CHEMICAL CHANGES AND PERFORMANCE OF IRON-ELECTROLYSIS FOR GROUNDWATER REMEDIATION

A Thesis Presented

by

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ABSTRACT

Sustainable and effective technologies are required for remediation of contaminated groundwater. Iron electrolysis is a promising technology, which uses natural and low-cost materials, to enhance remediation of groundwater contaminated with chlorinated solvents.

A two-stage experimental program is conducted to evaluate chemical changes induced by iron electrolysis and its potential for enhanced electrochemical transformation of trichloroethylene (TCE). The first stage includes evaluation of changes in electrolyte pH, redox potential, and conductivity due to iron electrolysis in batch and sand-packed flow-through columns. The controlled variables selected for batch experiments include anode material (inert or iron), background electrolyte composition, electric current and polarity configuration. The controlled variables for flow-through experiments include anode material, current density, flow rate and background electrolyte composition.

The batch experiments are conducted in a glass electrochemical cell. The pH of mixed electrolyte is stable when inert (MMO) anode is used. When the iron anode is used, the pH for relatively low current density does not tend to show significant changes; however, the pH increases sharply under high current densities. Using iron anodes results in reducing electrolyte condition. Inert anode (MMO) produces an oxidizing environment when compared to iron anode due to oxygen release from the MMO anode. In addition, the distribution of pH and redox potential in the flow-through column is dependent on the applied current density and flow rate. Low flow rate does not produce significant changes in pH and redox potential until a specific
period of application. When steady state condition where reached, chemicals distribution in column were similar under different flow rates.

The second stage is focused on evaluation of the role of iron electrolysis on improved electrochemical dechlorination of TCE. The controlled variables for the second stage include the anode and cathode material types, current density and initial TCE concentration. Iron anodes enhance the reductive dechlorination of TCE on the cathode surface by creating favorable electrolyte conditions for TCE reduction. Combining porous copper cathodes and iron anodes show the best dechlorination rates. The dechlorination rate constants (k) increase with increase in applied current and decrease in initial TCE concentration.
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Chapter 1

Introduction

1.1 Overview

Chlorinated organic compounds (COCs) such as tetrachloroethylene (PCE) and trichloroethylene (TCE) are commonly found contaminants in soil, groundwater, sediment and other environmental media. According to the United States Environmental Protection Agency (USEPA) records, TCE has been found in 852 of 1430 National Priority List (NPL) sites \[1\]. Similarly PCE has been recorded in 771 of 1430 NPL sites \[2\]. COCs do not occur naturally in the environment. Their presence in the environment is mainly because of poor disposal practices from manufacturing and human use. Human exposure to chlorinated solvents may cause serious health problems because of their high toxicity levels. For this reason the USEPA has developed strict regulations concerning handling and disposing of chlorinated organic compounds. For example, the USEPA has set maximum contaminant level in drinking water at 0.005 mg L\(^{-1}\) for TCE and PCE to protect human health.

Over the last several decades, significant research has been conducted to remove COCs from the environmental media and control the potential human exposure or transform COCs to less-toxic/non-toxic by-products. Several remediation methods were evaluated for practicality, effectiveness (optimization, cost effectiveness, remediation efficiency and operation time), and environmental sustainability.
Electrochemical processes and electrochemically enhanced biological processes are considered effective methods for the treatment of chlorinated organic compounds in contaminated soil, water, sediment, and other environmental media. The contaminants can be transformed to less toxic by-products by direct oxidation, or reduction on the electrode surface. Other methods include indirect biological, chemical or physicochemical transformation in the electrolyte \cite{3,4}, such as electrochemically-assisted biological reduction \cite{5}, chemical reduction \cite{6}, electrocoagulation \cite{7}, electroflotation \cite{8} and electrofloculation \cite{9}.

Generally, research on electrochemical water treatment has shown that the efficiency of electrochemical processes is affected not only by electrode surface reactivity and reactions, but also by the temporary changes on the physical and (or) chemical properties of electrolyte. The performance of electrochemical remediation methods could be optimized by controlling the physicochemical conditions of the electrochemical redox system. The types of anode and the cathode materials have great influences on the chemical properties of the medium during electrochemical remediation process. Anode and cathode materials change the dominant electrolysis reactions and the type and concentration of the species in the electrolyte during treatment.

Although iron (cast iron, mild steel etc.) electrolysis is an important electrochemical treatment process having promising potential during the electrochemical remediation of chlorinated compounds like TCE, it was not evaluated in the literature. Iron electrolysis has been reported mostly for remediation of heavy metals with electrocoagulation technology and for remediation of chlorinated hydrocarbons with zero valent iron (ZVI). However, ZVI based technologies have some limitations regarding uncontrollable dechlorination potential during the treatment and fast
passivation of nano scale iron particles. Using separated iron anode and cathode may allow for a fast and controllable dechlorination rate by adjusting operating parameters.

1.2 Objectives of Research

The primary goals of this study are to define and evaluate chemical changes from iron electrolysis during electrochemical treatment of groundwater and compare the results with electrolysis by inert anodes. Moreover, the reductive TCE dechlorination efficiencies of different anode and cathode materials are assessed and reported. The specific research objectives are as follows:

- To define the temporal chemical changes in pH, ORP and conductivity with iron anodes in mixed and divided electrolytes with varying current densities, background electrolyte compositions and DC source polarity configuration.
- To compare iron anode with inert anode in terms of the induced chemical changes in batch electrochemical cells and flow-through column set-up.
- To define iron speciation and the iron dissolution efficiencies in varying electrolyte compositions and current densities in batch electrochemical cells.
- To evaluate TCE dechlorination efficiencies of different anode and cathode materials and to evaluate the current densities and initial TCE concentration effects on the dechlorination rate constants during electrochemical treatment process with iron anodes.
1.3 Organization of Thesis

This thesis consists of five chapters. Chapter 1 includes an introduction about chlorinated contaminants (mostly TCE and PCE) found in the USA to understand the necessity to develop new remediation methods. Electrochemical processes are also introduced and the role of anode and cathode materials is emphasized. The goals and objectives of the research are defined in Chapter 1. Chapter 2 presents the general physical and chemical properties of chlorinated solvents with literature review of remediation methods. Subsequently, an overview of electrochemical remediation of TCE and the use of iron in remediation processes is presented. Chapter 3 describes the experimental methods and procedures, materials and experimental apparatus in detail. Moreover, the lists of experiments with variables and experimental conditions are provided. Chapter 4 presents the results and discussion of experiments. Chapter 5 provides the summary of the results, conclusions and future work recommendations.
Chapter 2

Background Review

2.1 Introduction

The chlorinated solvents, such as tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC), are commonly found contaminants in the environment. Several remediation technologies have been developed to clean up these contaminants. Among these methods, electrochemical methods such as electrochemical reduction and oxidation are most promising and can transform chlorinated contaminants to non-toxic hydrocarbons. Electrochemical methods depend on the proper selection of the anode and cathode materials to enhance dechlorination efficiency. In this chapter, the physical and chemical properties of commonly found chlorinated contaminants are discussed. A general description of commonly used remediation technologies is presented with a discussion of advantages and limitations. Technologies that involve the use of iron are then briefly explained. Lastly, reported studies from the literature on electrochemical reduction, also known as electrochemical reductive dechlorination, are summarized.
2.2 Basic Physical and Chemical Properties of Chlorinated Ethenes

Chlorinated ethenes such as PCE, TCE, DCE and VC are synthetic chemicals that have favorable properties and are widely used for industrial purposes. A summary of basic physical and chemical properties of these ethenes is presented in Table 2.1. However, improper disposal of these chemical results in significant soil and groundwater contamination in the US. Some of these chemical are persistence and their removal and remediation from contaminated media is a challenge.
Table 2.1 Physical and chemical properties of chlorinated ethenes

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Tetrachloroethene</th>
<th>Trichloroethene</th>
<th>cis-1,2-Dichloroethene</th>
<th>trans-1,2-Dichloroethene</th>
<th>Vinyl Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbreviation</td>
<td>PCE</td>
<td>TCE</td>
<td>cis-1,2-DCE</td>
<td>trans-1,2-DCE</td>
<td>VC</td>
</tr>
<tr>
<td>CAS Registry Number</td>
<td>127-18-4</td>
<td>79-01-6</td>
<td>156-59-2</td>
<td>156-60-5</td>
<td>75-01-4</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C₂Cl₄</td>
<td>C₂HCl₃</td>
<td>C₂H₂Cl₂</td>
<td>C₂H₂Cl₂</td>
<td>C₂H₃Cl</td>
</tr>
<tr>
<td>Molar Weight</td>
<td>165.83</td>
<td>131.4</td>
<td>96.95</td>
<td>96.95</td>
<td>62.5</td>
</tr>
<tr>
<td>Appearance @20 °C</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless liquid</td>
<td>Colorless gas</td>
</tr>
<tr>
<td>Odor</td>
<td>Ethereal</td>
<td>Ethereal; sweet</td>
<td>Ethereal, slightly acrid</td>
<td>Ethereal, slightly acrid</td>
<td>sweet</td>
</tr>
<tr>
<td>Density, g/ml @ 20 °C</td>
<td>1.6227</td>
<td>1.465</td>
<td>1.2837</td>
<td>1.2565</td>
<td>0.9106</td>
</tr>
<tr>
<td>Boiling Point, °C</td>
<td>121</td>
<td>86.7</td>
<td>60.3</td>
<td>48</td>
<td>-13.37</td>
</tr>
<tr>
<td>Melting Point, °C</td>
<td>-19</td>
<td>-87.1</td>
<td>-80.5</td>
<td>-50</td>
<td>-153.8</td>
</tr>
<tr>
<td>Vapor Pressure, mmHg</td>
<td>18.47 (@25 °C)</td>
<td>74 (@25 °C)</td>
<td>180 (@20 °C)</td>
<td>265 (@20 °C)</td>
<td>2530 (@20 °C)</td>
</tr>
<tr>
<td>Solubility in water, g/L @25 °C</td>
<td>0.15</td>
<td>1.366</td>
<td>3.5</td>
<td>6.3</td>
<td>2.763</td>
</tr>
<tr>
<td>Henry Constant, atm-m³/mol @25 °C</td>
<td>0.018</td>
<td>0.011</td>
<td>0.0041</td>
<td>0.0094</td>
<td>0.0278</td>
</tr>
<tr>
<td>Log Kₗw</td>
<td>3.4</td>
<td>2.42</td>
<td>1.86</td>
<td>2.09</td>
<td>1.36</td>
</tr>
<tr>
<td>Log Kₗoc</td>
<td>2.2-2.7</td>
<td>2.03-2.66</td>
<td>1.69</td>
<td>1.56</td>
<td>1.99</td>
</tr>
</tbody>
</table>

The table is summarized using the information on website: [http://www.atsdr.cdc.gov/](http://www.atsdr.cdc.gov/)
2.3 Remediation of Trichloroethylene

2.3.1 Air Sparging and Biosparging

Air sparging is an in-situ remediation technology for physical removal of volatile organic compounds and fuels. Air or oxygen is injected into the saturated zone to volatilize and transfer groundwater contaminants to the vadose zone. Injected air increases oxygen concentration in saturated and unsaturated soil and enhances aerobic biodegradation of the contaminants. This technology is generally coupled with a soil vapor extraction system which enables extraction of volatilized vapor from the vadose zone [10]. Figure 2.1 shows general components of air sparging system combined with the soil vapor extraction system.

