PERCHLORATE DEGRADATION USING PARTIALLY OXIDIZED TITANIUM IONS AND ION EXCHANGE MEMBRANE HYBRID SYSTEM

A Dissertation

by

SUNG HYUK PARK

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2010

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Bill Batchelor
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ABSTRACT

Perchlorate Degradation Using Partially Oxidized Titanium Ions
and Ion Exchange Membrane Hybrid System. (May 2010)
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Chair of Advisory Committee: Dr. Bill Batchelor

Perchlorate has entered human and environmental food chains and has received a great deal of attention because of its toxicity to humans. In this study, chemical degradation of perchlorate was investigated using partially oxidized titanium ions (Ti^{2+} and Ti^{3+}) in solutions and as part of an ion exchange membrane reactor system. Aqueous titanium ions (Ti^{2+} and Ti^{3+}) were applied to remove perchlorate ions and its destructive mechanism, reaction kinetics, and the effect of environmental factors were investigated. Titanium ions were able to degrade perchlorate ions very rapidly with half life less than one hour under conditions of high acid concentrations. A new reactor system with an ion exchange membrane was adapted to apply better the reactions of perchlorate destruction to water treatment practice. A novel treatment method was developed by integrating partially oxidized titanium ions with an ion exchange membrane, and it is named the Titanium and Membrane Hybrid System (TMH System). The results shown in this research demonstrate the feasibility of TMH System for perchlorate reduction. The perchlorate ions were rapidly adsorbed onto the ion exchange membrane and diffused through it, but they were reduced by titanium ions in the degradation zone relatively slowly. To enhance the overall rate of reaction, high concentrations of acid and Ti(III) are needed, but transport of hydrogen ions through the anion permeable membrane was observed and would be greater at higher acid concentrations. The proposed mathematical model predicts the performance and behavior of the TMH system for different physical and chemical conditions. It successfully described adsorption, diffusion and reduction of perchlorate in the system. This model could be used as an important tool for process design and optimization.

DEDICATION

This dissertation is dedicated

to my Father Jung-Soon Park, mother Young-Hee Yoon,

and my wife Eun-Kyoung Yoo.

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I would like to express my sincere gratitude to my advisor, Dr. Bill Batchelor. I believe that it is one of the greatest blessings in my life to meet him and pursue a degree with his advice. I will remember his warm heart to teach students, keen sight on environmental problems, and faithful attitude for everything with his job.

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CHAPTER I

INTRODUCTION

1.1 Statement of Purpose

Perchlorate (ClO_4^-) is an emerging contaminant that has been found in surface and groundwater and it has become a very controversial contaminant, because there is controversy over whether the government should regulate it by establishing a drinking water standard for it [1]. Perchlorate in the environment is known to come from manmade sources and natural sources [2]. Across the United States, perchlorate has been found in 153 public water systems and 25 states as of January 2005 [2]. Because of its high oxidizing power, it is commercially used in solid rocket fuels, munitions, commercial explosives, fireworks, and flares. Its use in military applications has resulted in a number of DOD (Department of Defense) facilities being heavily contaminated by perchlorate [2, 3]. Furthermore, medical or pharmaceutical procedures may use potassium perchlorate, water and wastewater treatment could generate perchlorate as a byproduct, and landfills that have received waste water contaminated with perchlorate could be a source [3]. Recently, trace levels of perchlorate were widely detected in milk, breast milk, tobacco products, fertilizers and even vegetables [4-7]. In Asia, perchlorate is also becoming an environmental and health concern [8-10].

This dissertation follows the style of *Environmental Science and Technology*.

As for the Republic of Korea, the first preliminary assessment for perchlorate has been conducted for surface waters, drinking waters and wastewater treatment plant effluents. The highest level of perchlorate found in surface water was 60 µg/L and in drinking water it was 35 µg/L [8]. In the case of Japan, the maximum concentration of perchlorate found in metropolitan drinking water sources was 2,300 µg/L in 2007 [10]. As for Texas, it is known that groundwaters from 56 counties in northwest Texas and eastern New Mexico contains up to 200 µg/L of perchlorate [1]. These studies imply that perchlorate contamination is potentially global and that additional evaluation of the extent of contamination should be considered.

Perchlorate has entered human and environmental food chains and has received a great deal of attention because of its toxicity to humans [11]. It blocks iodine uptake by the thyroid gland due to the similar sizes of the iodine and perchlorate molecules. Lowered uptake of iodine results in inhibition of the normal production of thyroid hormones [12]. Thyroid hormones are reported to play a crucial role in human metabolism, reproduction, growth and function of the cardiovascular and central nervous systems. Women of child bearing age are especially vulnerable and the American Thyroid Association recommends that they consult their doctors to determine their proper thyroid hormone standing [2, 13].

Because of these toxic effects, the USEPA established an official human reference dose for perchlorate at 0.0007 mg/kg-day in 2005 and this equates to a Drinking Water Equivalent Level (DWEL) of 24.5 µg/L. Also, several states have developed health-based goals for perchlorate that range from 1 to 14 µg/L and perchlorate is listed as a candidate for possible regulation in the future [13]. The health-based goals are 1 µg/L for Massachusetts, 6 µg/L for California and 14 µg/L for Arizona. Texas has established an action level at 17 µg/L [2]. However, the efforts for federal regulation of perchlorate are controversial. In October 2008, USEPA made a preliminary determination not to regulate perchlorate in drinking water and it brought out numerous critical comments [14]. In January 2009, they issued an interim health advisory for perchlorate of 15 µg/L and EPA published a supplemental request for comments to analyze data related to regulatory determination of perchlorate in August 2009 [15, 16].

A variety of technologies have been developed for perchlorate remediation. Among them, ion exchange is a very effective method for removing perchlorate ions from water and it is listed as Best Available Technology (BAT) for perchlorate treatment [17]. However, conventional ion exchange treatment requires that the resins be regenerated with a brine solution, which becomes contaminated with perchlorate and requires additional treatment. Oak Ridge National Laboratory developed a method for reducing perchlorate-rich brine, but it needs elevated temperature (up to 200˚C) and high pressure (up to 20 atm) [11, 18]. They also demonstrated the process at a field site in California and showed high efficiency. Their recent technique for destroying perchlorate in the regenerant solution was also effective, but it also needs a high-temperature reactor (190˚C) to enhance the chemical reaction with ferrous ions [19].

Other chemical treatment technologies have been developed to treat perchlorate. Catalytic reduction, electrodialytically assisted catalytic reduction, and stabilized zero-valent iron nanoparticles have been investigated and have shown good efficiency, but they all need special conditions such as low pH, high temperature or expensive catalysts [20-24]. Biological treatment is another effective way to degrade perchlorate in water. In this process, perchlorate is used as an electron acceptor in microbial redox reactions. However, biological processes are difficult to use in high salinity water such as ion exchange brine. Besides, application of microbial processes to drinking water treatment is difficult due to public concerns with microbial pathogens.

Drs. Kramer and Lee developed a novel treatment method for destroying perchlorate. They showed that perchlorate can be successfully reduced to chloride during pitting corrosion of Ti(0) that is induced electrochemically. However, the presence of chloride and bromide inhibit the process so it is not applicable to waters such as ion exchange regenerant solutions [17]. Furthermore, the high voltages required would result in high costs for power. However, they showed that the mechanism for perchlorate reduction in this process is conversion of Ti(0) into oxidized ions such as Ti(II) and Ti(III), which reduce perchlorate in solution. Until recently, very little was known about the aqueous chemistry of Ti(II), but a method for producing Ti(II) has been developed and its ability to reduce various contaminants has been examined [25, 26]. Several studies have shown that Ti(II) was an effective reductant for compounds that are difficult to degrade and this is the basis for examining the ability of Ti(II) to reduce perchlorate. Also, Ti(II) could be effective in destroying various other oxidized contaminants such as nitrate, chromate, chlorinated organics, selenate and arsenate. A treatment process for perchlorate that is based on partially oxidized titanium ions has several potential advantages. First, they are stable and easily applicable to solutions with high ionic strength such as waste ion exchange regenerant. Second, they could be applied to other oxidized contaminants.

In this study, Chapters III and IV describe how partially oxidized titanium ions (Ti^{2+} and Ti^{3+}) are applied to remove the perchlorate ions. In order to develop a novel technology for perchlorate treatment, this study investigates the perchlorate destruction mechanism, reaction kinetics and effect of environmental factors. In chapter V, a reactor system with an ion exchange membrane is adapted to better apply the reactions of perchlorate destruction to water treatment practice. This technology is named the ‘Titanium and Membrane Hybrid System (TMHS)’ and it operates by having perchlorate adsorb to the membrane, diffuse through it and be reduced by titanium ions in a solution that is optimized to promote the rate of reduction. Also, a physicochemical model was developed to analyze the system and predict its behavior.

1.2 Research Objectives

The goal of this research is to develop a novel treatment technology for the destruction of perchlorate in contaminated water using multivalent titanium and ion exchange membrane. The objectives of this study are: 1) Optimize methods for producing Ti(II) that is effective in degrading perchlorate; 2) Characterize destruction of perchlorate by Ti(III) ; 3) Determine the ability of a Titanium Membrane Hybrid System to provide for perchlorate treatment. Successfully achieving this goal will provide data that demonstrates the feasibility of using Ti(II) and Ti(III) with an ion exchange membrane to treat perchlorate and the potential for treating other oxidized contaminants.

This data will form the basis for completing the process development stage in which the process will be evaluated at larger scales. Ultimate development and demonstration of a perchlorate treatment process based on partially oxidized titanium ions and ion exchange membrane has the potential to provide a lower cost method of destroying perchlorate in contaminated ground and surface waters, ion exchange regenerant solutions and other contaminated media.

1.2.1 Ti(II) production and perchlorate degradation

Previous research on divalent titanium has been generally limited to solid state compounds such as nonstoichiometric titanium oxide TiO_x, the hydride TiH_2 as well as halides TiF_2 and $TiCl_2$ [25]. However, a general method for producing aqueous state Ti(II) is available in the literature but it has not been optimized. Thus, the objective of this phase of study is to provide an optimum condition for producing Ti(II) solution and reducing perchlorate using it. Over 50 batch kinetic experiments were conducted to investigate the effects of acid type, acid concentration, F/Ti(0) molar ratio, catalyst concentration on perchlorate degradation. Accomplishment of this objective provided fundamental data to describe the kinetics of perchlorate destruction by Ti(II) under numerous process conditions. The data obtained in this step described degradation kinetics of perchlorate and were used to develop kinetic models. It successfully predicted the performance of the treatment process under a range of different environmental conditions.

1.2.2 Perchlorate degradation using Ti(III)

Little information is available on the aqueous chemistry of Ti(III). Perchlorate was once evaluated as a reductant for Ti(III) in dilute solution, but additional studies were not conducted [27]. Other research conducted on Ti(II) and Ti(III) could not conclude lucidly which is the stronger reductant. One of the research efforts showed that five oxidants out of eight reacted more rapidly with Ti(II) than Ti(III), two oxidants reacted more rapidly with Ti(III) and one exhibited a similar reaction rate with both [26]. Another research project showed that rate constants for reduction of hypervalent chromium species by Ti(II) and Ti(III) are similar [28]. Thus, this phase of study focused on the investigation of perchlorate reduction rates with Ti(III). To enhance understanding of the basic characteristics of aqueous solutions of the reductant, UV spectrophotometer study was conducted and sets of kinetic experiments were conducted. Also, ionic strength was controlled to investigate its effect on reaction rate and several metal catalysts (Mo, Cu, Ni, Re and W) were evaluated for their ability to enhance the reaction rate.

1.2.3 Titanium Membrane Hybrid System for perchlorate treatment

Ion exchange and membrane process such as electrodialysis, reverse osmosis or nanofiltration are commonly used for removal of oxyanions like nitrate or bromate [29]. However, the contaminants are not destroyed, but accumulate in the brine solution. Thus, research has been conducted on coupling ion exchange with biological treatment process using the concept of an ion exchange membrane bioreactor [29, 30]. In this study, a Titanium Membrane Hybrid System (TMH System) is developed for perchlorate treatment. This system is composed of a semi-permeable membrane that separates two solutions. One solution contains contaminated water that contains perchlorate and the other contains a reductant and has optimal conditions for perchlorate degradation. The membrane works as a barrier to separate the reaction media from the media being treated, but also as a method to transport perchlorate to the solution with reductant and optimal reducing conditions. Data obtained in pursuit of this objective were used to develop a physicochemical model that can describe transport and degradation of perchlorate in the membrane reactor. The model was used to predict perchlorate adsorption, diffusion and degradation under different conditions. This objective led to successful development of a practical treatment process based on the reaction of multivalent titanium ions with perchlorate in TMH System.

CHAPTER II

BACKGROUND

2.1 Perchlorate Sources and Occurrence

Perchlorate is produced for use in a range of materials including solid fuel for rockets, munitions, commercial explosives, fireworks, air bag inflators, and flares [2]. It has been utilized in the United States national defense and space programs. Ammonium perchlorate or potassium perchlorate had been used as a major component in almost all solid rocket fuel, missile propellants and thousands of military combat munitions [31]. They are very widely produced in U.S. and allied countries because of their much lower costs than any other candidate replacements currently available or being developed [31]. According to the USEPA’s estimates, 90 percent of the perchlorate manufactured in the United States is produced for use by the military and NASA [32].

Perchlorate may be also be formed as a byproduct of drinking water chlorination with sodium hypochlorite [2]. There appear to be natural sources of perchlorate contamination as well. It is a component in Chilean nitrate fertilizer [2] and it has been shown by laboratory experiments to possibly be formed by various atmospheric processes [33]. This research showed that perchlorate could be formed from chloride aerosols by electrical discharge and by exposing aqueous chloride ions to a high concentration of ozone [33].

The increased ability to measure perchlorate at low concentrations has led to detections of perchlorate in ground and surface waters over a wide range of the US. Over 150 public water supplies in 25 states have detected perchlorate in their water [2]. The contamination is widespread, but is greatest in California, Texas, New Jersey, and New York as shown in Figure 2.1 [34].

Figure 2.1. Occurrences of perchlorate in US as of September 2004 [34].

Concentrations of perchlorate as high as 160,000 µg/L have been measured at military facilities, including the Longhorn Army Ammunition Plant and the Naval Weapons Industrial Reserve Plant in Texas [2].

Perchlorate has also been detected in food, such as milk, breast milk, tobacco products and leafy vegetables [4, 6, 7, 35, 36]. Data sources for perchlorate detection in 27 foods and beverages from FDA’s 2005 survey are available at its website [36].

2.2 Toxicity and Regulations of Perchlorate

Perchlorate is toxic to humans because it interferes with the ability of the thyroid gland to incorporate iodine, which is required by the thyroid to produce a number of hormones necessary for proper body function. This mode of action also describes the animal toxicity of perchlorate. Without sufficient thyroid iodide, an infant cannot produce enough thyroid hormone for its developmental needs [37, 38]. During early life, the successful development of the neurosystem is dependent on thyroid hormones [37].

Based on the toxicological data, a report by a committee of the National Research Council (NRC) suggested a reference dose for perchlorate in February 2005 at 0.0007 mg/kg/day that results in a drinking water equivalent level (DWEL) of 24.5 µg/L [2]. A reference dose is defined as a “scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans” and a DWEL assumes that all of a contaminant comes from drinking water.

Several states have developed health-based goals for perchlorate that range from 1 to 14 µg/L [2]. In March 2004 for the first time, California set a drinking water public health goal of 6 µg/L. Seven states have their own advisory, health-based, and/or other levels as shown in table 2.1 but do not yet have drinking water standards [2].

Table 2.1 Perchlorate levels [2].

	Concentrations (µg/L)	**Type of advisory levels**
AZ	14	Health based goal
CA	6	Health based goal
MA	1	Health based goal for sensitive populations
MD	1	Health based goal
NM	1	Drinking water screening level
NV	18	Cleanup standard for groundwater
TX	17	Cleanup standard for groundwater

The regulation process for perchlorate in drinking water standard continues to be controversial. In 2008 August, USEPA determined not to regulate perchlorate with a conclusion that “a national primary drinking water regulation for perchlorate would not present a meaningful opportunity for health risk reduction for persons served by public water systems” [39]. After a national outpouring of critical comments, they are again researching the occurrence of perchlorate in state-wide public water systems, evaluating exposures from sources other than drinking water, and indentifying the health effects on various age groups. In January 2009, EPA issued an interim health advisory level at 15 µg/L "while the agency evaluates the opportunity to reduce risks through a national primary drinking water standard" [40]. On August 2009, EPA published a Supplemental request for Comments Federal Register notice to seek additional ways to analyze data related to the regulatory determination of perchlorate. They are focusing on the re-evaluation of perchlorate exposure to infants and developing children, in addition to pregnant women and their developing fetuses. EPA's final decision seems to be a determination to regulate [16].

2.3 Perchlorate Chemistry

Perchlorate is an anion which has a chlorine atom at its center that is bonded to four oxygen atoms with tetrahedral geometry. It is usually associated with ammonium (NH_4^+), potassium (K^+), or sodium (Na^+) and these salts are very soluble in water. The physical and chemical properties of the perchlorate compounds are summarized in table 2.2.

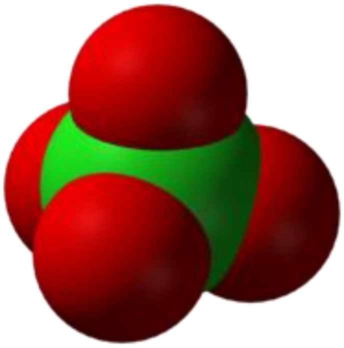


Figure 2.2. Molecular structure of perchlorate ion (ClO_4^-).

Table 2.2. Physical and chemical properties of perchlorate compounds [2].

Properties	**Ammonium perchlorate (NH_4ClO_4)**	**Potassium perchlorate ($KClO_4$)**	**Sodium perchlorate ($NaClO_4$)**	**Perchlorate acid ($HClO_4$)**
Molecular weight	117.49	138.55	122.44	100.47
Taste/Odor	Odorless	Slightly salty	Odorless	Strong odor
Density	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.77 g/cm^3
Solubility at 25 °C	200 g/L	15 g/L	2096 g/L	Miscible in cold water
Volatility	Nonvolatile	Nonvolatile	Nonvolatile	Volatile

Perchloric acid ($HClO_4$) has a pK_a of 1.77 [41], so perchlorate will be present as the perchlorate ion (ClO_4^-) at environmental pH. Perchlorate is recognized as having a very weak tendency to form complexes with metals, so perchlorate salt solutions are often used to provide a background electrolyte for water chemistry experiments [13]. Furthermore, it has little tendency to precipitate as a solid, so it tends to be found in aqueous solution and is mobile in the environment. Therefore, the perchlorate ion tends to remains in groundwater and moves with the flow of water. However, perchlorate is preferred by ion exchangers over most monovalent anions and some divalent ions such as sulfate [42].

