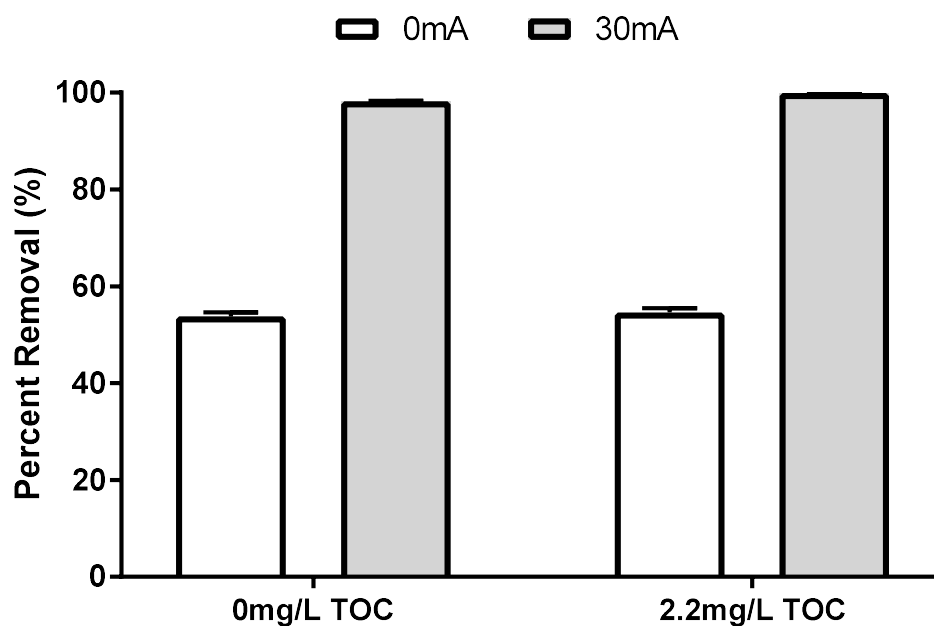


Figure 5.14: Arsenic removal using electrolysis-RO with 0 or 30 mA electrolytic treatment with and without TOC. The values shown are the means of three tests ± 1 standard deviation. Some error bars are not visible due to the small standard deviation. The NaCl concentration in feed water was 500 mg/L, pH was 7.36.

6. CONCLUSIONS

Arsenite removal using a XLP RO membrane (Dow Chemical, USA) was approximately 40 to 54%, which does not meet the goal of 98% removal (based on an initial concentration of 360 $\mu\text{g/L}$ and a final concentration of 10 $\mu\text{g/L}$). Significantly improved arsenic removal (more than 98%) was attained using electrolytic oxidation at 30 mA DC current (although the influence of water quality on optimal operating current should be evaluated in future studies). The improvement in performance was associated with the electrolytic oxidation of As(III) to As(V), which is much more effectively removed using RO treatment. The main oxidant responsible for the electrolytic oxidation of As(III) was shown to be free chlorine, while no evidence was found to support the presence of other oxidants. Additionally, a novel NF-based approach to rapid differentiation between As(III) and As(IV) was validated as part of the study.

The impact of several water quality parameters on the electrolysis-RO process was assessed. Chloride concentrations significantly impacted arsenic removal, as they are directly linked to the generation of the free chlorine oxidant responsible for converting As(III) to the more readily removable As(V). Chlorine generation efficiency declined as chloride concentrations dropped. Feed water alkalinity, ferrous and NOM concentrations did not significantly impact arsenic removal in the electrolysis-RO membrane system. The reaction of sulfide and arsenic is able to generate ionized species, which significantly improved arsenic removal using RO membranes, even without electrolytic oxidation (and application of current did not provide any additional benefit in this case).

For efficient operation of these systems, the feed water chloride concentration must be sufficient to generate enough free chlorine to satisfy stoichiometric requirements

for As(III) oxidation. Notably, the presence of reduced matter must be accounted for as it will compete with arsenic during the oxidation reactions, and the amount of free chlorine must be sufficient to satisfy this competition.

This study demonstrated the feasibility of electrolytic oxidation (as a mechanism to generate free chlorine) as a pretreatment for RO membranes in order to improve arsenic removal. 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 more complex, and realistic water matrices should be evaluated, including assessment of the generation of free chlorine in low chloride, high TDS feed water. An additional scenario of interest is high hardness feed water, wherein the risk of electrode scaling (and subsequently diminished electrode life) is higher.