Biosparging uses indigenous microorganism to biodegrade organic constituents in the saturated zone. Air and nutrients are injected to enhance biological activity of the microorganism used for biodegradation of contaminants that are dissolved in groundwater, adsorbed below the water table and within the capillary zone. Biosparging is similar to air sparging however air sparging removes contaminants using physical processes from the medium; biosparging uses biodegradation processes [11].

Air sparging and biosparging are known to clean up volatile organic compounds (VOCs) and BTEX compounds. The effectiveness of pulsed air sparging technology for the remediation of TCE contaminated groundwater in a sandy aquifer was investigated in laboratory experiments. The air was pulsed into the sandy aquifer on daily basis. Based on the results of this study, 95% of the aqueous TCE was removed [12]. The mass transfer mechanism and the effect of system
variables of air sparging on TCE removal have been reported. According to this study, air-injection rate is increasing TCE removal up to an equilibrium point, after this optimum point, the air-injection rate does not have a significant effect on the TCE removal rate $^{[13]}$. 

Figure 2.1 Air sparging system with soil vapor extraction $^{[14]}$
2.3.2 In-Situ Bioremediation

In-situ groundwater bioremediation is a technology that requires contribution of indigenous microorganisms to enhance biodegradation of organic constituents in the saturated zone. It is an effective method to degrade organic compounds dissolved in water. Bioremediation requires 1) electron acceptor (oxygen, nitrate); 2) nutrients (nitrogen, phosphorus); and 3) an energy source (carbon) \[15\].

Figure 2.2 shows a schematic diagram of in-situ groundwater remediation system using injection wells. Groundwater is extracted by using wells and treated dissolved constituents then it is mixed with nutrients and electron acceptors. Afterwards, it is re-injected into the groundwater by wells. In situ bioremediation has been applied to clean up sediments, soil, groundwater and other environmental media contaminated with organic contaminants such as benzene, toluene, tetrachloroethylene (PCE), trichloroethylene (TCE) and polycyclic aromatic hydrocarbons (PAHs).

The effectiveness of this system depends on the hydraulic conductivity, the contaminant type and the location of the contamination in the subsurface. In-situ bioremediation is most effective in high permeable aquifers because of the ease of distribution of essential substrates. Less permeable aquifers need longer time for clean up. The physical and chemical characteristics of the contaminant play a significant role on the performance of the in-situ bioremediation. The biodegradability of the contaminants is a measure of its ability to be metabolized by microorganisms. The heavy metals do not have the ability to be degraded by bioremediation. The water solubility, partitioning coefficient and adsorption characteristics of contaminants are other
chemical properties that have influence on the in-situ bioremediation efficiency. Groundwater pH, temperature and mineral content affect the microbial activity. Optimal microbial activities are occurring at neutral pH conditions. Extreme groundwater temperature values influences the microbial activities negatively\(^{[15]}\).

Figure 2.2 Schematic of in-situ groundwater bioremediation system
2.3.3 Monitored Natural Attenuation (MNA)

Monitored Natural Attenuation is defined by the USEPA as the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. USEPA considers natural attenuation as an alternative remediation method for other viable remediation methods. Some other terms including “intrinsic remediation”, “intrinsic bioremediation”, “passive bioremediation”, “natural recovery” and “natural assimilation” can be used instead of “natural attenuation”. [16]

Natural attenuation is a combination of a variety of chemical, physical and biological processes. Processes that only reduce the concentration of the contaminant are termed “nondestructive” such as volatilization, hydrodynamic dispersion and sorption. Other processes reduce the mass of contaminants such as biodegradation and abiotic degradation; these are termed “destructive”. [16]

The advantages of MNA are in-situ destruction of contaminants, lesser volume of remediation wastes, applicability to all or part of the given site and lower overall remediation cost. The disadvantages of MNA include a longer clean-up time frame, costly and complex site characterization processes, and potential change of hydrologic and geochemical conditions over time.

MNA may be an effective way to remediate the several organic and inorganic contaminants under favorable conditions. Aerobic and anaerobic biological processes show a significant role in the removal of organic contaminants. Natural attenuation of PCE and TCE with a combination of
aerobic and anaerobic biotransformation has been reported at a test site, Area 6 at Dover Air Force (Dover, DE)\textsuperscript{[17]}.

### 2.3.4 In-Situ Chemical Oxidation

Chemical oxidation is defined as the contact between oxidizing chemicals with subsurface contaminants to remediate the contamination. Some oxidizing agents such as potassium ferrate\textsuperscript{[18]}, ozone\textsuperscript{[19]}, hydrogen peroxide\textsuperscript{[20]}, and potassium permanganate\textsuperscript{[21]}, and persulfate\textsuperscript{[22]} have been reported effective on the chemical oxidation of TCE. Delucca et al.\textsuperscript{[18]} reported oxidation of TCE by 30 mg/L ferrate concentration at 23 °C and at pH 8.3. TCE oxidation reaction can be accelerated by adding catalyst such as mixing ferrous ions with hydrogen peroxide (Fenton’s reagent). The reactions between ferrous ($Fe^{2+}$) and hydrogen peroxide ($H_2O_2$) produces several oxidants. The possible reactions occurring in $Fe^{2+}/H_2O_2$ solution are as following:

\begin{align}
Fe^{2+} + H_2O_2 & = Fe^{3+} + HO^- + HO^\cdot \quad (2.1) \\
Fe^{2+} + HO^\cdot & = Fe^{3+} + HO^- \quad (2.2) \\
H_2O_2 + HO^\cdot & = H_2O + HO_2 \quad (2.3) \\
Fe^{2+} + HO_2 & = Fe^{3+} + HO_2^- \quad (2.4) \\
Fe^{2+} + HO_2 & = Fe^{2+} + H^+ + O_2 \quad (2.5) \\
Fe^{3+} + H_2O_2 & = Fe^{2+} + HO_2 + H^+ \quad (2.6)
\end{align}

Hydroxyl radicals ($HO^\cdot$), hydroperoxyl radicals ($HO_2^\cdot$), hydrogen peroxide($H_2O_2$), and oxygen ($O_2$) are all oxidants\textsuperscript{[23]}. Hydroxyl radical ($HO^\cdot$) is a very unstable and strong oxidant causing it
to immediately react with target organic compounds and oxidize them. The rate constant of the hydroxyl radical with TCE is $4 \times 10^9$ M$^{-1}$ s$^{-1}$. The rate constant of TCE oxidation can be enhanced by combining different oxidants such as ozone with hydrogen peroxide or ozone with UV radiation, which is called as advanced oxidation process (AOP). The rate constant of ozone (O$_3$) with TCE is 17 M$^{-1}$ s$^{-1}$ which is much less than that of hydroxyl radical.[24] Yasunaga et al. [24] reported that TCE oxidation efficiency of O$_3$/H$_2$O$_2$ system is only 40% better than that of O$_3$. The overall reaction between O$_3$ and H$_2$O$_2$ is the production of hydroxyl radicals as following:

$$2O_3 + H_2O_2 = 2HO^+ + 3O_2 \quad (2.7)$$

Ozone can be used with UV radiation to enhance oxidation of TCE as well. Ozone absorbs UV radiation at a 254 nm wavelength and produces hydrogen peroxide, the hydrogen peroxide finally decomposes to hydrogen radical which is a strong oxidant. [25] Potassium permanganate is another chemical utilized for TCE oxidation. The oxidation of TCE with permanganate follows the sequential reactions as following [26]:

$$C_2HCl_3 + MnO_4^- \rightarrow I \rightarrow aCA + MnO_2 + 3Cl^- \quad (2.8)$$

$$aCA \rightarrow bCO_2 \quad (2.9)$$

where

a and b: stoichiometric coefficients

I: Cyclic complex

CA: various carboxylic acids

The effectiveness of chemical oxidation depends on the strength of the oxidant, contact time of the oxidant with contaminants and site hydrogeologic conditions. The oxidant should be
transformed to the target zone without consumption. The total oxidant demand should be estimated carefully for full transformation of the contaminant. The targeted location has to be explored and characterized to not deliver the oxidant to a non-targeted zone. [27]

The primary advantages are:

- Rapid in-situ destruction of the contaminants
- No significant waste production except Fenton’s
- Reduced operation and monitoring cost
- Minimal disturbance to site operations

Some disadvantages are [28]:

- Higher initial and overall cost compared to other in-situ treatment technologies
- Ineffectiveness in low permeability soils.
- Production of significant amount of explosive off-gas by Fenton’s Reagent
- Health and safety concerns associated with applying oxidants
- Significant amount of oxidants loss as a result of reacting with non-toxic organics
- Possibly change of aquifer geochemistry (reduction of porosity of aquifer with precipitation)
2.3.5 Soil Vapor Extraction

Soil vapor extraction (SVE) is an in situ remediation method that reduces the concentration of volatile compounds in petroleum products that were absorbed in the vadose zone of soil. A negative pressure gradient is created by applying vacuum, which causes movement of volatile compounds towards the extraction well. It is also called as “soil venting” or “vacuum extraction”. [29]

The permeability of the soil and constituent volatility controls the effectiveness of SVE. Coarse-grained soils (e.g. sands) have greater permeability than fine-grained soils (e.g., clays or silts) and a lower vapor flow. Soil structure and stratification are important parameters that affect where the soil vapor will flow within the soil matrix under extraction conditions. SVE is not effective below the groundwater level making depth an important parameter for the SVE method. The moisture content may also reduce the air flow as a result of reduction in permeability of the soil. The more volatile (higher vapor pressure and less boiling points) the petroleum constituents are, the easier to clean up with SVE [29]. Soil heterogeneity must be considered to the applicability of SVE due to its limitations in effectiveness in changes of the soil characteristics. The SVE system has been proven as an effective method for treatment of volatile contaminants such as PCE [30] and TCE [31]. A pilot SVE system was installed at a landfill within Savannah River Site to evaluate TCE removal and the criteria for site closure have been met at the end of the process [32].
SVE has several advantages in terms of applicability. In addition, vacuum extraction can be combined with other remediation technologies such as air sparging and bioremediation. It does not need any excavation; therefore it can be used under buildings and other difficult to reach areas. SVE is a cost effective technology with minimal disturbance to site operations. However, it is less effective when applied to low-permeability soil and during the treatment of only unsaturated zone.\textsuperscript{29}

2.4 The use Iron for Water Treatment

2.4.1 Zero Valent Iron (ZVI)

Zero valent iron (ZVI) is effective for reductive dechlorination of chlorinated organic compound. ZVI systems can be installed as permeable reactive barriers perpendicular to the flowing paths of contaminated groundwater providing practical alternatives in comparison to traditional pump-and-treat method. Over the past decades, ZVI has been reported as effective for dechlorination of a variety of chlorinated organic contaminants\textsuperscript{33-37}, the most significant advantages being that the dechlorination reaction can proceed under ambient environmental condition and its high efficiency for a wide range of contaminants.

Two redox reactions may result in chlorinated organic compounds-iron-water mix. The first redox reaction is the reduction of water by oxidation of zero valent iron (Equation 2.9). The second one is the reduction of water by oxidation of iron (Equation 2.10).

\[ Fe^0 + 2H_2O = Fe^{2+} + 2OH^- + H_2 \quad (2.9) \]
Zero valent iron is highly reduced, that is why thermodynamically, Equation 2.10 is more favorable for many chlorinated contaminants \(^{[38]}\).