Perchlorate is an oxidized compound with oxidation number of +7. Thermodynamically, it is a strong oxidant, based on its high E_h^0/pe^0 [41].

$$ClO_4^- + 8\,H^+ + 8\,e^- = Cl^- + 4\,H_2O \qquad E_h^0 = 1.19 \text{ volt},\ pe^0 = 20.2$$

The oxidizing ability of perchlorate is utilized in producing solid rocket fuels, munitions, fireworks and flares where the redox reactions occur at high temperature. However, perchlorate is a poor oxidant at room temperature due to kinetic limitations [13]. Although reactions are slow and require extreme conditions, there are reports of perchlorate being reduced chemically. A summary of the half-lives for perchlorate reduction by various reductants is shown in Table 2.3. These half-lives were calculated assuming that the initial concentrations of reductant and perchlorate were 10^{-4} M and 10^{-5} M, respectively.

Mahdi et al. evaluated methylrhenium oxides (CH_3ReO_2) to reduce perchlorate at pH 0 and 25℃. They found that the rate of the overall reaction was controlled by the first step, which was an oxygen abstraction from perchlorate to form chlorate (Equation 2.1). They measured a second order rate constant of 7.3 $M^{-1}s^{-1}$ based on Equation 2.2 [31, 43]. The half-life of perchlorate with this reaction is 0.26 hr assuming a reductant concentration of 10^{-4} M and this is the fastest reaction reported in the literature before 2003. This result is important because the very rapid reaction occurred at room temperature, even though it was at very acidic conditions.

$$CH_3ReO_2 + ClO_4^- = CH_3ReO_3 + ClO_3^- \tag{2.1}$$

$$\frac{d[ClO_4^-]}{dt} = -k[CH_3ReO_2][ClO_4^-] \tag{2.2}$$

Kallen et al. investigated the kinetics of perchlorate reduction by $Ru(H_2O)_6^{2+}$. They proposed that rate of reaction is independent of $[H^+]$ concentration in the range of

0.088-0.297 M and decreases with higher ionic strength to a limit near 0.26 M [44]. The rate of reaction depends on the concentrations of Ru^{2+}, ClO_4^- and Cl^- as shown in their proposed rate equation (2.4). The half life of perchlorate was calculated as 12.5 days.

$$2Ru^{2+} + ClO_4^- + 2H^+ = 2Ru^{3+} + ClO_3^- + H_2O \qquad (2.3)$$

$$\frac{d[ClO_4^-]}{dt} = -\frac{k[Ru^{2+}][ClO_4^-]}{1 + K[Cl^-]} \qquad (2.4)$$

Ti(III) was evaluated as a reductant for perchlorate by Duke et al. and Wagner et al., but its reaction rate was too slow to be used for treatment process [27, 45]. All reports shown in Table 2.3, except that for CH_3ReO_2, used concentrations of hydrogen ions that were less than 1.0 M. This table documents that chemical reduction of perchlorate with the reductants that have been tested is usually too slow to be used as a treatment process. The one exception is the reaction with CH_3ReO_2 (methylrhenium dioxide). However, a treatment process is unlikely to be developed with this reductant, because it is not generally available and would probably be too expensive if it were available.

Table 2.3. Summary of chemical reduction of perchlorate and calculated half lives.

Reductant	**Typical Half-life**[a]	**Conditions**	**Reference**
CH_3ReO_2	0.26 hr	25°C , pH 0	[43, 46]
Fe(0)	252 day	25°C, $[HClO_4]$=1M, [Fe(0)]=.037 M	[43, 47]
Ru(II)	12.5 day	25°C, $[H^+]$ = 0.09-0.30 M	[44, 48]
Sn(II)/Mo	890 day	25°C, $[H_2SO_4]$ = 2.5 M, [Mo] (catal yst) = 10^{-5}M	[49]
Ti(III)	53 day	50°C, $[H^+]$ = 0.2-1.0 M	[27, 46]
Ti(III)	668 day	25°C, $[H^+]$ = 0.1 M	[45]
Ti(III)-Hedta	2000 day	25°C, $[H^+]$ = 0.1 M	[45]
V(II)	4400 day	49.95°C, $[H^+]$ = 0.11 M	[50]
V(III)	14,000 day	49.95°C, $[H^+]$ = 0.11 M	[50]

[a] initial concentrations of reductant and perchlorate assumed to be 10^{-4} M and 10^{-5} M

Since 2003, several methods for more rapid degradation of perchlorate were developed. They include using reductants such as Fe(II), elemental iron (Fe(0)), ZVI nanoparticles, hydrogen gas with catalyst, and Ti(III) with β-alanine [18, 20, 22, 23, 51, 52]. The experimental conditions and rate constants are shown in Table 2.4 as reported in literature. The half-lives were calculated from reported values of pseudo first-order rate constants. To increase the rate of reaction, elevated temperature [18, 22, 23, 52], high pressure [18], and catalysts such as 5.9% Re/Pd [20] and β-alanine [52] were applied. The half-lives of perchlorate are less than 2.1 hours for all cases. The fastest method was from Oak Ridge National Laboratory and it has half-life of 0.13 hour. Many novel treatment methods were developed and are being developed to overcome the ‘barrier’ of rapid perchlorate degradation.

Table 2.4. Summary of rapid chemical reaction of perchlorate since 2003.

Reductant	**[Reductant]** **(mM)**	**[ClO_4^-]** **(mM)**	**T** **(°C)**	**k[a]** **(hr^{-1})**	**Half life** **(hr)**	**Conditions**	**References**
Fe(II)+HCl	1,392	87	200	5.23	0.13	$[H^+]$=4M	[18]
Elemental Iron	unknown	0.5	200	1.57	0.44	pH = 7.4	[22]
ZVI nanoparticle	32.2	0.1	110	0.984	0.70	Al, Cu, Co, Ni, Pd, Re have no effect	[23]
H_2 gas + Re + Pd/C	Continuously injected	2	25	0.34	2.04	pH=2.7, [Catalyst]=2g/L	[20]
Ti(III) + β-alanine	40	1	50	1.08	0.64	[β-alanine]=120 mM, optimal pH=2.3	[52]

[a] Pseudo-first order rate constant in all cases

2.4 Perchlorate Treatment Technologies

2.4.1 Physical treatment process

Physical treatment processes remove perchlorate from contaminated media without changing it chemically. Considerable progress has been made in developing treatment methods for removing perchlorate from drinking water, groundwater, and surface water. Some technologies are proven and commercially available, while others are still in the research and development levels. The following are representative physical processes for treatment of perchlorate-impacted water: ion exchange, reverse osmosis, nanofiltration / ultrafiltration and ion exchange membrane.

2.4.1.1 Ion exchange

Ion exchange is the most proven and widely accepted physical process [2]. During ion exchange, perchlorate ion is exchanged with another ion, typically chloride. The following is the principal ion exchange reaction of perchlorate with a strong base resin in the chloride form [2].

$$R_4N^+Cl^- + ClO_4{}^- = R_4N^+ClO_4{}^- + Cl^- \qquad (2.5)$$

When perchlorate-contaminated water contacts the resin, perchlorate ions stick to the resin and release chloride ions. However, the resin releases perchlorate ions when it is exposed to concentrated chloride solution. This reversal is used to regenerate spent resins and it produces a perchlorate-concentrated brine that needs further treatment. In recent years, pilot and full-scale systems based on ion exchange have been evaluated at government, military, and private facilities, but they all requires replacement of exhausted resin or regeneration of spent resin and treatment for the contaminated brine [2, 42].

2.4.1.2 Reverse Osmosis (RO) / nano and ultra Filtration

RO is a physical separation method that has long been used to remove ions from drinking-water supplies [53]. In this technology, high pressure is applied to reverse the osmosis process and it forces water molecules to go through the semi-permeable membrane from the contaminated water into cleaner water. RO can be used as a pretreatment step to further reduce perchlorate concentrations from water treated by other technologies including bioreactors and ion exchange, and other filtration membranes [2]. Reverse osmosis membranes are expected to be used widely in the future due to improvement of materials and decrease of cost [53]. Nanofiltration and ultrafiltration are similar to RO, but the pore sizes of the membranes are larger and operating pressures are lower than RO [2]. Their use for perchlorate treatment is not popular yet, but transport phenomena of perchlorate ions through NF, UF and RO membranes have been investigated [54-58] .

2.4.1.3 Ion exchange membrane

Ion exchange membranes have been used widely in numerous industrial fields and have huge potential for being used in new areas due to the adaptability of polymer membranes [59]. Based on their application, ion exchange membranes can be classified into three categories, as shown in table 2.5.

Table 2.5. Overview of ion exchange membrane applications [59].

Processes	**Applications**
Mass separation process	Donnan dialysis, Diffusion dialysis, Electrodialysis
Chemical synthesis process	Chlorine-alkaline electrolysis, hydrogen and oxygen production by water electrolysis
Energy conversion and storage processes	Fuel cells, electrical batteries

It is reported that ion exchange membranes can remove specific charged inorganic ions such as nitrate, sulfate, fluoride and bicarbonate [60]. Also, some research has been conducted on perchlorate degradation using an ion exchange membrane bioreactor [29, 60]. This system combines Donnan dialysis and biological degradation and its feasibility has been evaluated for simultaneous degradation of perchlorate and nitrate from drinking water [29, 60].

2.4.2 Chemical processes

In recent years, many strong reductants for perchlorate reduction have been investigated and their kinetic data are shown in Table 2.4. Zero-valent iron nanoparticles successfully degraded perchlorate in water or ion exchange brine at elevated temperature (90~95℃) within 7 hours, but no metal catalysts (Al, Cu, Co, Ni, Pd, or Re) were effective in improving the reaction rates [23]. Gu et al. developed a new methodology for perchlorate degradation by Fe(II) in a $FeCl_3$-HCl solution at an elevated temperature and/or pressure and showed that the reaction rate could be increased by controlling temperature and pressure [18]. Elemental iron was also evaluated by Oh et al. and perchlorate was removed in 1 hour at 200℃ with microwave heating [22]. However, all the above reactions need very high temperature and/or pressure. Hurley et al. researched a catalytic reaction with mild conditions, but they had to use expensive catalyst such as 5 % palladium and 13% rhenium to obtain fast reaction [20]. Very recently, a method that uses Ti(III) as a reductant with β-alanine as a catalyst was developed and it achieved complete degradation of perchlorate in 2.5 hour at 50 ℃. Another study combined electrodialysis and catalytic reduction [21]. These types of combined processes are the major approaches used in developing perchlorate remediation and treatment technologies in recent years [61].

2.4.3 Biological processes

Biological reduction of perchlorate has been studied widely and shown to be successful for large scale applications to perchlorate contaminated groundwater and soil [62]. As for ex-situ remediation, a general review of pilot and full-scale applications of bioreactors is available [63]. Several kinds of biological reactors, such as CSTR (Continuous flow Stirred Tank Reactor), PBR (Packed Bed Reactor), FBR (Fludized Bed Reactor), were reviewed for application to perchlorate degradation. In-situ remediation technologies have also been used to treat perchlorate contaminated groundwater and have been shown to be effective [2, 11]. However, no large-scale biological drinking water treatment plants exist in the United States due to concerns for microorganisms remaining in the water after treatment [17].

2.5 Titanium Chemistry

Titanium can exist in several redox states. The zero-valent or metallic titanium (Ti(0)) has a strong tendency to form a tight oxide film on its surface, which nearly eliminates the ability of the metal to undergo further redox reactions [64]. This kinetic limitation means that Ti(0) is not an effective reductant and will not be oxidized when placed in solutions of typical oxidants such as oxygen. However, if a high enough cathodic (positive) potential is imposed on the metallic titanium, it will oxidize by a mechanism called pitting corrosion, where the oxide film is broken. The potential where oxidation begins under given solution conditions is called the pitting potential.

The stable form of titanium in oxidized solutions is Ti(IV). Under reducing conditions, Ti(II) (Ti^{2+}) and Ti(III) (Ti^{3+}) can form [64]. Ti(0), Ti(II) and Ti(III) can all act as reductants, but Ti(0) and Ti(II) are particularly strong reductants thermodynamically [41].

$$TiO_2(s) + 4\,H^+ + 4\,e^- = Ti + 2\,H_2O \qquad E^0 = -2.132 \text{ volt}, pe^0 = -36.14$$

$$TiO_2(s) + 4\,H^+ + 2\,e^- = Ti^{2+} + 2\,H_2O \qquad E^0 = -0.502 \text{ volt}, pe^0 = -8.51$$

$$TiO_2(s) + 4\,H^+ + e^- = Ti^{3+} + 2\,H_2O \qquad E^0 = 0.398 \text{ volt}, pe^0 = 6.74$$

Ti(0), Ti(II) and Ti(III) are all sufficiently strong reductants to have the thermodynamic ability to reduce perchlorate [41].

$$ClO_4^- + 8\,H^+ + 8\,e^- = Cl^- + 4\,H_2O \qquad E^0 = 1.389 \text{ volt}, pe^0 = 23.55$$

Since any of the three titanium species that are not fully oxidized (Ti(0), Ti(II), Ti(III)) could be released from a titanium electrode during pitting corrosion, all of them are potential reductants for perchlorate during electrochemical treatment. Ti(II) could remove an oxygen atom from perchlorate in a single step and form chlorate (ClO_3^-), which has been observed to be reduced more than one thousand times more rapidly than perchlorate [46].

$$Ti^{2+} + ClO_4^- = TiO^{2+} + ClO_3^-$$

This type of oxygen-abstraction method of chemical reduction is theorized to be the mechanism for the rapid reduction of perchlorate by methylrhenium dioxide [43] and the slow reduction by other metals [65]. Therefore, Ti(II) is hypothesized to be the active reductant formed during pitting corrosion of titanium metal during electrochemical destruction of perchlorate.

Very little is known about the aqueous chemistry of Ti(II) and what is known has been reported recently [25, 26, 66, 67]. Its presence in aqueous solution was demonstrated by Kölle and Kölle in 2003, who developed a method for producing Ti(II) by dissolution of Ti(0) in the presence of fluoride. They characterized the visible absorbance spectra of Ti(II) as having maxima near 430 nm and 650 nm.

$$2\ Ti + 6\ F^- + 6\ H^+ = Ti^{2+} + TiF_6^{2-} + 3\ H_2$$

Yang and co-workers have used this procedure to generate Ti(II) and examine its ability to reduce a variety of compounds, but they have not investigated perchlorate as an oxidant [26, 28, 66, 67]. They calculated the concentration of Ti(II) in their solutions by having it react completely with $[Co(NH_3)_5F](ClO_4)_2$ and measuring the concentration of the product ($CoCl_4^{2-}$) by its absorbance at 692 nm [28].

$$Ti + 2Co^{3+} = Ti^{4+} + 2Co^{2+}$$

They compared reaction rate constants to determine whether Ti(II) or Ti(III) was the faster reductant. Their kinetic studies showed that Ti(II) reacted more rapidly with five oxidants ($[NDS\cdot]^{2-}$, Bzqn, $CoA_5(H_2O)^{3+}$, CoA_5F^{2+}, CoA_5Cl^{2+}) and Ti(III) reacted more rapidly with two oxidants (CHBzqn, $Co(C_2O_4)_3^{3-}$) [26]. Recently, Dhar et al. evaluated reduction of Cr(IV), Cr(V) and Cr(VI) by Ti(II) and Ti(III) and they concluded that reaction rates of both reductants are ‘remarkably similar’ [28]. Thus, it is not clear which is generally the faster reductant.

CHAPTER III

PERCHLORATE DEGRADATION USING DIVALENT TITANIUM

3.1 Introduction

Aqueous perchlorate ion is well known for remarkable inertness at normal temperature toward many reducing complex-forming agents, so perchlorate salt solutions are often used to provide a background electrolyte for water chemistry experiments [13]. Furthermore, it has little tendency to precipitate as a solid, so it tends to be found in aqueous solution and is mobile in the environment. Although redox reactions are slow and require extreme conditions, there are a few studies of perchlorate being reduced chemically using transition metal ions, zero-valent metals and several metal electrodes [27, 44-47, 50]. However, the chemical reduction of perchlorate is usually too slow to be used as a treatment process. Other studies have reported reduction of perchlorate at faster rates, but they need high temperature, pressure, or both [18, 22]. It has been reported that the high activation energy of perchlorate results in its low reactivity in redox reactions [13]. The high activation energy originates from its molecular structure and electronic configuration. Perchlorate ion has a tetrahedron structure in which the chlorine atom is surrounded with four oxygen atoms that defend it from direct attack by chemical reductants [17].

Titanium can exist in four oxidation states: 0, II, III and IV. The zero-valent or metallic titanium (Ti(0)) has a strong tendency to form a tight oxide film on its surface, which nearly eliminates the ability of the metal to undergo further redox reactions [64]. Therefore, Ti(0) is not an effective reductant by itself and will not be oxidized when placed in solutions of typical oxidants such as oxygen. A new treatment method using titanium metal has been developed for destroying perchlorate [17]. If a high enough cathodic potential is imposed on the metallic titanium, it will be oxidized by a mechanism called pitting corrosion, where the oxide film is broken. Thus, perchlorate reduction was believed to be caused by an active reductant (e.g. dissolved Ti(II)) [17]. However, the presence of chloride and bromide greatly inhibit the rate of perchlorate reduction, thus its application to waters such as ion exchange regenerant containing high concentration of chloride might not be economical [17]. Also, the high voltages required for development of pitting corrosion on Ti(0) result in high energy cost. Research on developing this process showed that ions such as Ti(II) and Ti(III) produced by partial oxidation of Ti(0) can be effective reductants for perchlorate in the aqueous state. Very little is known about the aqueous chemistry of Ti(II), but a method for producing Ti(II) has been developed and its ability to reduce various contaminants has been examined by several researchers [25, 26, 66, 67]. Kölle and Kölle developed a method for producing Ti(II) by reductive dissolution of Ti(0) in the presence of fluoride and characterized the visible absorbance spectra of Ti(II) as having maxima near 430 nm and 650 nm.

$$2\ \mathrm{Ti} + 6\mathrm{H}^{+} + 6\mathrm{F}^{-} = \mathrm{Ti}^{2+} + \mathrm{TiF}_6^{2-} + 3\mathrm{H}_2 \qquad (3.1)$$

Yang and co-workers have used this procedure to generate Ti(II) and examined its ability to reduce a variety of compounds, but they have not investigated perchlorate as an oxidant [26, 66, 67].

