EFFECT OF NATURAL ORGANIC MATTER, METAL IONS, AND NITRATE ON ELECTROCHEMICAL DECHLORINATION OF TRICHLOROETHYLENE

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By

NOUSHIN FALLAHPOUR

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ABSTRACT

Groundwater is susceptible to pollution due to improper waste disposal. Groundwater contamination continues to be a problem in areas where population relies on groundwater as a major source of drinking water. Development of technologies, such as *in situ* electrochemical transformation to clean contaminated groundwater is of great importance. Electrochemical systems, which mainly consist of two or more arranged electrodes that are immersed in wells in groundwater, are of interest because of their ability to manipulate redox conditions to transform contaminants into non-toxic forms.

Aquifers in karst regions are very susceptible to contamination and present a significant exposure routes due to presence of fissures and channels that facilitate contaminant transport under high flow rate. Trichloroethylene (TCE), a toxic chlorinated solvent that causes major health problems, is present in many contaminated aquifers including many that reside in karst regions. Treatment of aquifers contaminated with TCE is difficult in the presence of other contaminants, such as chromate, selenate, and nitrate, which interfere with TCE transformation and degradation mechanisms. Moreover, presence of natural organic matter (NOM) in the groundwater can influence transformation of TCE and other contaminants. Therefore, it is important to evaluate transformation of TCE in the presence of contaminant mixtures in groundwater.

In this study, a series of experiments are conducted to (1) evaluate the effect of co-existing organic and inorganic compounds on the electrochemical dechlorination of trichloroethylene (TCE) in simulated karst media; and (2) assessment of the impacts of high groundwater flow rates in the presence of palladium (Pd) catalyst on TCE transformation rate and the accumulation of precipitates.
A small-scale flow-through limestone column is used to simulate a karst aquifer media to evaluate dechlorination of TCE in the presence of organic and inorganic compounds. Iron anode was used to produce ferrous ions and promote reducing conditions in the column. Various current intensities (30, 60, and 90 mA) were applied under the flow rate of 1 mL min\(^{-1}\) and initial TCE concentration of 1 mg L\(^{-1}\). Under the same testing conditions, presence of chromate has the highest influence on TCE removal followed by selenate and then nitrate. The reduction of TCE under 90 mA current, 1 mL min\(^{-1}\) flow rate, and 1 mg L\(^{-1}\) initial TCE concentration, was inhibited in the presence of humic acids due to competition for direct electron transfer and/or reaction with atomic hydrogen produced at the cathode surface by water electrolysis. The use of iron anode creates favorable conditions for TCE reduction but produces aggregates in combination with ferrous ions, which may impact the long-term performance of the remedial system.

A vertical acrylic column, with Pd pellets placed on the cathode surface, was used to investigate the impacts of Pd-based catalysis for the removal of TCE under high flow rate (1 L min\(^{-1}\)). The effects of electrode materials and current intensities on precipitation, pH and ORP are assessed. The following electrode materials and arrangements were tested: (a) two MMO electrodes as an anode and a cathode, (b) a cast-iron anode and a MMO cathode, and (c) a cast-iron anode and a copper foam cathode. Current intensities of 500, 250, 125, and 62 mA were tested under the flow rate of 1 L min\(^{-1}\) and 5 mg L\(^{-1}\) of initial concentration of TCE. Under the conditions of 1 L min\(^{-1}\) flow, 500 mA current, and 5 mg L\(^{-1}\) initial concentration of TCE, removal efficacy using iron anodes (96%) is significantly higher than that of mixed metal oxide (MMO) anodes (66%) because the iron anode supports reduction conditions by electrolysis. Two types of cathodes (MMO and
copper foam) in the presence of Pd/Al₂O₃ catalyst under various currents (250, 125, and 62 mA) were used to evaluate the effect of cathode materials on TCE removal efficacy. The similar removal efficiencies were achieved for both cathodes, but more precipitation generated with copper foam cathode. Palladium improved TCE degradation by 120% for 250 mA, 100% for 125 mA, 100% for 62 mA, under the conditions of using an iron anode followed by a copper foam cathode with 1 L min⁻¹ flow rate. The high velocities of groundwater flow can have important implications since the groundwater flow rate can significantly fluctuate, especially in karst aquifers. The optimization of the electrochemical systems for successful operation under high flow rates allows the robustness and great flexibility for the application. It is assumed that the high flow rate would favor the transformation of contaminants since it would flush out precipitates and prevent clogging.
Chapter 1  Introduction

1.1. Overview

Soil and groundwater contamination is an ongoing environmental problem in the United States, especially in areas that rely on groundwater for their drinking water source (USEPA, 1998). Presence of contaminants, such as chlorinated solvents, hexavalent chromium, selenates, and nitrates in groundwater pose a significant health risk to humans and a burden on the environment (Gandhi et al., 2002). Chlorinated volatile organics such as trichloroethylene (TCE), tetrachloroethylene (PCE), dichloroethylene (DCE) and vinyl chloride are among the most common contaminants at Superfund and other contaminated groundwater sites in the US (Chen et al., 2003; USEPA, 2005). Presence of these contaminants in soil and groundwater is due to improper disposal and poor handling during production and transformation. Once introduced to the environment, their fate and transport through environmental media (air, water and soil) can be very complex. For example, when TCE is released to the environment, it will either evaporate or penetrate the soil into the groundwater and move downward by gravity as a dense non-aqueous phase liquid (DNAPL) through an aquifer until it reaches an impermeable layer (Teerakun et al., 2001). Due to its physico-chemical properties, TCE is a persistent contaminant and has negative impacts on human health and the environment (Gandhi et al., 2002).

Groundwater remediation is the cleanup of contaminated groundwater to levels that are in compliance with regulatory limits (King et al., 2012). There are several essential principals to select an applicable treatment method to treat a contaminated site. The most important aspects are addressing site characterization and risk assessment prior to selecting
an effective remedial procedure. There is fairly extensive literature on *in situ* and *ex situ* technologies to remediate contaminated groundwater. *In situ processes* treat soils and ground water in place, without removal. *In situ* remediation requires a detailed understanding of existing subsurface conditions in order to be effective. The *in situ* approach requires manipulation to create environmental conditions that enhance the degradation of the contaminants into less harmful products. *In situ* processes may reduce the costs of materials handling and some environmental impacts may be reduced, however, *in situ* processes may be limited by the ability to control or manipulate the physical and chemical environment in place (ITRC, 2002). On the other hand, *ex situ processes* involve the removal of the contaminated media to a treatment area. For example, groundwater is extracted by wells, treated on the surface, and pumped back in the subsurface by injection wells, percolation basins, or similar means (King et al., 2012).

Most chlorinated compounds can be transformed to non-toxic substances with various reductive biological (Lee, and Batchelor, 2002), chemical (Stroo and Ward, 2010) or electrochemical processes (Chen et al., 2003, Mao et al., 2011, Mao et al., 2012) that are subcategories of either *in situ* or *ex situ* technologies. Different types of technologies for TCE remediation, including pump and treat, *in situ* air sparging, *in situ* flushing, ion exchange, bioventing, monitored natural attenuation, and permeable reactive barriers (PBRs) have been used to prevent spreading of TCE from contaminating groundwater.

Some groundwater pollution occurs naturally. Water percolating through soils picks up naturally-occurring minerals, salts, and organic compounds (Saracino et al., 2002). The toxic metal chromium, for instance, is commonly found in the sediments or
rock and can be present in groundwater at concentrations that exceed safe levels for drinking water. Contamination of water resources by selenium (Se) may result from natural processes or anthropogenic activities. The oxidation of sulfide minerals is usually a major source for an increase in Se concentrations in groundwater because Se is strongly chalophilic and thus groundwater concentration tends to be highly variable. Nitrate is very soluble in water and not readily adsorbed by soil, so it is typically very mobile in the subsurface environment and it can move easily into groundwater, which is the primary source of drinking water in United States.

Due to an increasing demand for more agricultural/industrial production and other resources because of a higher living standard and increased population, the discharge of nitrogen compounds such as inorganic nitrogen (e.g., ammonia/ammonium, nitrogen oxide, and nitrate) and organic nitrogen (e.g., urea, amines and protein) via water use also rises (Galloway et al., 2003). Presence of these substances in groundwater negatively impacts the removal of target chlorinated contaminant but there is still a limited knowledge on the effect of coexisting compounds on remediation, especially in karst aquifers (Liu et al., 2008). The efficiency of an electrochemical system for TCE removal is influenced by the presence of strong oxidants such as chromate, selenate, and nitrate because the layer of sediments at the surface of the electrodes prevents electron transfer reactions and lessens dechlorination rate.

Karst aquifers constitute 25% of the earth’s groundwater resources (Green et al., 2004). Contaminants that easily enter karst aquifers through thin soils or via swallow holes, can quickly spread over large distances due to rapid and turbulent flow in the conduit network. On the other hand, the flow of ground water in karst terrains is unpredictable.
Groundwater flow in conduits and fractures of karst aquifers differs radically from flow in other aquifers. Such flow is generally faster than in other aquifers; extreme velocities of 2300 m/hr (7500 ft/hr) have been observed, while a range of 10 to 500 m/hr (30 to 1500 ft/hr) is typical for many conduits (Quinlan, 1987). Thus the effects of leakage or a spill of hazardous material on water quality in a karst aquifer can be sensed at great distances in less than a day. Consequently, karst aquifers are important routes of contaminant exposure for humans and wildlife.

Several physical-chemical and biological processes proposed to manage TCE and other inorganic contaminants can be only marginally cost-effective for some pollutants, and are often limited by being relatively slow and inefficient, along with being environmentally disruptive in nature (Pant and Pant, 2010). Thus, developing alternatives for remediation of contaminated sites should target not only by chlorinated solvents (e.g., TCE and PCE), but also other co-existing substances such as chromate, selenate, nitrate and natural organic matters present in the aquifers. A system of permeable reactive barriers (PBRs), an in situ treatment for groundwater contamination, has received considerable attention because of being cost-effective and environmentally friendly containment technology for groundwater remediation. Electrochemical dechlorination of chlorinated aliphatic organic compounds by metals and catalysts and the pathways of dechlorination at various electrodes in electrochemical cells have been reported as one the most effective alternatives (Al-Abed and Fang, 2006).

PRBs are mainly designed to treat contaminated groundwater, which is moving through permeable soil and sediments due to natural gradient. Electrochemical reactive barriers contain electrodes as the reactive medium to degrade chlorinated organics into
less-toxic compounds. Electrochemical processes maybe applied in the form of permeable reactive barrier for groundwater remediation, sometimes referred to as electrically induced redox barrier or e-barrier that consists of closely placed electrodes across the flow direction of contaminated groundwater (Sale et al., 2005). As the plume of contaminated groundwater passes through the barrier, the dissolved contaminants are subject to sequential oxidation-reduction or reduction-oxidation, depending on the sequence of the charges applied to the electrode set. Electrochemical treatment methods have attracted attention since they can offer options to treat wide range of organic pollutants.

Electrochemical processes have potential ability to treat a broad range of contaminants through sequential oxidation and reduction reactions without any chemicals injection into the subsurface as electrochemical remediation uses electrolysis. They also have the potential to be cost effective as the electrochemical remediation system can be powered by renewable energy sources like solar power. More than a pair of electrodes can be used to enhance the contaminant transformation process and the rate of electrochemical reactions can be controlled by adjusting current intensity which further regulate groundwater chemistry to achieve desired conditions for the degradation of target contaminants. Iron electrodes have shown promise for in situ electrochemical remediation of contaminated subsurface (Cho and Park, 2005).
1.2. Objectives of Research

The primary goal of this research is to develop a remediation strategy using low-level electricity to induce electrolysis in groundwater and transform contaminants to non-toxic or less-toxic products without adverse effects on the environment. The research objectives are focused on the development of electrochemical processes for treatment of TCE in the presence of a mixture of contaminants in karst aquifers. Specifically, this research investigates:

(1) the influences of presence of a mixture of contaminants and natural organic matter on hydrochlorination of TCE in simulated groundwater and

(2) the influence of high flow rate on TCE removal by enhanced hydrochlorination via Pd catalysis.

To achieve the objectives, a specific set of experiments were proposed for the electrochemical to:

- Evaluate the effect of process variables such as current density, flow rate, and initial concentration of co-existing compounds on TCE removal efficiency in a limestone column (as experimental set-up) designed to simulate the channel flow in karst aquifer.

- Test the effect of current intensity and electrode materials and arrangements on precipitation, pH and ORP changes in a circulated system.

- Investigate the performance of a circulated system under high flow rate by introducing Pd-catalyst to enhance hydrodechlorination of TCE.
1.3. Organization of Thesis

A brief review of the content of the thesis is given below. Chapter 1 includes a brief introduction of the groundwater contamination and challenges in karst aquifer, and introduce the objectives of this research. Chapter 2 includes a comprehensive literature review of physical and chemical properties of TCE as a chlorinated hydrocarbon present in aquifers, different available remediation technologies with focus on electrochemical transformation processes. Subsequently, an overview of TCE transformation, especially, electrochemical reactive barrier, role of iron anode and its influences on the environment, and the effect of other co-existing organic and inorganic compounds on TCE remediation are discussed. Chapter 3 describes the experimental methods and procedures, analytical methods, and sampling processes. The experimental apparatus is explained in details and the chemicals and instruments are listed. Chapter 4 presents the results from flow-through experiments for the evaluation of the presence of a mixture of contaminants and natural organic matter on hydrochlorination, including TCE removal efficiency as well as the results for the enhanced circulated hydrochlorination system under high flow rate the using Pd catalyst. Various variables such as current density, flow rate, catalyst type, and electrode configurations have been investigated. Chapter 5 provides the summary of the results, conclusions and future work recommendations.
Chapter 2  Literature Review

2.1. Release of Chlorinated Compounds into the Environment

Around 50% of the United States population uses groundwater as drinking water source (Maupin et al., 2014). However, groundwater is very susceptible to pollutants. Even though groundwater is plentiful in some areas, it may not be usable as a drinking water supply if its quality has been changed by contamination. Contaminants can enter aquifers by infiltration from surface water through soils, sediments, and porous rocks and direct flow from both surface water in fractured-rock or karst area and improperly built wells. Water that infiltrates through the soil, carries naturally-occurring minerals, ions, and organic compounds, which can result in contaminated ground water, either by establishing a pathway or a conduit for pollutants entering a well from surface drainage or by establishing hydraulic connection between aquifers of varying quality (Saracino et al., 2002).

Groundwater contamination also results from many sources including man-made ones such as current and past oil and gas production practices, agricultural activities, industrial and manufacturing processes, and domestic activity. For instance, extensive use of pesticides and fertilizers use in agricultural areas can cause their migration into groundwater over time. Mining wastes, generated during the extraction and processing of minerals, are another major source of groundwater contamination (Stewart, 2009).