7. BIBLIOGRAPHY

- Akin, I., Arslan, G., Tor, A., Cengeloglu, Y., & Ersoz, M. (2011). Removal of arsenate [As(V)] and arsenite [As(III)] from water by SWHR and BW-30 reverse osmosis. *Desalination*, 281, 88–92. <http://doi.org/10.1016/j.desal.2011.07.062>
- Alert, E. (2006). Arsenic toxicity, (June 1990).
- Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S. A., & Jefferson, B. (2013). The impact of background organic matter and alkalinity on the degradation of the pesticide metaldehyde by two advanced oxidation processes: UV/H₂O₂ and UV/TiO₂. *Water Research*, 47(6), 2041–2049. <http://doi.org/10.1016/j.watres.2013.01.022>
- Baker, D. E., & Chesnin, L. (1975). Chemical Monitoring of Soils for Environmental Quality and Animal and Human Health. *Advances in Agronomy*, 27, 305–374. [http://doi.org/10.1016/S0065-2113\(08\)70013-0](http://doi.org/10.1016/S0065-2113(08)70013-0)
- Berg, M., Tran, H. C., Nguyen, T. C., Pham, H. V., Schertenleib, R., & Giger, W. (2001). Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat. *Environmental Science & Technology*, 35(13), 2621–2626. <http://doi.org/10.1021/es010027y>
- Bergmann, M. E. H., & Koparal, A. S. (2005). Studies on electrochemical disinfectant production using anodes containing RuO₂. *Journal of Applied Electrochemistry*, 35(12), 1321–1329. <http://doi.org/10.1007/s10800-005-9064-0>
- Bergmann, M. E. H., Rollin, J., & Iourtchouk, T. (2009). The occurrence of perchlorate during drinking water electrolysis using BDD anodes. *Electrochimica Acta*, 54(7), 2102–2107. <http://doi.org/10.1016/j.electacta.2008.09.040>
- Bhaskar Raju, G., Thalamadai Karuppiyah, M., Latha, S. S., Latha Priya, D., Parvathy, S., & Prabhakar, S. (2009). Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics. *Desalination*, 249(1), 167–174. <http://doi.org/10.1016/j.desal.2008.08.012>

- Brown, K. G., & Ross, G. L. (2002). Arsenic, drinking water, and health: a position paper of the American Council on Science and Health. *Regul Toxicol Pharmacol*, 36(2), 162–174. <http://doi.org/10.1006/rtph.2002.1573>
- Cadena, F., & Peters, R. W. (1988). Evaluation of Chemical Oxidizers for Hydrogen Sulfide Control. *Journal WPCF (Water Pollution Control Federation)*, 60(7), 1259–1263. <http://doi.org/10.2307/25043633>
- Chatterjee, A., Das, D., & Chakraborti, D. (1993). A study of ground water contamination by arsenic in the residential area of behala, calcutta due to industrial pollution. *Environmental Pollution*, 80(1), 57–65. [http://doi.org/10.1016/0269-7491\(93\)90010-L](http://doi.org/10.1016/0269-7491(93)90010-L)
- Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and Purification Technology*, 38(1), 11–41. <http://doi.org/10.1016/j.seppur.2003.10.006>
- Chen, W., & Lu, H. (2010). 台灣地下水之氧化還原狀態與砷濃度 The Redox Condition and Arsenic Concentration in, 56(2), 57–70.
- Choong, T. S. Y., Chuah, T. G., Robiah, Y., Gregory Koay, F. L., & Azni, I. (2007). Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desalination*, 217(1–3), 139–166. <http://doi.org/10.1016/j.desal.2007.01.015>
- Conrad, F. (2013). Arsenic Removal from Drinking water, (Mcl), 1–54.
- Criaud, A., & Fouillac, C. (1989). The distribution of arsenic (III) and arsenic (V) in geothermal waters: Examples from the Massif Central of France, the Island of Dominica in the Leeward Islands of the Caribbean, the Valles Caldera of New Mexico, U.S.A., and southwest Bulgaria. *Chemical Geology*, 76(3), 259–269. [http://doi.org/10.1016/0009-2541\(89\)90095-8](http://doi.org/10.1016/0009-2541(89)90095-8)
- Deborde, M., & von Gunten, U. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanisms: A critical review. *Water Research*, 42(1–2), 13–51. <http://doi.org/10.1016/j.watres.2007.07.025>
- Dhar, R. K. (1997). Groundwater Arsenic Calamity in Bangladesh.