Matheson and Tratynek \(^{[37]}\) suggested three possible pathways effective for dechlorination of chlorinated compounds (Figure 2.3). The first pathway (Figure 2.3A) involves the electron transfer from the metal surface to adsorbed contaminants. The second pathway (Figure 2.3B) is the reduction of the contaminant by intermediate product of corrosion (Fe\(^{2+}\)) in aqueous system. The third pathway (Figure 2.3C) is the reductive dechlorination by produced hydrogen as a product of corrosion with water.

\[
RCl + Fe^0 + H^+ = Fe^{2+} + RH + Cl^- \quad (2.10)
\]
Figure 2.3 The proposed pathways by Matheson and Tratynek \cite{37} for reductive dehalogenation.
Arnold and Roberts \cite{Arnold1997} reported detailed pathways and kinetics for reduction of chlorinated compounds by ZVI. Figure 2.4 shows the proposed pathways with hydrogenolysis and reductive β-elimination being two main mechanisms. Hydrogenolysis is the replacement of a halogen by hydrogen. ZVI involves the transferring of two electrons in hydrogenolysis. Reductive β-elimination is the release of two chloride atoms, accompanied by the formation of an additional carbon-carbon bond. As seen in Figure 2.4, reductive β-elimination and hydrogenolysis can proceed simultaneously during the reduction of PCE and TCE. Hydrogenation is the addition of two hydrogen atoms to the two across carbon atoms. The reduction of acetylene to ethene can be given as an example to hydrogenation.
Figure 2.4 The proposed pathways for the chlorinated ethylenes and intermediate products during reduction by ZVI \cite{39}
2.4.2 Electrocoagulation

Electrocoagulation is an electrochemical treatment process that removes contaminants from wastewater by complex physical and chemical processes. Electrocoagulation has been reported as an alternative remediation method for the treatment of wastewater, such as dairy wastewater \[40\] and the effluents containing phenol compounds \[41\], nitrogen and phosphorus \[42\], and mercury(II) \[43\], heavy metals \[44-46\], oil wastes \[47\], textile dyes \[48\], nitrate \[49\], arsenic \[50\].

The basic principle of the electrocoagulation is the destabilization of the contaminants with the coagulant formed by the oxidation of the sacrificial anode \[51\]. The anode material can be iron or aluminum. The treatment efficiency of the process highly depends on the anode type and chemical properties of the effluents. For instance, the iron dissolution rate increases for acidic pHs, however the aluminum dissolution rate is several orders higher in alkaline pHs compared to acidic and neutral pHs \[52\]. The removal efficiencies of Mercury (II) with iron and aluminum anodes has been compared and concluded that iron anodes provided faster treatment although the efficiencies are the similar for aluminum and iron anodes \[43\].

Electrocoagulation processes have several advantages and drawbacks \[51\]. The advantages are as follows:

- being easily operable and implementable
- Low maintenance and operating cost
- Not requiring any chemical addition
• Needing low current that’s why can be run by green processes like solar panel

• Enhancing the flotation capability

The main drawback of the electrocoagulation process is that it requires the replacement of the sacrificial anodes periodically and needs the minimum conductivity to maintain the efficiency of the process.

2.4.3 Electrochemical Reductive Dechlorination

Over the last decades, the electrochemical reductive dechlorination of contaminants has been extensively reported because of its long service life and high dechlorination efficiency. Electrochemical reduction occurs mostly on the surface of the cathode: therefore the reduction efficiencies of aqueous contaminants are heavily dependent on the cathode material. For instance, cathode materials such as silver \[^{53}\], iron \[^{54}\], copper \[^{54, 55}\], palladium \[^{56}\], Pt- or Pd-coated ceramic \[^{57}\], bare and polymer coated nickel \[^{58}\] and mixed metal oxide (MMO)-coated titanium mesh cathodes \[^{59}\] demonstrate different performances for reductive electrolytic dechlorination of chlorinated solvents in aqueous solution. The electrolyte pH and constituting components also impact the efficiency of electrochemical treatment of water contaminated by chlorinated hydrocarbons \[^{60}\]. Al-Abed and Fang \[^{60}\] reported that acidic pH increases the reduction rate of TCE in an electrolyte not involving proton and electron reactions like potassium chloride. However, with the electrolytes involving proton and electron reactions, pH value affected the dechlorination rate through proton limitation and electron competition.
Li and Farrell\textsuperscript{[6]} reported the rate limiting mechanisms for TCE and carbon tetrachloride (CT) on the surface of iron cathode. They recognized that the primary pathway for the reduction on the cathode was the indirect reduction involving atomic hydrogen. Therefore, the significant amount of dechlorination can occur only at the potential, which is high enough for hydrogen evolution.

2.5 Need for Further Research

Because of the severity and urgency of soil and groundwater contamination, new effective, environmentally friendly and sustainable methods should be developed. Although the electrochemical dechlorination efficiencies of several cathode materials have been reported, the effects of the anode material to the electrolyte redox potential and cathodic dechlorination efficiencies have not been reported. Depending on the anode type, the redox potential and chemical properties of the electrolyte can be manipulated to provide optimum conditions for reductive dechlorination. The redox potential greatly affects the dechlorination of TCE at the cathode.

Further research is required to understand the effects of the type of anode materials (inert or iron) on chemical properties of the electrolyte and the cathodic dechlorination of TCE. Moreover, the cathodic reduction of TCE with several cathode materials has been reported separately, a comparative scientific research for different combinations of anode and cathode materials is required.
Chapter 3

Materials and Methods

3.1 Introduction

This chapter describes the experimental procedures followed to investigate the electrode materials effect on temporal chemical changes and on TCE dechlorination rate by electrochemical processes. In this chapter, chemicals/reagents and materials used in the study are described. Experimental procedures and analytical methods utilized during the experiments are also explained in detail.

The experiments are conducted in two phases: (i) electrode effects on temporal chemical changes (Section 3.2), and (ii) electrode effects on TCE degradation (Section 3.3). Three different experimental set-ups were designed for this study. Electrode effects on temporal changes were investigated in batch set-ups and in sand-packed flow-through columns. pH and ORP values were key measurements in the first phase of the study. The other significant parameters that were analyzed include the mass of iron dissolution during iron electrolysis and iron speciation in the
electrolyte. Chemical analysis method (phenantroline method) was selected to measure the concentration of iron. Different anode and cathode materials were investigated in the second phase of the study. Gas chromatograph and ion chromatograph were used to analyze the concentration of chlorinated compounds, hydrocarbons and chloride ions.

### 3.2 Electrode Effects on Temporal Chemical Changes

The electrode effects on the temporal chemical changes (pH, ORP, conductivity) in electrolyte were evaluated (i) in batch setup, and (ii) in sand packed flow through column setup. Below is a description of the batch and flow experimental setups.

#### 3.2.1 Batch Experiment for Chemical Changes

#### 3.2.1.1 Materials

Cast gray iron (McMaster Carr, USA) and mixed metal oxides (mesh type, 3N International, USA) were used as electrodes. The working surface area for the each electrode was 7 cm$^2$ with a length of 7 cm. The surface of iron electrodes were polished with sand paper, etched in 1.3 M HCl, and then washed several times with distilled water prior to assembly.

The chemicals and reagents used include NaCl (100%, Fisher Scientific), Na$_2$SO$_4$ (99%, BDH), NaHCO$_3$ (99-100%, Fisher Scientific), o-Phenantroline (0.25% w/v, LabChem Inc.),
hydroxylamine hydrochloride (98.5%, Fisher Scientific), ammonium acetate (98.1%, Fisher Scientific), hydrochloric acid (37.3%, Fisher Scientific), and glacial acetic acid (99.9%, Fisher Scientific). All the solutions were prepared by deionized water and without pH adjustment.

3.3.1.2 Experimental Methods and Procedures

An experimental program (Table 3.1) was designed to evaluate the effect of electrode type, current density, background electrolyte composition and polarity reversal on temporal changes in the pH and redox potential. To understand temporal changes in the electrolyte, the current density is evaluated and discussed with respect to electrolyte volume (mA L$^{-1}$), instead of using current density based on electrode surface.

The divided- and mixed-electrolyte batch experiments were conducted in a glass electrochemical cell with two electrode compartments as shown in Figure 3.1. In each compartment, the liquid and headspace volume were 200 mL and 100 mL, respectively. Gas from electrolysis was collected in 150 mL syringe connected to each compartment to maintain a closed system. The electrodes were placed in parallel such that the working surfaces were face to face. The center to center spacing between anode and cathode was 13 cm. The electrical current was applied by Agilent E3612A DC power supply. In the divided-electrolyte, the anolyte and catholyte were isolated by a Nafion® membrane (Nafion® 112, ElectroChem Inc, USA). The anolyte and catholyte compartments were continuously stirred at the same speed during testing. pH and ORP values were recorded routinely with microprobes. The final conductivity was measured using conductivity probe.
Table 3.1 The experiment list for investigation of temporal chemical changes with batch set-up

<table>
<thead>
<tr>
<th>Variables</th>
<th>Exp. No</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte (0.02 M)</th>
<th>Current (mA L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Types</td>
<td>1</td>
<td>MMO</td>
<td>MMO</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MMO</td>
<td>MMO</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
</tr>
<tr>
<td>Background Electrolyte</td>
<td>5</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>NaCl-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na(HCO₃)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td>Current Density</td>
<td>8</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>37.5</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>112.5</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-mixed</td>
<td>150</td>
</tr>
<tr>
<td>Polarity Reversal</td>
<td>12</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na₂(SO₄)-divided</td>
<td>112.5</td>
</tr>
</tbody>
</table>
Figure 3.1 Divided glass electrochemical cell: 1) cathode side; 2) anode side; 3) electrolyte; 4) gas release port to the syringe; 5) magnetic stirrer; 6) membrane connection; 7) sampling port.
3.2.2 Sand-Packed Flow-Through Column Experiment for Chemical Changes

3.2.2.1 Materials

The column was machined using 6.3 cm (2.5 in.) cast acrylic cylinder tube (McMaster Carr, USA) in the machine shop at Northeastern University. The column is composed of different sections to place the electrodes accordingly. PVC pipe fittings (McMaster Carr, USA) were used to connect the sections of the column. The pipe fittings were machined so that the electrodes are vertical to the flow direction as shown in Figure 3.2. Mixed metal oxide mesh electrodes and cast gray iron electrodes were cut in 8.3 cm diameter circle as in Figure 3.3. The iron electrodes were perforated to maintain water flow through the electrodes. The column was packed with quartz sand for the flow through column experiment (Ottowa testing sand). The solution was pumped with peristaltic pump (Cole-Parmer, USA) equipped with 0.89 mm and and 1.42 mm inner diameter tygon autoanalysis tubing (Cole-Parmer). The tubing allows flow rate between 0.36 to 4.9 mL min\(^{-1}\).