Chlorinated solvents have played a role in the world’s industrial societies for more than 70 years where the majority of products made of metals or incorporating electronic components undergo some form of cleaning processes using solvents to remove residuals from fabrication (Mohr et al., 2010). Improper use and disposal of chlorinated solvents have caused significant groundwater contamination. Chlorinated volatile organics are the
most frequently encountered organic contaminants at Superfund and other groundwater contaminated sites in the United States (Chen et al., 2003).

2.2. Properties of Chlorinated Solvents and Co-existing Contaminants

Chlorinated solvents, which can be present as dense non aqueous phase liquids (DNAPLs), are composed of single or multi-component chlorinated hydrocarbon (Figure 2.1), and were used since the early 1900s for a wide variety of purposes, from cleaning of machinery, clothes and electronic parts to use in chemical manufacturing as degreaser (Kueper et al., 2004; Stroo and Ward, 2010).

![Figure 2.1. Chemical structures of some common chlorinated solvents](image-url)
The behavior of chlorinated solvents is a function of their physical and chemical properties. The properties that make chlorinated solvents problematic with regards to groundwater contamination include density, solubility, viscosity, and surface tension. At room temperature (25°C), most chlorinated solvents are colorless liquids with the density greater than that of water (1 kilogram per liter). Chlorinated solvents are heavier than water and with densities ranging from 1100 kg.m⁻³ to 1600 kg.m⁻³ (Kueper, 2004, Fetter, 2001) causing their downward migration below the water table. Likewise, the level of solubility refers to the process through which organic phases (pure or mixture of several organic liquids) are gradually released into groundwater. Most chlorinated solvents can be classified as sparingly soluble in water. In general, as the number of chlorine atoms on a compound increases, the aqueous solubility decreases. Environmental variables such as temperature, salinity, and presence of other organic substances could influence chlorinated solvents solubility. Viscosity is the measurement of the resistance of a fluid to flow and it is inversely proportional to temperature. Chlorinated solvents are less viscose (0.57-1.0 cP) than water (1.0 cP) (Kueper et al., 2004), which results in faster penetrating through the subsurface and easier migration. The surface tension of chlorinated solvents (20-40 dynes cm⁻¹) compared to water (73 dynes cm⁻¹) significantly impacts how chlorinated solvents penetrate the capillary zone and migrate through the saturated zone (O’carroll et al., 2007).
Figure 2.2. Distribution of potential DNAPL-accumulation sites in a hypothetical karst setting (EPA, 2016)

Figure 2.2. shows a schematic of the distribution of DNAPLs and their dissolved phase at a site with permeable surface soil layer. DNAPLs downward migration in the unsaturated (vadose) zone will result in residuals contamination and will eventually encounter groundwater. Aquifers include porous materials like sand and gravel leading to DNAPLs continuous downward migration. When DNAPLs reach impervious layers like clay, it will pool on top of these layers. However, based on the chemical properties of soil layers and soil particles that define different capillary forces, both the solvent and water will follow unpredictable pathways. Thus, knowing the particular surface location where a chlorinated solvent exists is not sufficient to locate DNAPLs source contamination because of the erratic paths it may follow (Stroo and Ward, 2010, Baird et al., 2005).

2.2.1. TCE

Examples of chlorinated solvents that are important groundwater pollutants include PCE and TCE. PCE has been widely used in the dry-cleaning industry and have been used
for aluminum cleaning, sulfur recovery, paint removal, and textile industry, moreover, TCE has been considered as one of the best solvents for cleaning and degreasing because of its effectiveness (Doherty, 2000). It has been also contained in many household products such as shoe polish and disinfectants. The physical and chemical properties of TCE affect its movement and fate in the environment. TCE is a non-flammable, colorless liquid with a sweet odor and burning taste that has been used in adhesives and metal cleaning and degreasing industries (Doherty, 2000). TCE transformation may produce other chlorinated byproducts such as dichloroethylene, chloromethane, and vinyl chloride that are toxic. In 2005, the United States Environmental Protection Agency completed its Final Health Assessment for TCE and released a list of new TCE toxicity values (USEPA, 2014). Proper understanding of TCE properties in addition to other considerations such as site characteristics are necessary for effective treatment of TCE contaminated sites. Table 2.1. lists TCE properties compared to water.

Table 2.1. Physical and Chemical Properties of trichloroethylene in comparison to water (McKenzie, 2013)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TCE</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C₂HCl₃</td>
<td>H₂O</td>
</tr>
<tr>
<td>Liquid density at 20 °C</td>
<td>1460 kg.m⁻³ (a)</td>
<td>998 kg.m⁻³ (a,b)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.0057 g.(cm.s)⁻¹ (b,c)</td>
<td>0.010050 g.(cm.s)⁻¹ (d)</td>
</tr>
<tr>
<td>Aqueous solubility</td>
<td>1100 mg.L⁻¹ (c)</td>
<td>Not defined</td>
</tr>
<tr>
<td>Surface tension with air</td>
<td>29.5 dynes.cm⁻¹ (a)</td>
<td>72.0 dynes.cm⁻¹ (a)</td>
</tr>
<tr>
<td>Maximum Contaminant Level</td>
<td>0.005 mg.L⁻¹ (a)</td>
<td>Not defined</td>
</tr>
</tbody>
</table>

a Ajo-Franklin, Geller, Harris (2006).
b Jackson and Dwarakanath (1999).
As a result of its properties, TCE spills will produce contamination in many forms, for example as highly concentrated free product, a trail of residual saturation moving more or less vertically through saturated zone, and as dissolved molecules in groundwater. These forms will impact the fate and transport of dissolved phase TCE through groundwater systems.

2.2.2. Other Contaminants: Chromate, Selenate, and Nitrate

Various land uses and human-made activities supply the basis for chemical accumulation in watershed all across the landscape. A variety of hazardous substances, complex mixtures of natural and anthropogenic chemicals, have been identified as sources of groundwater contamination causing human health threats, including (1) toxic organics such as halogenated compounds, benzenes and polycyclic aromatic hydrocarbons (PAHs); (2) inorganic nonmetallic ions such as nitrate, perchlorate, and fluoride; and (3) heavy metals such as lead, chromium, and arsenic (Mao et al., 2012). Over 40% of superfund sites include mixtures of organic and heavy metal contaminants (Wu et al., 2008). Other kinds of mixed contaminants are also often reported (Fernandes et al., 2009; Wang et al., 2010). Assessment and management of the risks of exposure to complex chemical mixtures in the environment are priorities for human and environmental health organizations. The current lack of information on the composition and variability of environmental mixtures and a limited understanding of the combined effects of multiple chemical exposures are fundamental obstacles to timely identification and prevention of adverse human and ecological effects of exposure to chemical mixtures (USGS, 2015).
One of the most important environmental issues today continues to be the level of groundwater contamination with heavy metals because of their toxicity even at low concentrations (Marcovecchio et al., 2007; Wongsasuluk et al., 2014). Heavy metals are generally more persistent than organic contaminants and they can become mobile in soils based on the soil pH and their speciation. Over the past few decades, many documented remediation technologies were applied to treat organic and inorganic pollutants in soil and groundwater (Khan et al., 2004, Diels et al., 2005). These technologies can be categorized into (1) containment to prevent the transport of contaminants when the other options are not physically or economically feasible for a site, (2) immobilization to reduce the mobility of contaminants, (3) chemical and/or biological process that include oxidation, reduction, and neutralization reactions to change the oxidation state of metal, and (4) physiochemical treatment that include electrokinetic remediation, which operates by low density current that passes through electrodes inserted into the subsurface to effect movement of water, ions and particulates through the soil. Due to coexistence of different contaminants, strategies to address contamination mixtures in groundwater require considering not only the properties of individual contaminant, but also the complexity of their interactions (Mao et al., 2012).

Among heavy metals, Cr (VI) is one of the most toxic and carcinogenic chemical elements and is considered by the World Health Organization as a priority toxic chemical (Allan and Kukacka, 1995). Trivalent Cr(III) is a micronutrient, which forms sparingly soluble hydroxide precipitates under conditions prevalent in most surficial aquifers, however, hexavalent Cr(VI) is a known carcinogen, which does not adsorb readily, and its relatively high concentrations are often found in aquifers impacted by Cr contamination.
There are various technologies available to remove chromium from water such as reduction, chemical or electrochemical precipitation, and ion exchange (Rengaraj et al., 2002, Mao et al., 2012). The formation of precipitates within an electrochemical reactive barrier can potentially impact system performance by means of accumulation on the reactive material surface and further decreasing effective reactive surface area. Simultaneous treatment of organic and inorganic contaminants provides an additional level of efficiency to the electrochemical reactive barrier treatment system (Mao et al., 2012).

Release of selenium by anthropogenic disturbances, including mining, agricultural activities and industrial waste disposal, can lead to contamination of aquifers (Hayashi et al., 2009). A variety of physical, chemical and biological treatment technologies have been shown to remove selenium from water (CH2M HILL, 2010). Since reduction of Se(VI) by elemental iron, and precipitation of elemental selenium (Se⁰) is favored thermodynamically, the elemental iron and selenate/selenite redox reaction in water (as an electrochemical cell) will essentially produce a variety of ferrous and ferric iron products that will either directly reduce the selenate to selenite then to elemental selenium, or adsorb the selenite to the ferric amorphous solids, which further produces precipitates and clogs the system and prevent further reactions (CH2M HILL, 2010). This increases the complexity of how to determine applicable selenium removal technologies to a wide variety of industries. Information exchange among and within industries is needed to advance technologies for selenium removal, including the need to consider process engineering principles applied to both the science behind the physical, chemical treatment technology, and an overall system configuration for the core treatment technology.
Nitrogen is the most common element used as a fertilizer supplement for agricultural, turf, and garden use and those nitrogen fertilizers normally exist in the forms of either commercial or animal waste (ITRC, 2000). In dealing with the nitrate problem in subsurface waters, there are two options for achieving safe nitrate level: (1) non-treatment techniques that consist of blending drinking waters with cleaner waters to bring the nitrate concentration down to a safer level, (2) using treatment processes that include two major categories: (i) reduction technologies like biological denitrification and chemical reduction, both of which transform nitrate through reduction to other nitrogen species, preferably to nitrogen gas and (ii) removal technologies such as ion exchange, reverse osmosis, and electrodialysis, which remove nitrate and other constituents to a concentrated waste stream requiring disposal (Jensen et al., 2012). There is an extensive research focused on the use of zero valent iron (ZVI) in different forms of application such as powered iron, stabilized iron nanoparticles and iron filings for chemical reduction (Hao et al., 2005, Xiong et al., 2009). While nitrate cannot be completely removed from groundwater, the use of treatment methods such as ion exchange and the adoption of preventative measures will help to reduce nitrates to biologically safe levels (Tong and He, 2013).
2.3. Karst Groundwater Resources

Karst aquifers constitute 25% of the earth’s groundwater resources (Green et al., 2004). Karst aquifers consist of bedrocks made up of soluble rocks (e.g. limestone or dolomite) and are often structured by conduits and cavities that have been created or expanded by dissolution of the carbonate. Groundwater management technologies that are appropriate for porous media are often insufficient for karst aquifers because of its essentially different characteristics. These characteristics make karst aquifers well-known for intrinsic vulnerability to groundwater contamination which is due to soil and vegetation cover and upper layer capacity to introduction and transport of contaminants and is independent from the nature of contaminants and the contamination scenarios (Ghasemizadeh, 2015). Contaminant transport mostly occurs along preferential flow pathways that are basically inaccessible location because of the high degree of heterogeneity of karst aquifers which makes them behave very differently from other aquifers. The convergent nature of flow in karst aquifers may result in contamination becoming concentrated in conduits that can affect plant and animal life exists in the area as well as human health by contaminating drinking water supplies (USEPA, 1988). Therefore, protection and investigation method are required for these aquifers to protect human health as they carry vulnerable freshwater resources.

Although the contamination of groundwater is a serious problem and a large majority of the United States population relies on groundwater as a safe, drinkable source of water, it doesn’t always receive the attention necessary to address it until it has impacted a community (USGS, 2000). The process of cleaning contaminated groundwater can be very costly. To protect the community at large spills groundwater contamination should be
addressed and contained as quickly as possible following the release (Element Environmental Solution Inc., 2015).

2.4. Remediation Technologies

Groundwater is a valuable source of drinking water, which is used extensively for agricultural and industrial applications. Thus, remediation of contaminated groundwater is critical in order to protect human health and the environment and it is of the utmost importance to properly characterize the site, and such a characterization includes defining the site’s geology, hydrology, and contamination, potential releases to the environment, and locations and demographics of nearby populations (Reddy and Cameselle, 2009). This requires a thorough understanding of both the subsurface conditions and the benefits/disadvantages of the selected remedial technology. Several technologies exist for the remediation of contaminated groundwater including pump and treat, air sparging, \textit{in situ} chemical oxidation/reduction, monitored natural attenuation, permeable reactive barriers, and \textit{in situ} electrochemical remediation (e-barrier). Many of these technologies are used in combination and other innovative technologies are being developed (Stroo and Ward, 2010). There are many factors such as site specific hydrogeology and contaminant conditions, desired cleanup levels, remedial time, and cost that must be considered in selection of the proper remediation technology for a specific site.
2.4.1. *Ex Situ* Treatment - Pump and Treat

Pump and treat has been the most common method for groundwater clean-up. Pump and treat systems operate by pumping groundwater to the surface, removing the contaminants, and then either recharging the treated water back into the ground or discharging it to a surface water body or municipal sewage plant (Suthersan, 1999). Although, pump and treat systems have been operated at various sites, the data collected mention that the performance drastically decreases over time, while it may be successful during initial stages of implementation.

Pump and treat requires simple equipment, however, some concerns with pump and treat include lingering residual contamination, biofouling of extraction wells and associated treatment stream that can severely affect system performance, high cost of treating large quantities of wastewater, and high operation and maintenance costs (USEPA, 1996).

Pump and treat application is well documented (Bass et al., 2000, Hattan et al., 2003) practically in all environmental settings. Undesirably, the performance of pump and treat systems are always uncertain and has proven difficult to achieve until subsequent monitoring provide the necessary information to determine whether the cleanup goals will be achieved. By presenting basic concepts of pump and treat technology, an in-depth understanding of hydrology and groundwater engineering is required to design and operate a pump and treat system for groundwater remediation.
2.4.2. *In Situ* Physical Treatment - Air Sparging

Air sparging is an *in situ* remedial technology to reduce volatile compounds concentration, which is both adsorbed to soil and dissolved in groundwater. Air sparging treatment (Figure 2.3) involves the injection of contaminant-free air directly into saturated zone to transfer contaminants to the vadose zone (ITRC, 2005).