- Ding, M., Szymczyk, A., & Ghoufi, A. (2016). Hydration of a polyamide reverse-osmosis membrane. *Journal of Membrane Science*, 501, 248–253.
<http://doi.org/10.1016/j.memsci.2015.12.036>
- Dodd, M. C., Vu, N. D., Ammann, A., Le, V. C., Kissner, R., Pham, H. V., ... Von Gunten, U. (2006). Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: Relevance to drinking water treatment. *Environmental Science and Technology*, 40(10), 3285–3292. <http://doi.org/10.1021/es0524999>
- Driehaus, W., Seith, R., & Jekel, M. (1995). Oxidation of arsenate(III) with manganese oxides in water treatment. *Water Research*, 29(1), 297–305.
[http://doi.org/10.1016/0043-1354\(94\)E0089-O](http://doi.org/10.1016/0043-1354(94)E0089-O)
- Duarte, A. A. L. S., Cardoso, S. J. A., & Alçada, A. J. (2009). Emerging and innovative techniques for arsenic removal applied to a small water supply system. *Sustainability*, 1(4), 1288–1304. <http://doi.org/10.3390/su1041288>
- EPA. (2000). National Primary Drinking Water Regulations Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring Proposed Rule, 1–97.
- EPA. (2012a). 2012 Edition of the Drinking Water Standards and Health Advisories.
http://doi.org/EPA_822-S-12-001
- EPA. (2012b). EPA 2012. *Annual Reports Section “C” (Physical Chemistry)*.
http://doi.org/EPA_822-S-12-001
- Feenstra, L., & Erkel, J. Van. (2007). Arsenic in groundwater : Overview and evaluation of removal methods. *International Groundwater Resources Assessment Centre*, (December), 1–23.
- Feng, C., Sugiura, N., Shimada, S., & Maekawa, T. (2003). Development of a high performance electrochemical wastewater treatment system. *Journal of Hazardous Materials*, 103(1–2), 65–78. [http://doi.org/10.1016/S0304-3894\(03\)00222-X](http://doi.org/10.1016/S0304-3894(03)00222-X)
- Fisher, R. S., & Mullican, III, W. F. (1997). Hydrochemical Evolution of Sodium-Sulfate and Sodium-Chloride Groundwater Beneath the Northern Chihuahuan Desert, Trans-

- Pecos, Texas, USA. *Hydrogeology Journal*. <http://doi.org/10.1007/s100400050102>
- Frey, M. M., Owen, D. M., Chowdhury, Z. K., Raucher, R. S., & Edwards, Marc, A. (1998). Cost to utilities of a lower MCL for arsenic. *American Water Works Association*, 90(3), 89.
- Fujioka, T., Oshima, N., Suzuki, R., Price, W. E., & Nghiem, L. D. (2015). Probing the internal structure of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight into the transport of water and small solutes. *Journal of Membrane Science*, 486, 106–118. <http://doi.org/10.1016/j.memsci.2015.02.007>
- Geucke, T., Deowan, S. A., Hoinkis, J., & Pätzold, C. (2009). Performance of a small-scale RO desalinator for arsenic removal. *Desalination*, 239(1–3), 198–206. <http://doi.org/10.1016/j.desal.2008.03.018>
- Gholami, M. M., Mokhtari, M. A., Aameri, A., & Alizadeh Fard, M. R. (2006). Application of reverse osmosis technology for arsenic removal from drinking water. *Desalination*, 200(1–3), 725–727. <http://doi.org/10.1016/j.desal.2006.03.504>
- Harvey, C. F., Ashfaq, K. N., Yu, W., Badruzzaman, A. B. M., Ali, M. A., Oates, P. M., ... Ahmed, M. F. (2006). Groundwater dynamics and arsenic contamination in Bangladesh. *Chemical Geology*, 228(1–3 SPEC. ISS.), 112–136. <http://doi.org/10.1016/j.chemgeo.2005.11.025>
- Heffron, J., & Heffron, J. (2015). Removal of Trace Heavy Metals from Drinking Water by Electrocoagulation Removal of Trace Heavy Metals from Drinking Water by Electrocoagulation, (April).
- Hofmann, R., & Andrews, R. C. (2006). Impact of H₂O₂ and (bi)carbonate alkalinity on ammonia's inhibition of bromate formation. *Water Research*, 40(18), 3343–3348. <http://doi.org/10.1016/j.watres.2006.07.032>
- Hughes, M. F. (2002). Arsenic toxicity and potential mechanisms of action. *Toxicology Letters*, 133(1), 1–16. [http://doi.org/10.1016/S0378-4274\(02\)00084-X](http://doi.org/10.1016/S0378-4274(02)00084-X)
- Jeong, J., Kim, C., & Yoon, J. (2009). The effect of electrode material on the generation of