3.2.2.2 Experimental Methods and Procedures

Table 3.2 presents a summary of the experiment variable to evaluate the effect of anode type, current density, flow rate and electrolyte composition on temporal chemical changes (pH and ORP) in flow through column setup. The main aim of this part is to understand the distribution of the chemical changes under flow and to mimic electrolysis in groundwater.
Figure 3.2 shows the schematic of the column. The column consists of 3 pieces. The pieces are combined using pipe fitting flanges and bolts. The flange was drilled from the side and 4 stainless steel screws were inserted through these holes to provide electrical connection between the electrodes and DC source as shown in Figure 3.2. The total length of the column is 82 cm and the inner diameter is 6.3 cm. Six sampling ports were fabricated using Swagelok fittings and septa; 1 before anode; 3 between anode and cathode; and 2 after cathode. Electrodes, 8.3 cm (3.25 in.) in diameter, were placed parallel to each other and vertical to the flow direction to provide 1-D transport of the electrolysis compounds and to maintain homogeneous distribution of the electric fields. The distance between anode and cathode was 24 cm. Total amount of sand used for each experiment was around 4 kg, and the bulk density of air-dry sand in column before the experiment was 1.56 g cm\(^{-3}\). After the column was assembled, the solution was pumped through the column until the sand in the column was saturated. Then, the DC source was turned on and the pH and redox potential variables were measured by collecting 0.5 mL liquid solution from each sampling port.
### Table 3.2 The experiment list with sand-packed flow-through column set-up

<table>
<thead>
<tr>
<th>Variables</th>
<th>Exp. No</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte (0.02 M)</th>
<th>Current (mA)</th>
<th>Flow Rate (mL min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Types</td>
<td>13</td>
<td>MMO</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Current Density</td>
<td>15</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>40</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>80</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>18</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>3.2 ± 0.2</td>
</tr>
<tr>
<td>Background Electrolyte</td>
<td>21</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na₂(SO₄)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>Cast Iron</td>
<td>MMO</td>
<td>Na(HCO₃)</td>
<td>20</td>
<td>1.2 ± 0.2</td>
</tr>
</tbody>
</table>
Figure 3.2 Schematic of sand-packed flow-through column
3.2.3 Analytical Methods

The pH and the oxidation reduction potential (ORP) were measured by microelectrodes probes (Microelectrodes Inc., USA), an aliquot of 0.5 mL electrolyte was sampled from compartments for pH and ORP measurements.

Total dissolved iron and precipitated iron concentration were determined using 1, 10 Phenantroline method \[^{[62]}\]. For the measurement of total dissolved ferrous ions concentration, 1 mL sample taken from cell was filtered with 0.45 µm syringe filter and immediately diluted by 0.05 M H\textsubscript{2}SO\textsubscript{4} solution, then placed in centrifuge tubes. Afterwards, 200 µL ammonium acetate buffer (14.30 g ammonium acetate and 40 mL glacial acetic acid in 150 mL distilled water) and 1 g L\textsuperscript{-1} phenantroline solution were added subsequently to the centrifuge tube. The absorbance of
solution at 510 nm wavelength was measured using UV-VIS spectrophotometer (UVmini-1240, Shimadzu). For measurement of the total dissolved iron concentration (ferrous and ferric), 25 µL hydroxylamine hydrochloride (15 g of hydroxylamine hydrochloride in 150 mL distilled water) was added to the filtered sample as a reductant and the sample was mixed for 5 minutes to allow all ferric ions to reduce to ferrous ions. Then, the same reagents (ammonium acetate buffer and phenantroline) were added prior to spectrophotometer measurement. For the determination of concentration of total iron precipitates, 1 mL samples were collected from electrochemical cell and were placed in 1.5 mL centrifuge tube and 100 µL concentrated HCl was added to the tube. The tube was stored for 1 day to allow all forms of iron precipitates to dissolve. The sample was then subjected to the same procedure explained above to measure the total iron concentrations (dissolved and solid form).

3.3 Electrode Effects on Electrochemical TCE Dechlorination

3.3.1 Materials

The chemicals and reagents used include TCE (99.5%, Sigma-Aldrich), cis-DCE (97%, Sigma-Aldrich), VC (analytical standard, 200 µg mL$^{-1}$ in methanol, Supelco), hydrocarbon gas standard (analytical standard, 1% (w/w) methane, ethane, ethane, acetylene in nitrogen, Supelco), NaHCO$_3$ (99-100%, Fisher Scientific), NaCl (100%, Fisher Scientific), Na$_2$SO$_4$ (99%, BDH), . Saturated TCE solution was prepared as stock solution by dissolving TCE in double-distilled water (18 MΩ cm). The stock solution was kept in 20 ºC temperature to maintain 1.07 mg mL$^{-1}$
dissolution concentration. The conductive materials used as anode (Figure 3.4) include cast gray iron (McMaster Carr, USA), mixed metal oxide (mesh type, 3N International, USA), lead dioxide. The cathode materials are copper foam (60 pores per inch (PPI), 99.5%, Aibixi Ltd., China), iron foam (45 PPI, 98% iron, 2% nickel, Aibixi Ltd., China), nickel foam (60 PPI, 99.9%, Lyrun Ltd., China), vitreous carbon foam (100 PPI, ERG, USA), copper plate (99.9%, VWR) and pure iron plate (3N5 purity, ESPI metals, USA) (Figure 3.5). The foam materials were cut as 4 cm length, 1 cm width, and 0.3 cm thickness. The working surface area of the plates was 4 cm² with 4 cm length and 0.1 cm thickness. A piece of copper wire was attached to the electrodes to connect to the DC source. Glass tube, 10 cm long, was placed around the electrode connection and filled with epoxy to prevent connection corrosion. The surface of the iron electrodes were polished with sand paper, etched in diluted HCl solution (10% by weight) and washed several times with distilled water. The copper foam electrodes were soaked in diluted H₂SO₄ solution (3 % by weight) and cleaned with 2% Micro-90 cleaning solution (Cole-Parmer, USA) and then washed several times with distilled water prior to assembly.
**Figure 3.4** The anode materials from left to right: lead dioxide, cast iron, and MMO.

**Figure 3.5** The cathode materials from left to right: vitreous carbon foam, iron foam, copper foam, nickel foam, pure iron plate, and copper plate.
3.3.2 Experimental Procedures

The experimental plan was designed to evaluate the effect of different anode and cathode materials, the effect of current and initial TCE concentration on TCE transformation (Table 3.3). TCE transformation experiments were conducted in undivided glass electrochemical cell (Figure 3.6) at ambient room temperature (25 °C). The liquid and headspace volume were 115 mL and 67 mL, respectively. Although 150 mL syringe was connected to the electrochemical cell to enable gas expansion during electrolysis, no gas expansion was observed during 5 hours electrolysis. The anode and cathode were pretreated prior to assembly and placed in parallel position with 1.7 cm distance to obtain homogeneous distribution of current on electrodes. The appropriate amount of electrolyte solution (0.01 M NaHCO₃ for most of the experiments) was added, and then the solution was spiked with saturated TCE solution. The solution was stirred 30 minutes with Teflon coated one inch magnetic stirring bar with a speed of 500 rpm to allow TCE equilibrium between aqueous and gas phase. The initial concentration of TCE was checked by withdrawing aqueous sample. The electric current was then applied and TCE concentration and hydrocarbon gases concentrations were routinely measured. For some of the experiments pH and ORP values were measured during the electrolysis by taking 0.2 mL aqueous sample. The final pH, ORP, conductivity and chloride ion concentration were measured for most of the experiments.
Table 3.3 The experiment list for electrode effects on the TCE dechlorination

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Anode Material</th>
<th>Cathode Material</th>
<th>Current (mA)</th>
<th>Electrolyte condition</th>
<th>Initial TCE Concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>NA</td>
<td>NA</td>
<td>no current</td>
<td>NA</td>
<td>39</td>
</tr>
<tr>
<td>23</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>24</td>
<td>PbO₂ anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>25</td>
<td>MMO anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>26</td>
<td>Cast iron anode</td>
<td>Porous iron</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>27</td>
<td>Cast iron anode</td>
<td>Pure iron (plate)</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>28</td>
<td>Cast iron anode</td>
<td>Porous nickel</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>29</td>
<td>Cast iron anode</td>
<td>Porous carbon</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>30</td>
<td>Cast iron anode</td>
<td>Copper plate</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>31</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>32</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>33</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>34</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>20</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>35</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>36</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>37</td>
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<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>20</td>
</tr>
<tr>
<td>38</td>
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<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>39</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>40</td>
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<td>Porous copper</td>
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<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>41</td>
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<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>42</td>
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<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>43</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>39</td>
</tr>
<tr>
<td>44</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>5</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
<tr>
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<td>Porous copper</td>
<td>10</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
<tr>
<td>46</td>
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<td>Porous copper</td>
<td>20</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
<tr>
<td>47</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>30</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
<tr>
<td>48</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>60</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
<tr>
<td>49</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>90</td>
<td>0.01 M Na(HCO₃)</td>
<td>74</td>
</tr>
</tbody>
</table>
Figure 3.6 A schematic of the electrochemical cell. 1) cathode; 2) anode; 3) sampling port; 4) to expandable syringe; 5) stir bar; 6) gas-tight adapter; 7) electrolyte (115 mL); 8) headspace of cell (67 mL)

3.3.3 Analytical Methods

Aqueous TCE, DCE, VC concentration were determined using purge and trap method with gas chromatograph instrument (SRI GC 8610C, USA) (Figure 3.7), which is equipped with photo ionization detector (PID) and MXT-VOL stationary column (L=15 m, inner diameter=0.53 mm, DF=3). Helium was used as carries gas which was pretreated with a gas filter. The purge and trap autosampler system was equipped with carbon-sieve trap and Tenax™ trap, which enable the detection of highly volatile compounds like VC. 50 μL aqueous samples were withdrawn from the electrochemical cell and injected in 5 mL distilled water in glass tube. The glass tube was loaded immediately to the 10 ports auto-sampler. The solution was purged at flow rate 1.5 mL
min⁻¹ for 5 minutes before injection to the trap. The GC was set to hold at 40 °C for 6 minutes, and then ramp to 60 °C in 2 minutes, hold at 60 °C for 10 minutes.

Hydrocarbon gases in the headspace of the electrolytic cell were analyzed by Model 310 GC (SRI, USA) with flame ionization detector (FID) and Haysep-T column (Figure 3.8). 100 μL gas taken from the headspace was injected to the GC directly through on-column port. The Model 310 GC was set to increase the temperature from 40 °C to 140 °C at a rate of 15 °C min⁻¹, hold it at 140 °C for 1 minute, and cool to 40 °C at a rate of 20 °C min⁻¹.

Chloride ion concentration was analyzed by Dionex DX-120 ion chromatograph. 0.5 mL aqueous sample was taken from the electrolytic cell after each experiment and the sample was diluted to 5 mL and filtered with 0.45 μm pore size filter paper prior to analysis.

pH and oxidation-reduction potential (ORP) values were measured with microprobes (Microelectrodes Inc., USA) as shown in Figure 3.9 and corresponding meters, and initial and final conductivity values were measured by using corresponding conductivity meter and probe.
Figure 3.7 Gas chromatograph instrument with autosampler for measurement of concentration of dissolved gas compounds
Figure 3.8 Gas chromatograph for the measurement of hydrocarbon gases concentrations

Figure 3.9 pH and redox microprobes with reference electrodes
Chapter 4

Results and Discussion

4.1 Introduction

This chapter presents a summary and discussion of the experimental results in two parts. Section 4.2 discusses the differences between iron electrolysis and water electrolysis in terms of chemical changes without any TCE contaminated water sample. Section 4.3 discusses the dechlorination efficiency of different anode and cathode materials and optimizes the reductive dechlorination of TCE by selecting proper anode and cathode materials.
4.2 Electrode Effects of Temporal Changes in pH and ORP

4.2.1 Batch Experiment for Chemical Changes

4.2.1.1 Effect of Electrode Types

Temporal chemical changes in divided- and mixed-electrolytes were evaluated in 0.02 M NaSO$_4$ background electrolyte. As shown in Figure 4.1a, the pH of mixed electrolyte with inert electrodes did not change significantly since the H$^+$ produced at the anode neutralizes the OH$^-$ produced at the cathode. The electrolyte pH with iron electrodes increased to 10.5 (Figure 4.1b) because there is no or limited formation of H$^+$ ions at the iron anode to neutralize the OH$^-$ released from the cathode. Instead, the dissolution of iron is the dominating reaction on the anode as given by,

$$\text{Fe} - 2\text{e}^- = \text{Fe}^{2+} \quad (4.1)$$

Depending on the pH, ferrous ions may subsequently form ferrous hydroxides (Fe(OH)$_2$(s), $pK_{so} = 15.1$) $^{[63]}$. The ORP data in Figure 4.1 show critical differences. The ORP values of the mixed electrolyte with inert electrodes decreased from 217 mV to 160 mV in the first 2 hours then stabilized around 150 mV (Figure 4.1a). In contrast, the ORP of the mixed electrolyte with iron electrodes steadily dropped to -444 mV in 5 hours (Figure 4.2b), showing buildup of reducing electrolyte condition.