![Figure 2.3. Schematic of an *in situ* air sparging system combined with soil vapor extraction (EPA, 2012)](image)

Chlorinated solvents such as TCE, often have low water solubility and high vapor pressure, which make them easily responsive to air sparging system. The effectiveness of pulsed air sparging technology for the remediation of TCE contaminated groundwater in a sandy aquifer was investigated in laboratory experiments (Ciblak, 2011). Based on studies (ITRC, 2005), air sparging could be used to effectively remove dissolved phase chlorinated
solvents such as TCE. Like other common remedial technologies, there are both advantages and limitations to the application of air sparging system. Some advantages to air sparging include the following (ITRC, 2005); it has been recognized as an effective remedial technology by the regulatory community and its implementation is relatively simple due to possible use of low-cost well-installation techniques. In other words, if applied properly, air sparging can be a low-maintenance in situ remediation method with a reasonable cleanup time frame (Bass et al., 2000). Although in situ air sparging seems very simple process at a very first step, includes air injection into the contaminated aquifer to enhance removal efficiency, there are some conditions that under which air sparging is not recommended:

- Conditions with hydraulic conductivity less than $10^{-3}$ cm/s (Suthersan, 2000)
- Contaminants present are non-strippable or non-biodegradable
- Conditions with the presence of low permeability layers overlying zones with higher permeability

It is important to be careful about the potential for uncontrolled migration of vapor contaminants because air sparging increases the rate of contaminant volatilization. Therefore, air sparging couples with Soil Vapor Extraction (SVE), which applies vacuum to extract the vapors from vadose (unsaturated) zone.

2.4.3. In Situ Chemical Oxidation

One of the most advanced technologies to remediate the concentration of targeted contaminants from soil and groundwater to acceptable levels defined by EPA, is in situ
chemical oxidation (ISCO), which could be introduced as injecting strong oxidants into the soil or groundwater to treat chemical contaminants. The remediation of certain organic substances such as chlorinated solvents (trichloroethylene and tetrachloroethylene), and gasoline-related compounds (benzene, toluene, ethylbenzene, MTBE, and xylenes) by ISCO is possible based on research and development that still continue, however, the effectiveness of ISCO is highly dependent on various factors such as site characteristics and oxidant delivery system (Stroo and Ward, 2010).

A wide range of groundwater contaminants react either moderately or highly with the ISCO method, and ISCO can also be used in a variety of different situations (e.g. unsaturated and saturated ground, above ground or underground, etc.), so it is a popular method to use (Huling and pivetz, 2006).

### 2.4.3.1 Potassium and Sodium Permanganate

Among all oxidants that have been applied for this process, hydrogen peroxide (H2O2), potassium and sodium permanganate (KMnO4, NaMnO4), sodium persulfate (Na2S2O8), and Ozone (O3) are the most common ones.
Table 2.2. Characteristics of chemical oxidants used for destruction of organic contaminants (Huling and Pivetz, 2006).

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidant chemical</th>
<th>Commercial form</th>
<th>Activator</th>
<th>Reactive species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanganate</td>
<td>KMnO₄ or NaMnO₄</td>
<td>Powder, liquid</td>
<td>None</td>
<td>MnO₄⁻</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>H₂O₂</td>
<td>Liquid</td>
<td>None, Fe(II), Fe(III)</td>
<td>OH⁻, O₂⁻, HO₂⁻</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃ (in air)</td>
<td>Gas</td>
<td>None</td>
<td>O₃, OH⁻</td>
</tr>
<tr>
<td>Persulfate</td>
<td>Na₂S₂O₈</td>
<td>Powder</td>
<td>All above</td>
<td>S₂O₈²⁻, SO₄⁻⁻⁻</td>
</tr>
</tbody>
</table>

Permanganate is a common chemical oxidant that has been used in the treatment of water and wastewater, as well as industrial and organic chemistry for a long time (e.g. Singh and Lee, 2001). It is also a selective reagent, which means its applicability depends on both target contaminant chemical structure and readiness for permanganate attack (Singh and Lee, 2001; Waldemer and Tratnyek, 2006). Generally, permanganate reaction is dependent on system pH according to the following reactions (Siegrist et al., 2010):

\[
\begin{align*}
\text{MnO}_4^- + 8H^+ + 5e^- & \rightarrow \text{Mn}^{2+} + 4H_2O \quad \text{pH} < 3.5 \quad (\text{Eq. 2.1}) \\
\text{MnO}_4^- + 2H_2O + 3e^- & \rightarrow \text{MnO}_2(s) + 4OH^- \quad 3.5 < \text{pH} < 12 \quad (\text{Eq. 2.2}) \\
\text{MnO}_4^- + e^- & \rightarrow \text{MnO}_4^{2-} \quad \text{pH} > 12 \quad (\text{Eq. 2.3})
\end{align*}
\]

Many aspects of permanganate ISCO have been investigated such as its chemical reactions and degradability of organic contaminant of concern (Siegrist et al., 2010). Permanganate is capable of degrading a wide variety of contaminants, especially,
chloroethenes and to a lesser extent PAHs. It should be noted that the byproduct formation may impact subsurface permanganate and contaminant transport process as it is able to foul the injection devices, lessen the permeability, and generate preferable flow pathways (MacKinnon and Thomson, 2002; Li and Schwartz, 2004; Heiderscheidt et al., 2008).

2.4.3.2. Hydrogen Peroxide

Generally, hydrogen peroxide and Fenton oxidation would be a great option to transform or decompose organic chemicals as it may produce a wide variety of free radicals, which have both oxidation and reduction potentials, through catalytic process. A wide range of organic compounds (e.g., halogenated aliphatic) are treatable with hydrogen peroxide due to its non-selective nature and the variety of its reactions. While hydrogen peroxide has shown a strong capability to treat a wide variety of contaminants, other factors such as high concentration of present constituents in soil and groundwater could affect the ISCO process by out-competing with target contaminants for oxidant and decrease or cease contaminant degradation.

In situ application of this oxidant results in a dramatically more complex chemistry that has many steps including the following (Pignatello et al., 2006; Siegrist et al., 2010):

\[
Fe^{2+} + H_{2}O_{2} \rightarrow Fe^{3+} + OH^- + OH^o \tag{Eq. 2.4}
\]
\[
OH^o + H_{2}O_{2} \rightarrow H_{2}O + HO_2^* \tag{Eq. 2.5}
\]
\[
HO_2^* + H_{2}O_{2} \rightarrow H_{2}O + O_2 + OH^o \tag{Eq. 2.6}
\]
\[
Fe^{2+} + OH^o \rightarrow Fe^{3+} + OH^- \tag{Eq. 2.7}
\]
\[
HO_2^* \leftrightarrow O_2^- + H^+ \tag{Eq. 2.8}
\]
This general sequence and reactions continue to occur simultaneously till the H₂O₂ is fully consumed (USEPA, 2006). In order to achieve a significant removal rate in ISCO system, these reactions need to last long enough for the target contaminant to be degraded.

Physical factors such as temperature and oxygen gas evolution have the potential to impact effectiveness of using hydrogen peroxide for ISCO. The role of natural organic matter (NOM) has been investigated in several studies (Crimi and Siegrist, 2005; Rivas, 2006) because NOM can enhance or limit the mass transport, mass transfer, and the reaction kinetics involved in the hydrogen peroxide treatment process. Chloride also has a negative effect on the system by both scavenging radicals by hydrogen peroxide reaction and complexing with iron (Sigrist et al., 2010). Under optimized conditions, hydrogen peroxide reactions aim to complete degradation of the VOCs to produce carbon dioxide, water and salts but it is not always the case, as many organic contaminants require multiple oxidation steps to become completely mineralized. The commonly observed byproducts for a wide range of organic contaminants include low molecular weight carboxylic acids, such as formic acid, oxalic acid, acetic acid, and others (Huling et al., 2000; Zazo et al., 2005).

2.4.3.3. Sodium Persulfate

Persulfate salt is a strong oxidant and dissociates in water as persulfate onions (S₂O₈²⁻). It is more powerful than hydrogen peroxide and more stable in the subsurface as
compared to H$_2$O$_2$ and O$_3$ (Huling and Pivetz, 2006). Although persulfate has a strong reduction potential and provide strong free radicals intermediates, its reactions should take place on a timescale designed for ISCO remediation to achieve the most favorable degradation pathway of VOCs (ITRC, 2005). The feasibility of using ISCO to degrade TCE and PCE is extensively investigated, as they are common groundwater contaminants (Krembs, 2008). The stoichiometry of the direct sodium persulfate oxidation of TCE requires three moles of sodium persulfate per mole of TCE and is described as illustrated below (Siegrist et al., 2010):

$$3 \text{Na}_2\text{S}_2\text{O}_8 + \text{C}_2\text{H}_4\text{O}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 9\text{H}^+ + 3\text{Cl}^- + 3\text{Na}^+ + 6\text{SO}_4^{2-} \quad (\text{Eq. 2.11})$$

In the context of this discussion, it is still required to broadly explore how persulfate application impacts the subsurface environment while there are proofs regarding: (1) how manganese dioxide solids (byproduct of using permanganate) can precipitate and change both permeability and flow pattern in the subsurface (MacKinnon and Thomson, 2002; Heiderscheidt, 2005) and (2) the significant off-gassing that may occur by using hydrogen peroxide which affect permeability and oxidant distribution (Heiderscheidt, 2005). Nonetheless, persulfate shows great promise in both the basis of field applications and laboratory studies to be able to efficiently and effectively degrade many organic contaminants of concern (Siegrist et al., 2010).
2.4.3.4. Ozone

Ozone is a tri-molecular oxygen (O₃), a gas under atmosphere conditions, and is about 12 times more soluble than O₂ and it is notably a strong oxidant (Reisen and Arey, 2002). Being a strong oxidant helps it reacting in both gas and aqueous phase through direct oxidation as well as free radical intermediates. This feature creates a variety of different reaction pathways to degrade organic contaminants.

![Ozone process schematic diagram](U.S. EPA, 1986)

Ozone may react with organic compounds via two predominant reaction pathways: direct reaction between ozone and organic compounds (Reisen et al., 2002), or catalytic decomposition to form free radicals, which may further react with organic contaminants (Choi et al., 2002; Reisen and Arey, 2002). All chlororethenes have high rates of reaction with ozone (Schaal and Hey, 2002). Increasing chlorine substitution will decrease the rate constant of O₃, and in the case of TCE and PCE, the rate constants are already so low that
at short reaction times common in treatment processes there is very little destruction (Dablow and Rowland, 2004).

ISCO systems usually involve a mixture of contaminants such as NOM, inorganic minerals, and other components, all of which may react with ozone and compete for ozone or its free radicals, so it is not easy to predict the contaminant removal based only on kinetic (Choi et al., 2002; Shin et al., 2004). HSN and Masten (2001) reported that ozone was degrading NOM in a consumable trend. Likewise, the oxidation of NOM may offer tradeoffs, as more ozone is required to treat high NOM content, but they may also promote other mechanisms capable of destroying contaminants by extremely degrading humic substances into smaller molecules. Although ISCO systems using ozone are an emerging technology to many contaminants of concern, in situ ozonation may require feasibility tests to assess the optimum quantities of O\textsubscript{3} without detrimental side effects such as metal mobilization or unacceptable by products prior to field application (USEPA, 2006).

2.4.4. Monitored Natural Attenuation (MNA)

Biodegradation is the result of microbiologically catalyzed redox reactions in which the contaminant is served either as an electron donor or acceptor in a biochemical reaction. Monitored Natural Attenuation (MNA) relies on natural process to decrease the concentration, toxicity and mobility of contaminants in soil and groundwater unaided by deliberate human intervention (Stroo and Ward, 2010; USEPA, 2012a). MNA has been applied with about 60% of projects combined with source treatment and 40% as a solely remediation (USEPA, 2012b). Biodegradation of chlorinated solvents by either naturally
occurring or artificially enhanced process is an applicable alternative for site remediation. However, it is often considered to be too slow to provide effective contaminant removal in most chlorinated sites particularly with DNAPL residues without aggressive pre-treatments and it also results in partial dechlorination with producing cis-DCE and vinyl chloride intermediates (USEPA, 2000).

MNA is a relatively a low-cost process because it requires little labor and the lack of active management limits costs. On the other hand, its primary limitation is the anticipated clean up time that must be reasonable compared to that of other more active clean up methods as it is known as a relatively slow process. Monitored natural attenuation at a particular site is discovered, described and documented, but it is not designed as an active remedy would be because it is a matter of seeing and understanding what is already there, and then being able to share that quantitative understanding of the behavior of the contaminants with others (USEPA, 2012b). The selected remedy must adequately protect human health and result in the cleanup of target contaminants and their degradation products based on their toxicity.

2.4.5. In Situ Chemical Reduction

Permeable reactive barriers (PRBs) were first introduced in the 1990s with the installation of a pilot scale barrier in Borden, Ontario, followed by the first full scale barrier installed in 1995 in Sunnydale, CA (Henderson and Demond, 2007). The PRB wall is filled with reactive material to intercept and decontaminate plumes in the subsurface. However, PRB barriers are used to support biodegradation (biobarriers), sorption (e.g., zeolite) and/or
chemical reduction. PRBs are usually used to implement reducing materials like zero-valent iron (Fe$^0$), the reactive media that converts contaminants to non-toxic or immobile species because of its ability to degrade dissolved chlorinated ethenes such as perchloroethylene (PCE), trichlorethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC) via reductive dechlorination mechanism (Reddy and Camselle, 2009). As the water flows through the barrier, geochemical reactions effectively break down or remove the contaminants of interest by either adsorption, chemically or biologically degradation and once the chemical process is complete, the remediated water continues downstream via natural flow (Yeh et al., 2010).

![Figure 2.5. Basic layout design of a PRB within a contamination plume (EPA, 1998)](image)

There are several limitations of PRBs which include limited understanding about long term performance of in situ application. Reactivity of the material can be reduced due to the ZVI particles surface coating because of biological or chemical precipitation. Also, there is potential for plume bypassing the PRB as a result of clogging seasonal changes in
Several important factors must be assessed if using PRB remediation technology is a concrete option, including the nature of the contaminant and the availability of persistent material in terms of reactivity for relatively long time periods, as well as the mobility, toxicity, and stability of the transformation products resulting from the contaminant and media interactions.