In this present work, the basic characteristics of Ti(II) solutions were examined, methods to optimize its production were developed, and its ability to reduce perchlorate was evaluated. Also, several metal catalysts were evaluated for enhancing the Ti(II)-perchlorate reaction and a kinetic model was proposed to predict the rate of perchlorate reduction and how it is affected by environmental factors. A treatment process for perchlorate that is based on partially oxidized titanium ions has potential advantages, because these ions are stable and the process that uses them is easily applicable to solutions with high ionic strength such as waste ion exchange regenerant. The objectives of research reported in this chapter are to: 1) Optimize methods for producing Ti(II); 2) Characterize destruction of perchlorate by Ti(II); 3) Evaluate the ability of metal catalysts to promote faster reaction; 4) Model the chemical reduction of perchlorate using Ti(II).

3.2 Materials and Methods

3.2.1 Chemicals

All experiments were conducted in an anaerobic chamber filled with a mixed gas containing 5 % hydrogen and 95 % nitrogen. Deionized water was purged with 99.99 % argon for 2 hours and kept in an anaerobic chamber until use. Sodium perchlorate, titanium powder (325 mesh, 99.98%), hydrofluoric acid (48%), hydrochloric acid (37-38%), sulfuric acid (5 N), potassium fluoride (99%), sodium molybdate (Na_2MoO_4), copper(II) chloride dehydrate ($CuCl_22H_2O$), nickel chloride hexahydrate ($NiCl_26H_2O$), ammonium perrhenate (NH_4ReO_4) and sodium tungstate (Na_2WO_4) have been purchased from Fisher Scientific. All chemicals were used as received without further purification unless otherwise noted.

3.2.2 Batch reactor

Batch kinetic experiments were conducted in 250-mL polyethylene bottles (Nalgene). Solution volume was 100 mL and 1 mL of sample was taken at specific time intervals. Glass-wares were not used during the experiments in order to avoid possible reactions with HF. Ti(II) solutions were prepared using the method of Kölle and Kölle[25], which is conducted by dissolving Ti(0) powder with F^- in the presence of various concentrations of HCl and H_2SO_4. The HCl and H_2SO_4 were used directly or diluted with deionized water to achieve appropriate concentrations. The F^- concentrations were adjusted by dissolving designated amounts of KF in acid solutions. Times for complete dissolution of Ti(0) particles will vary from several minutes to hours depending on initial concentrations of Ti(0), H^+, and F^-. All Ti(II) solutions were prepared in polyethylene bottles that had enough head space to prevent overflow of solutions due to violent hydrogen gas evolution. Attempts were made to enhance perchlorate reduction with Ti(II) by adding 1 mM of Na_2MoO_4, $CuCl_22H_2O$, $NiCl_26H_2O$, NH_4ReO_4 and Na_2WO_4.

3.2.3 Analytical procedures

Concentrations of perchlorate were determined using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column. Since many samples contained high concentrations of F^-, Cl^- or SO_4^{2-}, there were interferences in the analysis of reduction products of ClO_4^- such as ClO_3^-, ClO_2^- and Cl^-. Additionally, some samples contained high concentrations of H^+ and dissolved Ti ions that could damage the analytical and guard column if analyzed directly. Therefore, these samples were immediately diluted with 1.0 ~ 1.5 N NaOH in order to precipitate dissolved Ti metal ions. The precipitated sample was filtered with 25-mm diameter nylon filter (Whatman, 0.22 µm) and stored in a refrigerator until analysis. Absorption spectra of Ti(II) solutions were measured using a UV-VIS spectrophotometer (Hewlett Packard G1103A).

3.3 Results and Discussion

Previous research on divalent titanium (Ti^{2+}) has been generally limited to solid state compounds and very little is known on aqueous chemistry of Ti(II). A general procedure for producing aqueous divalent titanium has been published and it is based on dissolving titanium metal in acids that contains HF as shown in equation (3.1). However, the method is not optimized for producing Ti(II) solutions. Thus, the objectives of this research are to discover optimal conditions for production of Ti(II) solutions, apply them to degradation of perchlorate ions and examine the chemical reduction mechanism. Two kinds of experiments were conducted to achieve these objectives. First, UV spectra of Ti(II) solutions were studied to investigate the basic characteristics of solutions produced under different conditions. Second, batch kinetic experiments were conducted and the data were used in nonlinear regressions to estimate the amount of Ti(II) produced and values of the reaction rate constants. Because ‘the aqueous chemistry of Ti(II) is almost unknown’[25], there is no quantitative method yet to measure its concentration analytically so nonlinear regression were used to estimate the concentration of Ti(II) initially present in the solutions by their abilities to degrade perchlorate. Relationships were determined between the concentration of Ti(0) added and the concentration of Ti(II) formed, as well as between the concentration of HCl and the concentration of Ti(II) formed. These relationships were used to specify initial concentrations of Ti(II) for some experimental data sets, where it could not be accurately determined by regression.

Experiments were conducted if four stages. The first stage included studies of UV spectra and batch kinetic experiments that evaluated the effects of two acid types (HCl, H_2SO_4), two acid concentrations (1 N, 5 N) and two Ti(0) concentrations (80 mM, 160 mM). The second stage further evaluated the effects of concentration of Ti(0) (10, 25, 50, 100, 200 mM), concentration of acid (1.2, 1.9, 4.7, 8.2, 10 N), and acid type (HCl, H_2SO_4). The third stage of this research investigated the effect of F/Ti(0) molar ratio (0.5, 1.0, 2.0, 3.0, 6.0, 10.0) on the production of Ti(II) and the ability of Ti(II) to reduce perchlorate to chloride. In the last stage, metal catalysts (Mo, Cu, Ni, Re, W) were tested for their ability to enhance the rate of chemical reaction between perchlorate and Ti(II).

The experimental data for perchlorate concentration as functions of time were analyzed by non-linear regressions to evaluate a second-order kinetic model and to determine its coefficient. The second-order kinetic model was applied to a batch reactor to generate the differential equation that describes how the concentration of perchlorate should change during experiments. The reaction rate coefficient k was obtained by least-squares non-linear regression using MATLAB (MathWorks Inc.) function “nlinfit”.

Solutions to the model were determined using the MATLAB function “ode45” which solves equation (3.2) numerically by a fourth order Runge-Kutta method. The stoichiometry shown in equation (3.3) is used to express the concentration of the titanium ion in terms of the concentration of perchlorate to give a differential equation in one independent variable that can be solved.

$$\frac{d[ClO_4^-]}{dt} = -k[ClO_4^-][Ti^{2+}] \tag{3.2}$$

$$4Ti^{2+} + ClO_4^- + 8H^+ \ \rightarrow\ 4Ti^{4+} + Cl^- + 4H_2O \tag{3.3}$$

The nonlinear regression procedure chooses parameters to minimize the sum of squared residuals (SSR). A relative fitting error parameter (RFEP) was calculated using SSR in order to numerically compare the fitting error among data sets. It is the ratio of the standard deviation of the data points about regression line divided by the average value of the data. As such, it represents the ratio of an average error to the average value. Smaller values represent better fits (lower errors) of the model to the data.

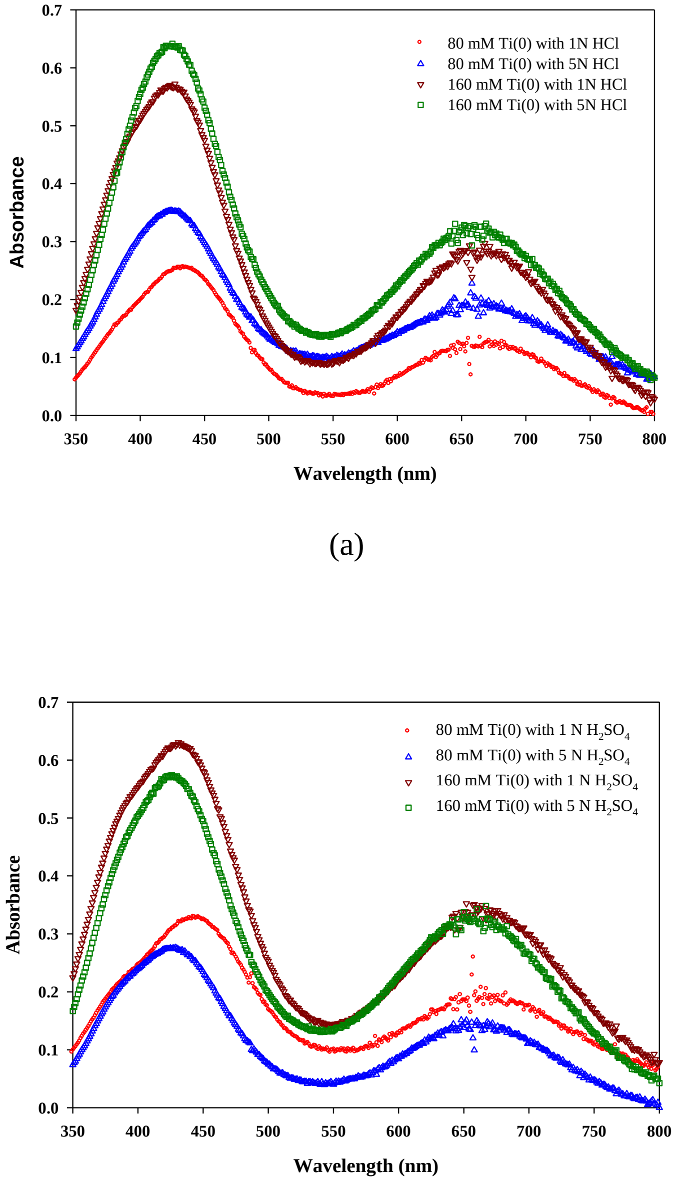
$$RFEP = \frac{\sqrt{\frac{SSR}{n-2}}}{\overline{C}} \tag{3.4}$$

where SSR is the Sum of Squared Residuals; n is number of data points; $\overline{C}$ is the average perchlorate concentration

3.3.1 Effect of acid type, acid concentration and Ti(0) concentration

According to the published report on the method for producing Ti(II) which is shown in equation (3.1) [25], concentrations of initial titanium, proton and fluoride could influence on production of Ti(II) in solution. Thus, the effects of acid concentration and acid type, and initial Ti(0) concentrations on the absorption spectrum of Ti(II) were investigated. Solutions of both HCl and H_2SO_4 at concentrations of both 1 N and 5 N were used with initial Ti(0) concentration of 80 mM and 160 mM. Fluoride concentrations were three times higher than Ti(0) concentrations, which is based on the stoichiometric equation (3.1) for production of Ti(II).

Figure 3.1 shows that the absorption spectra of Ti(II) solution have two peaks at 430 nm and 660 nm. When the concentration of Ti(0) increases from 80 mM to 160 mM, the absorption of the two peaks increased with by a factor of 2 for both kinds of acids. This indicates that the amount of Ti(II) produced is proportional to the amount of metallic titanium consumed. Also, when the concentration of HCl increases from 1 N to 5 N, the absorption of the two peaks increased for both concentrations of titanium. This indicates that the concentration of HCl influences the production of Ti(II). Comparing Figures 3.1(a) and 3.1(b) shows that higher H^+ concentrations produce higher absorbance at both peaks when HCl is used as proton source. This indicates that higher concentrations of HCl enhance the production of Ti(II) ions. In contrast, when H_2SO_4 is used, higher H^+ concentrations generate lower absorbance at both peaks.



(a)

(b)

Figure 3.1. Absorption spectra of Ti(II) solutions produced by (a) HCl and (b) H_2SO_4 at two concentrations and at two initial concentrations of Ti(0). Molar ratio of F/Ti(0) is 3.

To investigate the ability of Ti(II) to reduce perchlorate, batch kinetic experiments were conducted. Figures 3.2 and 3.3 show perchlorate degradation by Ti(II) using two different acids at two concentrations. The acid types were the same as those used to develop the UV spectra (Figure 3.1). Figure 3.2 shows that perchlorate was removed gradually over time and higher HCl and initial Ti(0) concentrations resulted in faster rates of perchlorate reduction. The experimental data (perchlorate concentration as function of time) were analyzed by nonlinear regression to further investigate the chemical reaction mechanism. Values of rate constants (Equation 3.2) and initial concentrations of Ti(II) were calculated using MATLAB to best fit the experimental data for experiments 1-8 that were shown in Figures 3.2 and 3.3. These values are presented in Table 3.1 with their 95% confidence intervals and they are shown in Figure 3.4. Points with confidence intervals in Figure 3.4(a) represent the initial concentrations of Ti(II) that were determined by regression for different doses of Ti(0) when two different concentrations of HCl were used. Figure 3.4(a) shows that these initial concentrations of Ti(II) are proportional to Ti(0) concentrations for both 1 N and 5 N HCl. Figure 3.4(b) replots the data in Figure 3.4(a) to show the effect of HCl concentrations. It shows that HCl concentration also increases the production of initial Ti(II) for both Ti(0) concentrations. Figure 3.4(c) shows that higher HCl concentration increases the rate constant, but that there is no effect of initial concentration of Ti(0) to be seen.

Accordingly, two assumptions were made based on these results: 1) the amount of Ti(II) produced is proportional to the dose of Ti(0), 2) the amount of Ti(II) produced increases linearly with HCl concentrations. The first assumption is reasonable because the experimental data showed a linear increase with zero intercept. The second assumption is justified because there is no available literature data that describes the relationship between Ti(II) and HCl and the linear assumption is the simplest relationship for two points. Two lines in Figure 3.4(a) are linear regression lines based on the first assumption applied with two different HCl concentrations (1N and 5 N). Equations (3.5) and (3.6) are equations for those linear regression lines. They will be used to predict the initial Ti(II) concentration in experiments with 300 mM of Ti(0) The calculated concentrations of Ti(II) expected with a dose of 300 mM Ti(0) were plotted in Figure 3.4(a) and (b) using rectangular symbols without error bars. These two points were used with the second assumption to develop Equation (3.7) in order to predict initial Ti(II) concentrations with different HCl concentrations when the dose of Ti(0) is 300 mM.

$$Ti(II)_0 = 0.248 \times Ti(0)_0 \qquad R^2=0.982 \quad \text{in 1 N HCl} \tag{3.5}$$

$$Ti(II)_0 = 0.384 \times Ti(0)_0 \qquad R^2=0.999 \quad \text{in 5 N HCl} \tag{3.6}$$

$$Ti(II)_0 = 10.2 \times [HCl] + 64.3 \quad \text{With 300 mM Ti(0)} \tag{3.7}$$

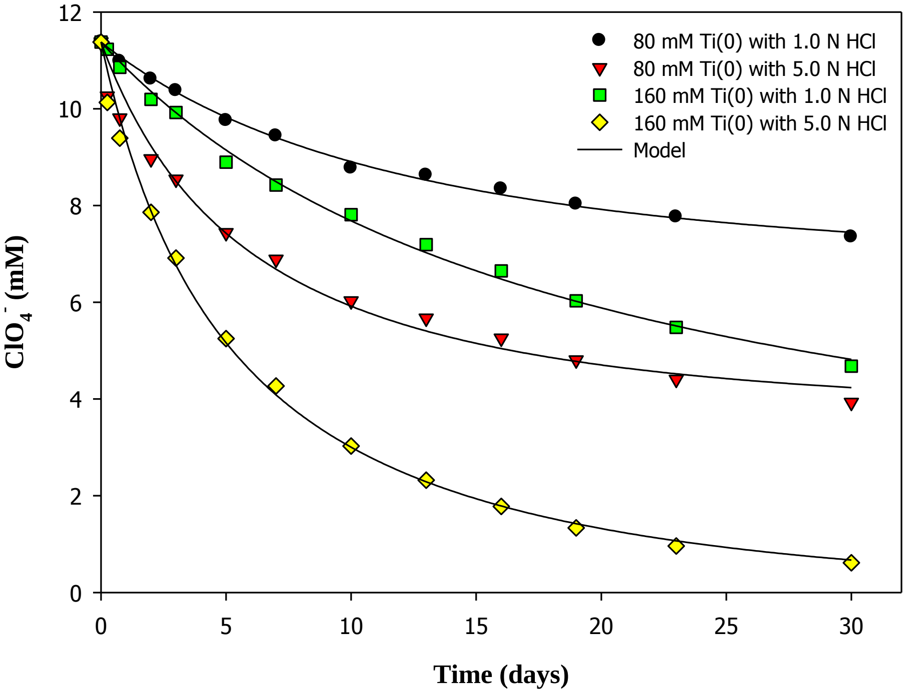


Figure 3.2. Perchlorate reduction by Ti(II) solutions produced in HCl. Molar ratio of F/Ti(0) is 3. The solid lines represent model predictions.