When the anolyte and catholyte were divided by a membrane (Figure 4.1a), the pH in the anolyte was acidic ($\approx 2$) and that in the catholyte was alkaline ($\approx 11.5$) when MMO electrodes were used.
The iron anode limits the change in the anolyte pH due to little or no H⁺ production. A slight decrease was observed in the first 2 hours in the anolyte (Figure 4.1b). This could be explained by the oxidation of the ferrous species by the dissolved oxygen in electrolyte. The formation of solid ferric hydroxides (pKₘₐₓ of Fe(OH)₃ (s) is 38.8) [63] induces the production of protons, leading to a slight pH drop, as given by:

$$4Fe^{2+} + 10H_2O + O_2(g) = 4Fe(OH)_3(s) + 8H^+ \quad (4.2)$$

As shown in Figure 4.1a, the ORP of the anolyte with MMO anode was highly oxidizing (∼450 mV) due to oxygen production from water electrolysis by the inert anode. By contrast, the anolyte ORP was low and more chemically reducing (11 mV, Figure 4.1b) with an iron anode. The main reason is that ferrous ions, instead of protons and oxygen gas, were produced at the anode. Ferrous species show reducibility to consume the oxidative components, such as dissolved oxygen (Equation 4.2), in the electrolyte. Furthermore, with increasing pH, the reducibility of ferrous species (such ferrous hydroxides) increases progressively. [63] Changes in pH and ORP values in catholyte were consistent for both inert and iron electrodes because cathodic reactions are the same. The pH increased to 11.5 and the ORP decreased to -340 mV in one case and -250 mV in the other case (Figure 4.1). The reducing potential (negative ORP) is due of the production of hydrogen gas and the basic environment.

The above observations show significant difference on the effect of using iron (reactive) versus MMO (inert) electrodes on the pH and redox change of the electrolytes. Water oxidation is the main reaction at the anode of inert electrodes, therefore oxygen gas (O₂) and hydrogen ion (H⁺) are produced at the anode of inert electrodes. Iron dissolution is the governing reaction at the anode of iron electrodes and ferrous ions (Fe²⁺) are produced as main product. The main cathodic
reaction is water reduction that is same for iron and inert electrodes. The oxidation rates of iron and the flux of ferrous ions per electrolyte volume are controlled by the electric current. The rate can be calculated following Faraday’s law,

\[
J_{Fe(II)}^{e} = \frac{\alpha}{n_{Fe(II)}V_{a}F} = \frac{\alpha}{2V_{a}F} \quad (4.3)
\]

\[
\alpha = \frac{2V_{a}FJ_{Fe(II)}^{e}}{l} \quad (4.4)
\]

\[
\bar{\alpha}_{0\rightarrow t} = \frac{2V_{a}FJ_{Fe(II)}^{e}}{l\Delta t} \quad (4.5)
\]

where \( J_{Fe(II)}^{e} \) is the rate of electrolytic oxidation (in mol/m\(^3\) s) of Fe(0) into Fe(II), \( n_{Fe(II)} \) is the number of electron transferred, \( V_{a} \) is the volume of the anolyte (for divided-electrolyte) or total electrolyte volume (for mixed electrolyte), \( I \) is the electric current, \( \alpha \) is instant iron dissolution efficiency and \( \bar{\alpha}_{0\rightarrow t} \) is the average iron dissolution efficiency from time zero to time \( t \). In Equation 4.3 the current is divided by the electrolyte volume to evaluate the current per volume of electrolyte (A m\(^{-3}\)). This is mainly because it is important to evaluate the impact of electrolysis on the dynamics of electrolyte chemistry.

Other electrolysis reactions may occur at the anode include the oxidation of ferrous (Equation 4.6, \( E^{0} = 0.77 \) V vs. SHE) and the water decomposition (Equation 4.7, \( E^{0} = 1.23 \) V vs. SHE).

\[
Fe^{2+} = Fe^{3+} + e^{-} \quad (4.6)
\]

\[
2H_{2}O = 4H^{+} + O_{2} + 4e^{-} \quad (4.7)
\]

Comparing the electrochemical standard potential shows that the electrolytic transform of iron to Fe(II) has a significantly lower standard potential (+0.44 V). Therefore, oxidation of Fe(0) to
Fe(II) is the dominant electrolytic reaction at the anode. As a result, the electrolyte pH and redox potential significantly change due to the ferrous species.

Figure 4.1 pH and ORP profiles in divided-electrolyte and mixed-electrolyte, 0.02 M Na$_2$SO$_4$ background electrolyte, 112.5 mA L$^{-1}$ current density (a) MMO electrodes (b) Iron electrodes.
4.2.1.2 Effect of Background Electrolyte on Iron Electrolysis

The electrolyte composition has significant effects on chemical and physicochemical change induced by iron electrolysis due to the complexation of ferrous and ferric ions with existing anions and the precipitation of produced solid species. Mixed-electrolyte experiments were conducted using 0.02 M NaCl, Na₂SO₄ and NaHCO₃ solution and change in electrolyte pH and ORP values were recorded. In addition, iron speciation and the average iron dissolution efficiency (\( \bar{\alpha} \)) within 5 hours in different background electrolytes were compared. In Figure 4.2a, the pH of mixed bicarbonate solution was stable around 8 in the first 4 hours due to its buffer capacity. Afterwards, the buffer capacity was exceeded by the OH⁻ released from the cathode and pH increased to 8.9. The pH values of the mixed sulfate and chloride electrolytes increased steadily as a result of electrolysis. At the end of the experiment, the pH of Na₂SO₄ (\( \approx 10.5 \)) electrolyte was slightly higher than that of the chloride solution (\( \approx 10.0 \)).

Initially, the ORP value of the mixed bicarbonate solution was lower (87 mV) than sulfate and chloride solutions (Figure 4.2a). Over time, the sulfate electrolyte showed a constant decrease in the ORP and, by the end of testing, the sulfate electrolyte was the most reducing (-444 mV).

Although chloride, sulfate and carbonate anions can form ferrous ions complexes, based on the equilibrium data, the primary metal ligands in the solution were ferrous hydroxides (Table 4.1). Some ferrous ions can be further oxidized to ferric ions with the presence of dissolved oxygen. Ferric ions produce some ferric complexes with existing ligands as well. Ferric hydroxides precipitations (yellow to brownish color) were observed at the early stage of the experiment and
ferrous hydroxides precipitations (dark green color) were observed at the end of the experiment. Dissolved iron, ferrous and ferric precipitates are summarized in Table 4.2 for varying electrolyte composition. Dissolved iron was not observed in the bicarbonate solution because of the high initial pH (≈8). Dissolved iron was detected in sulfate solution (7.3%) and in chloride solution (4.4 %) in the first hour, however, at the later stages of experiments, all dissolved iron precipitated due to pH increase. At the end of 5-hours electrolysis, the ratio of ferrous precipitates to ferric precipitates was higher in chloride and sulfate solutions compared to bicarbonate solution that leads more reducing condition. Total iron concentrations were 8.9 mM for sulfate solution, 6.9 mM for chloride solution and 9.6 mM for bicarbonate solution. The average iron dissolution efficiencies were 85%, 66% and 92% in sulfate, chloride and bicarbonate solutions, respectively.
Table 4.1 The equilibrium constants of the ferrous and ferric complexes with sulfate, chloride and bicarbonate anions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$+2H$_2$O = 2H$^+$+Fe(OH)$_2$ (aq)</td>
<td>-20.494</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{3+}$+2H$_2$O = 2H$^+$+Fe(OH)$_2$ $^+$</td>
<td>-5.75</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe$^{2+}$+3H$_2$O =3H$^+$+Fe(OH)$_3$ $^-$</td>
<td>-30.991</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{3+}$+3H$_2$O =3H$^+$+Fe(OH)$_3$ (aq)</td>
<td>-15</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe$^{3+}$+4H$_2$O = 4H$^+$+Fe(OH)$_4$ $^-$</td>
<td>-22.7</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>2Fe$^{3+}$+2H$_2$O =2H$^+$+Fe$_2$(OH)$_3$ $^{2+}$</td>
<td>-2.894</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>3Fe$^{3+}$+4H$_2$O = 4H$^+$+Fe$_3$(OH)$_4$ $^{5+}$</td>
<td>-6.288</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{2+}$+Cl$^-$ = FeCl$^+$</td>
<td>-0.2</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{3+}$+Cl$^-$ =FeCl$^{2+}$</td>
<td>1.48</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{2+}$+H$_2$O =H$^+$+Fe(OH)$^+$</td>
<td>-9.397</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{3+}$+H$_2$O =H$^+$+Fe(OH)$_2$ $^{2+}$</td>
<td>-2.02</td>
<td>LiuMill99</td>
</tr>
<tr>
<td>Fe$^{3+}$+2SO$_4$ $^{2-}$ = Fe(SO$_4$)$_2$ $^-$</td>
<td>5.38</td>
<td>Nord 90</td>
</tr>
<tr>
<td>Fe$^{2+}$+SO$_4$ $^{2-}$ =Fe(SO$_4$) $^2$ (aq)</td>
<td>2.39</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{3+}$+SO$_4$ $^{2-}$ =Fe(SO$_4$) $^+$</td>
<td>4.25</td>
<td>NIST 46.7</td>
</tr>
<tr>
<td>Fe$^{2+}$+CO$_3$ $^{2-}$+H$^+$ =FeHCO$_3$ $^+$</td>
<td>11.429</td>
<td>NIST 46.7</td>
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</table>
Table 4.2 Iron speciation in sulfate, chloride and bicarbonate solutions at different times, 112.5 mA L\(^{-1}\) current density, mixed-electrolyte (total volume 400 ml), and two iron electrodes

<table>
<thead>
<tr>
<th>Time, h</th>
<th>0.02 M Na(_2)SO(_4)</th>
<th>0.02 M NaCl</th>
<th>0.02 M NaHCO(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolv ed Iron, %</td>
<td>Fe(^{2+}) precipitates, %</td>
<td>Fe(^{3+}) precipitates, %</td>
</tr>
<tr>
<td>1</td>
<td>7.3</td>
<td>13.2</td>
<td>79.5</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>33.5</td>
<td>66.5</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>45.0</td>
<td>55.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>52.4</td>
<td>47.6</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>59.7</td>
<td>40.3</td>
</tr>
</tbody>
</table>
Figure 4.2 pH and ORP profiles (a) in different electrolyte compositions using iron electrodes, 112.5 mA L\(^{-1}\) current density, mixed-electrolyte; (b) with different current densities (mA L\(^{-1}\)), using iron electrodes, in 0.02 M Na\(_2\)SO\(_4\) mixed-electrolyte.
4.2.1.3 Effect of Different Current Densities on Iron Electrolysis

The electrolyte pH slightly decreased from 5.6 to 4.9 for the lowest current density (37.5 mA L\(^{-1}\)) in the first 2 hours (Figure 4.2b) because ferrous ions oxidation with existing oxygen leads H\(^+\) production. The pH value then increased slightly to 5.8 and stabilized. When the current density is increased, OH\(^-\) production and the pH at the cathode increase. The maximum observed pH was 10.7 for 150 mA L\(^{-1}\) (Figure 4.2b). The ORP values for different current densities also showed similar trends with pH. The most reducing solution was observed under 150 mA L\(^{-1}\). According to the pe-pH diagram \(^{[63]}\) of iron species, the basic pH enables more Fe(OH)\(_2\)\(_{(s)}\) precipitation and a more reducing condition (lower ORP).