- oxidants and microbial inactivation in the electrochemical disinfection processes. *Water Research*, 43(4), 895–901. <http://doi.org/10.1016/j.watres.2008.11.033>
- Kang, M., Kawasaki, M., Tamada, S., Kamei, T., & Magara, Y. (2000). Effect of pH on the removal of arsenic and antimony using reverse osmosis membranes. *Desalination*, 131(1–3), 293–298. [http://doi.org/10.1016/S0011-9164\(00\)90027-4](http://doi.org/10.1016/S0011-9164(00)90027-4)
- Kim, M. J., & Nriagu, J. (2000). Oxidation of arsenite in groundwater using ozone and oxygen. *Science of the Total Environment*, 247(1), 71–79. [http://doi.org/10.1016/S0048-9697\(99\)00470-2](http://doi.org/10.1016/S0048-9697(99)00470-2)
- Košutić, K., Furač, L., Sipos, L., & Kunst, B. (2005). Removal of arsenic and pesticides from drinking water by nanofiltration membranes. *Separation and Purification Technology*, 42(2), 137–144. <http://doi.org/10.1016/j.seppur.2004.07.003>
- Kraft, a, Stadelmann, M., Blaschke, M., Kreysig, D., Sandt, B., Schro, F., & Rennau, J. (1999). Electrochemical water disinfection Part I: Hypochlorite production from very dilute chloride solutions. *Journal of Applied Electrochemistry*, 29, 861–868. <http://doi.org/10.1023/A:1003650220511>
- Kurihara, M. (2008). New Advancement of Seawater Desalination Reverse Osmosis Membranes (SWRO), (March).
- Kurtio, P., Komulainen, H., Hakala, E., Kahelin, H., & Pekkanen, J. (1998). Urinary excretion of arsenic species after exposure to arsenic present in drinking water. *Archives of Environmental Contamination and Toxicology*, 34(3), 297–305. <http://doi.org/10.1007/s002449900321>
- Li, L., Van Genuchten, C. M., Addy, S. E. A., Yao, J., Gao, N., & Gadgil, A. J. (2012). Modeling As(III) oxidation and removal with iron electrocoagulation in groundwater. *Environmental Science and Technology*, 46(21), 12038–12045. <http://doi.org/10.1021/es302456b>
- Li Puma, G., & Yue, P. L. (2003). Modelling and design of thin-film slurry photocatalytic reactors for water purification. *Chemical Engineering Science*, 58(11), 2269–2281.

[http://doi.org/10.1016/S0009-2509\(03\)00086-1](http://doi.org/10.1016/S0009-2509(03)00086-1)

M A Jun, Li Xue Yan, Cheng Zhong lin, Q. F. (2006). Removal of 2-Methylisoborneol in Drinking Water by Ozonation.

Malaeb, L., & Ayoub, G. M. (2011). Reverse osmosis technology for water treatment: State of the art review. *Desalination*, 267(1), 1–8. <http://doi.org/10.1016/j.desal.2010.09.001>

Mandal, B. (2002). Arsenic round the world: a review. *Talanta*, 58(1), 201–235. [http://doi.org/10.1016/S0039-9140\(02\)00268-0](http://doi.org/10.1016/S0039-9140(02)00268-0)

Manning, B. A., Fendorf, S. E., Bostick, B., & Suarez, D. L. (2002). Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environmental Science and Technology*, 36(5), 976–981. <http://doi.org/10.1021/es0110170>

Marshall, W., & Vol, M. (1945). The Electrolytic Oxidation of Arsenic (III) in Acid Solution, 1, 1–3.

Martínez-Huitle, C. A., & Brillas, E. (2008). Electrochemical alternatives for drinking water disinfection. *Angewandte Chemie - International Edition*, 47(11), 1998–2005. <http://doi.org/10.1002/anie.200703621>

Matschullat, J. (2000). Arsenic in the geosphere – a review.

Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents-A critical review. *Journal of Hazardous Materials*, 142(1–2), 1–53. <http://doi.org/10.1016/j.jhazmat.2007.01.006>

Na, L. I., Maohong, F. A. N., Johannes, V. L., Basudeb, S., Hongqun, Y., & Huang, C. P. (2007). Oxidation of As (III) by potassium permanganate, 19, 783–786.

Nas, B., & Berktaý, A. (2010). Groundwater quality mapping in urban groundwater using GIS. *Environmental Monitoring and Assessment*, 160(1–4), 215–227. <http://doi.org/10.1007/s10661-008-0689-4>

Ng, J. C., Wang, J., & Shraim, A. (2003). A global health problem caused by arsenic from natural sources, 52, 1353–1359. [http://doi.org/10.1016/S0045-6535\(03\)00470-3](http://doi.org/10.1016/S0045-6535(03)00470-3)

- Ning, R. (2002). Arsenic removal by reverse osmosis. *Desalination*, 143(3), 237–241.
[http://doi.org/10.1016/S0011-9164\(02\)00262-X](http://doi.org/10.1016/S0011-9164(02)00262-X)
- Nordstrom, D. K. (2002). Worldwide Occurrences of Arsenic in Ground Water, 296(June), 64–65. <http://doi.org/10.1007/b101867>
- Nyhus, K. J., Wilborn, A. T., & Jacobson, E. S. (1997). Ferric iron reduction by *Cryptococcus neoformans*. *Infection and Immunity*, 65(2), 434–8. Retrieved from <http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=174613&tool=pmcentrez&rendertype=abstract>
- O'Day, P. a, Vlassopoulos, D., Root, R., & Rivera, N. (2004). The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proceedings of the National Academy of Sciences of the United States of America*, 101(38), 13703–13708. <http://doi.org/10.1073/pnas.0402775101>
- Oliveira, F. H., Osugi, M. E., Paschoal, F. M. M., Profeti, D., Olivi, P., & Zanoni, M. V. B. (2007). Electrochemical oxidation of an acid dye by active chlorine generated using Ti/Sn(1-x)Ir x O₂ electrodes. *Journal of Applied Electrochemistry*, 37(5), 583–592. <http://doi.org/10.1007/s10800-006-9289-6>
- Panizza, M., & Cerisola, G. (2004). Influence of anode material on the electrochemical oxidation of 2-naphthol: Part 2. Bulk electrolysis experiments. *Electrochimica Acta*, 49(19), 3221–3226. <http://doi.org/10.1016/j.electacta.2004.02.036>
- Petrusevski, B., Sharma, S., Schippers, J., & Shordt, K. (2001). *Arsenic in Drinking Water*. [http://doi.org/10.1016/S0273-1223\(99\)00432-1](http://doi.org/10.1016/S0273-1223(99)00432-1)
- Quansah, R., Armah, F. A., Essumang, D. K., Luginaah, I., Clarke, E., Marfoh, K., ... Dzodzomenyo, M. (2015). Association of arsenic with adverse pregnancy outcomes/infant mortality: A systematic review and meta-analysis. *Environmental Health Perspectives*, 123(5), 412–421. <http://doi.org/10.1289/ehp.1307894>
- Ransom, Richland, and S. C. (2013). Five-Year Review Report Fourth Five-Year Review Report for Arsenic Trioxide Superfund Site, (September).

- Ratnaike, R. N. (2003). Acute and chronic arsenic toxicity, 391–397.
<http://doi.org/10.1136/pmj.79.933.391>
- Seo, E. T., Nelson, R. F., Fritsch, J. M., Marcoux, L. S., Leedy, D. W., & Adams, R. N. (1966). Anodic Oxidation Pathways of Aromatic Amines. Electrochemical and Electron Paramagnetic Resonance Studies. *J. Am. Chem. Soc.*, 88(1965), 3498–3503.
<http://doi.org/10.1021/ja00967a006>
- Shi, H., Shi, X., & Liu, K. J. (2004). Oxidative mechanism of arsenic toxicity and carcinogenesis. *Molecular and Cellular Biochemistry*, 255(1–2), 67–78.
<http://doi.org/10.1023/B:MCBI.00000007262.26044.e8>
- Sirés, I., Brillas, E., Oturan, M. A., Rodrigo, M. A., & Panizza, M. (2014). Electrochemical advanced oxidation processes: Today and tomorrow. A review. *Environmental Science and Pollution Research*, 21(14), 8336–8367. <http://doi.org/10.1007/s11356-014-2783-1>
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source , behaviour and distribution of arsenic in natural waters, 17, 517–568.
- Smith, A. H., Hopenhayn-Rich, C., Bates, M. N., Goeden, H. M., Hertz-Picciotto, I., Duggan, H. M., ... Smith, M. T. (1992). Cancer risks from arsenic in drinking water. *Environmental Health Perspectives*, 97(6), 259–267.
<http://doi.org/10.1289/ehp.9297259>
- Song, S., Lopez-Valdivieso, a., Hernandez-Campos, D. J., Peng, C., Monroy-Fernandez, M. G., & Razo-Soto, I. (2006). Arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite. *Water Research*, 40(2), 364–372.
<http://doi.org/10.1016/j.watres.2005.09.046>
- Sorlini, S., & Gialdini, F. (2010). Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine. *Water Research*, 44(19), 5653–5659.
<http://doi.org/10.1016/j.watres.2010.06.032>