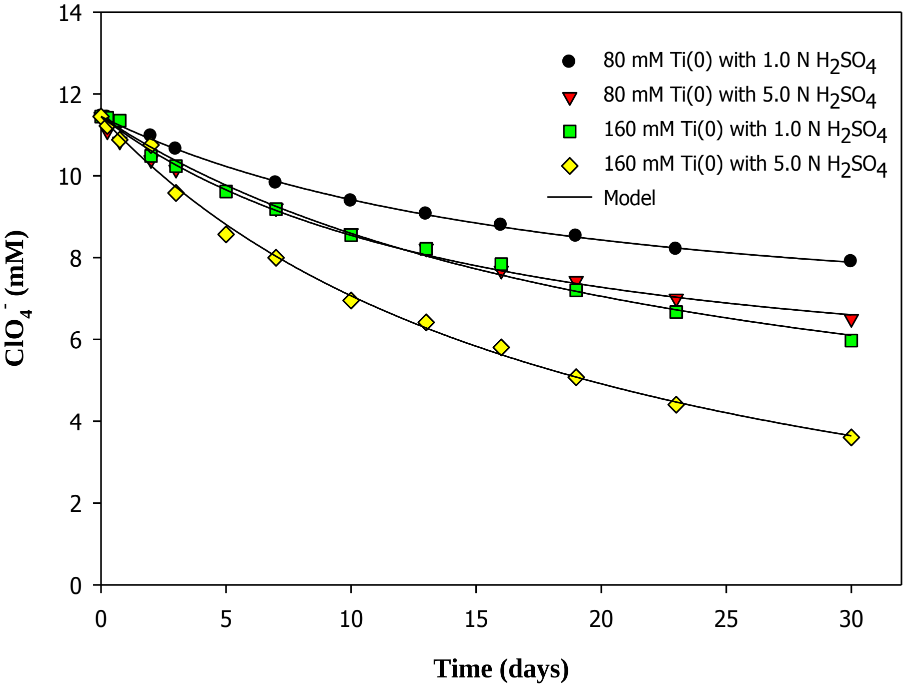
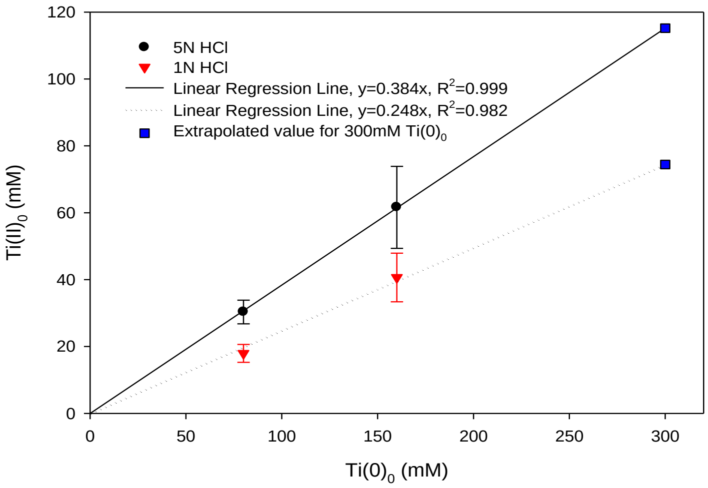
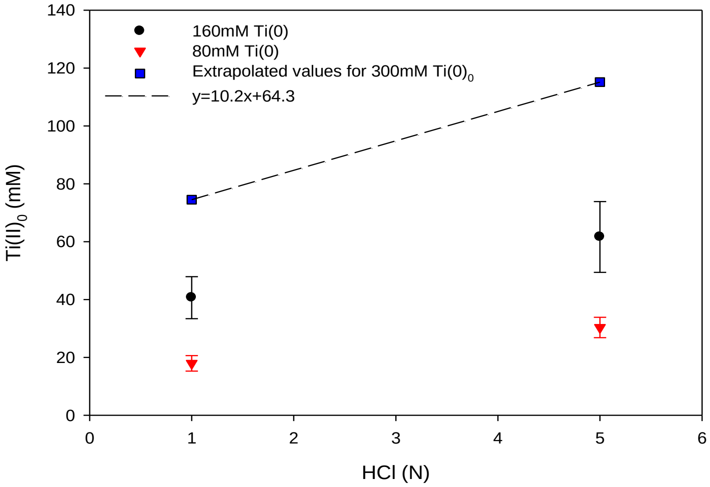


Figure 3.3. Perchlorate reduction by Ti(II) solutions produced in H_2SO_4. Molar ratio of F/Ti(0) is 3. The solid lines represent model predictions.



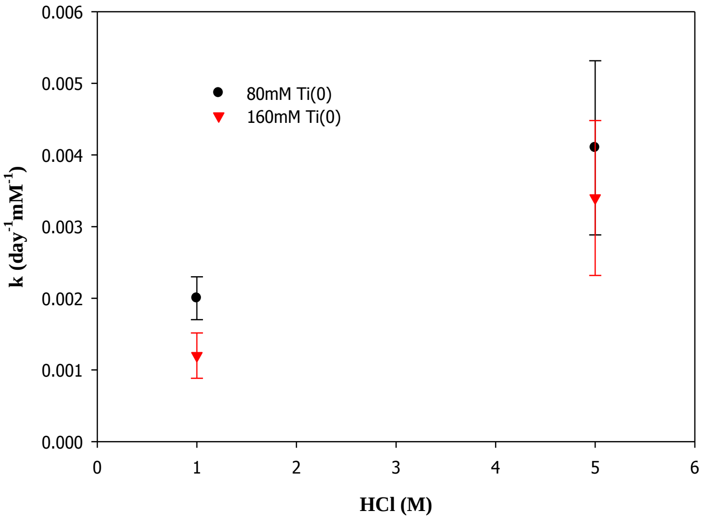
(a)



(b)

Figure 3.4. (a) Initial concentration of Ti(II) obtained by non-linear regression as a function of initial Ti(0) concentration for different HCl concentrations.

(b) Initial concentration of Ti(II) obtained by non-linear regression as a function of HCl concentration for different initial concentrations of Ti(0).

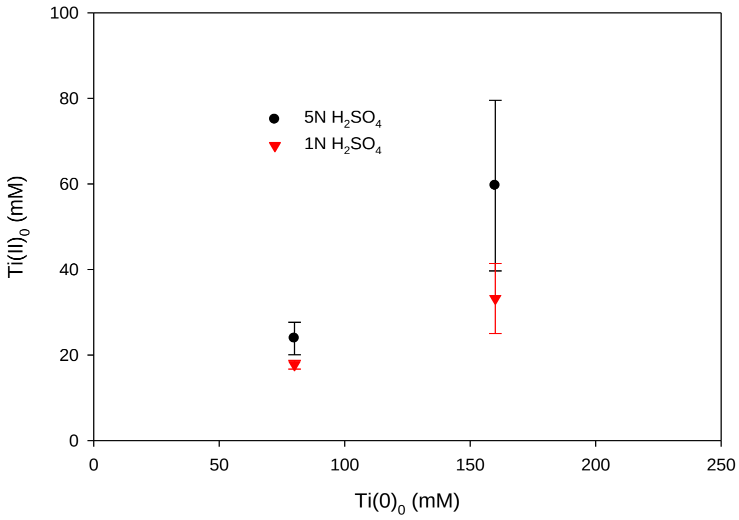


(c)

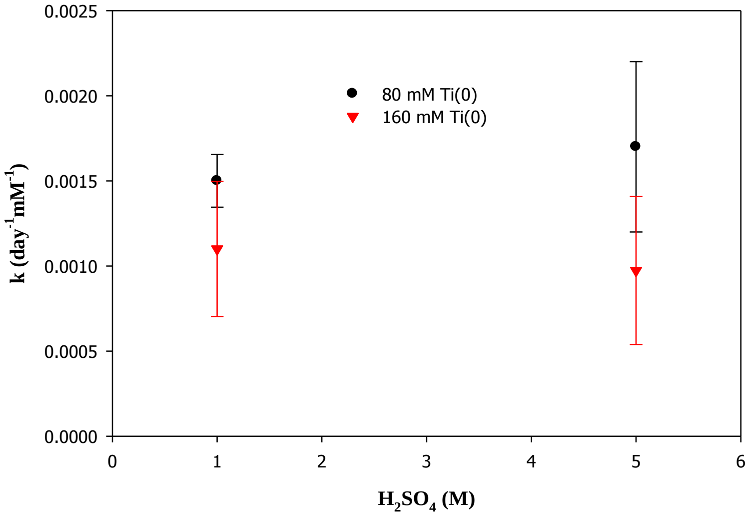
Figure 3.4 Continued. (c) Perchlorate reduction rate constant as function of HCl concentrations for different initial concentrations of Ti(0). Error bars are 95% confidence intervals.

Figure 3.3 shows perchlorate reduction observed when H_2SO_4 was used to prepare Ti(II). Comparing Figures 3.2 and 3.3, the Ti(II) solution produced with HCl shows faster reduction of perchlorate than that produced with H_2SO_4. Faster reduction could be the result of formation of more Ti(II) or the presence of conditions that result in faster reaction at the same concentration of Ti(II).

Figure 3.5(a) shows that initial concentrations of Ti(II) determined by the regressions are higher for higher initial Ti(0) concentrations. This means that a higher dose of Ti(0) increases the production of Ti(II) when sulfuric acid is used, similarly to what was observed when HCl was used. However, there appears to be a small overlap of the 95% confidence limits for the initial concentrations of Ti(II) in 1 N H_2SO_4 and 5 N H_2SO_4 when 160 mM of Ti(0) was used. Thus, it is not necessarily true that the effect of H_2SO_4 concentration is significant to the production of Ti(II). Figure 3.5(b) shows that the confidence limits for both pairs of data points overlap each other, so there is no significant effect of Ti(0) on the rate constant. Thus, it is not possible to distinguish significant effects of concentrations of Ti(0) and H_2SO_4 on perchlorate reaction rate constants with the given data.



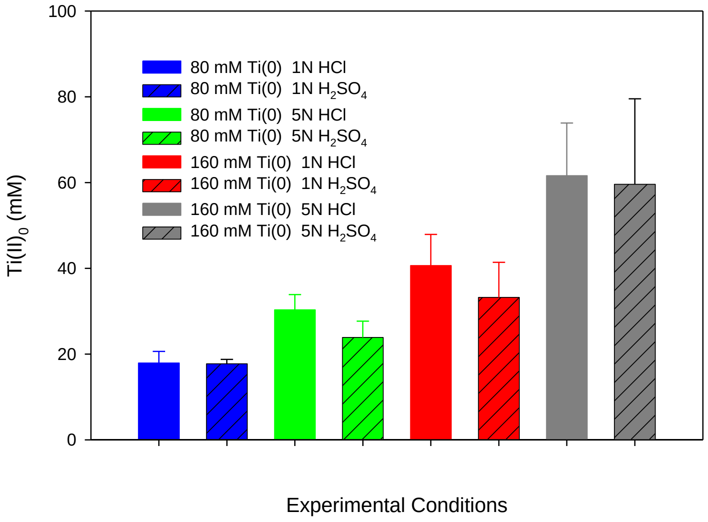
(a)



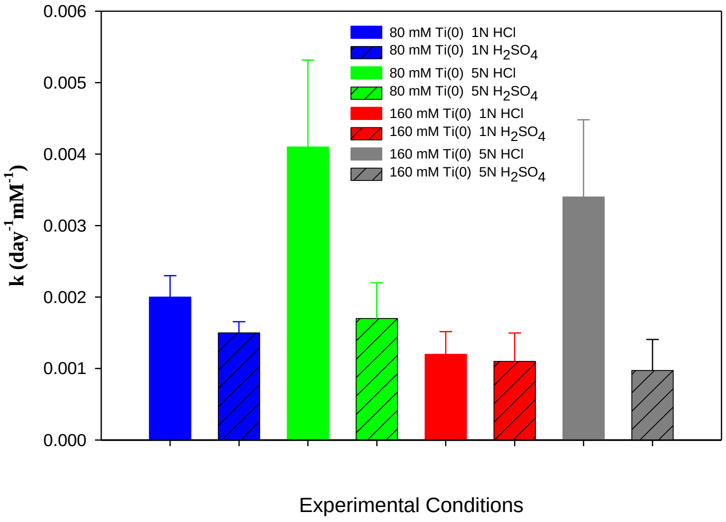
(b)

Figure 3.5. (a) Initial concentration of Ti(II) obtained by non-linear regression as a function of initial Ti(0) concentration for different H_2SO_4 concentrations (b) Perchlorate reduction rate constant as function of H_2SO_4 concentrations for different initial concentrations of Ti(0). Error bars are 95% confidence intervals.

To evaluate the effect of each acid type on production of initial Ti(II) and reduction of perchlorate, Figure 3.6 was drawn with the same data used to produce Figures 3.4 and 3.5. The concentrations of Ti(II) produced with HCl and H_2SO_4 have a maximum difference of 21% when Ti(0) concentration is the same (Figure 3.6(a)). However, Figure 3.6(b) shows that the reaction rate constants with H_2SO_4 are significantly smaller than those with HCl when 5 N acid was used at the same Ti(0) concentrations. The maximum difference in rate constants caused by acid type is 78%, when 160 mM of Ti(0) and 5 N of acid were used. This means that the slower reaction of perchlorate in the presence of H_2SO_4 is not due to a smaller amount of Ti(II) being produced, but to a slower reaction rate when H_2SO_4 is present. This difference could be the result of different pH in these solutions. The pK_a values for HCl and H_2SO_4 are both about the same (pK_a = -3), but the second pK_a for H_2SO_4 is 1.96 [68]. Therefore, when concentrations of HCl and H_2SO_4 are equal on an equivalent basis and greater than or equal to 1 N, more hydrogen ions will be released in solutions of HCl and this could enhance the rate of perchlorate reduction.



(a)



(b)

Figure 3.6. (a) Comparison of initial Ti(II) concentrations for different conditions. (b) Comparison of perchlorate reaction rate constant for different conditions. Same color means equal acid concentrations but different acid types.

3.3.2 Further investigation on the effect of Ti(0) and HCl concentration

To investigate the effect of Ti(0) concentration on perchlorate degradation further, additional experiments were conducted for five different Ti(0) concentrations (10, 25, 50, 100, 200 mM) and four different HCl concentrations (1.2, 1.9, 4.7, 8.2 M). The results are shown in Figures 3.7 and 3.8. Figure 3.7 shows that perchlorate was completely degraded when the dose of Ti(0) was higher than 25 mM in the presence of 10 N HCl. Figure 3.8 shows complete degradation for all HCl concentrations when the Ti(0) dose was 300 mM. Higher concentrations of Ti(0) and HCl result in faster degradation of perchlorate.

The kinetic data were analyzed by calculating concentrations of initial Ti(II) and reaction rate constants. In the previous section, nonlinear regressions were used to calculate both initial Ti(II) concentrations and rate constants for experiments 1-8. These experiments showed that the concentration of perchlorate approached equilibrium, which means that all Ti(II) present initially was oxidized. Therefore, the experimental data contains sufficient information for a regression to determine the initial concentration of Ti(II) from the change in perchlorate concentration and reaction stoichiometry (Equation 3.3). This approach provides a good estimate of the initial Ti(II) concentration and results in more accurate calculation of rate constants. However, the kinetic experiments in this section (experiments 9-17) were faster and the initial perchlorate ions were completely degraded. Thus, it is difficult a regression to determine how much Ti(II) was present initially. Figure 3.7 shows five experiments with different Ti(0) concentrations and only of the one with the smallest Ti(0) (10 mM) approached equilibrium without complete degradation of perchlorate. Therefore, a nonlinear regression was used to calculate both initial Ti(II) concentration and rate constant for this experiment, but could not be used for the other experiments at higher Ti(0). The Ti(II) concentrations for experiments at higher Ti(0) (25, 50, 100, 200 mM) were calculated by assuming that the initial Ti(II) concentration would be proportional to the dose of Ti(0). The initial Ti(II) concentration obtained for at dose of 10 mM was used to develop Equation (3.8).

$$Ti(II)_0 = 0.32 \times Ti(0)_0 \tag{3.8}$$

for experiment 9-13

Figure 3.8 shows complete degradation of perchlorate for all HCl concentrations using a Ti(0) dose of 300 mM. Thus, it is difficult to estimate the concentration of initial Ti(II) by regression and the stoichiometric ratio between Ti(II) and perchlorate. Equation (3.7) was used to calculate initial Ti(II) concentrations and these values were used to calculate rate constants using nonlinear regression. The calculated values are shown in Table 3.1. Figure 3.9 shows that the rate constant increases when the concentration of HCl increases. Although there are no reports in the literature on reactions between perchlorate and Ti(II), a few researchers have studied perchlorate reduction by aqueous Ti(III) and they reported that the reaction rate constant increased linearly or with a second-order dependence on hydrogen ion concentration [27, 45, 51].

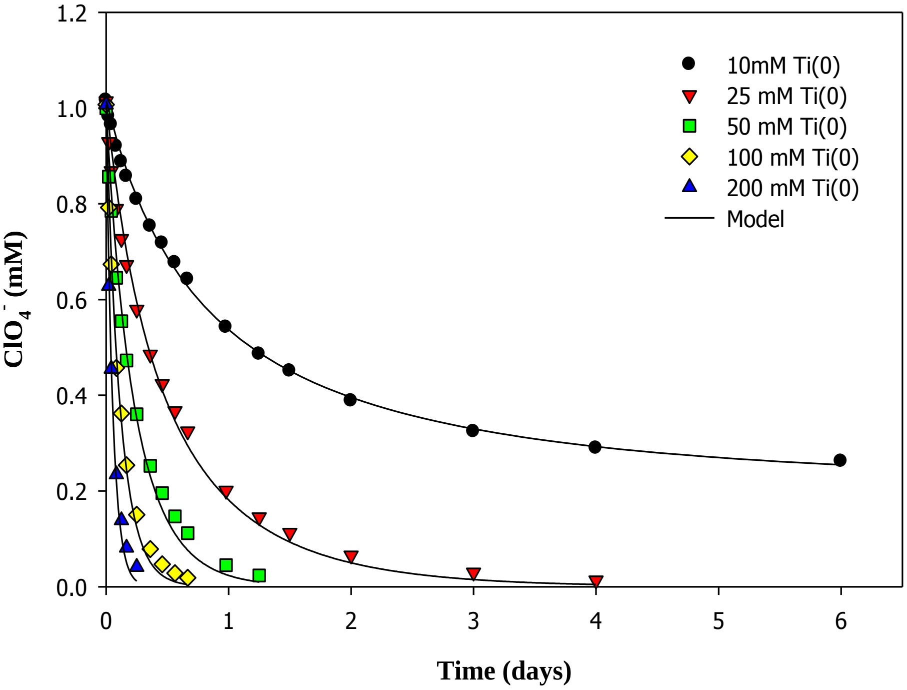


Figure 3.7. Influence of initial Ti(0) concentration on perchlorate reduction by Ti(II) produced in 10 N HCl. Molar ratio of F/Ti(0) is 0.1. The solid lines represent model predictions.

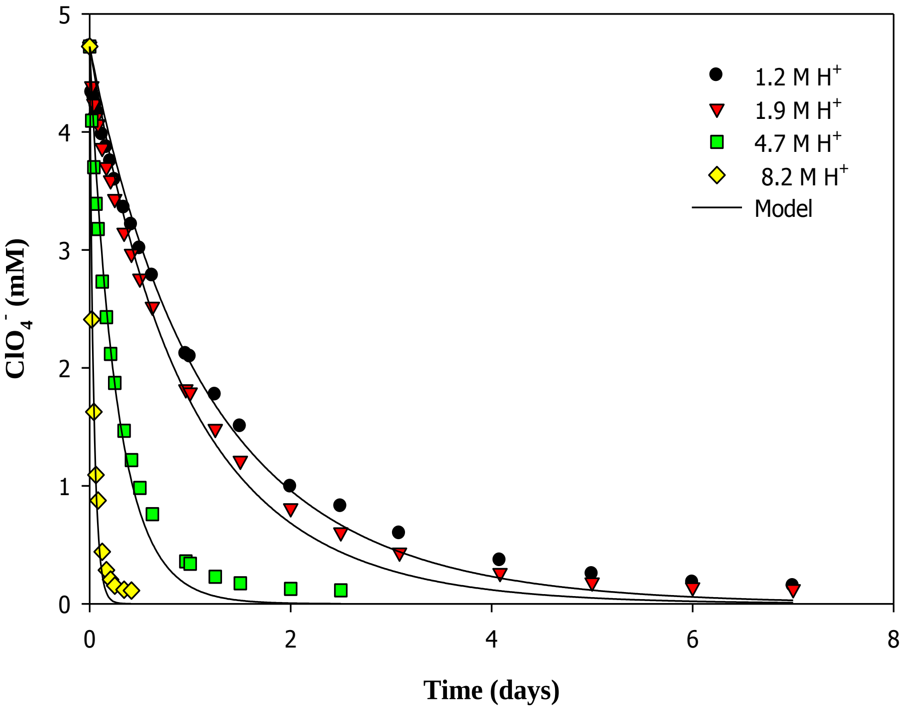


Figure 3.8. Influence of HCl concentration on perchlorate reduction by Ti(II). $[Ti(0)]_0$ is 300 mM, Molar ratio of F/Ti(0) is 0.1. The solid lines represent model predictions.