2.5. Electrochemical Remediation Technologies

2.5.1. Introduction to Electrochemical Remediation Technologies for Chlorinated Solvents

In spite of the efforts made to develop new processes for groundwater remediation, they are often found to be costly, energy intensive, ineffective, and could also cause other environmental pollution as their intermediates might be more toxic. An alternative can be the application of electrochemical technologies for groundwater treatment because of the versatility, environmental compatibility and potential cost effectiveness among other conventional technologies. The feasibility of electrochemical remediation has been evaluated for many hazardous inorganic pollutants, such as chromium, copper, and zinc (Rajkumar et al., 2005, Mao et al., 2012). Electrochemical transformation of dissolved organics has attracted a considerable interest due to the method's ability to control and manipulate groundwater redox conditions (Alshawabkeh and Sarahney, 2005; Petersen et al., 2007; Alshawabkeh, 2009; Gilbert et al., 2010; Scialdone et al., 2010; Mao et al., 2011;
The motivation to develop electrochemical remediation technologies stems from (Petersen et al., 2007);

(i) The potential ability to treat a broad range of contaminants through sequential oxidation and reduction reactions;

(ii) The avoidance of the injection of chemicals into the subsurface as electrochemical remediation uses a clean reagent, the electron, as a reactant;

(iii) The potential to produce a cost effective remediation alternative to current options, given that the remediation system can be powered by renewable energy sources (e.g., solar power);

(iv) The ability to use more than a pair of electrodes to enhance the contaminant transformation performance; and

(v) The rate of electrochemical reactions at the electrodes can be controlled by adjusting the electrical potential difference between electrodes, thus the groundwater chemistry can be regulated to achieve desired conditions for the degradation of target contaminants. 

For the above reasons, electrochemistry can be considered as an alternative for the management of groundwater pollution problems. Different mechanisms may be considered as discussed below.
2.5.1.1. Electrochemical Oxidation

Electrochemical oxidation is performed by the action of strong oxidants, similar to chemical destruction, but the \textit{in situ} electro-generation allows better efficiency of the abatement of the organic substrates (Martinez-Huitle and Ferro, 2006). Two different mechanisms can be distinguished for organics oxidation; direct oxidation, where pollutants exchange electrons directly with the anode surface without involvement of other substances, and indirect electrochemical oxidation, where organic pollutants do not exchange electrons directly with the anode surface but rather through the mediation of electroactive species that act as intermediates for electrons shuttling between the electrode and the organic compounds (Panizza and Cerisola, 2009). The mechanism that is tentatively proposed for the direct electrolytic oxidation of TCE consists of the following steps: TCE diffusion to the electrode surface where it undergoes a single electron oxidation, subsequent conversion which involves reaction of TCE radical and/or other reaction intermediates with hydroxyl radicals that produced at the anode surface via oxidation of H$_2$O or OH (Chen et al., 2003). A few studies focus on electrochemical oxidation for TCE removal (Yuan et al., 2012b; Lakshmipathiraj et al., 2012; Yuan et al., 2013). Yuan et al. (2013) investigated the performance of a new electro-Fenton process with Ti-based mixed metal oxides (Ti/MMO) cathode, a dimensionally stable electrode, for degrading contaminants of emerging concerns (CECs) in aqueous solutions. In other recent investigations (Yuan et al., 2011 and Yuan et al., 2013), a specially configured three-electrode electrolytic system that can automatically produce localized acidic condition in the reaction zone and neutral effluent after treatment was developed. This system (Yuan et al., 2011 and Yuan et al., 2013) may overcome the barrier of acidity requirement to some
extent, however, Pd catalyst can be used to enable electro-Fenton process for TCE oxidation when pH < 4. This is achieved in a flow-through reactor by employing three electrodes with current splitting. Oxidation supported by Pd catalyst is given by (Rajic et al., 2014);

\[
H_2 + O_2 \leftrightarrow H_2O_2 \quad \text{(Pd-catalyst)} \quad \text{(Eq. 2.12)}
\]

\[
H_2O_2 \leftrightarrow +2OH^\circ \quad \text{(Pd-catalyst)} \quad \text{(Eq. 2.13)}
\]

\[
H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + OH^\circ + H_2O \quad \text{(Eq. 2.14)}
\]

\[
TCE + OH^\circ \rightarrow \text{oxidation products} \quad \text{(Eq. 2.15)}
\]

The idea of indirect electrolysis is to prevent electrode fouling, so pollutants are oxidized through the mediation of electrochemically generated redox reagents that act as an intermediary for electrons shuttling between the electrode and the organics (Panizza, and Cerisola, 2009). Different factors such as the potential at which the intermediate species is produced, intermediate generation rate and its reaction rate with the pollutant, and the pollutant adsorption rate are critical for obtaining high efficiencies in indirect electrolytic oxidation processes (Panizza, and Cerisola, 2009). Generally speaking, the mediated indirect electrochemical approach is more favorable due to avoiding the minor problems of electrode fouling and/or corrosion; so, it can be considered more effective than the direct one.
2.5.1.2. Electrochemical Reduction

Although the oxidative electrochemical processes are more widely used and studied, since they generally lead to the total degradation (mineralization) of the compounds, the electro-reductive treatments attract interest because they might potentially lead to the partial recovering/recycling of chemicals or to the production of value-added substances (Cabot et al. 2004; Titov et al. 2006). Generally, electrochemical reduction kinetics is directed by transport of the target chemical to the cathode surface, the rate of charge-transfer to the surface, or a combination of the two (He et al., 2004). The water electrolysis at the cathode leads to the hydrogen evolution via electrochemical hydrogen adsorption where atomic hydrogen is chemically adsorbed on active site of the electrode surface (Rajic et al., 2016). Therefore, the main reaction pathways for the electroreductive cleavage of the carbon–halogen bond lead to total or partial dehalogenated products with the formation of C–H and/or single, double and triple C–C bonds according to the prevailing coupling or elimination reactions (Rondinini and Vertova, 2010).

\[
\begin{align*}
H_2O + e^- & \rightarrow H^+ + OH^- \quad \text{(Atomic hydrogen formation)} \quad \text{(Eq. 2.16)} \\
H^+ + H^\circ & \rightarrow H_2 \quad \text{(Hydrogen evolution)} \quad \text{(Eq. 2.17)} \\
2H^\circ + RCl & \rightarrow RH + H^+ + Cl^- \quad \text{(Hydrochlorination)} \quad \text{(Eq. 2.18)}
\end{align*}
\]

Most of the literature has focused on cathodic conversion of chlorinated aliphatic hydrocarbons to the corresponding dehalogenated hydrocarbons (Li and Farrell 2000; Petersen et al., 2007; Mishra et al., 2008; Mao et al., 2011, 2012a, 2012b). Different cathode (Mao et al., 2012b) and anode materials (Mao et al., 2011) were investigated to
improve TCE reduction. Resembling electrochemical oxidation, there are two electrochemical reductive mechanisms: direct electron transfer, which occur heterogeneously via electron transfer between targeted chemical species and solid-state electrodes (Gent et al., 2012) and indirect electron transfer, which takes place via electrolytic production of atomic hydrogen on the cathode surface (Wang and Farrell, 2003). The type of reductive electron transfer mechanism is highly related to thermodynamic characteristics of the target compound, applied electrode potential and electrode material (Ciblak, 2015). Although laboratory and pilot tests have been successful, industrial applications of these methods are still limited, due to relatively high energy consumption of the electrochemical methods (Panizza, and Cerisola, 2009).

2.5.2. Electrolytic Reactive Barrier for Groundwater Remediation

Electrochemical technologies offer an alternative solution to many environmental problems in the process industry, because electrons provide a versatile, efficient, cost-effective, easily automatable, and clean reagent (Panizza, and Cerisola, 2009). Electrochemical technologies appear to have reached a promising state of development and can be effectively used for remediation and purification of aquatic media polluted with organic compounds (Chen, 2004; Martinez-Huitle, and Ferro, 2006).

2.5.2.1. Electrolytic Reactive Barrier for TCE Transformation

The concept of an electrolytic reactive barrier (e-barrier), a novel technology, is that of a permeable reactive barrier applied fundamental electrochemical aspects including
low voltage direct current to treat contaminated soil and groundwater (Stroo and Ward, 2010). The active component of electrolytic reactive barriers consists of closely spaced permeable electrodes installed in a trench vertical to the direction of groundwater flow carrying the contaminant plume, similar to PRBs. A low electric potential applied to the electrodes induces oxidizing conditions at the anode electrodes and reducing conditions at the cathode electrodes. Solar-powered direct current is sufficient to promote the degradation reactions and provide oxidizing conditions at the anode (positive electrode) and reducing conditions at the cathode (negative electrode).

Figure 2.6. Electrochemical remediation of target contaminant with iron anode (Alshawabkeh and Mao, 2014)

A wide range of redox-sensitive contaminants such as metal ions, nitrate, chlorinated ethenes (TCE), and energetic compounds may be treated using the electrolytic barriers. Several studies have illustrated that the treatment is achieved through
electrochemical transformation of contaminants such as TCE and PCE into thermodynamically stable forms like ethene, ethane, and acetylene at the cathode of electrochemical reactors (Gu et al., 2002). Rajic et al. studied the use of the bipolar electrodes to enhance electrochemical degradation of trichloroethylene (TCE) in an undivided, flow-through electrochemical reactor. The bipolar electrode, which forms when an electrically conductive material polarizes between feeder electrodes that are connected to a direct current source and creates an additional anode/cathode pair in the system, showed enhancing the improve electrochemical treatment of contaminated groundwater and enhance the TCE removal efficiency (Rajic et al., 2015). The performance of different commercially available cathode materials, which provide large electrode surface area and important properties for field application of the electrochemical technology such as iron (Fe), copper (Cu), nickel (Ni), aluminum (Al), and carbon (C) was also evaluated (Rajic et al., 2016). Electrode polarity reversal, a technique that is based on defined time intervals of operation under reversed electrode polarity, has been investigated to control electrokinetic remediation of heterogeneous media to control electrode fouling due to CaO and CaCO3 formation (Gilbert et al., 2010). Rajic et al. (2016) studied and optimized TCE removal from groundwater using electrode polarity reversal in the presence of Pd catalysts.

In order to achieve a complete degradation of target compounds and any intermediates that pose on environmental health, the applied voltage can be adjusted to manipulate water chemistry (Alshawabkeh, 2009). Under electric current applied, decomposition of water that takes place at the surface of electrodes, generates oxygen gas and hydrogen atom (H+) due to oxidation at anode surface as well as hydrogen gas and hydroxyl ions (OH-) due to reduction at cathode surface as shown by the following
reactions;

\[ 2H_2O \rightarrow O_{2(gas)} + 4H^+_\text{(aq)} + 4e^- \quad E^\circ = -1.229 \, V \quad \text{(Anode Oxidation)} \quad \text{(Eq. 2.12)} \]

\[ 4H_2O + 4e^- \rightarrow 2H_{2(gas)} + 4OH^-\text{(aq)} \quad E^\circ = -0.828 \, V \quad \text{(Cathode Reduction)} \quad \text{(Eq. 2.13)} \]

The net effect of these reactions is to reduce the contaminant concentration and furthermore reduce the contaminant flux. It should be noted that electrochemical transformation may occur either at the anode or the cathode like organic compounds that can undergo both reductive and oxidative dechlorination. Such transformation reactions are dependent on the conditions of groundwater chemistry, however, anode-cathode configuration sequence affect the reactions greatly. Rajic et al. (2015b) investigated the effect of electrode sequence in a mixed flow-through electrochemical cell to improve the hydrodechlorination of trichloroethylene in aqueous solutions. Enhanced reaction rates found in this study imply that a mixed flow-through electrochemical cell with multiple cathodes up stream of an anode is an effective method to promote the reduction of TCE in groundwater (Rajic et al., 2015b).

Removal of chlorinated compounds is complicated due to their potential dissociation characteristics and sorption to the soil (Ulsamer, 2011). TCE can be dechlorinated either via multiple reaction pathways such as hydrogenolysis, beta-elimination, alpha-elimination, and hydrogenataion or other reactions of interest (e.g. precipitation and complexation reactions of the minerals) that result in passivation of reactive material due to competition for reaction site and clog the pore spaces (Arnold and Roberts, 2000).
A series of reactions that occur at or near the anode surface of a target compound such as TCE, may include direct oxidation, as well as the oxidation of water to generate oxygen and H\(^+\) ions (Figure 2.7). The more H\(^+\) is produced, the lower the pH will be around the anode. However, cations (such as calcium) may react with oxygen and precipitate at the anode surface while oxygen may be off-gas (Stroo and Ward, 2010).

\[
C_2HCl_3 + 13H_2O \rightarrow 2CO_2(aq) + 6e^- + 3Cl^- + 9H_3O^+ \\
\text{(Eq. 2.14)}
\]

\[
2H_2O \rightarrow O_2(aq) + 4e^- + 4H^+ \\
\text{(Eq. 2.15)}
\]

\[
HCO_3^- + H_3O^+ \rightarrow CO_2(aq) + 2H_2O \\
\text{(Eq. 2.16)}
\]

\[
CO_2(aq) \rightarrow CO_2(g) \\
\text{(Eq. 2.17)}
\]
As mentioned, hydrogenolysis is a pathway for TCE and PCE degradation that generally do not happen under regular conditions and require high pressure and temperature, or a catalyst to promote the reactions. Hydrogenolysis is not a favorable pathway because the C-Cl bond and aliphatically bond halogenated hydrocarbons are resistant to hydrogenolysis at acidic or neutral conditions, which is not the case in most electrochemical systems. Below are the hydrogenolysis reactions involved in a zero valent systems treating chlorinated hydrocarbons (Sale et al., 2005):

\[
\begin{align*}
C_2Cl_4 + H_2 &\rightarrow C_2Cl_3H + H^+ + Cl^- & \text{(PCE to TCE)} \\
C_2Cl_3H + H_2 &\rightarrow C_2Cl_2H_2 + H^+ + Cl^- & \text{(TCE to trans, cis 1,2-DCE)} \\
C_2Cl_2H_2 + H_2 &\rightarrow C_2ClH_3 + H^+ + Cl^- & \text{(1,2-DCE to vinyl chloride)} \\
C_2Cl_2 + H_2 &\rightarrow C_2ClH + H^+ + Cl^- & \text{(dichloroacetylene to chloroacetylene)} \\
C_2ClH + H_2 &\rightarrow C_2H_2 + H^+ + Cl^- & \text{(Chloroacetylene to acetylene)} \\
C_2ClH_3 + H_2 &\rightarrow C_2H_4 + H^+ + Cl^- & \text{(vinyl chloride to ethylene)}
\end{align*}
\]

Hydrogenolysis usually is ignored in groundwater modeling as it is not the dominate pathway for chlorinated hydrocarbon removal based on experimental data. However, it is one of the most important pathways to consider as most of the toxic daughter products, which possibly making the barrier less effective, will be produced via hydrogenolysis. Beta-elimination that involves the exchange of electrons is the responsible
pathway for creation of different hydrocarbons. Reductive alpha-elimination is similar to beta-elimination except it is the alpha C-Cl bonds that are affected instead of the beta C-Cl bonds. Hydrogenation, addition of hydrogen to a compound by reducing the triple or double bond between two carbons (Arnold and Roberts, 2000), is another important mechanism.