Dissolved iron species are detected in the electrolyte after 1 hour (Figure 3) for all current densities. As electrolysis progresses, the dissolved iron gradually disappears and only 37.5 mA L\(^{-1}\) shows dissolved iron after 5 hours electrolysis. The data is in agreement with the pH data in Figure 2b. According to the pH data, the pH values after 2 hours under 37.5 mA L\(^{-1}\) and 75 mA L\(^{-1}\) were less than 7, which allows the presence of the dissolved ferrous ions.
**Figure 4.3** Iron speciation at different current densities (37.5, 75, 112.5, 150 mA L\(^{-1}\)). The asterisk (*) means under detection limit.
4.2.1.4 Polarity Reversal with Iron Electrolysis

Polarity reversal is a convenient and useful method to clean the scale and fouling on electrode, and prevent the passivation of iron electrode. The effect of polarity reversal of iron electrolysis on redox and pH conditions in divided anolyte and catholyte is also evaluated. After application of the current for 5 hours, the polarity was reversed for the next 5 hours. In the first 5 hours, the pH in the anolyte dropped from 5.4 to 4.2 in 2 hours and then increased up to 5.8 (Figure 4.4a) due to the formation of ferrous and ferric hydroxides; and the pH in the catholyte increased up to 12 (Figure 4.4b) due to water electrolysis. After polarity reversal, the pH in the new catholyte (Figure 4.4a) was stable for about one hour because the OH\(^-\) being produced is reacting with existing ferrous and ferric ions. The pH then sharply increase up to 12 since and all ferrous ions immediately precipitated mostly in the form Fe(OH)\(_2\)\(_{(s)}\). As shown in Figure 4.4b, the pH change in the new anolyte was not significant for 2 hours, but the pH dropped after that because of precipitation of ferrous hydroxides. The final pH in the anolyte was around 6.5 (Figure 4.4b).

The ORP value in the anolyte (Figure 4.4a) decreased to -150 mV in the first 5 hours due to ferrous production at the anode, and the ORP in the catholyte (Figure 4.4b) dropped to below -300 mV in the first 5 hours due to H\(_2\)\(_{(g)}\) generation in basic environment. When the polarity was reversed, the ORP in the new catholyte (Figure 4.4a) continued to decrease to -600 mV while the pH increased. The ORP in the anolyte (Figure 4.4b) was stabilized at around -400 mV. At the end of the experiment, neutral pH and highly reducing environment (Figure 4.4b) was achieved in the anolyte.
Figure 4.4 pH and ORP profiles under polarity reversal using iron electrodes, 112.5 mA L$^{-1}$ current density and 0.02 M Na$_2$SO$_4$ background electrolyte (a) first 5 hours served as anolyte then polarity reversed and then served as catholyte from 5 hours to 10 hours (b) first 5 hours served as catholyte then polarity reversed served as anolyte from 5 hours to 10 hours.
4.2.2 Sand-Packed Flow through Column Experiment for Chemical Changes

4.2.2.1 Effect of Electrode Types

Temporal chemical changes in sand-packed flow-through column with iron and MMO (inert) anodes were evaluated in 0.02 M Na₂SO₄ electrolyte with flow rate 1.2 ml min⁻¹. Electrolyte was passing first through the anode and secondly through the cathode (Figure 3.2). Figure 4.5 shows the distribution of pH and ORP values in the column for different times (4 h, 6 h, 10 h, 16 h).

As shown in Figure 4.5a, the pH of the electrolyte between the electrodes with iron anode did not change significantly, which is almost the same as the influent pH. The pH after cathode increased sharply to 11.3 (Port 5) in 4 hours due to OH⁻ production at the cathode. The pH for last port (Port 6) after 4 hours was still similar to the initial value (5.9) because produced OH⁻ ions did not reach to the last port. It took 6 hours for the OH⁻ ions to reach the last port and generate a basic environment (pH=11.8). At this time, the whole section after cathode was alkaline. The pH in pore water in the first port after the cathode dropped to around 5.6 (Figure 4.5a) after 10 and 16 hours because ferrous ions produced at the anode were transported up to this port with advection and the carried ferrous ions mostly reacted with OH⁻ and precipitated as Fe(OH)₂(s) in the highly alkaline zone.

On the other hand, when MMO anode was used, the pH between the electrodes decreased to 2.8 (Figure 4.5b) due to water oxidation at the anode. pH decreased at Port 1 before anode as well due to H⁺ diffusion from the anode and H⁺ production due to little electric field at the outer surface of the anode. The pH of the region beyond the cathode decreased after 10 hours and 16
hours because $H^+$ flux from the anode reached to the ports after cathode (Port 5 and Port 6) and neutralized the OH$^-$ released from the cathode.

The main differences between pH distribution in the column with iron anode and MMO (inert) anode are:

- No or little pH drop was observed between the electrodes and before the anode when iron anode was used. However, highly acidic environment between the electrodes and slight pH drop before the anode were seen when MMO anode was used.
- After a certain time, pH drop was observed around the cathode when iron anode was which was an indication of precipitation (mostly in the form of ferrous hydroxides) was around the cathode. However, pH drop was observed not only around the cathode but also all section after the cathode due to water formation when MMO (inert) anode was used.

The ORP value with MMO anode increased (Figure 4.5b) from 254 mV (influent value) up to 371 mV for the port before the anode (Port 1) and up to 480 mV between the electrodes in 4 hours due to $O_2(g)$ release from the MMO anode. The ORP value after the cathode was relatively reducing (-246 mV for Port 5 and -119 for Port 6) after 4 hours due to the alkaline condition. Then, ORP started to increase up to 427 mV for Port 5 and 164 mV for Port 6 in 16 hours because $O_2$ flux from the MMO anode reached Port 5 and Port 6. In contrast, the ORP value with iron anode dropped (Figure 4.5a) from 254 mV to 200 mV for the port just before anode (Port 1) and 100 mV between the electrodes in 4 hours. The ORP value after the cathode dropped from 254 mV to -194 mV for Port 5 and 206 mV for Port 6 in 4 hours. After that, ferrous ion release
from the anode reached to Port 5 and Port 6 and made redox potential more reducing compared to MMO anode (after 16 hours: -33 mV for Port 5 and -106 mV for Port 6).

The main differences between ORP distribution in the column with iron and MMO (inert) anode are:

- The ORP value was highly oxidizing before anode and between the electrodes when MMO anode was used. However, the ORP was relatively more reducing before anode and between the electrodes when iron anode was used.
- The ORP value was reducing after the electrodes at the early stage of the experiment when MMO electrode was used. Then, the ORP started to increase and made the whole column oxidizing until the end of testing (16 hours). However, the ORP after the cathode was reducing at the early stage of the experiment and at the end of the experiment.
Figure 4.5 pH and ORP profiles for 4 different instant times (4 h, 6 h, 10 h and 16 h) in flow-through column set-up, 20 mA current, 0.02 M Na₂SO₄ background electrolyte and 1.2 mL min⁻¹ flow rate (a) using iron anode (b) using MMO (inert anode)
4.2.2.2 Effect of Current Density

Figure 4.6 shows the distribution of pH and ORP in the column with iron anode for 3 different currents (20 mA, 40 mA and 80 mA) and 4 different times (4 h, 6 h, 10 h and 16 h). The pH decrease between the electrodes was not significant for all three current densities. pH values between the electrodes decreased from 5.73 to around 5 in 4 hours (Figure 4.6a). Then, pH was stable around 5 in 16 hours for all current densities and did not show significant differences for different current densities (Figure 4.6d) because the main reaction at the anode was iron dissolution and no or little H+ production at the iron anode. The slight drop in pH data was because of the ferric hydroxides formation with the presence of dissolved oxygen (Equation 4.2). pH value after the cathode showed a similar trend for 4 and 6 hours. pH values at Port 5 were 5.63 for 20 mA, 5.73 for 40 mA and 11.2 for 80 mA in 10 hours (Figure 4.6c). This pH drop for low current densities was due to ferrous hydroxides precipitation observed after the cathode. Relatively high current density (80 mA) did not show significant pH drop.

The redox potential between the electrodes was more reducing for high current density (80 mA) because of more ferrous ions release at the anode (Figure 4.6). The ORP dropped (Figure 4.6a) to -194 mV, -268 mV and -263 mV in 4 hours for 20 mA, 40 mA and 80 mA, respectively. The current density and anodic reactions effects were more dominant at the later stage of the experiment. After 16 hour, the ferrous flux reached to Port 5 and Port 6 and the redox potential at Port 6 was -106 mV, -190 mV and -286 mV for 20 mA, 40 mA and 80 mA, respectively.
Figure 4.6 pH and ORP profiles for different currents (20 mA, 40 mA and 80 mA) in flow-through column set-up, iron anode, 0.02 M Na₂SO₄ background electrolyte and 1.2 mL min⁻¹ flow rate (a) time= 4 hours (b) time=6 hours (c) time=10 hours (d) time=16 hours
Figure 4.6 pH and ORP profiles for different currents (20 mA, 40 mA and 80 mA) in flow-through column set-up, iron anode, 0.02 M Na₂SO₄ background electrolyte and 1.2 mL min⁻¹ flow rate (a) time= 4 hours (b) time=6 hours (c) time=10 hours (d)time=16 hours
4.2.2.3 Effect of Flow Rate

Figure 4.7 shows the distribution of the pH and ORP in the column for three different flow rates (1.2 mL per min, 2 mL per min and 3.2 mL per min) for three different times (1 h, 2 h and 4 h). The pH between the electrodes and after the cathode (Figure 4.7a) did not show significant changes for relatively low flow rates (1.2 mL min\(^{-1}\) and 2 mL min\(^{-1}\)) because the flux of electrolysis products did not reach to the sampling ports in 1 hour. However, the pH increased up to 10.94 at Port 5 for the flow rate 3.2 mL min\(^{-1}\). The pH between the electrodes started to decrease slightly (Figure 4.7b) for all flow rates in 2 hours. The pH values at Port 5 were alkaline for all flow rates (Figure 4.7c). At that time, the pH of lower flow rate showed more basic pH (11.27 for 1.2 mL min\(^{-1}\), 10.97 for 2 mL min\(^{-1}\) and 10.9 for 3.2 mL min\(^{-1}\)).