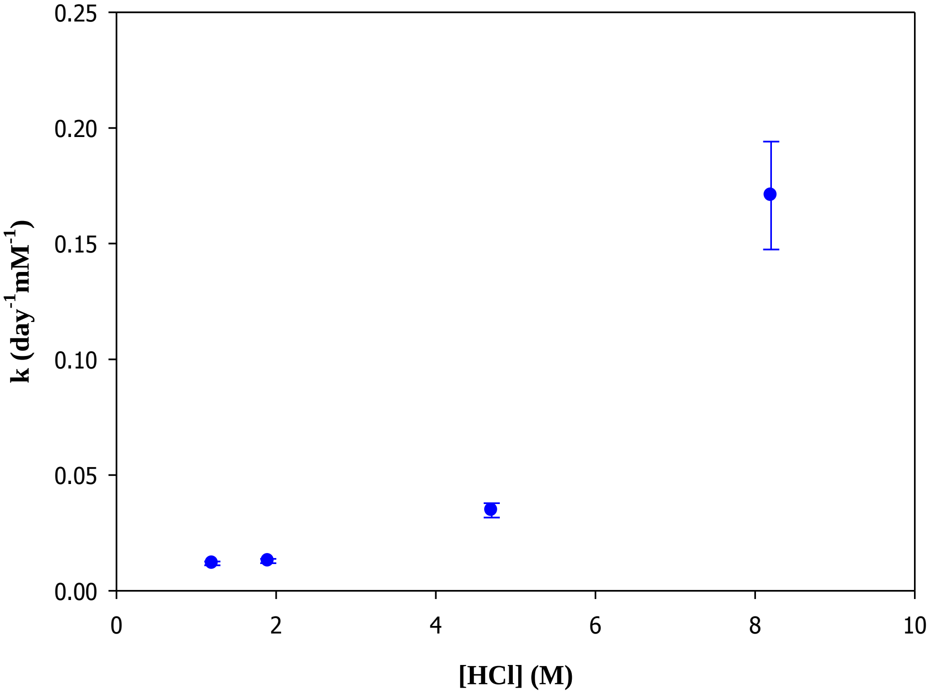


Figure 3.9. Perchlorate reduction rate constant with different HCl concentrations.

Error bars are 95% confidence intervals.

3.3.3 Effect of F/Ti(0) molar ratio

To investigate the effect of fluoride concentrations on production of Ti(II), six different concentrations were used with 5 N HCl, resulting in six different F/Ti(0) molar ratios (0.5, 1, 2, 3, 6, and 10). Figure 3.10 shows the absorption spectra of Ti(II) solutions produced under these conditions and they show how F^- influences both adsorption bands. When the F/Ti(0) molar ratio decreases, the absorbance at 430 nm gradually decreases and the peak is shifted to longer wavelength, while the absorbance of the peak at 660 nm decreases and shifts to shorter wavelength. However, at the lowest F/Ti(0) molar ratio of 0.5 (25 mM F^-), the peak at the lower wavelength is shifted to 480 nm, which is similar to the wavelength of peak absorbance of Ti(III) solutions, which is reported at 500 nm [51]. This implies that Ti(III) might be present in these solutions. Figure 3.11 shows the absorption spectra of Ti(II) solutions produced in 5 N H_2SO_4 solutions with various F/Ti(0) molar ratios (1, 2, 3, 6, and 10). These absorption spectra are not identical to those for Ti(II) solutions produced with 5 N HCl. When the F/Ti(0) molar ratio decreases, the two peaks became closer to each other, but did not form one peak, as was observed with HCl.

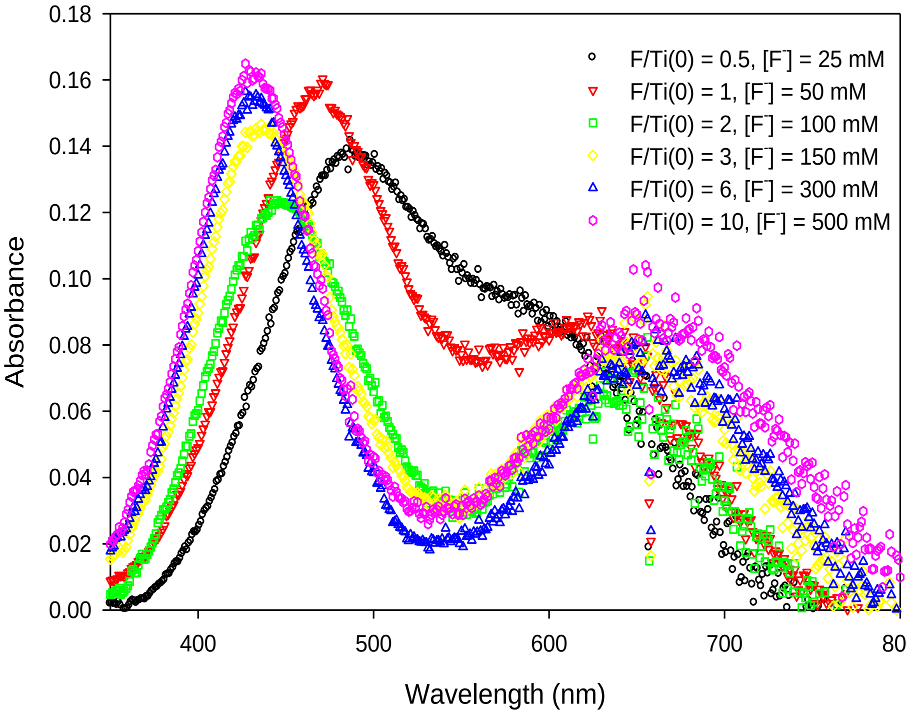


Figure 3.10. Influence of F/Ti(0) molar ratio on absorption spectra of Ti(II) in 5 N HCl solutions. [Ti(0)]$_0$ is 50 mM.

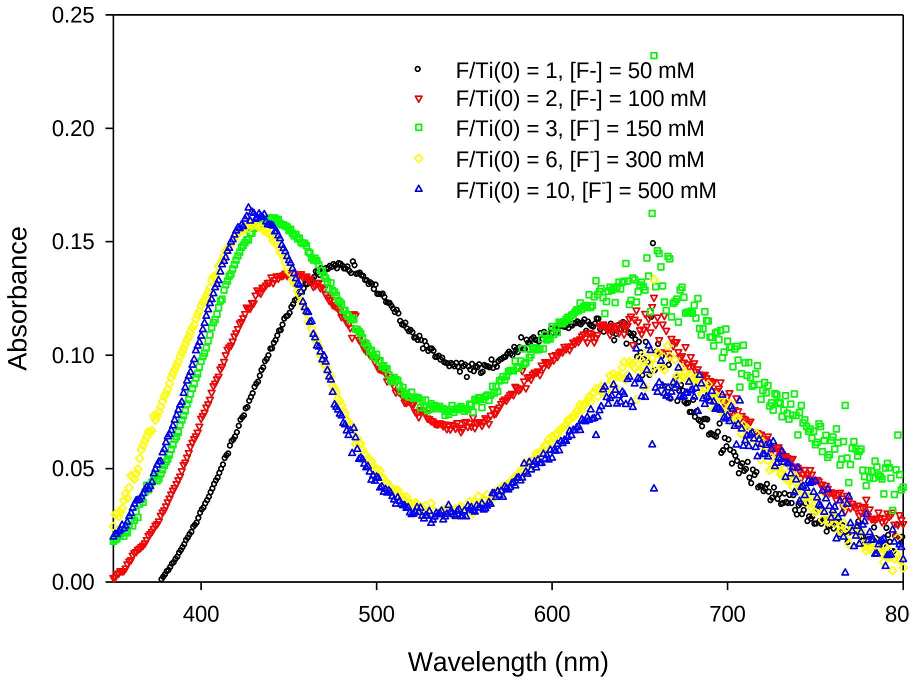


Figure 3.11. Influence of F/Ti(0) molar ratio on absorption spectra of Ti(II) in 5 N H_2SO_4 solutions. $[Ti(0)]_0$ is 50 mM.

Figure 3.12 shows results of batch kinetic experiments to examine perchlorate degradation with Ti(II) solutions having a range of F/Ti(0) ratio. The rate of perchlorate reduction is increased by decreasing the F/Ti(0) molar ratio. The faster reaction rate with lower F/Ti(0) ratio could be due to more production of Ti(II) or to a higher reaction rate constant. This means that fluoride can influence either the production of Ti(II) or its reaction with perchlorate, or both. The differences of maximum absorbance with different F/Ti(0) molar ratio in Figures 3.10 and 3.11 support the conclusion that F/Ti(0) molar ratio have some effect on production of Ti(II).

Kölle and Kölle proposed that 2 M Ti(0) dissolves with HF to make 1 M of Ti^{2+} and 1 M of Ti^{4+}. They explained that Ti^{4+} complexes with fluoride to make TiF_6^{2-}. The color of solutions of Ti(II), Ti(III) and Ti(IV) are known to be green, brownish red, and colorless, respectively [25]. In this present study, only a green color was observed throughout numerous batch experiments, so it is believed that Ti(III) was not present. According to another experimental study on complex formation between Ti(IV) and fluoride, $[Ti(OH)_2F]^+$, TiF_4^0 and $[TiHF_6]^{-1}$ are favorably produced with equilibrium constants equal to $10^{2.2}$, $10^{8.4}$ and $10^{11.5}$, respectively [69]. Another study on reactions between Ti(IV) and fluoride showed that complexes are formed such as $[TiOF(H_2O)_4]^+$, $[TiOF_2(H_2O)_3]$, $[TiF_3OH(H_2O)_2]$, $[TiF_4(H_2O)_2]$, $[TiF_5(H_2O)]^-$ and TiF_6^{2-} with formation constant with $10^{6.0}$, $10^{2.2}$, $10^{3.2}$, $10^{4.0}$, $10^{13.0}$, and $10^{2.2}$, respectively [70]. Additional researches support the formation of Ti(IV)-F complexes with different conditions [71-73]. Thus, it is believed that fluoride ions are depleted by reaction with Ti^{4+} in the experimental range of F/Ti(0) ratio in this present study.

Even though much fluoride exists in the solution, it will exist as HF (pK_a=3.17 >> pH). A previous study on proton-fluoride association in sodium perchlorate media (0~3 M) showed favorable formation of HF and HF_2^- with formation constants equal to $10^{3.0}$ and $10^{0.6}$ [74]. HF is known to be very stable in solutions with high concentrations of sodium perchlorate media (2~8 M) [75]. This stability has made perchlorate the most employed medium for fluoride equilibria studies [75]. All of this means that HF is favorably formed in aqueous perchlorate media and does not react with perchlorate. Therefore, it is reasonable to assume that F/Ti(0) does not influence concentrations of perchlorate and Ti(II), and consequently would not affect the reaction rate constant of perchlorate with Ti(II).

Accordingly, initial concentrations of Ti(II) used in the kinetic model were assumed to depend on fluoride concentration, but the rate constants were assumed to be independent of fluoride concentration. Results of nonlinear regressions to calculate initial Ti(II) concentrations are shown in Table 3.2 and Figure 3.14. Figure 3.13 shows that the rate of perchlorate degradation is only slightly increased by decreasing the F/Ti(0) molar ratio when sulfuric acid was used to produce Ti(II), compared to a bigger effect when HCl is used (Figure 3.12). The initial concentrations of Ti(II) and the reaction rate constants were calculated using same procedure described above and the values are shown in Table 3.2 and Figure 3.14. Figure 3.14 shows how the F/Ti(0) molar ratio influences the initial concentration of Ti(II) produced by both acids. Lower molar ratios of F/Ti(0) enhance the production of Ti(II) and HCl was more effective than H_2SO_4 in producing Ti(II).

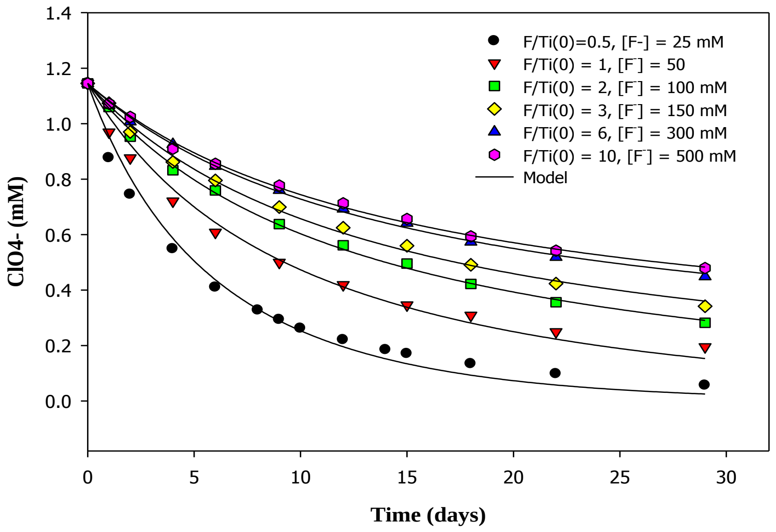


Figure 3.12. Influence of F/Ti(0) molar ratio on perchlorate reduction by Ti(II) in 5 N HCl solutions. $[Ti(0)]_0$ is 50 mM. The solid lines represent model predictions.

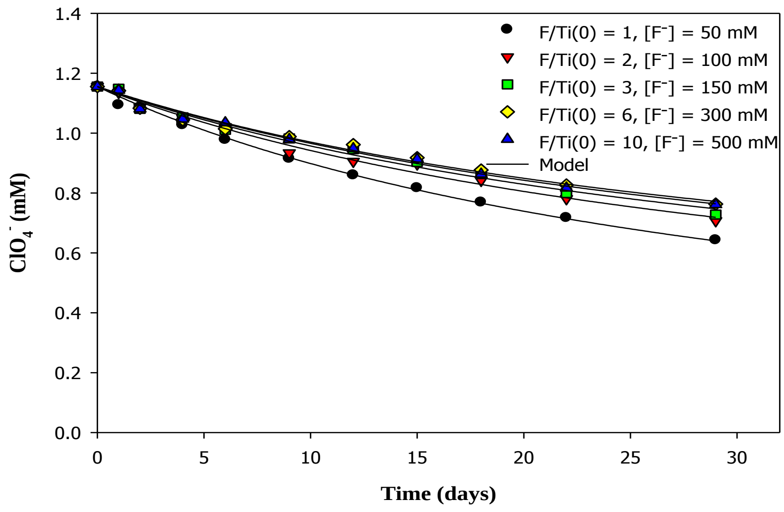


Figure 3.13. Influence of F/Ti(0) molar ratio on perchlorate reduction by Ti(II) in 5 N H_2SO_4 solutions. $[Ti(0)]_0$ is 50 mM.

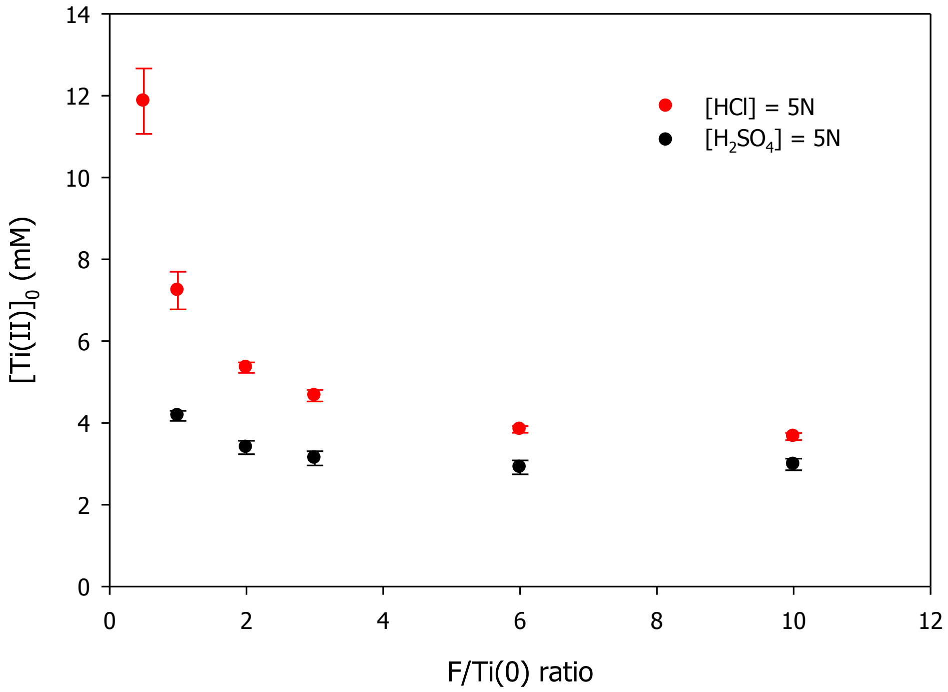


Figure 3.14. Initial concentration of Ti(II) with different F/Ti(0) molar ratio.

Error bars are 95% confidence intervals.

3.3.4 Effect of metal catalysts

Several metals (molybdenum, copper, nickel, rhenium, tungsten) were tested for their catalytic effect on perchlorate reduction by Ti(II) and the results are shown in Figures 3.15 and 3.16. Only rhenium was observed to have a catalytic effect on perchlorate degradation. The experimental conditions and values for rate constants are shown in Table 3.2. Initial concentration of Ti(II) was calculated using equation (3.5).