Electrochemical technologies have reached such a state that they are comparable with other technologies and also benefit from their impressive advantages such as versatility, environmental compatibility, and cost. First, the power cost is low and there are both in situ and ex situ options feasible. The reaction condition can be manipulated to have a desired water quality by adjusting the applied voltage between electrodes. Undesired precipitates that may result in electrode plugging can be removed by applying reverse polarity periodically. Also, being applicable to low-permeability soils, heavy metals, and organic contaminants as well as in any of their combination (contaminant mixture) is also one of its main advantages (Acar and Alshawabkeh, 1993; Mao et al., 2012). In contrast, its initial capital cost may be higher than that of other remediation technologies due to its complex electrochemical transformation process. The depth of the contaminant plume is another factor that may limit its application as it may not be economically feasible. As new field demonstrations and applications are undertaken, the growing body of knowledge is expected to provide additional insights into the optimal installation methods and operational procedures, the contaminants that can be treated, and the long-term costs and performance of e-barriers (Stroo and Ward, 2010).
2.5.2.2. Iron Corrosion, Precipitation and Complexation

Electrochemically induced iron barrier treatment is feasible since iron has high reductive efficiency over chlorinated organic solvent. The selection of iron type can have a large impact on the efficiency of an electro-reductive barrier. Purity and surface area important qualities that have the ability to affect treatment efficiency. Cast iron and sponge iron are two types of iron commonly used. Iron corrosion by water is the chemical reaction that creates the favorable environment for precipitation of minerals. A modified iron electrocoagulation process using a foam cathode was investigated for enhanced reduction of soluble, reducible contaminants in wastewater (Mao et al., 2015). In this scientific research, the ability of the enhanced system to treat TCE and nitrate that pose a low potential for precipitation or adsorption was validated as well as the effect of anode type on electrochemical coagulation of soluble contaminants. The role of iron anode in electrochemical dechlorination of aqueous trichloroethylene (TCE) was evaluated using batch mixed-electrolyte experiments (Mao et al., 2011). A significantly higher dechlorination rate, up to 99%, was reported when iron anode and copper foam cathodes are used. In contrast to the oxygen-releasing inert anode, the cast iron anode generates ferrous species, which regulate the electrolyte to a reducing condition (low ORP value) and favor the reduction of TCE, however, the main products of TCE electrochemical reduction on copper foam cathode include ethene and ethane (Mao et al., 2011). When zero valent iron reacts with water, the pH within the barrier increases rapidly and Eh levels drop to less than -100 volts (Ulsamer, 2011, Mao et al., 2012). The high pH and low Eh (reducing environment) favor these precipitation reactions. The first reaction of interest is the corrosion of Fe\(^0\) by water. This reaction quickly affects the water equilibrium reactions and
causes an increase in the pH. The increased amount of OH- ions will then react with dissolved carbonic acid, and bicarbonate species to buildup carbonate ions, which will eventually result in the precipitation of carbonate solid phases. This build-up can passivate iron surfaces and reduce flow rates due to a reduction of porosity and permeability. Some of the possible precipitation reactions are as follows (Ulsamer, 2011):

\[
CaCO_3 (\text{Aragonite}) \leftrightarrow Ca^{2+} + CO_3^{2-} \quad \text{(Eq. 2.26)}
\]

\[
Fe_2(OH)_2CO_3 (s) \leftrightarrow 2Fe^{2+} + CO_3^{2-} + H_2O \quad \text{(Eq. 2.27)}
\]

\[
Fe(OH)_2 (am) \leftrightarrow Fe^{2+} + H_2O \quad \text{(Eq. 2.28)}
\]

Laboratory column and field tests of Fe⁰ have indicated the formation of iron (oxy)hydroxides, iron sulfide minerals, calcite and siderite as potential mineral phases might impact iron reactivity and cause a decline in permeability within an iron treatment zone (Liu et al., 2007; Ulsamer, 2011; Ciblak et al., 2012).

2.5.2.3. Treatment of Inorganic Co-contaminants (Chromate, Selenate, Nitrate)

Traditional approaches to treating groundwater contaminated by dissolved inorganic constituents have involved removing the contaminant source, pumping, and treating plumes of contaminated groundwater or isolating the source area with low permeability barriers or covers but electric reactive barriers provide an alternative for in situ approach to replace or supplement these existing techniques (Blowes et al., 2000). A
novel reactive electrochemical flow system consisting of an iron anode and a porous cathode was proposed for the remediation of mixture of contaminants (e.g., chromate, selenate, nitrate, and arsenic) in groundwater (Mao et al., 2012).

Similar to all other groundwater contaminants, there are several conventional technologies for chromium removal that could be categorized into chemical treatment technologies, biological treatment technologies and physical–chemical treatment technologies (Chen et al., 2010). Compared with other technologies, electrochemical reactive barriers (e--barriers), with a reactive media emplaced for the separation of contaminants from ground- water, may create a passive treatment system and have become more competitive and economical for the contaminated ground- water remediation (Thiruvenkatachari et al., 2008). The most commonly used reactive media is zero-valent iron (Fe$^0$) because of its low cost, high reductive potential and high reactivity (Owlad and Aroua, 2009). Simultaneous treatment of organic and inorganic contaminants provides an additional level of efficiency to the reactive barrier treatment system.

Removal of selenate from solution is investigated in batch electrochemical systems using reactive iron anodes and copper plate cathode in a bicarbonate medium (Baek et al., 2013). Results from this study demonstrate that iron anodes not only generate a significant decrease in the oxidation–reduction potential (ORP) of the solution due to inhibiting oxygen generation, but also produce ferrous hydroxide, which is a major factor in the removal of selenate from solution.

The removal of nitrate can be accomplished by using physical, chemical, and biological methods, which consist of two major categories; reduction technologies that
include biological denitrification (BD) and chemical denitrification (CD), both of which transform nitrate through reduction to other nitrogen species, and removal technologies such as *in situ* reactive barriers (King et al., 2012, Mao et al., 2012). *In situ* technologies are generally more cost-effective than *ex situ* options while they have the ability to directly remediate the groundwater contaminant plume (King et al., 2012). Iron is being evaluated as a very potential reactive material for preventing the transport of a wide range of highly mobile contaminants into groundwater. The reduction of nitrate by iron is characterized by an increase in pH and consumption of hydrogen ions. pH is a significant controlling factor for this treatment method (Hao et al., 2005). Fe corrosion could trigger nitrate reduction, although the corrosion products would form a passivation layer on the surface which could slow down the reduction rate of nitrate (Hao et al., 2005). More research is required to determine possible inhibitory effects on treatment systems involving Fe and how to put this method into practice.
Chapter 3   Materials and Methods

3.1. Introduction

This chapter describes the experimental procedure followed to investigate the effect of chromate, selenate, nitrate, and humic substances as co-contaminants that are naturally present in aquifers on the efficiency of the electrochemical transformation of TCE using a limestone column to simulate the karst aquifer. This chapter also describes the procedure to study the effect of other factors such as the electrode material, high flow rate, and catalyst on precipitate formation and removal. A description of the components of experimental setup, chemicals, reagents, and materials used in this study is presented. Experimental procedures and analytical methods utilized during the experiments are also explained in detail.

The flowchart presented in Figure 3.1 depicts the research plan followed in this study. The experiments were conducted in two series: (1) evaluation of the effect of common co-existing organic and inorganic compounds on the electrochemical dechlorination of trichloroethylene (TCE) in karst media (Section 3.2); (2) the assessment of high velocities of groundwater flow on flush out of precipitation while using Pd pellets as catalyst for the remediation of groundwater contaminated with TCE (Section 3.3).
Figure 3.1. Flow chart of experiments flow for this research study

3.2. TCE and Co-contaminants in simulated Karst media

3.2.1. Materials

The chemicals used in this study include trichloroethylene (99.5 %, Sigma Aldrich), potassium dichromate (reagent grade, JT Baker), sodium selenate (99.8%, Alfa Aesar), sodium nitrate (reagent grade, JT Baker), sodium bicarbonate (reagent grade, Fisher
Chemical), humic acid (Alfa Aesar), and calcium sulfate (99.9%, JT Baker). Excess amount of TCE was dissolved in 18.2 MΩ.cm deionized water. This saturated solution was used to prepare aqueous TCE solution during experiments. Electrodes were cast iron (MacMas-Carr, USA) and copper foam (99.99%, 40 PPI, ERG, USA). The cast iron electrode used in this study was a cylinder rod with outer diameter of 0.95 cm. Before starting the experiment, iron anode was polished by coarse paper and the cathode was immersed by diluted HCL solution (10 wt%) and rinsed with distilled water prior to assembly.

3.2.2. Reactor Design and Experimental Methods

An experimental program (Table 3.1) was designed to evaluate the effect of naturally-occurring substances, initial concentration of co-existing compounds, and current density on electrochemical dechlorination of TCE in limestone column as a karst media illustration. As the precipitates formation is a pH-dependent factor, the pH was recorded during the experiment with probe continuously. However, its effect on the system was not investigated as it was beyond the scope for this research. For sure, the pH will affect the system and change the precipitates structure.
Table 3.1. Parameters and experiment conditions for electrochemical dechlorination of TCE in karst media

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCE plus Chromate</td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>5 mg L⁻¹</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>10 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>TCE plus Selenate</td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>2 mg L⁻¹</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>2 mg L⁻¹</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>TCE plus Nitrate</td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>2 mg L⁻¹</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>40 mg L⁻¹</td>
<td>---</td>
</tr>
<tr>
<td>TCE plus Humic Acid</td>
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<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
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<td>1 mg L⁻¹</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
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<td>2 mg L⁻¹</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5 mg L⁻¹</td>
</tr>
<tr>
<td>Mixture</td>
<td>90</td>
<td>1 mg L⁻¹</td>
<td>10 mg L⁻¹</td>
<td>5 mg L⁻¹</td>
<td>40 mg L⁻¹</td>
<td>---</td>
</tr>
</tbody>
</table>

* For all experiments listed above, 0.5 mM NaHCO₃ and 0.5 mM CaSO₄ were dissolved in deionized water as background electrolytes.
** Two electrode were used; cast iron anode and copper foam cathode.
*** For the mixture, the highest concentration of co-existing compounds was used based on experiments.

A flow-through column reactor that consists of limestone block with a flow channel of 2.5-inch inner diameter and 13-inch length was used (Figure 3.2). Limestone column was used to simulate a karstic aquifer media. The space between the electrodes that are placed face to face is 5 cm. Simulated groundwater was pumped through the column with a flow rate of 1 mL min⁻¹. The constant flow rate was maintained by using a peristaltic pump (Masterflex, model 7720066). To minimize the TCE loss by absorption, glass tube
and Viton pump tubing (Cole Parmer, USA) was used as a connection between all parts of the reactor.

Figure 3.2. Schematic of the flow-through system

Figure 3.3. a) An acrylic column, b) limestone block as a model of a karst media and c) cast iron anode and copper foam cathode
The surfaces of the iron electrode were polished by coarse paper and the cathode was immersed by diluted HCl solution (10 wt%) and rinsed with distilled water prior to assembly, and washed several times with distilled water. Oxidation-reduction potential (ORP) and pH probes recorded the effluent pH and ORP through the connection with the computer via the USB port. Simulated groundwater was prepared by dissolving 2 mL of saturated TCE solution in a 2 L aqueous solution containing 0.413 g L\(^{-1}\) NaHCO\(_3\) and 0.172 g L\(^{-1}\) CaSO\(_4\) (1 mg L\(^{-1}\) initial concentration of TCE). The prepared solution was stirred 30 minutes prior to start the experiment with magnetic stirring bar. The initial concentration of TCE was checked by taking 1 mL of the solution before the electricity starts. Chromate, selenate, and nitrate solutions were prepared by dissolving K\(_2\)CrO\(_4\) (JT Baker), Na\(_2\)SeO\(_4\) (Alfa Aesar), and NaNO\(_3\) (JT Baker) into deionized water, respectively. The aqueous stock solution of humic acids was prepared by dissolving 20 mg humic acids in 50 mL DI water. The humic acids stock solution was used to prepare solutions containing 1, 2, and 5 mg L\(^{-1}\) total organic carbon (TOC) originating from humic acids. At specific time intervals, 1 mL samples were taken from sampling port 3.

Various current intensities (30, 60, and 90 mA) were applied using an Agilent E3612A DC power supply under the conditions of 1 mL min\(^{-1}\) flow rate and 1 mg L\(^{-1}\) initial concentration of TCE according to the optimized system’s operation described in Mao et al., 2012. The most efficient current density (90 mA) was selected for conducting the experiments for this study. Control experiments were conducted without electricity under the same concentrations of contaminants suggested that the adsorption of contaminants on limestone block was limited (2.5%). All experiments were conducted at room temperature. Each set of experiments was repeated in triplicate to ensure reliability of the results.
Aqueous TCE concentration was measured by HPLC (1200 Infinity Series) equipped with a 1260 DAD detector. 1 mL of sample was diluted immediately after filtration (0.2 µm filter, Milipore) with 1 mL acetonitrile in a 2 mL vial for HPLC analysis. Selenate and nitrate ions were analyzed using an ion chromatography (IC) instrument (Dionex 5000) equipped with an AS20 analytical column. To measure the selenate and nitrate in a mixture, 1 mL of sample was taken for each and filtered and diluted to 5 mL prior to analysis (0.2 µm filter, Milipore). Dichromate ion was measured by diphenylcarbazide method using Hach Chroma Ver 3 reagent at 540 nm wavelength (UVmini-1240 spectrophotometer - Shimadzu). TOC was measured by total organic carbon analyzer (Shimadzu TOC-VWS). The amount of iron released during the experiment was calculated based on Faraday’s law.
3.3. TCE Hydrodechlorination Under High Flow Rate

3.3.1. Materials

Trichloroethylene (99.5%) was purchased from Sigma-Aldrich. Excess amounts of TCE were dissolved in deionized water (18 MΩ) produced by Millipore. This solution was used to prepare aqueous TCE solution during experiments. Palladium on alumina powder (1% wt. Pd, Sigma-Aldrich) with an average size of 3.2 mm was used as catalyst in flow-through experiments. The electrodes were cast iron (Macmaster-Carr, USA), mixed metal oxide (MMO), and copper foam (99.99%, 40 PPI, ERG, USA); all were 2 mm in thickness. Randomly distributed holes were drilled through the iron plate electrode for fluid flow.