- Stauder, S., Raue, B., & Sacher, F. (2005). Thioarsenates in sulfidic waters. *Environmental Science and Technology*, 39(16), 5933–5939. <http://doi.org/10.1021/es048034k>
- Table, P. (2004). Arsenic and Arsenic Compounds (Book), 2002.
- Teychene, B., Collet, G., Gallard, H., & Croue, J. P. (2013). A comparative study of boron and arsenic (III) rejection from brackish water by reverse osmosis membranes. *Desalination*, 310, 109–114. <http://doi.org/10.1016/j.desal.2012.05.034>
- Tribus, M., & Evans, R. B. (1962). Sorlini & Gialdini, 2010, (2), 62–63.
- Tu, Kha L., Long D. Nghiem, A. R. C. (2011). Boron removal by reverse osmosis membranes.
- Urase, T., Oh, J. I., & Yamamoto, K. (1998). Effect of pH on rejection of different species of arsenic by nanofiltration. *Desalination*, 117(1–3), 11–18. [http://doi.org/10.1016/S0011-9164\(98\)00062-9](http://doi.org/10.1016/S0011-9164(98)00062-9)
- Vrijenhoek, E. M., & Waypa, J. J. (2000). Arsenic removal from drinking water by a “loose” nanofiltration membrane. *Desalination*, 130(3), 265–277. [http://doi.org/10.1016/S0011-9164\(00\)00091-6](http://doi.org/10.1016/S0011-9164(00)00091-6)
- Walker, M., Seiler, R. L., & Meinert, M. (2008). Effectiveness of household reverse-osmosis systems in a Western U.S. region with high arsenic in groundwater. *Science of the Total Environment*, 389(2–3), 245–252. <http://doi.org/10.1016/j.scitotenv.2007.08.061>
- Wang, S., & Mulligan, C. N. (2006). Occurrence of arsenic contamination in Canada: Sources, behavior and distribution. *Science of the Total Environment*, 366(2–3), 701–721. <http://doi.org/10.1016/j.scitotenv.2005.09.005>
- Westerhoff, P., Chao, P., & Mash, H. (2004). Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Research*, 38(6), 1502–1513. <http://doi.org/10.1016/j.watres.2003.12.014>
- WHO. (2004). Arsenic and Arsenic Compounds (Book), 2002, 1–484.

- WHO. (2004). Arsenic in drinking-water. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, 84, 41–267. <http://doi.org/10.1016/j.kjms.2011.05.002>
- WHO. (2004). Guidelines for drinking-water quality, 3rd edition, 1, 516. [http://doi.org/10.1016/S1462-0758\(00\)00006-6](http://doi.org/10.1016/S1462-0758(00)00006-6)
- WHO. (2010). Exposure to Arsenic: A Major Public Health Concern. *Agriculture*, 5. <http://doi.org/10.1016/j.ecoenv.2011.12.007>
- Williams, M. E. (2003). A Review of Reverse Osmosis Theory. *EET Corporation and Williams Engineering Services Company, Inc*, 1–40.
- Wu, C., & Linden, K. G. (2010). Phototransformation of selected organophosphorus pesticides: Roles of hydroxyl and carbonate radicals. *Water Research*, 44(12), 3585–3594. <http://doi.org/10.1016/j.watres.2010.04.011>
- Yoshida, T., Yamauchi, H., & Fan Sun, G. (2004). Chronic health effects in people exposed to arsenic via the drinking water: Dose-response relationships in review. *Toxicology and Applied Pharmacology*, 198(3), 243–252. <http://doi.org/10.1016/j.taap.2003.10.022>