ORP data (Figure 4.7) is critical to understand the effect of flow rate on electrochemical dechlorination of chlorinated compounds. At the initial stage of testing (Figure 4.7b), ORP values between the electrodes were mostly oxidizing for low flow rates (at port 2 around 200 mV for 1.2 mL min\(^{-1}\), 152 mV for 2 mL min\(^{-1}\) and around 105 mV for 3.2 mL min\(^{-1}\)) because ferrous ion distribution through the column was not complete as a result of slow transport of the reducing compounds like ferrous ions in the column. As electrolysis continues, ferrous ion and other electrolysis compounds were transported and distributed through the column. As seen in Figure 4.7c, the ORP values between the electrodes were similar for all flow rates. This can be explained by the retention time of electrolyte in the electric fields. The same volume of electrolytes with lower flow rate was subjected to more electrolysis when compared to higher flow rate. On the other hand, the total mass of electrolysis compounds like OH- and Fe2+ released from the electrodes are the same for all flow rates at a specific time because current densities are same for all flow rates.
Figure 4.7 pH and ORP profiles for different flow rates (1.2 mL min\(^{-1}\), 2 mL min\(^{-1}\) and 3.2 mL min\(^{-1}\)) in flow-through column set-up, iron anode, 0.02 M Na\(_2\)SO\(_4\) background electrolyte and 20 mA current, (a) time= 1 hour (b) time=2 hours (c) time=4 hours
**Figure 4.7** pH and ORP profiles for different flow rates (1.2 mL min\(^{-1}\), 2 mL min\(^{-1}\) and 3.2 mL min\(^{-1}\)) in flow-through column set-up, iron anode, 0.02 M Na\(_2\)SO\(_4\) background electrolyte and 20 mA current (a) time= 1 hour (b) time=2 hours (c) time=4 hours
4.2.2.4 Effect of Electrolyte Composition

The electrolyte composition causes significant effect on the distribution of the chemical properties in the column due to precipitation and complexation of the ferrous and ferric ions with existing anions in the background electrolytes. Figure 4.8 shows the distribution of pH and redox potential in the column with two different background electrolytes (sodium bicarbonate and sodium sulfate) in time (1 h, 2 h, 4 h and 6 h). The pH dropped from 7.7 to 6.9 between the electrodes for bicarbonate solution (Figure 4.8b); however the pH decrease between the electrodes was not significant for sulfate solution. This behavior can be explained by precipitation zone of sulfate and bicarbonate solution. The decrease in pH with iron anode is mainly due to iron hydroxide precipitation. Initial pH values were 5.73 for sodium sulfate and 7.7 for sodium bicarbonate, therefore the zone of iron oxides precipitation differs for sulfate and bicarbonate solutions. Although it had high buffer capacity, the main precipitation products such as ferrous hydroxides and ferric hydroxides (green and yellowish color precipitates) were observed between the electrodes for sodium bicarbonate solution. On the contrary, precipitations were observed after the cathode for sulfate solution. Precipitation of highly reducible species like Fe(OH)$_2$ (s) greatly affects the ORP distribution in the column as well. As shown Figure 4.8b, the ORP at Port 2 dropped sharply from 87 mV to -187 mV for the bicarbonate solution. However, the ORP decreased at Port 2 from 254 mV to 140 mV for sulfate solution. Based on Figure 4.8, the redox potential is more reducing between the electrodes when bicarbonate was used as background electrolyte instead of sulfate. On the other hand, redox potential with sulfate solution was more reducing after the cathode compared to bicarbonate solution.
Figure 4.8 pH and ORP profiles for different background electrolyte composition (0.02 M Na$_2$SO$_4$ and 0.02 M NaHCO$_3$) in flow-through column set-up, iron anode, 20 mA current. (a) time= 1 hour (b) time=2 hours (c) time=4 hours (d) time=6 hours
4.3 Evaluation of Electrochemical TCE Dechlorination

4.3.1 Effect of Anode Type

Three types of anode materials (cast gray iron, lead dioxide and mixed metal oxide) were investigated by applying 90 mA constant current electrolysis in 10 mM sodium bicarbonate solution and their electrochemical efficiency to TCE degradation were compared in mixed electrolyte. Porous copper was used as cathode for this part of the study. As shown in Figure 4.9, after 5 hours electrolysis, the mass of TCE in the solution was reduced from 40 mg to 15.6 mg and 16.65 mg for lead dioxide (PbO$_2$) and mixed metal oxide (MMO) respectively. However, for iron anode, the TCE mass was under detection limit (0.1 mg) after the same period. The TCE degradation efficiencies of these 3 anode types were 61%, 57% and >99% for PbO$_2$, MMO and PbO$_2$.

The ORP value is the key parameter to understand the reason behind significant degradation efficiency of iron anode. The ORP values during electrolysis decreased to –750 mV (Figure 4.10) for iron anode due to production of reductive compounds such as Fe$^{2+}$ and Fe(OH)$_2$. These compounds have the potential to consume oxidative substances in the electrolyte such as dissolved oxygen and create very reducing condition. Reducing condition possibly enhances TCE degradation. However, PbO$_2$ and MMO anode types did not show significant decrease in redox potential (-37 mV for PbO$_2$ and -83 mV for MMO) compared to iron anode. As discussed in Section 4.2.1.1, PbO$_2$ and MMO are inert anodes, which mean the main anodic reaction is water decomposition (Equation 4.7), and the main products are protons and oxygen gas.
Continuous production of the oxygen gas at the anode possibly limits the degradation of TCE. Oxygen ($O_2$) has high oxidation potential so it is susceptible to reduction. The reduction potential of $O_2$ is 1.229 V vs SHE (Equation 4.9) higher than the reduction potential of TCE (0.42 V vs SHE) (Equation 4.10). Therefore, the reduction of $O_2$ is more favorable than TCE reduction in electrolyte which negatively effects TCE degradation.

$$O_2 + 4H^+ + 4e = 2H_2O \quad (4.9)$$

$$TCE + 2e^- = 1,1 - DCE \quad (4.10)$$

**Figure 4.9** Aqueous TCE (Ca) electroreductive dechlorination profile with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, initial TCE concentration 39 mg L$^{-1}$, 90 mA current, 0.01 M NaHCO$_3$ electrolyte. The control experiment conducted without electrical current.
Figure 4.10 The ORP profile with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO$_3$ electrolyte

The produced hydrocarbons (ethane, ethene, methane, acetylene) were monitored to understand the transformation mechanism of TCE. Ethane, ethene and methane were observed (Figure 4.11) as TCE transformation by-products. The more hydrocarbon gases indicate higher degradation rate when iron anode was used. Therefore, the atomic hydrogens (Equation 4.11) at the cathode mostly contribute the reduction of TCE (Equation 4.12), as given by:

$$H_2O - e = H^+ + OH^- \quad (4.11)$$

$$2H^+ + RCl = RH + H^+ + Cl^- \quad (4.12)$$
Figure 4.11 The concentrations of hydrocarbon gases after 0.5 hour with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO₃ electrolyte

According to our hypothesis, atomic hydrogen formation on the surface of the cathode is the main mechanism for TCE reduction. This hypothesis can be verified by checking molar ratios of produced hydrocarbons in the headspace. Ethene needs four hydrogen and ethane needs six hydrogen to be formed chemically. The more ethane gas (with 6 hydrogens) in the headspace means that the more atomic hydrogen is available for TCE reduction. As shown in Figure 4.12, the molar ratio of ethene to ethane was less than 1 (ethane concentration was higher than ethene concentration) for iron anode. However, ethene:ethane ratio with inert anodes showed different
behaviors. The ratios were 2.8 and 2 for PbO$_2$ and MMO respectively. Although the same amount of atomic hydrogen was produced under same electrolysis condition, less atomic hydrogen was used for TCE reduction for PbO$_2$ and MMO anode, which proves that some part of the atomic hydrogen was consumed by oxidative compounds in the electrolytes of PbO$_2$ and MMO anodes.

Figure 4.12 Molar ratio of ethane to ethane at time 0.5 h with variable anode types (cast iron, MMO, and lead dioxide) and copper foam cathode, 90 mA current, 0.01 M NaHCO$_3$ electrolyte
4.3.2 Effect of Cathode Type

Four foam materials (iron, nickel, copper, carbon) and two plates (copper, pure iron) were investigated as cathodes. Cast iron was used as anode material for all the experiments. Cathode materials were compared under 90 mA current in mixed-electrolyte cell with 10 mM bicarbonate solution. Figure 4.13 shows the performances of these cathode materials. Copper foam and iron foam showed the best efficiency during 5 hours electrolysis. The dechlorination efficiencies of the copper foam and iron foam were 99.7% and 95.6% respectively. In addition, the copper plate and pure iron plate surprisingly showed high performances (88.8% for copper plate and 82.1% for pure iron) despite of their limited surface area. Although carbon foam and nickel foam had high surface areas to be used for TCE reduction, their overall performances (82.4% for carbon and 74.9% for nickel foam) were not high compared to copper and iron foam.
Figure 4.13 Aqueous TCE (Ca) electroreductive dechlorination profile with variable cathode types and cast iron anode, initial TCE concentration 39 mg L$^{-1}$, 90 mA current, 0.01 M NaHCO$_3$ electrolyte.
As shown in Figure 4.13, pseudo-first order transformation kinetics was observed for different cathode materials. The pseudo-first order model for TCE degradation (Equation 4.13) can be modified for our experimental procedures as follows:

$$-d(V_a C_a + V_h C_h) = k C_a dt + g C_h dt \quad (4.13)$$

where:

- $C_a$: TCE concentration in aqueous solution (mg L$^{-1}$)
- $C_h$: TCE concentration in headspace (mg L$^{-1}$)
- $V_a$: the volume of the aqueous solution (L)
- $V_h$: the volume of the headspace (L)
- $k$: the first order rate constant for TCE degradation (L h$^{-1}$)
- $g$: the headspace expansion rate (L h$^{-1}$)
- $t$: the electrolysis process operation time (h)

Total amount of TCE at any time during the electrolysis is the sum of TCE in aqueous solution ($C_a$) and in headspace ($C_h$). TCE equilibrium between aqueous and gas stage can be expressed with Henry’s law (Equation 4.14) where $H_{TCE}$ is the dimensionless Henry’s constant.

$$C_h = H_{TCE} C_a \quad (4.14)$$

Equation 4.13 can be further simplified and rearranged by substituting Equation 4.14 into the Equation 4.13;

$$\ln \frac{C_{a(t)}}{C_{a(0)}} = -\frac{k + g H_{TCE} V_h}{V_a + V_h H_{TCE}} t$$

where:

- $C_{a(t)}$: TCE concentration in aqueous solution at time $t$
- $C_{a(0)}$: initial TCE concentration in aqueous solution (after partitioning equilibrium is reached)
The headspace expansion rate (g) can be assumed zero in our case because no expansion was observed during the experiments.

The final equation (Equation 4.15) for pseudo-first order model for TCE reduction is;

\[
\ln \frac{C_a(t)}{C_a(0)} = -\frac{k}{V_a + V_h H_{TCE}} t
\]

\[-\ln(C_{a(t)}/C_{a(0)})(V_a + V_h H_{TCE}) = k t \quad (4.15)\]

Figure 4.14 shows the plots of \(-\ln(C_{a(t)}/C_{a(0)})(V_a + V_h H_{TCE})\) versus time, the slope of this plots indicates the first order rate constant for TCE reduction.