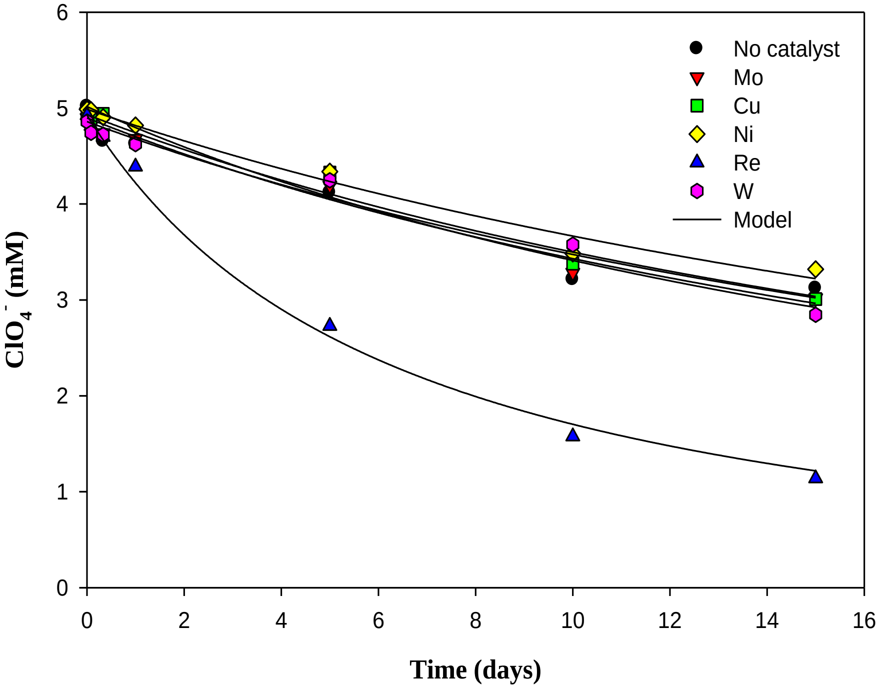


Figure 3.15. Perchlorate degradation using Ti(II) with catalysts.

$[Ti(0)]_0$ is 100 mM, [HCl] is 1.0 N, [HF] is 0.5 N, [Catalyst] is 1 mM, $[ClO_4^-]_0$ is 5 mM.

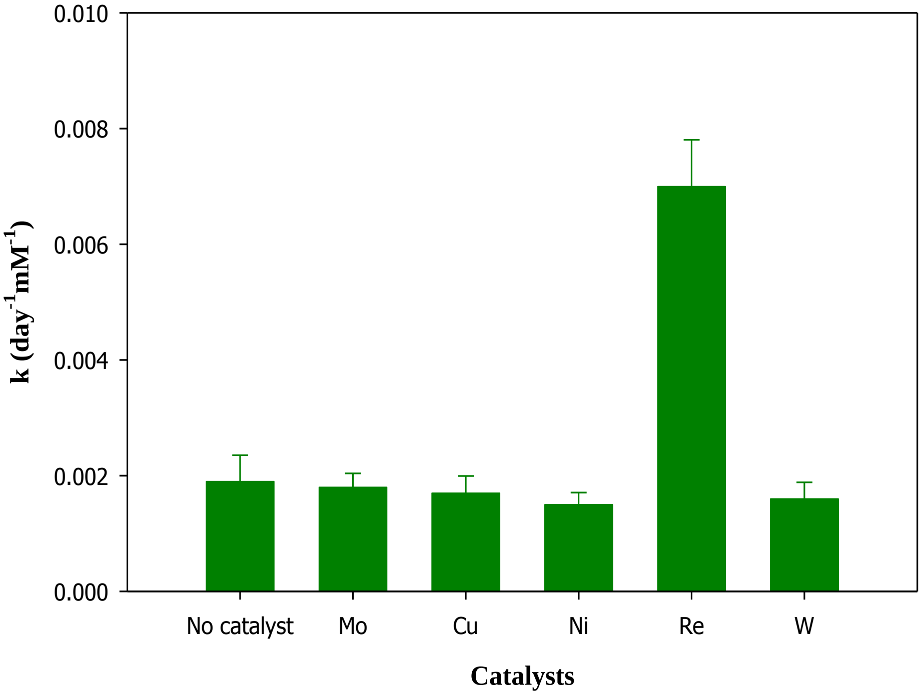


Figure 3.16. Perchlorate reduction rate constant with different kinds of catalysts.

Error bars are 95% confidence intervals.

Table 3.1 Comparison of perchlorate reducing systems with Ti(II).

Exp #	Ti(0) mM	$ClO_4^-{}_0$ mM	HCl or H_2SO_4 M	F^- mM	2nd order k[a] ± 95% C.I. $mM^{-1}day^{-1}$	$Ti(II)_0$[b] ± 95% C.I. mM	SSR[c] mM^2	RFEP[d]	Figure
1	80	11.4	[HCl]=1.0	240	2.00E-03±14.9%	17.9±7.4%	7.86E-02	9.00E-03	Figure 1(a) , 2, 4, 6
2	80	11.4	[HCl]=5.0	240	4.10E-03±29.6%	30.3±11.6%	1.35E+00	4.88E-02	
3	160	11.4	[HCl]=1.0	480	1.20E-03±26.4%	40.7±17.8%	2.01E-01	1.62E-02	
4	160	11.4	[HCl]=5.0	480	3.40E-03±31.8%	61.6±19.9%	7.18E-01	5.09E-02	
5	80	11.4	$[H_2SO_4]$=1.0	240	1.50E-03±10.3%	17.7±5.8%	1.63E-02	4.10E-03	Figure 1(b) , 3, 5, 6
6	80	11.4	$[H_2SO_4]$=5.0	240	1.70E-03±29.4%	23.9±16.0%	2.46E-01	1.73E-02	
7	160	11.4	$[H_2SO_4]$=1.0	480	1.10E-03±36.1%	33.2±24.6%	2.59E-01	1.69E-02	
8	160	11.4	$[H_2SO_4]$=5.0	480	9.73E-04±44.6%	59.6±33.3%	4.20E-01	2.47E-02	
9	10	1.02	[HCl]=10.0	1.0	1.63E-01±12.2%	3.2±3.0%	3.55E-02	1.55E-02	Figure 7
10	25	1.01	[HCl]=10.0	2.5	1.89E-01±8.2%	8.0	1.95E-02	6.19E-02	
11	50	1.00	[HCl]=10.0	5.0	1.89E-01±9.4%	16.0	1.53E-02	8.00E-02	
12	100	1.01	[HCl]=10.0	10.0	1.89E-01±8.0%	32.0	7.00E-03	7.47E-02	
13	200	1.01	[HCl]=10.0	20.0	1.98E-01±12.9%	64.0	6.40E-03	9.46E-02	
14	300	4.72	[HCl]=1.2	30	9.30E-03±7.2%	76.5	6.50E-01	6.57E-02	Figure 8, 9
15	300	4.72	[HCl]=1.9	30	1.09E-02±7.5%	83.7	7.09E-01	7.45E-02	
16	300	4.72	[HCl]=4.7	30	3.43E-02±9.0%	112.2	6.71E-01	1.11E-01	
17	300	4.72	[HCl]=8.2	30	1.99E-01±13.5%	147.9	3.39E-01	1.80E-01	
18	50	1.15	[HCl]=5.0	25	1.58E-02	11.7±6.73%	1.93E-02	1.03E-01	Figure 10, 12, 14
19	50	1.15	[HCl]=5.0	50	1.58E-02	7.23±6.37%	1.20E-02	6.35E-01	
20	50	1.15	[HCl]=5.0	100	1.58E-02	5.35±2.41%	1.70E-02	2.03E-02	
21	50	1.15	[HCl]=5.0	150	1.58E-02	4.66±3.09%	2.70E-02	2.37E-02	
22	50	1.15	[HCl]=5.0	300	1.58E-02	3.84±2.11%	1.10E-02	1.39E-02	
23	50	1.15	[HCl]=5.0	500	1.58E-02	3.66±2.33%	1.30E-02	1.48E-02	
24	50	1.16	$[H_2SO_4]$=5.0	50	6.96E-03	4.17±2.90%	1.10E-03	1.20E-02	Figure 11, 13, 14
25	50	1.16	$[H_2SO_4]$=5.0	100	6.96E-03	3.40±4.81%	2.30E-03	1.66E-02	
26	50	1.16	$[H_2SO_4]$=5.0	150	6.96E-03	3.13±5.55%	2.70E-03	1.78E-02	
27	50	1.16	$[H_2SO_4]$=5.0	300	6.96E-03	2.91±5.85%	2.70E-03	1.76E-02	
28	50	1.16	$[H_2SO_4]$=5.0	500	6.96E-03	2.98±4.74%	1.80E-03	1.46E-02	

[a] calculated by nonlinear regression. [b] Values with confidence intervals were calculated by nonlinear regression; Values without confidence intervals were estimated by linear equations (3.7) and (3.8). [c] Sum of Squared Residuals between measured and calculated concentrations of perchlorate. [d] Relative fitting error parameter.

Table 3.2. Comparison of perchlorate reducing systems with Ti(II) and catalysts.

Exp#	Ti(0) mM	ClO_4^- $_0$ mM	HCl N	F^- mM	Catalyst 1.0 mM	2nd order k ± 95% C.I. $mM^{-1}day^{-1}$	$Ti(II)_0$[a] mM	SSR mM^2	RFEP	Figure
29	100	5.0	1.0	500	No Catalyst	1.90E-03±23.9%	24.8	2.03E-01	4.76E-02	Figure 15, 16
30	100	5.0	1.0	500	Mo	1.80E-03±13.3%	24.8	5.67E-02	2.49E-02	
30	100	5.0	1.0	500	Cu	1.70E-03±17.3%	24.8	7.37E-02	3.12E-02	
31	100	5.0	1.0	500	Ni	1.50E-03±13.7%	24.8	5.38E-02	2.36E-02	
32	100	5.0	1.0	500	Re	7.00E-03±11.5%	24.8	6.63E-02	3.32E-02	
33	100	5.0	1.0	500	W	1.60E-03±17.8%	24.8	9.47E-02	3.26E-02	

[a] Equation (3.5) was used to calculate

3.4 Conclusions

This research has modified a procedure to produce Ti(II) and has developed data that helps to understand fundamental aspects of the kinetics of perchlorate destruction by Ti(II). Over 30 batch kinetic experiments were conducted to evaluate effects on perchlorate reduction kinetics of acid type, acid concentration, F/Ti(0) molar ratio, and catalyst type.

1) The amounts of Ti(II) produced using HCl and H_2SO_4 are similar when equivalent concentrations are used.

2) However, HCl was more effective than H_2SO_4 in promoting the ability of those solutions to degrade perchlorate when the concentration of acid was high.

3) Higher concentrations of Ti(0) produced higher concentrations of Ti(II), which resulted in more rapid perchlorate destruction.

4) Perchlorate reaction rate constants by Ti(II) increased with HCl concentrations.

5) Lower molar ratios of F/Ti(0) enhanced the production of Ti(II), which resulted in more effective reduction of perchlorate.

6) Most of the metals that were tested showed no catalytic effect on the rate of perchlorate reduction, but rhenium (Re) increased the degradation rate to a small degree.

7) Absorption spectra of the Ti(II) solutions formed by reaction of Ti(0) in the presence of acid and fluoride showed that as F/Ti(0) molar ratio decreased, the absorbance spectra shifted to become similar to that of Ti(III) solutions. This implies that Ti(III) might be present in these solutions.

CHAPTER IV

PERCHLORATE DEGRADATION USING TRIVALENT TITANIUM

4.1 Introduction

Results from Chapter III implied that Ti(III) might be present when solutions of acid and Ti(0) were mixed for the purpose of producing Ti(II). Chapter II reviewed the general chemistry of Ti(0) and Ti(III) and reported the results of studies on perchlorate reduction by Ti(III) under different conditions, but their reaction rates were too slow to be used for a treatment process. Also, chapter II compared Ti(II) and Ti(III) as reductants and showed that Ti(II) reacted faster with some oxidants, that Ti(III) reacted faster with for a few other oxidants and that their reaction rate constants were similar for some oxidants. Thus, this study will attempt to answer two questions. The first will be “which will be the faster reductant for perchlorate, Ti(II) or Ti(III)?” and the second will be ”how to make the reaction faster?”. Therefore, additional research was conducted to compare perchlorate degradation rates with Ti(II) and Ti(III) and to determine if the reaction rate could be increased. To make the reaction faster, ionic strength was controlled and several metals were evaluated as catalysts. Also, a solid acid catalyst was evaluated as an alternative source of hydrogen ions to avoid using a high concentration of a soluble acid. If the solid acid catalyst is effective as a source of hydrogen ions, it would be more convenient for use in a water treatment processes.

4.2 Materials and Methods

4.2.1 Chemicals

Sodium perchlorate ($NaClO_4$) was used in this research as a perchlorate source. Titanium trichloride (20% $TiCl_3$ by weight, 3% HCl by weight, Fisher Scientific) was used as Ti(III) source. To control the ionic strength, sodium chloride (NaCl) was used. Sodium molybdate (Na_2MoO_4), copper(II) chloride dehydrate ($CuCl_2{\bullet}2H_2O$), nickel chloride hexahydrate ($NiCl_2{\bullet}6H_2O$), ammonium perrhenate (NH_4ReO_4) and sodium tungstate (Na_2WO_4) were used as catalysts. Amberlyst-15(wet) ion exchange resin was used as a solid acid catalyst. All chemicals were purchased from Fisher Scientific and used as received without further purification. All experiments were conducted in an anaerobic chamber filled with a mixed gas containing 5% hydrogen and 95% nitrogen. Deionized water was purged with 99.99% argon for 2 hours and kept in an anaerobic chamber until use.

4.2.2 Analytical methods

Concentrations of perchlorate were determined using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column. Because many samples contained high concentrations of F^-, Cl^- or SO_4^{2-}, there were interferences in the analysis of reduction products of ClO_4^- such as ClO_3^-, ClO_2^- and Cl^-. Additionally, some samples contained high concentrations of H^+ and dissolved Ti ions that could damage the analytical and guard column if analyzed directly, so these samples were diluted with 1.0 to 1.5 N NaOH in order to precipitate dissolved titanium ions. The precipitated sample was filtered with 25-mm diameter nylon filter (Whatman, 0.22 µm).

4.3 Results and Discussions

4.3.1 Perchlorate reduction kinetics with Ti(II) and Ti(III)

Batch kinetic experiments were conducted to compare the ability of Ti(II) and Ti(III) to destroy perchlorate. The experimental data for perchlorate concentration as functions of time were analyzed by non-linear regressions to evaluate a second-order kinetic model and to determine coefficients for both perchlorate reduction by Ti(III). The second-order kinetic model was applied with a material balance for a batch reactor to generate the differential equation that describes how the concentration of perchlorate should change during experiments. The rate of perchlorate degradation was assumed to depend on concentrations of perchlorate and Ti(III) (Equation 4.1).

$$\frac{d[ClO_4^-]}{dt} = -k[ClO_4^-][Ti^{3+}] \tag{4.1}$$

$$8Ti^{3+} + ClO_4^- + 8H^+ = 8Ti^{4+} + Cl^- + 4H_2O \tag{4.2}$$

The reaction rate coefficient k was obtained by least-squares non-linear regression using MATLAB (MathWorks Inc.) function “nlinfit” for experiments with Ti(III). The concentration of Ti(III) in prepared solutions was used as the initial concentration in the kinetic model. Solutions to the model were determined using the

MATLAB function “ode45” which solves equation (4.1) numerically by a fourth order Runge-Kutta method. The stoichiometry shown in equation (4.2) was used to express the concentration of the Ti(III) in terms of the concentration of perchlorate to give a differential equation in one independent variable that can be solved.

The nonlinear regression procedure chooses parameters to minimize the sum of squared residuals (SSR). A relative fitting error parameter (RFEP) was calculated using SSR in order to numerically compare the fitting error among data sets. It is the ratio of the standard deviation of the data points about regression line divided by the average value of the data. As such, it represents the ratio of an average error to the average value. Smaller values represent better fits (lower errors) of the model to the data.

$$RFEP = \frac{\sqrt{\frac{SSR}{n-2}}}{\overline{C}} \qquad (4.3)$$

where SSR is the Sum of Squared Residuals; n is number of data points; and $\overline{C}$ is average perchlorate concentration.

Figure 4.1 shows the results of kinetic experiments with perchlorate and Ti(II) or Ti(III) and Table 4.1 shows the values of reaction rate constants by nonlinear regressions. The rate constants are not significantly different in experiments where 100 mM of Ti(0) was used to produce Ti(II) where 100 mM of Ti(III) was added when 1 N of HCl was used. However, the rate constant with Ti(III) is 50% higher than that of

Ti(II) when 5 N HCl was used. This shows that Ti(III) is more effective for perchlorate reduction at high HCl concentration. The lower reaction rate constant with Ti(II) may be due to less than complete conversion of Ti(0) to Ti(II). The concentrations of initial Ti(II) were calculated using equations (3.5) and (3.6) in Chapter III.

The higher concentrations of Ti(III) and HCl resulted in faster degradation of perchlorate. When the concentration of HCl increased from 1 N to 5 N, the rate constant increased about three-fold for experiments with 100 mM of Ti(III). Increasing the Ti(III) concentration with same HCl concentration increased the reaction rate, but not on its rate constant. When 5N HCl is used, the rate constants are similar for experiments with both 100 mM and 200 mM Ti(III). The model predictions showed relative fitting errors (RFEP) of less than 5% and the calculated rate constants have relative confidence intervals of less than 10%. This means that the model reasonably describes perchlorate degradation kinetics by Ti(III).

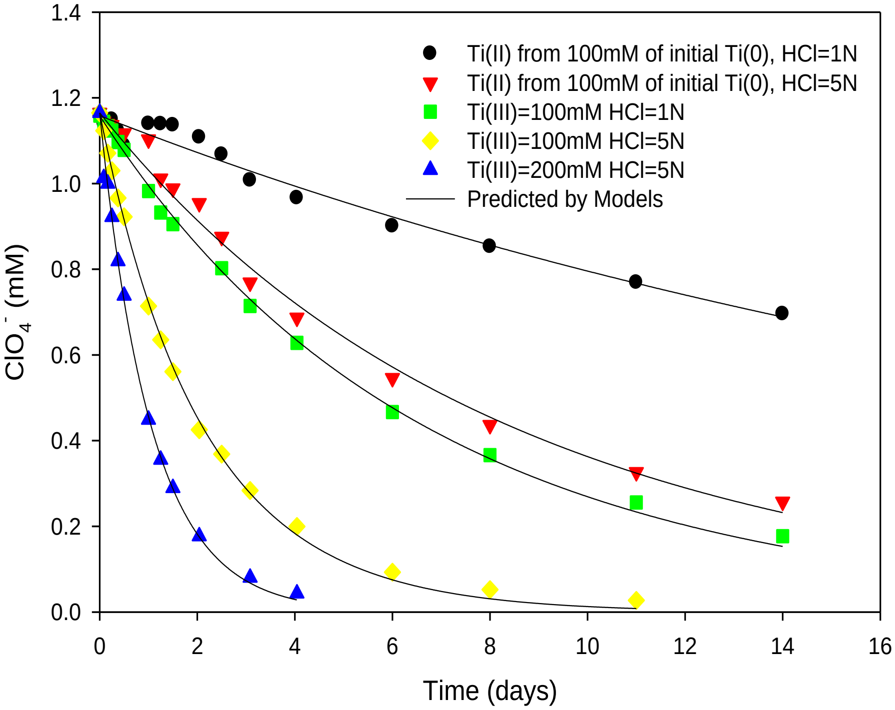


Figure 4.1 Perchlorate reduction by Ti(II) and Ti(III) solutions.