3.3.2. Reactor Design and Experimental Methods

A vertical acrylic column (3.175 cm inner diameter 30 cm length) (Fig.3.4) was used to simulate a continuously circulated system. The total volume of the column was 245 mL. MMO mesh, cast iron, and copper foam electrodes (a set of two electrodes as the anode and cathode was used for each experiment conducted), 3.170 cm diameter, were placed in parallel with respect to the flow direction at 9 cm and 11.3 cm from the bottom of the column. Iron electrodes were perforated to allow the water flow in the column. To hold the electrodes in place and convey electrical current, titanium rods were fabricated at electrode levels as electrical connections.
Two sampling ports were drilled after the cathode and after the Pd pellets filling the reactor; near the effluent. The column was prefilled with 4-mm glass beads with a porosity of 0.65. There were no glass beads between the electrodes to facilitate mixing of the electrolytes and limit development of high resistance zone. 10 g of Pd/Al₂O₃ pellets were placed on the cathode surface to investigate the role of palladium pellets on the transformation rate. Experiments were also conducted using iron anode and copper foam cathode without Pd catalyst for comparison.
The following electrode arrangements were tested: a) a cast-iron anode and a MMO cathode with Pd-catalyst, b) a cast-iron anode and a copper foam cathode with Pd-catalyst,
and c) a cast-iron anode and a copper foam cathode without Pd-catalyst. Table 3.2 presents a summary of the experimental variables used to evaluate the effect of cathode type, current intensity, catalyst, and flow rate on the dechlorination rate and precipitate formation in flow-through column setup.

Table 3.2. List of experiments under various electrode configuration and different current intensities that produce different amount of precipitation

<table>
<thead>
<tr>
<th>Variables</th>
<th>Anode</th>
<th>Cathode</th>
<th>Current (mA)</th>
<th>Precipitation (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Palladium Catalyst</em></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>500</td>
<td>2390</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>250</td>
<td>1264</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>125</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>MMO</td>
<td>62</td>
<td>381</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>Copper Foam</td>
<td>250</td>
<td>1101</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>Copper Foam</td>
<td>125</td>
<td>756</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>Copper Foam</td>
<td>62</td>
<td>419</td>
</tr>
<tr>
<td>No-Catalyst</td>
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<td>Copper Foam</td>
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<td>945</td>
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<tr>
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<td>Copper Foam</td>
<td>125</td>
<td>830</td>
</tr>
<tr>
<td></td>
<td>Cast Iron</td>
<td>Copper Foam</td>
<td>62</td>
<td>419.5</td>
</tr>
</tbody>
</table>

* 20 gr of Pd- pellets were used as a catalyst for the series of experiments mentioned above.
** For all experiments, the flow rate applied was 1 L min⁻¹.
*** Initial concentration of TCE was 5 mg L⁻¹ for all experiments.
Simulated groundwater was prepared by mixing 142 mg Na\(_2\)SO\(_4\) in a 2 L of deionized water (3 mM Na\(_2\)SO\(_4\)) along with addition of 2 mL of the saturated TCE stock solution to prepare a solution with 5 mg L\(^{-1}\) initial concentration of TCE. The solution was pumped up through the column with a flow rate of 1 L min\(^{-1}\) using a peristaltic pump (Masterflex, model 7720066) for 30 minutes before starting the electricity, to produce a uniform mixture of the contaminants in the column. To minimize TCE losses due to adsorption, a glass tube and Viton pump tubing (Cole Parmer, USA) were used to connect all parts of the reactor. Effluent was returned to the source bottle to be re-circulated through the column. At specific time intervals, 1 mL of aqueous solution was collected from two sampling ports. Various current intensities; 500, 250, 125, and 62 mA were tested under the conditions of 1 L min\(^{-1}\) flow rate and 5 mg L\(^{-1}\) initial concentration of TCE. Prior to set up assembly, the iron anode was polished by sand paper while the cathode was immersed in diluted HCL solution (10 wt %) and rinsed with distilled water. All experiments were conducted at room temperature. Each set of experiments was repeated in triplicate to ensure reliability of the results.

Aqueous TCE concentration was measured by HPLC (1200 Infinity Series) equipped with a 1260 DAD detector. 1 mL samples were diluted immediately after filtration (0.2 µm filter, Milipore) with 1 mL of acetonitrile in a 2 mL vial for HPLC analysis. Oxidation-reduction potential (ORP) and pH probes recorded the effluent pH and ORP through the connection with the computer via the USB port. ORP and pH were measured by microprobes and recorded every 30 seconds. Final removal efficiency (FRE) of the aqueous TCE was determined using the following equation:
\[ FRE = \frac{C_{aq(0)} - C_{aq(t)}}{C_{aq(0)}} \times 100 \% \]  \hspace{1cm} \text{(Eq. 3.1)}

Where \( C_{aq(0)} \) and \( C_{aq(t)} \) are the TCE concentration (mg L\(^{-1}\)) in the influent and effluent. All experiments were conducted at room temperature (20 °C). Each set of experiments was repeated in triplicate to ensure reliability of the results.
Chapter 4  Results and Discussion

4.1. Introduction

This chapter presents and summarizes results for two series of experiments each with specific laboratory set-up. The following sections describe (1) the effect of co-existing compounds, including metal ions such as chromate and selenate, and nitrate, as well as humic substances that are naturally present in aquifers, on electrochemical dechlorination of TCE in karst media, and (2) hydrochlorination of TCE in a circulated column under high flow rate with palladium pellets as catalyst to improve the system performance.

4.2. Electrochemical Dechlorination of TCE and Co-existing Compounds

4.2.1. Limestone Column vs. Acrylic Column

Remediation of chlorinated contamination is very difficult in a fractured rock like limestone due to the complexities imparted by the fractured bedrock in which groundwater flows. Consequently, any attempt to remove or destroy the contamination is dependent on the ability to understand and characterize the fracture framework in order to facilitate delivery of the remedial technology to the source material (Stephenson et al., 2006). To explore the viability of current system in such an environment (karst aquifer), an investigation of the use of this clean-up technology for a TCE-contaminated groundwater in a limestone, as well as, acrylic column was conducted (Figure 4.1).
Figure 4.1. Comparing of the percent removal of TCE under 1 mL min⁻¹ flow rate and different current intensity (30, 60, 90 mA) using acrylic and limestone experimental columns

Experiments have been conducted simultaneously to compare the removal rate of TCE in acrylic and limestone set-up. Figure 4.1. compares the final removal for TCE under the same operational conditions for both limestone and acrylic columns. The removal efficiency is higher using limestone rather than acrylic column under the same conditions. Generally, the larger-size colloids were more abundant and Ca-containing colloids were more important in the karst bedrocks (McCarthy and Shevenell, 1998). Considering the complex physical properties of cavities and fractures of karst aquifers, the potential exists for sorption of contaminants and metal ions onto solid phase to form colloids that have a significant role in contaminant transport (Warren and Zimmerman, 1993). From a remediation perspective, colloid-bound contaminants are more accessible for in situ
degradation by immobilization and proper chemical reactions since they are more easily attached in fractured or porous media due to the adhesive force binding the precipitates to the limestone surface and this is in agreement with published studies proving that enhanced remediation are likely to be more successful in fractured rather than granular formations (McCarthy and Shevenell, 1998; Shevenell and McCarthy, 2008). Therefore, the influences on TCE removal are due to limestone specific characteristics, such as higher surface area, that create complex network of preferential flow pathways, which may lead to TCE either sorption or higher reactivity within the treatment zone in the reactor. The removal rates seem to be slightly affected by the current intensity, which reflects that even the lower intensity of 30 mA is sufficient to produce the necessary reactivity for treatment. Control experiments were conducted without electricity under the same concentrations of contaminants suggested that the adsorption of contaminants on limestone block was limited (2.5%).

4.2.2. Effect of Humic Acids on TCE Reduction

TCE electro-reduction was evaluated in mixed electrolyte cells that provide advantages for in situ implementation of electrochemical groundwater treatment. The influence of presence of humic substances, which can be significant in karst aquifers, on the electrochemical reduction of TCE in groundwater was investigated. Fig. 4.2. shows the ratio of effluent by influent TCE concentration over time using an iron anode and a copper cathode in the presence of various concentration of humic acids (1, 2, and 5 mgTOC L⁻¹).
In the absence of humic acids, more than 90% of the TCE was transformed after 240 minutes of operation (Fig. 4.2). Increasing the amount of humic acids resulted in a decrease in dechlorination rate but the final removal is the same (around 78%). However, the removal rate is faster with presence of lower humic acid concentration, which implies that by increasing the initial concentration of humic acid, higher charge and energy is required to achieve the same TCE removal efficiency. Table 4.1 shows the required charge for various humic acid concentrations to achieve 78% removal for TCE.

Although the removal efficiency for the three humic acid concentrations are almost the same (Figure 4.2), the amount of charge required is slightly different that implies higher
energy is required. NOM suppresses contaminant reduction via reacting either directly with electrons or with H₂ produced at the cathode surface (Rajic et al., 2015) and alteration of surface electrostatic and reductive potentials (Klausen et al., 2003; Dries et al., 2005; Giasuddin et al., 2007). In this way, humic acids play a negative role as they may compete with target contaminant at the cathode surface and result in a decline in remediation rate of TCE. It was also reported that humic substances can inhibit reduction of chlorinated compounds in groundwater via zero valent iron due to competition between TCE and humic acid for adsorption on Fe⁰ surface sites (Rajic et al., 2015). Several studies have shown the negative effect of humic acid, a common component of NOM, on Fe activity for chlorinated hydrocarbon degradation, which is attributed to strong competition for reactive sites (Marconetto et al., 2004; Doong et al., 2006) and changing the reduction potential of surface sites (Liu et al., 2008).

Table 4.1 - Total charge required to achieve 78% removal for TCE under different initial concentration of humic acid, current intensity of 90 mA and flow rate of 1 mL min⁻¹

<table>
<thead>
<tr>
<th>Initial Concentration of Humic Acid (mg L⁻¹)</th>
<th>Time at which 78% removal is achieved (min)</th>
<th>Charge (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>198.75</td>
<td>1073</td>
</tr>
<tr>
<td>2</td>
<td>218.21</td>
<td>1178</td>
</tr>
<tr>
<td>5</td>
<td>227.52</td>
<td>1227</td>
</tr>
</tbody>
</table>

In addition, NOM could react with ferrous ions to produce Fe-humate precipitates which could contribute to the coverage of iron anode surface and surpass further production of ferrous species (Tang et al., 2014). Decrease in the formation of ferrous species affects the system’s ability to create reducing conditions that are necessary to support TCE degradation.
4.2.3. Role of Selenate, Dichromate, and Nitrate Reduction on TCE

Remediation

Table 4.2 summarizes the removal of TCE in the presence of nitrates, chromates and selenates as well as removal percentage for each contaminant by electrochemical redux using iron anode. The concentration profile for TCE and contaminants during the treatment is shown in Fig.3. All electrolysis experiments were conducted under an optimized condition (90 mA current, 1 mL min$^{-1}$ flow rate, and 1 mg L$^{-1}$ TCE) in the limestone column.

Table 4.2- The removal rate of target contaminants.

<table>
<thead>
<tr>
<th>Limestone Block- 90 mA- 1 mL/min- 240 min</th>
<th>Initial Concentration (mg/L)</th>
<th>Contaminant removal efficacy (%)</th>
<th>TCE removal efficacy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichromate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>&gt;99</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>&gt;99</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>&gt;99</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>Selenate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>&gt;99</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>83</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>71</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>72</td>
<td>81</td>
<td></td>
</tr>
</tbody>
</table>

The influence of tested concentrations of dichromate is higher than that of selenate or nitrate. The iron anode system is able to reduce different amounts of chromate in the solution (Table 4.2). Significant reduction of Se (VI) was achieved (around 100 and 83 % for 1 and 5 mg L$^{-1}$ initial concentration added, respectively). In addition, the removal rate for nitrate is around 70% for all initial concentrations.
Fig. 4.3 shows the concentration profile for TCE and contaminants during the treatment. During the reduction process, hexavalent chromium is being reduced to trivalent chromium, which further reacts with ferrous hydroxide present in simulated ground water due to iron anode reaction (Gandhi et al., 2002). Chromium hydroxide precipitations result in the loss of reactivity for TCE removal in our column because of covering the reactive surface of electrodes. These ions can be easily absorbed on the surface of iron (II) hydroxide where they are consequently reduced by Fe$^{2+}$, which result in poorly soluble products. The removal efficacy of TCE decreased intensely when the solution contains Cr (VI). In this study, the decay profiles under various initial concentrations (1, 5, and 10 mg L$^{-1}$ chromate) depicted that TCE removal rate decreased by 1.5 times in the presence of Cr (VI). The decrease in the removal efficiency can be attributed to the accumulation of Fe-Cr precipitates (Sarahney, 2007; Sarahney et al., 2012), which may result in a positive shift in corrosion potential, a declining rate of electron transfer, or the decrease of iron active surface area (Jeen et al., 2013).
Figure 4.3. Normalized TCE concentration profiles in the presence of (a) chromium (1, 5, and 10 mg L\(^{-1}\)), (b) selenate (1 and 5 mg L\(^{-1}\)), and (c) nitrate (2, 10, and 40 mg L\(^{-1}\)). All experiments were conducted under the same operational conditions (90 mA current, 1 mL min\(^{-1}\) flowrate, and 1 mg/L initial concentration of TCE).
By increasing the initial concentration of selenate, the capability of the system for removing both selenate and TCE reduction decreased. Although the removal efficacy of TCE is higher when the same amount of selenate added (Table 4.2) compared to chromium (Table 4.2), it is still lower than control experiment with no other contaminants (only TCE). This procedure suggests that the formation of chromium and selenate precipitates inhibit the iron anode system performance. Precipitation of minerals throughout the column, gradually decrease the reactivity of electrodes and permeability of the system and further limit the removal of contaminants (Handerson et al., 2007; Luo et al., 2010). The validity of the system for removal of TCE co-contaminated with selenate is presented in Fig 4.3-b. Reduction of selenate ions primarily relates to the iron anode and reducing environment containing ferrous species. Ferrous hydroxide can reduce Se (VI) and co-precipitate the produced elemental selenium (Mao et al., 2012). The remediation rate of TCE decreased by 15% when 5 mg L\(^{-1}\) of selenate was added. It can be concluded that the accumulation of precipitates not only can affect the access of contaminants to the electrode surface but also, decrease porosity and hydraulic conductivity, which in turn restricts groundwater flow (Jeen et al., 2013).

The results demonstrate that nitrate exerts a lesser influence on TCE remediation efficacy compared to selenate and chromate, which was also found by Vodyanitskii and Mineev (2013). It has been reported that TCE and nitrate are removed through the electrode-based electrochemical processes at the cathode surface, therefore their removal efficiencies are subject to the factors that are related to the mass transfer effect of contaminants on electrode/liquid interface, such as hydraulic residence time and surface area of the electrode (Mao et al., 2012). Further study by Lu et al. (2010) on TCE
degradation in the presence of nitrate indicated that higher nitrate concentration directed to an increased amount of precipitates that acted as a physical barrier and slowed degradation rate of TCE. In our study, adding nitrate to the synthetic ground water solution has the least significant influence on TCE removal efficiency, compared to presence of dichromate or selenate. As Fig 4.3-c shows that the remediation rate for TCE was negligibly influenced by nitrate presence, TCE removal efficiency decreased by approximately 5%. It is possible that nitrates are mostly removed via electrocoagulation process (Lacasa et al., 2011), which minimized their competition with TCE for the atomic hydrogen at the cathode.