The k values for these cathode materials are listed in Table 4.3.
Figure 4.14 Pseudo-first order TCE degradation kinetics with variable cathode materials and cast iron anode, the initial TCE concentration 39 mg L⁻¹, 90 mA current, 0.01 M NaHCO₃ electrolyte.
Table 4.3 The list of pseudo-first order rate constants and final dechlorination efficiencies for different anode and cathode materials.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
<th>FDE* (%)</th>
<th>$k$ (×10$^{-3}$ L h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper foam</td>
<td>Cast iron</td>
<td>&gt;99.7</td>
<td>212.5±3.8</td>
</tr>
<tr>
<td>Copper foam</td>
<td>MMO</td>
<td>57.2</td>
<td>NA</td>
</tr>
<tr>
<td>Copper foam</td>
<td>PbO$_2$</td>
<td>61.0</td>
<td>NA</td>
</tr>
<tr>
<td>Copper plate</td>
<td>Cast iron</td>
<td>88.8</td>
<td>64.6±2.2</td>
</tr>
<tr>
<td>Pure iron plate</td>
<td>Cast iron</td>
<td>82.1</td>
<td>54.4±2.2</td>
</tr>
<tr>
<td>Iron foam</td>
<td>Cast iron</td>
<td>95.6</td>
<td>90.1±1.6</td>
</tr>
<tr>
<td>Nickle foam</td>
<td>Cast iron</td>
<td>74.9</td>
<td>39.5±1.6</td>
</tr>
<tr>
<td>Vitreous carbon foam</td>
<td>Cast iron</td>
<td>82.4</td>
<td>54.1±3.7</td>
</tr>
</tbody>
</table>

*: FDE (Final Dechlorination Efficiency) = ($C_{a(0)}$ - $C_{a(5h)}$/ $C_{a(0)}$) ×100%
4.3.3 Effect of Current and Initial TCE Concentration

Initial TCE concentration and current density were evaluated using three different initial concentration levels (20, 39 and 74 mg L\(^{-1}\)) and 6 different current values (5, 10, 20, 30, 60, 90 mA). The iron anode and copper foam cathode were used in 10 mM bicarbonate solution. The first order rate constants and final dechlorination efficiencies are summarized in Table 4.5. As seen in Table 4.5, FDE values are increasing up to more than 99% as a result of increase in the applied current for all three initial TCE concentrations. As the initial concentration of TCE increases, the rate constants are generally decreasing for the same applied current value. To summarize, the rate constants are directly proportional to the applied current, however they are inversely proportional to the initial TCE concentration.

The rate of hydrodechlorination (\(r_{\text{TCE}}\)) on the iron surface proceeding with the participation of atomic hydrogen can be expressed as \(^{[61]}\) (Equation 4.16);

\[
r_{\text{TCE}} = k_{\text{TCE}} \Theta_H^n \Theta_{\text{TCE}}
\]

(4.16)

where \(\Theta_H\) and \(\Theta_{\text{TCE}}\) represent the surface coverage of adsorbed hydrogen (or atomic hydrogen) and adsorbed TCE, respectively, and \(n\) is the reaction order of hydrogen in the hydrodechlorination reaction. If the dechlorination of TCE on copper surface is assumed to be showing the same kinetics as Equation 4.15, the change in k values can be explained. As the applied current increases, more atomic hydrogens are produced and subsequently, the rate constants increase with an order of \(n\).
Table 4.5 The list of pseudo first order rate constants and final dechlorination efficiencies with different current densities and initial TCE concentration

| Current (mA) | \( C_{a(0)} \approx 20 \text{ mg L}^{-1} \) | | \( C_{a(0)} \approx 39 \text{ mg L}^{-1} \) | | \( C_{a(0)} \approx 74 \text{ mg L}^{-1} \) |
|---|---|---|---|---|---|---|
| | \( k \) (×10^{-3} \text{ L h}^{-1}) | FDE (%) | \( k \) (×10^{-3} \text{ L h}^{-1}) | FDE (%) | \( k \) (×10^{-3} \text{ L h}^{-1}) | FDE (%) |
| 5 | 51.55±6.03 | 65.9 | 19.39±1.67 | 42.2 | 18.98±1.92 | 38.7 |
| 10 | 57.51±1.25 | 83.9 | 39.81±3.13 | 72.1 | 45.58±1.33 | 76.5 |
| 20 | 116.5±4.06 | 98.0 | 113.8±11.49 | 99.2 | 64.45±3.62 | 84.6 |
| 30 | 150.12±2.7 | >99.4 | 149.33±2.96 | >99.7 | 105.18±1.89 | 96.7 |
| 60 | 241.4±6.49 | >99.4 | 128.24±4.67 | >99.7 | 150.05±5.13 | 99.2 |
| 90 | 287.6±9.58 | >99.4 | 212.51±3.81 | >99.7 | 245.15±7.23 | >99.8 |
Chapter 5

Conclusion

5.1 Summary of Work

An experimental program (total of 49 experiments) was conducted in two stages to evaluate the role of using iron anode electrolysis for electrochemical remediation of the TCE in groundwater.

In the first stage, chemical changes in the electrolyte as a result of iron electrolysis are evaluated in batch electrochemical setups and in flow-through column experiment. In this stage, the performance of iron anode was compared with inert anode. The testing variables include operating conditions, such as current density, electrolyte composition, polarity of DC and flow rate. A summary of the results of the batch scale experiments for the first stage are presented in Table 5.1.

In the second stage, TCE was selected as the target contaminant to evaluate the reductive dechlorination efficiency with iron electrolysis. Three different anode materials and six different cathode materials were investigated. The experiments examined the dechlorination efficiency of different electrode configurations, current densities and initial TCE concentrations. Table 5.2 summarizes the results of this stage.
5.2 Conclusions

When iron anode (corrosive) is used for electrochemical treatment of groundwater; highly reducing, basic electrolyte environment will develop. This environment is critical for reductive transformation of some contaminants. When mixed-metal-oxide (inert) anode is used, relatively oxidizing electrolyte environment and neutral pH is achieved. Electrolyte composition significantly affects the pH, ORP, iron speciation and electrolysis efficiency of iron electrolysis. Sulfate solution results in the highest pH value and most reducing ORP value compared to bicarbonate and chloride solutions. The bicarbonate electrolytes are more resistant to pH changes compared to sulfate and chloride solutions. The ORP values show similar trends for all these electrolyte composition. Polarity reversal can be engineered to control and/or maintain neutral pH and reducing environment with two-iron electrodes in divided-electrolyte cell.

In the flow-through column experiment, the main finding was that in the early stage of the experiment the pH and ORP distribution in the column show significant difference with different flow rates. However, as the experiment continues, the difference in the distribution of pH and ORP in the column becomes negligible with all flow rates. The reason is that the amount of produced electrolysis compounds are the same with all flow rates at a certain time because current density and electrolysis time are similar in all flow rates, assuming 100% iron dissolution efficiency. Only the distribution over time of electrolysis products differs as a result of different flow rates; therefore stable pH and ORP values are observed at specific times and flow rate effect became negligible.
Table 5.1 Summary of experimental results with different electrode materials, background electrolytes and current densities.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Current (mA L$^{-1}$)</th>
<th>pH (ini-fin)$^a$</th>
<th>ORP (mV vs Ag/AgCl) (ini-fin)$^a$</th>
<th>ζ (mS cm$^{-1}$) (ini-fin)$^a$</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MMO</td>
<td>MMO</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>112.5</td>
<td>5.4-5.7</td>
<td>217-156</td>
<td>4.01-4.07</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>MMO</td>
<td>MMO</td>
<td>Na$_2$(SO$_4$)-divided</td>
<td>112.5</td>
<td>5.4-2.5/5.4-11.4</td>
<td>271-449/275/(-251)</td>
<td>3.93-6.02/3.93-7.23</td>
<td>NA</td>
</tr>
<tr>
<td>3</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>112.5</td>
<td>5.5-10.5</td>
<td>217(-444)</td>
<td>4.02/4.05</td>
<td>85.1</td>
</tr>
<tr>
<td>4</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-divided</td>
<td>112.5</td>
<td>5.6-5.7/5.6-11.4</td>
<td>240-11/249/(-340)</td>
<td>4.03-3.21/4.03-7.96</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>112.5</td>
<td>5.5-10.5</td>
<td>217(-444)</td>
<td>4.02-4.05</td>
<td>85.1</td>
</tr>
<tr>
<td>6</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>NaCl-mixed</td>
<td>112.5</td>
<td>5.7-10.0</td>
<td>226(-385)</td>
<td>2.42-2.46</td>
<td>66.0</td>
</tr>
<tr>
<td>7</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na(HCO$_3$)-mixed</td>
<td>112.5</td>
<td>7.7-8.9</td>
<td>87(-299)</td>
<td>1.73-1.80</td>
<td>91.9</td>
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<td>8</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>37.5</td>
<td>5.6-5.8</td>
<td>188-52</td>
<td>4.05-4.11</td>
<td>87.1</td>
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<td>9</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>75</td>
<td>5.4-9.7</td>
<td>218(-376)</td>
<td>4.05-3.99</td>
<td>70.8</td>
</tr>
<tr>
<td>10</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>112.5</td>
<td>5.5-10.5</td>
<td>217(-444)</td>
<td>4.02-4.05</td>
<td>85.1</td>
</tr>
<tr>
<td>11</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-mixed</td>
<td>150</td>
<td>5.6-10.7</td>
<td>228(-494)</td>
<td>3.97-4.20</td>
<td>93.4</td>
</tr>
<tr>
<td>12$^b$</td>
<td>Cast Iron</td>
<td>Cast Iron</td>
<td>Na$_2$(SO$_4$)-divided</td>
<td>112.5</td>
<td>5.4-12/5.4-6.6</td>
<td>240(-572)/240(-389)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$: The first value is in the anolyte and second value is in the catholyte.

$^b$: The polarity of direct current was reversed so the initial values were in the anolyte and catholyte at the beginning of the experiment, final values were in the catholyte and anolyte at the end of the experiment.
In the second stage of the research, the dechlorination efficiency of variable anode and cathode materials are compared. The iron anode showed the most significant enhancing effect to the cathodic dechlorination efficiency. Furthermore, porous copper cathode show the best performance compared to other cathode materials. The pseudo-first order rate constants are observed for the dechlorination of TCE. Finally, it was recognized that the rate constant mainly depend on the applied current and initial TCE concentration. The dechlorination efficiency increased with an increase in applied current. However, initial TCE concentration affected the rate constant inversely.

Iron electrolysis provides a new concept to the electrochemical treatment process. Iron electrolysis can be utilized not only for the removal of the several contaminants but also as an enhancing factor for the reductive dechlorination of chlorinated compounds. Reported fast dechlorination of TCE with porous copper cathode-iron anode combination provides a promising technology for future treatment applications.
Table 5.2 The summary of the rate constants \((k)\) and Final Dechlorination Efficiencies (FDE)

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Anode Material</th>
<th>Cathode Material</th>
<th>Current (mA)</th>
<th>Initial TCE Concentration (mg L(^{-1}))</th>
<th>(k) ((\times 10^{-3} \text{ L h}^{-1}))</th>
<th>FDE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Cast iron anode</td>
<td>Porous copper</td>
<td>90</td>
<td>39</td>
<td>212.5±3.8</td>
<td>&gt;99.7</td>
</tr>
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<td>24</td>
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<td>74</td>
<td>245.15±7.23</td>
<td>&gt;99.8</td>
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</table>
5.4 Recommendations for Future Research

Using iron electrolysis for the treatment of the chlorinated compounds is a new concept and requires more research to develop better understanding. The following possible future research topics are recommended:

- The identification of iron oxide precipitates in detail during iron electrolysis to understand whether precipitates contribute to the dechlorination.
- The investigation of porosity loss in different soil types as a result of iron oxide precipitation to estimate potential changes in permeability of the system in aquifers.
- The optimization of the process in terms of the size, configuration, thickness of the electrodes.
References


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[45] Pogrebnaia, V.L.; Klimenko, A.A.; Bokovikova, T.N.; Tsymbal, E.P.; Pronina, N.P. Purification of


[47] Calvo, L.S.; Leclerc, J.P.; Tanguy, G.; Cames, M.C.; Paternotte, G.; Valentin, G.; Rostan, A.; Lapicque, F. An electrocoagulation unit for the purification of soluble oil wastes of high COD. Environmental Progress 2003, 22, 57-65.