Molar ratio of F/Ti(0) is 3. The solid lines represent model predictions

Table 4.1. Comparison of results of experiments on perchlorate reduction by Ti(II) and Ti(III).

Exp#	**[Ti(0)] (mM)**	**[Ti(III)] (mM)**	**$[ClO_4^-]_0$ (mM)**	**[HCl] (M)**	**$[F^-]$ (mM)**	**2nd order k[a] ± 95% C.I. ($mM^{-1}day^{-1}$)**	**$[Ti(II)]_0$[b] (mM)**	**SSR[c] $(mM)^2$**	**RFEP[d]**
1	100		1.16	1	300	1.60E-03±8.47%	24.8	9.80E-03	2.47E-02
2	100		1.17	5	300	3.20E-03±6.03%	38.4	1.21E-02	3.45E-02
3		100	1.17	1		1.50E-03±2.92%		2.80E-03	1.70E-02
4		100	1.17	5		4.90E-03±2.48%		2.40E-03	2.17E-02
5		200	1.17	5		4.80E-03±4.70%		4.70E-03	3.70E-02

[a] Calculated by nonlinear regression. [b] Calculated by equation (3.5) and (3.6) in Chapter III [c] Sum of Squared Residuals between measured and calculated concentrations of perchlorate. [d] Relative fitting error parameter.

4.3.2 Effect of ionic strength

Liu et al.'s study on perchlorate degradation with Ti(III) showed a four-fold increase in rate constant when ionic strength was increased from 1.0 M to 3.0 M [76]. Based on this result, it was hypothesized that ionic strength might be an important factor to enhance Ti(III)-perchlorate reaction kinetics. Three experiments were conducted to evaluate this hypothesis and their conditions are summarized in Table 4.2. Two experiments had the same acid concentration, but different ionic strength, and two experiments at the same ionic strength, but different acid concentrations. The acid was provided by HCl and ionic strength was adjusted with NaCl.

Figure 4.2 shows that rates of reactions are similar for Ti(III) solutions with different ionic strengths, but the same acid concentration. However, a faster reaction rate was observed at the higher acid concentration when ionic strength was the same. Values of the rate constants are shown in Table 4.2. These results demonstrate that faster degradation of perchlorate at high concentration of acid is not caused by the higher ionic strength, but by the higher concentration of hydrogen ions. In addition, there seems to be no significant inhibition of perchlorate degradation by sodium or chloride ions because the rate constants for experiment 6 and 8 are very similar. In fact, their 95% confidence limits overlap. Addition of 2 M NaCl did not influence the rate of reaction and its rate constant.

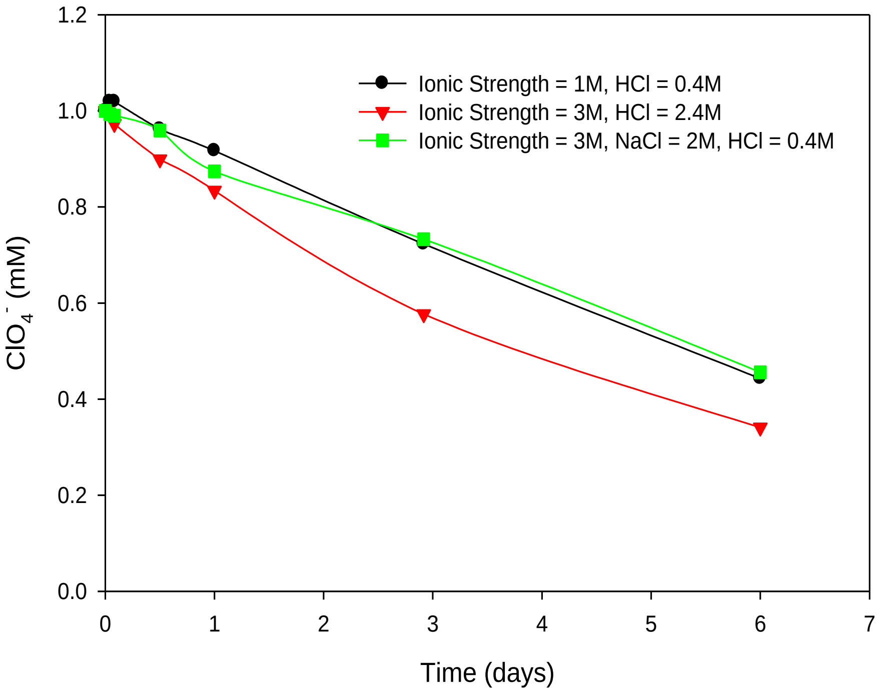


Figure 4.2. Perchlorate degradation using Ti(III) with different acid concentrations and ionic strengths. [Ti(III)] = 100 mM, [ClO_4^-] = 1 mM

Table 4.2. Comparison of results of experiments on perchlorate reduction by Ti(III) at different ionic strength.

Exp#	**[Ti(III)]** (mM)	**[ClO_4^-]** (mM)	**HCl** (mM)	**NaCl** (mM)	**Ionic Strength** (mM)	**2nd order k ± 95% C.I.** ($mM^{-1}day^{-1}$)	**SSR** ($(mM)^2$)	**RFEP**
6	100	1	400	0	1,000	1.30E-03±16.1%	5.10E-03	3.69E-02
7	100	1	2,400	0	3,000	1.90E-03±3.80%	3.70E-04	1.07E-02
8	100	1	400	2,000	3,000	1.20E-03±10.9%	2.30E-03	2.52E-02

4.3.3 Effect of metal catalysts

Five catalysts (Mo, Cu, Ni, Re, W) were examined for their abilities to enhance the rate of perchlorate degradation with Ti(III). Figure 4.3 shows that those metals have no catalytic influence on perchlorate degradation with Ti(III) under the conditions tested. Their rate constants are almost same, as shown in Table 4.3. However, the RFEP values are higher than 7% for all cases and 95% confidence intervals are around 20%. The uncertainty of the kinetic model is higher when applied to describing perchlorate degradation by Ti(III) with catalysts.

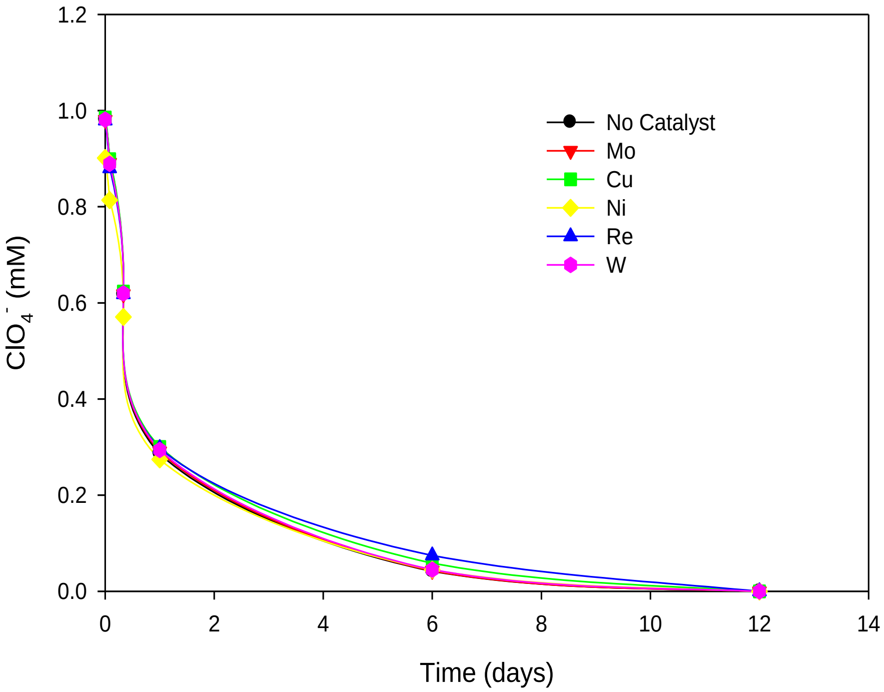


Figure 4.3. Perchlorate degradation using Ti(III) with catalysts at low F/Ti ratio.

[Ti(III)] = 200 mM, [HCl] = 6.0 N, [Catalyst] = 1 mM, [ClO_4^-] = 1 mM.

Table 4.3. Comparison of perchlorate reducing systems with Ti(III) and Catalysts.

Exp#	Ti(III) mM	ClO_4^- mM	Acid mM	Catalyst 1.0 mM	2nd order k	SSR mM^2	RFEP
9	200	1	6,000	No Catalyst	6.60E-03±19.0%	5.40E-03	7.83E-02
10	200	1	6,000	Mo	6.60E-03±18.7%	5.20E-03	7.68E-02
11	200	1	6,000	Cu	6.50E-03±21.7%	7.10E-03	8.80E-02
12	200	1	6,000	Ni	6.50E-03±19.3%	4.70E-03	7.87E-02
13	200	1	6,000	Re	6.50E-03±24.0%	8.60E-03	9.76E-02
14	200	1	6,000	W	6.50E-03±18.7%	5.20E-03	7.68E-02

4.3.4 Effect of solid acid catalysts

The high acid concentrations that were used in previous experiments would make it difficult to apply these reactions to a water treatment process. Thus, an alternative to high concentration of acids was sought and solid acid catalysts (SAC) were investigated, because they have been widely used as a replacement of acids such as HF, HCl, and H_2SO_4.

Cation exchange resins such as perfluorinated resinsulfonic acids are a type of solid acid catalyst that has been effectively used for reactions that require high acid concentration [77]. Amberlyst-15 is another type of cation exchange resin that has a higher capacity (120 $meqH^+g^{-1}$) and pore volume (4.8 mLg^{-1}) than those of perfluorinated resinsulfonic acids (0.10 $meqH^+g^{-1}$ and 0.78 mLg^{-1}) [77]. Amberlyst-

15 is a macroreticular sulfonated polystyrene-based ion-exchange resin with 20% divinylbenzene [77].

This experiment was conducted to examine the effect of SAC (amberlyst-15) on perchlorate degradation. Figure 4.4 shows that higher amounts of SAC resulted in slower perchlorate degradation, which was opposite of the result that was expected. The Ti(III) solution without SAC showed the fastest perchlorate degradation.

Also, the Ti(III) solutions with SAC had visibly less violet color than the Ti(III) solution without SAC. Ti(III) provides the violet color, so less color means that concentration of Ti(III) was reduced, probably due to adsorption onto the cation exchange resin.

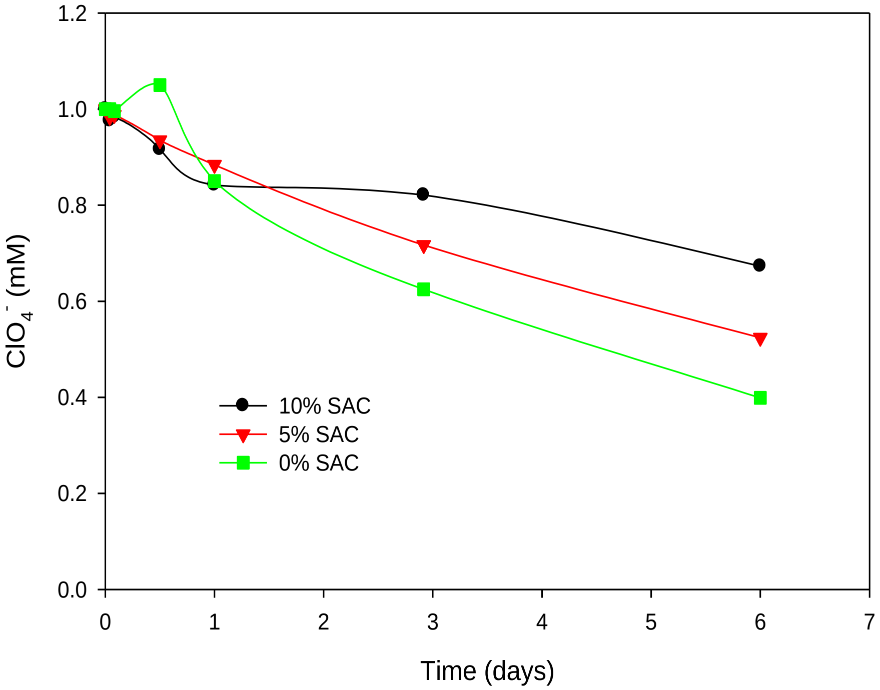


Figure 4.4 Perchlorate degradation using Ti(III) with solid acid catalysts.

[Ti(III)] = 100 mM, [HCl] = 0.06 N, [Amberlyst-15] = 0, 5, 10 w %, [ClO_4^-] = 1 mM

4.4 Conclusions

Experiments were conducted to compare the abilities of Ti(II) and Ti(III) to degrade perchlorate, to evaluate the potential for enhancing the perchlorate-Ti(III) reactions by control of ionic strength, and to evaluate effects of metal catalysts and solid acid catalysts on perchlorate reduction. Models were used to describe the chemical reactions and nonlinear regressions were used to acquire their rate coefficients. The conclusions from this study are as follows.

1) Ti(III) degraded perchlorate faster and with higher reaction rate constants than Ti(II) when 5 N of HCl was used.
2) Higher concentration of HCl increased the reaction rate and the rate constant for perchlorate reduction by Ti(III).
3) High ionic strength does not enhance the perchlorate-Ti(III) reaction, but high acid concentration does.
4) Sodium or chloride ions do not seem to inhibit perchlorate reduction by Ti(III).
5) Metals (Mo, Cu, Ni, Re, W) do not have catalytic effects on the perchlorate-Ti(III) reaction.
6) The solid acid catalyst decreased the reaction rate between perchlorate and Ti(III), possibly due to the reduction in the concentration of Ti(III) ions caused by removal by cation exchange.

CHAPTER V

PERCHLORATE DEGRADATION USING PARTIALLY OXIDIZED TITANIUM IONS AND ION EXCHANGE MEMBRANE HYBRID SYSTEM

5.1 Introduction

Ion exchange is the most widely used method for treatment of perchlorate-contaminated groundwater in order to meet the regulatory requirements [2, 11]. It has been used as a drinking water treatment process since the 1940s and is one of the first ex-situ technologies to be considered for remediation of perchlorate-contaminated water [11]. Many applications in full and pilot scales have been placed in operation for government, military and research facilities [11]. It is an equilibrium process and when the perchlorate laden resin is regenerated with concentrated chloride, perchlorate ion is displaced from the resin. This process produces a solution (brine) with a high concentration of perchlorate that needs further treatment.

The concept of ion exchange can be combined with biological treatment, electrodialytically assisted catalytic reduction, ion exchange membrane bioreactor, biological reduction by bacteria attached to ZVI and others for treatment of contaminants such as perchlorate, bromate, nitrate, and arsenic [21, 24, 29, 30, 60, 78-83]. Currently, hybrid systems of ion exchange and biological processes are some of the major methods for perchlorate treatment [24]. One of reviews on perchlorate remediation concluded that no single technology is ready to be used for perchlorate removal in drinking water systems and combinations of recent technologies seem to be more feasible [62].

Chapter III and Chapter IV showed that perchlorate ion can be reduced in Ti(II) or Ti(III) solution with high acid concentration. The rate of perchlorate reduction was faster with higher concentrations of acid and titanium. However, the high acid concentration makes it difficult to practically apply the method to a treatment process. To overcome this weakness, an ion exchange membrane can be used to separate the contaminated water from a solution with high concentrations of acid and titanium ion. The contaminated water could be a regenerant brine from an ion exchange process, the solution with high concentration of acid could contain trivalent titanium (Ti(III)), which has been shown to reduce perchlorate faster than divalent titanium(Ti(II)). The region with perchlorate is called the "contaminated zone" and the region with Ti(III) in which the reaction occurs is called the "degradation zone". The schematic of this Titanium and Membrane Hybrid System (TMH System) is shown in Figure 5.1.

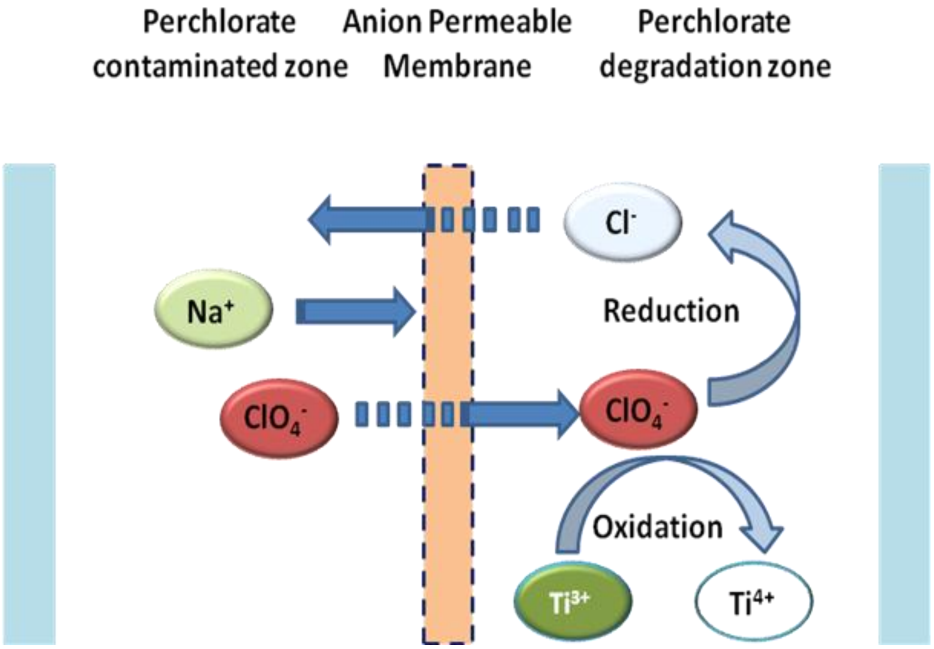


Figure 5.1 Conceptual diagram of a Titanium and Membrane Hybrid System.