4.2.4. Dichromate, Selenate, and Nitrate Removal

The removal of Cr(VI) from groundwater is mostly due to chemical reduction by electrogenerated ferrous, instead of direct electrochemical reduction on the cathode (Sarahney, 2007; Mao et al., 2012; Sarahney et al., 2012;). Iron atoms from the anode lose the electrons and form divalent ions that dissolve into the solution. Chromium hydroxide and probably other mineral precipitations result in the loss of reactivity for TCE removal in our column because of the action of covering the reactive surface of electrodes. These ions can be easily absorbed on the surface of iron (II) hydroxide where they are consequently reduced by Fe$^{2+}$, which results in poorly soluble products.

As shown in Figure 4.4., the reduction of reducing Cr(VI) to Cr(III) at three initial concentrations (1, 5, 10 mg L$^{-1}$) was completed within 40, 90, and 90 minutes of experiment, however, the rate of transformation is faster with lower initial concentration.
Figure 4.4. Chromate decay profile for different initial concentrations (1, 5, 10 mg L⁻¹) under the condition of 90 mA current intensity, 1 mL min⁻¹ flow rate, and 1 mg L⁻¹ initial concentration of TCE.

Reduction of Cr(VI) to Cr(III) by reaction with Fe ions, and subsequent precipitation of Cr(III) oxyhydroxides occurs through the reaction (Blowes et al., 2000; Sarahney, 2007):

$$\text{(1-x)Fe}^{3+}_{(aq)} + \text{xCr}^{3+}_{(aq)} + 2\text{H}_2\text{O} \rightarrow \text{Fe}_{(1-x)}\text{Cr}_x\text{OOH}_{(s)} + 3\text{H}^+_{(aq)}$$  \hspace{1cm} (Eq. 4.2)

Cr(VI) removal efficiencies decreased with the increase of the initial Cr(VI) concentrations because the Cr(VI) absorbed on anode surface prevented the iron from dissolving into water solution and providing the desirable reducing environment quickly.
Ferrous and ferric iron either directly reduce the selenate to selenite then to elemental selenium, or reduce the selenate to selenite and adsorb the selenite to the ferrihydrite or ferri-oxyhydroxide amorphous solids formed during the redox reaction with the iron, respectively (CH2M HILL, 2010).

The selenite concentration decay during the treatment is shown in Figure 4.5. Equation 4.3 summarizes the overall reactions of iron with selenate.

\[ 3Fe_{(s)}^0 + SeO_4^{2-} + 8H^+ \rightarrow 3Fe^{2+} + Se^0 + 4H_2O \]  

(Eq. 4.3)

Other oxidants such as carbonate, sulfate, nitrates, and phosphates can contribute to the oxidation of the iron (EPRI, 2009). They may also help form green rust which is an essential component for reduction of selenium.
Figure 4.5. Selenate decay profile for different initial concentrations (1, 5 mg L\(^{-1}\)) under the condition of 90 mA current intensity, 1 mL min\(^{-1}\) flow rate, and 1 mg L\(^{-1}\) initial concentration of TCE.

The nitrates removal efficiencies for 2, 10, and 40 mg L\(^{-1}\) initial concentration in an electrochemical system consisting of an iron anode and copper foam cathode under current intensity of 90 mA and flow of 1 mL min\(^{-1}\) after 3 h are 80%, 72 %, and 80%, respectively (Figure 4.6).
Figure 4.6. Nitrate decay profile for different concentrations (2, 10, 40 mg L⁻¹) under the condition of 90 mA current intensity, 1 mL min⁻¹ flow rate, and 1 mg L⁻¹ initial concentration of TCE.

The electro-reduction of nitrate at the cathode is a very complex process which starts with nitrate ion adsorption at the cathode (Eq. 4.4) and involves the simultaneous transfer of one electron and proton from a proton donor (e.g. water molecule, hydroxonium ion) that leads to a series of reactions where a number of products are possible: nitrite (Eq. 4.6), nitrogen monoxide (Eq. 4.7), nitrogen (Eq. 4.8), ammonia (Eq. 4.9) and hydroxyl amine (Eq. 4.10) (Rajic et al., 2016).

\[ \text{Eq. 4.4} \]
\[ \text{Eq. 4.5} \]
\[ \text{Eq. 4.6} \]
\[ \text{Eq. 4.7} \]
\[ \text{Eq. 4.8} \]
\[ \text{Eq. 4.9} \]
\[ \text{Eq. 4.10} \]
\[ \text{Eq. 4.11} \]
It has been reported that TCE and nitrate are removed through the electrode-based electrochemical processes at the cathode surface, therefore, the nitrate reduction mechanism is supported by H formation; related to the mass transfer effect of contaminants on electrode/liquid interface, such as hydraulic residence time and surface area of the electrode (Mao et al., 2012; Rajic et al., 2016). Also, the short retention time for the reaction in the flow through system and oxidation of reduction byproducts to nitrate adversely affect the reduction mechanism (Ding et al., 2015). The method by which the contaminant is sequestered will determine its long-term stability and will dictate if the reactive material and contaminants must be eventually removed from the aquifer, therefore, the preferred mechanism of removal is often precipitation of the target contaminant in an insoluble mineral phase, in which case, the long-term stability and solubility of that mineral must be assessed (Blowes et al., 2000).

4.2.5. Removal of TCE and a Mixture of Contaminants

The simultaneous transformation is observed for the solution containing a mixture of TCE, chromate, selenate, and nitrate (Figure 4.7). The treatment was conducted under optimized operational conditions (90 mA current, 1 mL min\(^{-1}\) flow rate, and 1 mg L\(^{-1}\) initial concentration of TCE) and for the highest initial concentration of chromate, selenate, and nitrate (10, 5, and 40 mg L\(^{-1}\)).
Figure 4.7. Normalized concentration profiles for TCE, nitrate, selenite, and chromium as a mixture. The experiment was conducted under the same operational conditions (90 mA current, 1 mL min\(^{-1}\) flow rate, and 1 mg L\(^{-1}\) initial concentration of TCE).

Using the experimental column, the Cr(VI) concentrations monitored at effluent decrease rapidly after the beginning of electrolysis and meet a steady-state concentration close to zero within 60 minutes of electrolysis. There is a similar pattern for selenate removal with a delay as the steady-state concentration is achieved after 210 min. Concentration profiles and removal efficacies at steady-state condition (100% for chromate, 90% for selenate, and 80% for nitrate) suggest that these contaminants can be removed simultaneously. To the contrary, the remediation rate of TCE decreased by 50% in the mixture of contaminants. Lower removal rate of TCE could be presumably due to
production of insoluble precipitates with ferrous species and also the competition for the reduction at the cathode surface.

**4.2.6. Summary**

Limestone block column experiments showed that there is an influence of limestone on TCE degradation. Results indicated that limestone block, a simulation of karst media, improve the removal efficiency of TCE up to 20% compared to acrylic column. The performance of iron anode and copper cathode system for TCE removal is influenced by the presence of humic acid and strong oxidants such as chromate, selenate, and nitrate. The influence on TCE removal is in the following order: humic acid, chromate, selenate, and nitrate. Dichromate and selenate are reduced to the insoluble ions, which presumably forms precipitates resulting in covering iron anode surface. The layer of sediments on iron anode prevents electron transfer reaction and lessen dechlorination rate. Humic acids also form aggregates in solution via cathodic reactions, which eventually out-compete with TCE for reduction and decrease or cease the degradation process. Thus, in humic acid-rich environments, the concentration of humic acid is a factor that requires monitoring in order to avoid any adverse impact in long-term in situ applications. It was also found that this system is capable of removing these contaminants as a mixture, while the remediation rate of TCE is significantly low (around 40%) compared to the control experiment (only TCE).

Since humic acid, metal ions, and nitrate are the most often co-existing compounds with TCE in groundwater, results obtained in this study can provide a better understanding of remediation process. Furthermore, notwithstanding the fact that current system is convenient to be applied for remediation of a mixture of contaminants, for field
implementation, more series of technical and engineering challenges should be considered in order to achieve the process, which is applicable for long-term performance. Although the limestone block is a simulation of a karst aquifer, it should be pointed out that the results mentioned here need to be tested in field conditions as different factors may impact the system significantly. Broad research is still needed to identify and address these issues.
4.3. Hydrochlorination of TCE under High Flow Rate in a Circulated Column

4.3.1. Effect of Anode on Dechlorination

The performance of two types of anode, MMO and cast iron, under the same operation conditions (500 mA current and 1 L min\(^{-1}\) flow rate) is presented in Figure 4.8. Iron anodes generate ferrous ions rather than O\(_2\), which support the reduction process (Eq. 4.1 and 4.2) (Gilbert et al., 2010; Yuan et al., 2013):

\[
\begin{align*}
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe}^0 \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \downarrow
\end{align*}
\]

(Eq. 4.12)

(Eq. 4.13)

MMO electrodes, in comparison with other types of electrodes such as iron, nickel, and copper, are more likely to retain their structure for a long-term operation; which is a key aspect of a successful remediation in the field (Peterson et al., 2007). However, using an inert anode generates oxygen gas, which competes with target contaminant for reaction with hydrogen and limits the dechlorination rate. The reduction potential of O\(_2\) (1.229 mV vs. SHE) (Bard, A.J. and Faulkner, L.R., 2001) is higher than that of TCE (Wiedemeier et al., 1999) (0.42 V vs. SHE from TCE to cis-DCE). The performance of two types of anode, MMO and cast iron, under the same operation conditions (500 mA current and 1 L min\(^{-1}\) flow rate) is presented in Fig.4.8.
Figure 4.8. Comparison of effect of MMO anode and iron anode on TCE degradation under the conditions of 500 mA current and 1 L min$^{-1}$ flow rate. This is a two-electrode design which both include MMO cathode and palladium pellets

The overall removal efficiency by MMO and iron electrodes was 66% and 96%, respectively. Lower removal efficacy was achieved with the MMO anode due to the inevitable generation of O$_2$, which limits the reductive transformation process. Higher ORP values (60 and 110 mV) appear in the electrolyte when MMO anode is used. These electrodes readily evolve oxygen and have low chemical activity for organics oxidation (Bagastyo et al., 2011). Using a cast iron anode improved the removal efficiency by 50% due to the development of a very reducing environment (-800 mV). The iron anode generates Fe$^{2+}$, while an inert anode produces O$_2$, therefore, there is no competition between O$_2$ and TCE while using an iron anode.
4.3.2. TCE Reduction on Cathode

The main degradation mechanism at the cathode is hydrochlorination, which involves the interaction between atomic hydrogen formed at the cathode and the reducible chemical species (e.g. TCE) (Zheng et al., 2012). During hydrodechlorination, chlorine atoms are removed and carbon-hydrogen bonds are formed, as given by:

\[
\begin{align*}
\text{H}_2\text{O} + e^- & \rightarrow \text{H}^+ + \text{OH}^- \quad \text{(Atomic hydrogen formation)} \\
\text{H}^+ + \text{H}^+ & \rightarrow \text{H}_2 \uparrow \quad \text{(Hydrogen evolution)} \\
2\text{H}^+ + \text{RCl} & \rightarrow \text{RH} + \text{H}^+ + \text{Cl}^- \quad \text{(Hydrodechlorination)}
\end{align*}
\]

(Eq. 4.14) (Eq. 4.15) (Eq. 4.16)

A variety of carbon materials (Al-Abed and Fang, 2006; Saez et al., 2010), elemental metal materials (Rajic et al., 2016) have been investigated as cathodes for reduction of chlorinated compounds. Copper and MMO cathodes were compared for electrochemical reduction of TCE with an iron anode. Table 4.3 summarizes the final removal efficiency of TCE hydrochlorination and the amount of precipitation for different electrode configurations and electric currents.
MMO cathodes with palladium pellets slightly improved the removal efficiency compared to the copper cathode. Under the lower current (125 and 62 mA), the copper cathode produced more precipitates compared to the MMO cathodes. Based on the results, current can be reduced to 62 mA to decrease the amount of precipitation and avoid further problems in aquifer while maintaining a satisfactory removal efficiency, and lowering the cost of energy applied.

Based on experimental results for a low flow rate system (1 mL min\(^{-1}\)), which is three order of magnitude slower) under the same conditions which have been reported simultaneously to compare the lower flow rate system with the higher one, the removal efficiency is the same for both high and low flow rate (about 88%), while the amount of precipitation is nearly doubled under the lower flow rate (1265 mg under 1 mL min\(^{-1}\) flow rate compared to 756 mg under 1 L min\(^{-1}\) rate). Therefore, the influence of both current, which determines the supply of H\(_2\) and the generation of Fe\(^{2+}\), and flow rate, which flushes
out the precipitates, should be optimized. Figure 4.9. a, b, and c show various strategies affect the TCE removal rate under the different current intensities applied.
Figure 4.9. Decay of the aqueous TCE concentration in the effluent under different electrode configurations. Curves refer to (a) iron anode-MMO cathode with Pd pellets, (b) iron anode, copper cathode including Pd pellets, and (c) iron anode, copper cathode without Pd pellets.
Higher current intensity increases removal rates but causes production of more precipitation (Table 4.3) and requires higher energy consumption. Optimum conditions are required to obtain high removal efficiency with minimal impact on the aquifer. These experiments imply that by dividing the current applied by two, the amount of precipitation decreased (Table 4.3). This means that it is viable to apply lower current to control the production of precipitates with the same removal efficiency.

4.3.3. Different Electrode Configuration and Current Intensities

The palladium hydrochlorination technique was investigated to improve treatment of TCE contaminated groundwater in flow through system. Current intensity and the use of catalyst (Pd pellets) are other parameters affecting removal efficiency significantly. The charge requirement for the transformation of TCE by MMO cathode and Pd pellets as a catalyst is comparable to the energy requirements for the electrochemical treatments without palladium under the same operational conditions.
Figure 4.10. Concentration profiles vs. charge under different electrode configurations and current applied

As seen in Figure 4.10, under a constant-charge, a lower removal rate is attained by increasing the applied current intensity. By using a cathode material, which provides higher cathodic potential, hydrogen evolution reaction consumes a big portion of the applied current, which negatively affects current efficiency (Ciblak, 2015). Furthermore, higher production rate for hydrogen atoms result in excessive release of gas bubbles that further prevents the mass transfer process, the main reduction mechanism for TCE reduction (Wuthrich et al., 2005). In addition, high current intensities can reduce the lifetime of the anode due to corrosion and increase the energy consumption due to increased cell
resistance. This is consistent with other literatures (Zhao et al., 2007; Ciblak, 2015). In conclusion, low current is preferable if the retention time of the contaminated water is not a primary concern. Also, under the higher current intensities, bubbles form at the surface of the electrodes and lower the active surface area (Wutrich et al., 2005). The bubble coverage of the cathode surface adversely affects hydrochlorination and can cause the decrease in overall TCE removal (Rajic et al., 2015a). The charge required to achieve 40% removal efficiency was calculated for different electrode configuration either with Pd pellets or not. Table 4.4 suggests that the iron anode and copper foam cathode system with no Pd pellets required significantly more charge for complete removal of TCE, than the other electrode materials containing Pd pellets at the surface of the cathode. Note that the charge required for iron anode and MMO cathode system using Pd pellets is slightly lower than that reported for copper foam cathode with Pd pellets.

Table 4.4. Charge required for various electrode configurations under 250, 125, and 62 mA current intensity

<table>
<thead>
<tr>
<th>Electrode Configuration</th>
<th>Current (mA)</th>
<th>Flow rate (L min⁻¹)</th>
<th>Voltage drop</th>
<th>Time at which 40% removal is achieved (min)</th>
<th>Charge (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron anode-MMO cathode- with Pd</td>
<td>250</td>
<td>1</td>
<td>1.1</td>
<td>42.5</td>
<td>40720</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>1</td>
<td>1.0</td>
<td>54.9</td>
<td>25880</td>
</tr>
<tr>
<td></td>
<td>62</td>
<td>1</td>
<td>0.4</td>
<td>72.6</td>
<td>16835</td>
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The electrochemical treatments require relatively low power levels (e.g., 10 W m$^{-2}$) compared to other electrically based remediation technologies, such as thermal heating (Gilbert and Sale, 2005). Results from this study indicate that by optimizing the current intensity, even as low as 62 mA, desired TCE transformation can be achieved while minimizing the amount of precipitates formation. Since the less precipitates formation is essential for in situ electrochemical process in terms of electrodes lifetime, energy consumption, remediation time, and cost; choosing an optimized current and proper catalyst material that exceed the remedial progress expectation, is of great importance to attaining a reasonable TCE removal rate.

### 4.3.4. Effect of Palladium Pellets

Palladium has a high hydrogen adsorption-dissociation capacity; it acts as a collector of hydrogen gas produced by cathodic hydrolysis of water. The active atomic H formed by dissociating H$_2$ effectively dechlorinates TCE. Palladium at the cathode surface was utilized to enhance TCE reduction in a flow-through system with an anode followed by a cathode electrode sequence. The removal efficiency for aqueous TCE concentration by palladium at cathode surface under different currents is shown in Table 4.3. TCE removal rates were 96%, 83% and 82% under 250 mA, 125 mA and 62 mA, respectively under the condition of using iron anode and copper foam cathode. Palladium improved TCE degradation by 120% for 250 mA, 100% for 125 mA, 100% for 62 mA, under the condition of using an iron anode followed by a copper foam cathode with 1 min$^{-1}$ flow rate.
TCE decay profile by different amounts of palladium at the cathode surface (MMO anode and MMO cathode were used) is shown in Figure 4.11.

![Normalized TCE Concentration (mg/L) vs Time (min)](image)

Figure 4.11. Effect of doubling the amount of Pd on TCE removal efficiency using iron anode and MMO cathode system under the condition of 500 mA current, 1 L min⁻¹ flow rate

The results indicate the influence of Pd catalyst on the performance of electrochemical system. The removal rates slightly increased in the presence of 20 g Pd used compared to 10 g Pd (10%). When MMO anode and MMO cathode were used and the amount of Pd pellets was doubled, the removal rate only improved by 10%. This small improvement compared with the added cost of Pd pellets could be addressed because of the MMO is a higher overpotential material, which produces hydrogen very slowly. On the other hand, the role of Pd as a hydrogen collector completely depends on the hydrogen release rate. It suggests that in larger scale application in the field, using an optimum
amount of Pd with other operation conditions is necessary for efficient implementation. To sum up, as the precipitates could cover the surface of Pd over time, there needs to be more consistent and global effort to identify site characterization and groundwater physiochemical properties which could affect long-term reactivity of Pd pellets. Additionally, development of simple and cost-effective methods to recover Pd-pellets reactivity could be a significant challenge and further research will be required to improve the functionality of Pd-pellets as catalyst in electrochemical remediation systems.

4.3.5. pH and ORP Changes

Fig.4.12 shows ORP and pH changes under various electrode configurations while other parameters remain constant under a flow rate of 1 L min\(^{-1}\) and 250 mA.
Figure 4.12. Effluent pH and ORP changes under different electrode configurations. Experiments were conducted with 250 mA current and 1 L min⁻¹ flow rate.

The effluent ORP values continuously decrease to a very reducing environment when an iron anode is used. Anodic reaction under these conditions generates ferrous ions, which further react with hydroxyl to form Fe(OH)₂ and then uptake O₂ to produce Fe(OH)₃, thus providing a reducing condition. The most reducing environment (ORP close to -800 mV) took place when MMO cathode and Pd pellets were applied with an iron anode. In comparison, when copper cathode is used with palladium pellets, the similar ORP conditions appear but the rate differs. This is probably due to the difference between the hydrogen evolution potential of MMO and that of copper cathode.
The effect of current on pH and ORP is presented on Fig. 4.12. This figure shows changes resulting from the most effective electrode configuration, which is coupled of iron anode and MMO cathode plus palladium particles under different current intensities.

Figure 4.13. Time profiles of electrolyte pH and ORP at different electrolysis currents

The higher current can accelerate the reaction rate within the reactor; therefore, an increase in current results in higher pH values and drops ORP values. Increasing the current provides more Fe ions and improves $\text{OH}^-$, and $\text{H}^+$ evolution and both anodic and cathodic reactions occur quickly. Moreover, as the electrical current is responsible for $\text{H}_2$
production, an increase in current intensity generates more H₂, resulting in more active H on the Pd surface and higher dechlorination rate.

4.3.6. Precipitate Formation

Generated ferrous ions, one of the main products during iron electrolysis, react with existing anions in the electrolyte and precipitate in the form of various iron oxides, such as iron hydroxide, ferric lepidocrocite, and magnetite (Sarahney, 2007; Sarahney et al., 2012). The generated iron precipitates and the entrapment of gas during electrolysis may adversely affect the physical characteristics of the aquifer, such as permeability. In this section, the effect of iron electrolysis on precipitate formation that latter impact the soil porosity was evaluated in the flow-through column.

Although the presence of ferrous ions leads to formation of a reducing environment, it also results in precipitates, which may gradually cover the surface of electrodes and decrease the removal rate of contaminants. In order to assess the impact of precipitations on the process development, iron based precipitates under different experimental operational conditions were collected. Experiments were conducted with various electric currents, and electrode material arrangement and the result are presented in Table 4.3.

Within the text. In field applications, the pumps that are used in wells generate flow rates higher than a gallon per minute (USEPA, 2005). Therefore, investigating the influence of high flow rates (on the order of liters per minute) on the efficiency of the transformation process is needed. In systems using the iron anode, the inevitable limitation of the iron performance is provided by the corrosion of zero-valent iron and deposition of minerals,
which decrease the reductive capacity and clog the system (Vodyanitskii., 2014; Ciblak, 2015). It is assumed that the high flow rate would favor the transformation of contaminants since it would flush out precipitations and prevent clogging.

### 4.3.7. Summary

This study demonstrates that a two-electrode system containing iron anode can effectively remove TCE in groundwater under a flow rate of 1 L min\(^{-1}\). However, the amount of precipitation might be a limiting factor and should be controlled. The effects of electrode materials and current intensity, on precipitation, pH and ORP are presented in the study. The best design for Pd-catalytic dechlorination of TCE includes iron anode, MMO cathode, and palladium due to the high removal efficacy attained with their combined use (96%, 92%, 90%, and 84% when the current is 500, 250, 125, and 62 mA, respectively). Additionally, under low current (62 mA), fewer precipitates are produced. Implementing this system in the field requires considering other aspects. Proper evaluation of influent flow rate is required for equipment design. High flow rate systems utilize more supplies, which consume more energy and would be costly but the system optimized to operate under higher flows would be sufficiently flexible to endure natural variations in groundwater flow. Although, this system is effective even under 62 mA, further research is required to identify possible strategies to address other potential barriers to dechlorination within aquifers.
Chapter 5 Conclusion

5.1. Summary of Work

Groundwater is a major source for irrigation and drinking water. However, it is susceptible to pollution because of inappropriate waste disposal practices as contaminants can enter aquifers by several means, including infiltration of surface water through soil and sediments, as well as, direct flow from surface water especially in karst terrain (USEPA, 1998). Since contaminants can easily enter the karst aquifers seeking through thin soils and can rapidly move through conduit networks. Karst aquifers are always vulnerable to contaminants and difficult to rely on as freshwater resources. Therefore, certified protection and investigation method are required for these aquifers to protect human health as they carry vulnerable freshwater resources. Due to simultaneous existence of different contaminants in groundwater, strategies to treat contamination mixtures require considering not only the properties of individual contaminants, but also the complexity of their interactions (Mao et al., 2012). Electrochemical processes are effective for removal of chlorinated ethylenes such as TCE, which is widely used as cleaning solvents, and heavy metals (such as Se and Cr) from ground water. In addition, natural organic matter (NOM) is present throughout the ecosystem and can move into soil and groundwater.

This research validates treatment of a broad range of contaminants through electrochemically induced oxidation and/or reduction reactions under variable flow conditions without any chemical injection. The ultimate goal is developing a sustainable and environmentally-friendly electrochemical technology, which can be powered by renewable energy sources such as solar power. A novel reactive electrochemical flow system consisting of an iron anode and a porous cathode is evaluated for removal of
mixture of contaminants in groundwater. A small-scale flow-through limestone column was used to evaluate the effect of common coexisting organic (e.g. humic acid) and inorganic compounds (e.g. chromate, selenate, and nitrate) on the dechlorination of trichloroethylene in groundwater by electrochemical induced reduction using iron anode. The changes in the effluent TCE concentration and other chemical concentrations were monitored together with operating conditions, including applied current intensity. Simultaneous removal of TCE together with other contaminants were measured.

This study also evaluated the effect of rapid flow rate, expected in the conduit network within karst aquifers, on TCE removal by enhanced hydrochlorination using Pd catalyst. Operating parameters such as electrode materials (inert or iron anode, and inert or copper cathode), current intensity, and Pd catalysis application were also investigated. The electrode couple (iron anode and inert MMO cathode with Pd pellets) with the best TCE removal performance was selected for further testing.

5.2. Conclusions

Based on the results of this research, the following specific conclusions can be drawn:

- Higher removal of TCE is attained using limestone columns rather than acrylic columns under the same flow conditions due to limestone specific characteristics; higher surface area that create complex network of preferential flow pathways and the larger-size colloid-bound contaminants that are more accessible for in situ degradation, both may lead to higher TCE losses due to either sorption or higher reactivity within the treatment zone in the reactor.
• Humic acids play a negative role on electrochemically induced chlorinated hydrocarbon degradation by inhibiting reduction due to competition between TCE and humic acid. Increasing the amount of humic acids decreases the dechlorination rate but the final removal is the same (up to 78%).

• Although TCE removal rates in the presence of different humic acid concentrations are almost the same, the removal rate is faster with presence of lower humic acid concentration, which suggests that higher charge and energy is required to achieve the same TCE removal efficiency in the presence of higher initial concentration of humic substances.

• The transformation profiles under various initial chromate concentrations (1, 5, and 10 mg L\(^{-1}\) of chromate) depicted that removal efficacy of TCE decreased intensely in the presence of Cr (VI) in the solution. Increasing the initial concentration of selenate reduces the capability of the system for TCE reduction. Chromium hydroxide, selenate, and probably other minerals precipitations result in the loss of reactivity for TCE due to precipitates covering the reactive surface of electrodes. As TCE and nitrate are removed through the electrochemical processes at the cathode surface, presence of nitrate relatively affects the TCE removal rate. The influence of presence of these chemicals on TCE removal is in the following order: chromate, selenate, and nitrate.

• The \textit{in situ} electrochemical system containing an iron anode, is capable of reducing
Cr(VI) to Cr(III) at three initial concentrations (1, 5, and 10 mg L$^{-1}$) completely within 40, 90, and 90 minutes of experiment, however, the rate of transformation is faster with lower initial concentration. Significant reduction of Se (VI) was also achieved (up to 100% and 83% for 1 and 5 mg L$^{-1}$ initial concentrations, respectively). In addition, the removal rate for nitrate is up to 70% for all initial concentrations.

- The removal rate of TCE decreased by 50% in the presence of mixture of other contaminants. However, concentration profiles and removal efficacies at steady state conditions (100% for chromate, 90% for selenate, and 80% for nitrate) suggest that these contaminants can be removed simultaneously. Lower removal rate of TCE could be presumably due to production of insoluble precipitates with ferrous species and also the competition for the reduction at the cathode surface.

- The iron anode showed the highest dechlorination efficiency for TCE reductive transformation. Furthermore, the inert MMO cathode showed better performance in terms of precipitates formation and removal efficiency compared to porous copper cathode. When an iron anode is coupled with an inert MMO cathode in presence of palladium pellets as catalyst, the TCE dechlorination rate increases significantly while producing less precipitates.

- Palladium has a high hydrogen adsorption-dissociation capacity; it acts as a collector of hydrogen gas produced by cathodic hydrolysis of water and improves TCE
degradation. The removal rates slightly increased in the presence of 20 gr Pd used compare to 10 g Pd (10%), which suggests that in larger scale application in the field, using an optimum amount of Pd with other operation conditions is necessary for efficient implementation.

- pH and ORP changes are significantly dependent on current intensity applied during iron electrolysis. The highest pH and the most reducing environment (lowest ORP) are achieved under 500 mA operational condition compared to 250 mA, 125 mA, and 62 mA applied currents. However, the pH and ORP values show similar trends for all four different current intensities applied.

- TCE reduction mechanism is supported by H formation; related to the mass transfer effect of contaminants on electrode/liquid interface, such as hydraulic residence time and surface area of the electrode. Therefore, slightly higher TCE removal efficiencies reached at a lower flow rate suggests that the short retention time for the reaction in the high flow through system adversely affects the reduction mechanism. In the contrary, higher flow rate favors TCE treating capacity by enhancing the mass transport of the target contaminant, a main mechanism for TCE reduction. Lower removal rate of TCE could be presumably due to production of insoluble precipitates with ferrous species and also the competition for the reduction at the cathode surface. It is assumed that the high flow rate would favor the transformation of contaminants since it would flush out precipitates and prevent clogging.
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