This system combines ion-selective membrane dialysis and chemical degradation. The advantage of this system is that the ion exchange membrane keeps the contaminated water from the high concentration of acid and titanium(III) that is used for reduction of perchlorate.

The objective of this study is to determine the ability of a Titanium Membrane Hybrid System to destroy perchlorate. To evaluate the behavior of the TMH system, batch kinetic and equilibrium experiments were conducted to evaluate how effectively it destroys perchlorate. Completing this objective can provide information to evaluate the practicality of using a system in which perchlorate is transported from the contaminated water through a semi-permeable membrane to a solution in which conditions are optimized for perchlorate reduction. As for perchlorate transport, the effective diffusivity of perchlorate through nanofiltration and ultrafiltration membranes has been measured with several salts (KCl, K_2SO_4, $CaCl_2$) and an average value of 8.2 E-10 cm^2/s has been reported for pH 4 to 10 [55, 57].

The present work proposes the TMH system for the first time and discusses its use for perchlorate removal and the mechanism of removal. Experimentally, batch experiments investigated the physical transport of perchlorate, its adsorption behavior, and its chemical reduction by partially oxidized titanium ions. Also, the physical and chemical behavior of the system was modeled and the model was solved numerically.

5.2 Materials and Methods

5.2.1 Experimental set-up

5.2.1.1 Membranes

Three different kinds of membranes; Neosepta AMX, ACS and ACM from Tokuyama corp. were used throughout this study. Mechanical properties of the membranes and their practical applications are shown in Table 5.1. The membranes were stored in a 1.0 M NaCl solution for 1 hr before being used in an experiment in order to avoid wrinkling or excessive tension.

Table 5.1. Mechanical properties of membranes.

	AMX	**ACS**	**ACM**
Type	Strongly basic anion permeable	Strongly basic anion permeable	Strongly basic anion permeable
Characteristics	High mechanical strength	Mono anion perm-selective	Proton blocking
Electric Resistance (Ω-cm^2)	2.4	3.8	2.6
Burst Strength (MPa)	≥0.25	≥0.15	≥0.15
Thickness (mm)	0.14	0.13	0.11

5.2.1.2 Reactor

For a batch experiment, an equilibrium type dialysis cell from Scienceware was used as a reactor. Each compartment had a 10-mL volume and 21-cm^2 area of contact with the membrane. A syringe and tube were used for injecting process solutions into each compartment. Samples of 20 µL were taken by autopipet and diluted with deionized water to 10 mL.

5.2.1.3 Chemicals

All experiments were conducted in an anaerobic chamber filled with a mixed gas containing 5 % hydrogen and 95 % nitrogen. Deionized water was purged with 99.99 % argon for 2 hours and kept in an anaerobic chamber until use. Sodium perchlorate ($NaClO_4$), sodium chloride (NaCl), titanium chloride ($TiCl_3$) and hydrochloric acid (37-38%) were purchased from Fisher Scientific. The concentrations in contaminated zone were 1.0 mM for sodium perchlorate and 1.0 M for sodium chloride. The concentrations in the degradation zone were 0.2 M titanium chloride and 1.0 M hydrochloric acid.

5.2.2 Analytical methods

The concentrations of perchlorate were analyzed using a Dionex 500 ion chromatograph equipped with a 4-mm Dionex AS–16 analytical and guard column, auto sampler, a CD 20 conductivity detector, 1000-µL sample loop and an ASRS 300-4 mm self regenerating suppressor. A 50 mM NaOH solution was used as an eluent and its flow rate was 1 mL/min.

5.2.3 Modeling

A model for the Titanium and Membrane Hybrid System (TMH System) is developed in this chapter that describes three steps for perchlorate transport and reaction: adsorption to an ion exchange membrane, diffusion through it, and reduction by trivalent titanium. This mathematical model that describes physical and chemical behaviors was originally developed and solved numerically by others. This model has been applied to the experimental data from the TMH system to acquire values of model parameters using nonlinear regression.

The ion exchange membrane adsorbs perchlorate ions selectively and the adsorbed ions diffuse through the membrane. Perchlorate ions diffuse from the boundary of membrane with the contaminated zone through the membrane to the boundary of the membrane with the degradation zone. Then they are desorbed into the degradation zone and begin to react with trivalent titanium and hydrogen ions as shown in Figure 5.1. The physical and chemical modeling of TMH system is important in evaluating the efficiency of using it as a treatment technology. The model can help identify importance of different mechanisms in the entire system by predicting the behavior of perchlorate ions under different conditions.

The purpose of this modeling is to mathematically describe the physical and chemical behavior of perchlorate ions in the TMH system and to acquire important parameters that govern the system's behavior.

5.2.3.1 General material balance

A general material balance equation for diffusion through a film with adsorption but without other reaction is shown in Equation (5.1).

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{\varepsilon} \frac{\partial q}{\partial t} \tag{5.1}$$

where C is concentration on liquid volume basis (M/L^3), D_e is the effective diffusivity (L^2/T), ρ_b is bulk density of film (M/L^3) and ε is porosity of film.

Apply the chain rule to the term to $\frac{\partial q}{\partial t}$,

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \tag{5.2}$$

Substitute equation (5.2) to equation (5.1),

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \tag{5.3}$$

Rearrange,

$$\frac{\partial C}{\partial t}\left(1 + \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial C}\right) = D_e \frac{\partial^2 C}{\partial x^2} \tag{5.4}$$

$$\frac{\partial C}{\partial t} = \frac{D_e}{\left(1 + \frac{\rho_b}{\epsilon} \frac{\partial q}{\partial C}\right)} \frac{\partial^2 C}{\partial x^2} \tag{5.5}$$

The Langmuir model is adopted as the adsorption isotherm, because its basic assumptions are applicable to TMH system in following aspects; 1. Perchlorate does not form multi layers of adsorbate, 2. Perchlorate ions behave as an ideal solute because it is very inert and does not readily react with any reductant, 3. Adsorption sites are uniformly distributed due to uniform manufacturing, 4. There are no interactions between perchlorate molecules. Because there are high concentrations of chloride along with perchlorate in the solution, a multi-component Langmuir sorption equilibria between main component and competing component with concentration C_c can be used. Then,

$$q = \frac{Q_0 bC}{1 + b_c C_c + bC} \tag{5.6}$$

If the concentration of the competing ion is relatively constant, then using $K=1+b_cC_c$,

$$q = \frac{Q_0 C}{K + C} \tag{5.7}$$

Then,

$$\frac{\partial q}{\partial C} = \frac{Q_0 K}{(K + C)^2} \tag{5.8}$$

Substituting equation (5.8) to equation (5.5),

$$\frac{\partial C}{\partial t} = \frac{D_e}{\left(1 + \frac{\rho_b}{\epsilon}\frac{Q_0 K}{(K + C)^2}\right)}\frac{\partial^2 C}{\partial x^2} \tag{5.9}$$

This can be converted to non-dimensional form by multiplying by $L^2/D_e^0C^0$ and rearranging,

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \frac{p_1}{\left(1 + \frac{p_2}{(p_3 + \bar{C})^2}\right)} \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} \tag{5.10}$$

where, $\bar{C} = \frac{C}{C^0}$, $\bar{t} = \frac{tD_e^0}{L^2}$, $\bar{x} = \frac{x}{L}$, C^0= standard concentration (initial concentration), D_e^0 = standard effective diffusivity, L = thickness of film, $p_1 = \frac{D_e}{D_e^0}$, $p_2 = \frac{\rho_b Q_0 K}{\epsilon (C^0)^2}$ and $p_3 = \frac{K}{C^0}$

5.2.3.2 Application with film between two solutions with reaction in one solution

To solve the general balance equations for the TMH system, boundary conditions and initial conditions are needed. Simple assumptions for the boundaries of the film are that the concentration of perchlorate concentration at the boundary of the membrane with the contaminated zone is same as the concentration of perchlorate in the contaminated zone ($C(x=0) = C_a$) and that the concentration of perchlorate at the boundary of membrane with the degradation zone is same as the concentration of perchlorate in the degradation zone ($C(x=L) = C_b$).

A material balance on the contaminated zone where no reaction occurs is shown by Equation (5.11).

$$V_a \frac{dC_a}{dt} = \varepsilon A D_e \frac{\partial C}{\partial x}_{x=0} \tag{5.11}$$

where V_a is the volume of solution in the contaminated zone, C_a is the concentration of perchlorate in the contaminated zone, C is concentration of perchlorate in the membrane, x is distance into the membrane, and A is contact area of the membrane.

Make dimensionless by multiplying by $L^2/V_aC^0D_e^0$ and rearranging,

$$\frac{d\overline{C_a}}{d\bar{t}} = p_1 p_4 \frac{\partial \bar{C}}{\partial \bar{x}}_{\bar{x}=0} \tag{12}$$

where: $p_4 = \frac{\varepsilon AL}{V_a}$

A material balance on the degradation zone, where a pseudo first-order reaction removes the compound gives:

$$V_b \frac{dC_b}{dt} = -\varepsilon A D_e \frac{\partial C}{\partial x}_{x=L} - V_b k' C_b \tag{13}$$

In Chapters III and IV, the rate of perchlorate reduction was assumed to be proportional to concentrations of initial perchlorate and titanium ions, thus the second order reaction model was used. However, the concentration of titanium(III) ions used in experiments with the TMH system were two hundred times higher (200 mM) than the perchlorate concentration (1.0 mM) for all experiments, so a pseudo-first order rate equation can be applied. The rate constant (k´) in equation (5.16) is the product of the second-order rate constant (k) and concentration of titanium(III) ions; $k' = k[Ti(III)]$.

Equation (5.15) can be made dimensionless by multiplying by $L^2/V_bC^0D_e^0$ and rearranging,

$$\frac{d\overline{C_b}}{d\bar{t}} = -p_1 p_5 \frac{\partial \bar{C}}{\partial \bar{x}}_{\bar{x}=1} - p_6 \overline{C_b} \tag{5.14}$$

where: $p_5 = \frac{\varepsilon AL}{V_a}$, $p_6 = \frac{kL^2}{D_e^0}$

5.2.3.3 Solution by orthogonal collocation

Steady-state diffusion problems in one space dimension are normally described by ordinary differential equations, usually of second order, with two boundary conditions, which are applied at two locations in space. Orthogonal collocation is a numerical method for solving problems whose solutions are steep. It has been proved to be useful for diffusion and reaction related problems. Material balance equations can be solved by applying it on finite elements.

Choose the number of two internal nodes to be used per element. Two internal nodes will be used in this example. When there is a steep profile in the domain, it is recommended that non-uniform finite element meshes be used.

Let “x” identify boundary nodes at each elements, and “o” identify internal nodes in elements as shown in Figure 5.2.

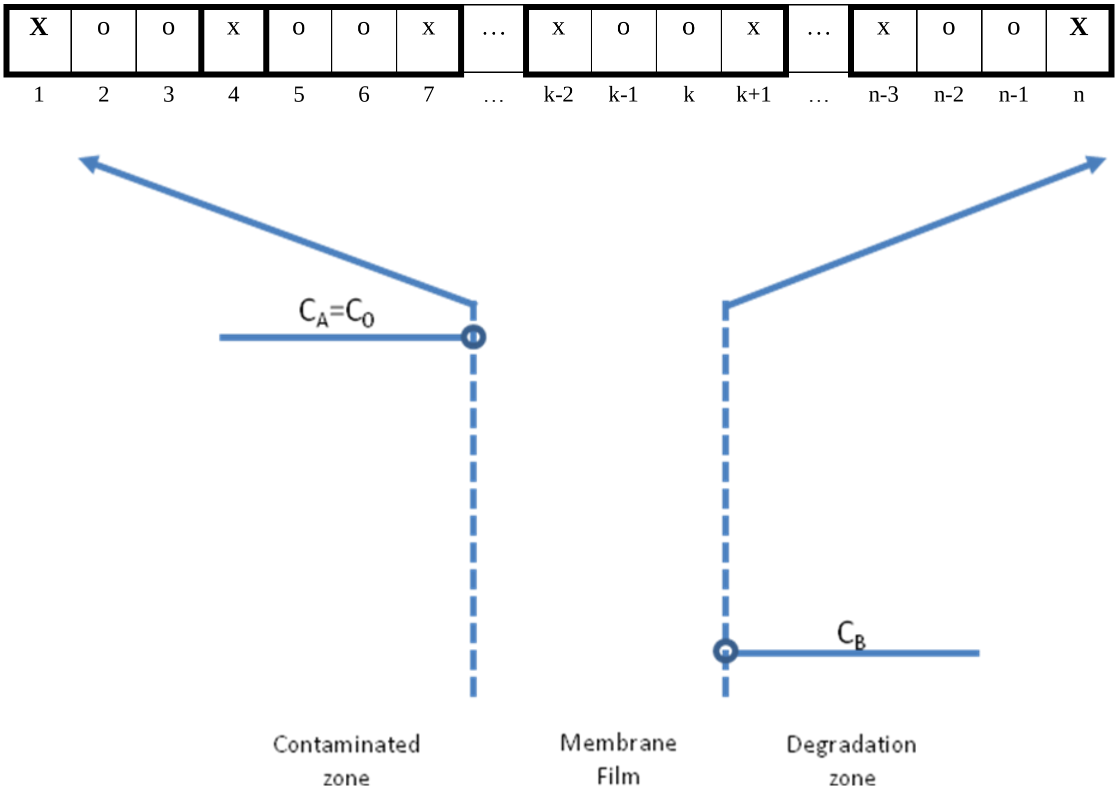


Figure 5.2 Model of transport of material from contaminated zone to the degradation zone through a membrane with n-nodes. Each small box represents a node and a group of four nodes makes one element (bold box).

x represents collocation points at the boundaries at each element; **X** represents collocation points at the boundaries of the domain; o represents collocation points in the interior of an element; n is the number of nodes

Node 1 is the boundary with solution A.

$$\frac{d\overline{C_1}}{d\bar{t}} = p_1 p_4 \frac{\partial \bar{C}}{\partial \bar{x}}_{\bar{x}=0,i=1} \tag{15}$$

Applying orthogonal collocation to calculate the derivative,

$$\frac{d\overline{C_1}}{d\bar{t}} = \frac{p_1 p_4}{h_e}\left(A_{1,1}\overline{C_1} + A_{1,2}\overline{C_2} + A_{1,3}\overline{C_3} + A_{1,4}\overline{C_4}\right) \tag{16}$$

where, h_e = width of element = 1.0/(number of elements) = 3/(n-1),

$$A = \begin{pmatrix} -7 & 8.196 & -2.196 & -1 \\ -2.732 & 1.732 & 1.732 & -0.732 \\ 0.732 & -1.732 & -1.732 & 2.732 \\ -1 & 2.196 & 8.196 & -7 \end{pmatrix}$$

A is the matrix used in orthogonal collocation that will give a vector of first derivatives when multiplied the vector of concentrations in an element [84].

For all internal nodes (i):

$$\frac{\partial \bar{C}}{\partial \bar{t}} = \frac{p_1}{\left(1 + \frac{p_2}{(p_3 + \bar{C})^2}\right)} \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} \tag{17}$$

Applying orthogonal collocation to calculate the second derivative:

For nodes i=k-1:

$$\frac{\partial \overline{C_{k-1}}}{\partial \bar{t}} = \frac{p_1}{h_e^2\left(1+\frac{p_2}{(p_3+\overline{C_{k-1}})^2}\right)}\left(B_{2,1}\overline{C_{k-2}} + B_{2,2}\overline{C_{k-1}} + B_{2,3}\overline{C_k} + B_{2,4}\overline{C_{k+1}}\right) \tag{18}$$

For nodes i=k

$$\frac{\partial \overline{C_k}}{\partial \bar{t}} = \frac{p_1}{h_e^2\left(1+\frac{p_2}{(p_3+\overline{C_{k-1}})^2}\right)}\left(B_{3,1}\overline{C_{k-2}} + B_{3,2}\overline{C_{k-1}} + B_{3,3}\overline{C_k} + B_{3,4}\overline{C_{k+1}}\right) \tag{5.19}$$

where, $B = \begin{pmatrix} 24 & -37.18 & 25.18 & -12 \\ 16.39 & -24 & 12 & -4.392 \\ -4.392 & 12 & -24 & 16.39 \\ -12 & 25.18 & -37.18 & 24 \end{pmatrix}$

B is the matrix used in orthogonal collocation to calculate the second derivatives when multiplied times the concentrations in an element [84].

For nodes that are boundaries between elements (i=k+1, for k=3 to n-4), the flux leaving one element (i-1) must equal the flux entering the adjacent element (i). Assuming that diffusivity remains constant in the film, Fick's law gives:

$$\left(\frac{d\bar{C}_i}{d\bar{t}}\right)_{m-1} = \left(\frac{d\bar{C}_i}{d\bar{t}}\right)_{m} \tag{5.20}$$

Applying orthogonal collocation to calculate the derivatives:

$$A_{4,1}\overline{C_{k-2}} + A_{4,2}\overline{C_{k-1}} + A_{4,3}\overline{C_k} + A_{4,4}\overline{C_{k+1}} = A_{1,1}\overline{C_{k+1}} + A_{1,2}\overline{C_{k+2}} + A_{1,3}\overline{C_{k+3}} + A_{1,4}\overline{C_{k+4}} \tag{5.21}$$

For the final node (i=n), that is the boundary with the solution B:

$$\frac{d\overline{C_n}}{d\bar{t}} = -p_1 p_5 \frac{\partial \bar{C}}{\partial \bar{x}}_{\bar{x}=1} - p_6 \overline{C_n} \tag{5.22}$$

Applying orthogonal collocation to calculate the derivative,

$$\frac{d\overline{C_n}}{d\bar{t}} = -\frac{p_1 p_5}{h_e}\left(A_{4,1}\overline{C_{n-3}} + A_{4,2}\overline{C_{n-2}} + A_{4,3}\overline{C_{n-1}} + A_{4,4}\overline{C_n}\right) - p_6 \overline{C_n} \tag{5.23}$$

Then, we can solve for C (perchlorate concentration) numerically because we have n unknowns and n equations. The dynamic material balance equations have been converted to ordinary differential equations (ODEs) by applying orthogonal collocation on finite elements, using elements with two internal nodes. Experimental data for perchlorate concentration in both sides of reactors over time were analyzed by using nonlinear regressions to evaluate the model. The parameters that govern adsorption, diffusion and reaction are the Langmuir adsorption coefficients (Q_0, K), effective diffusivity (D_e), and pseudo fist-order reaction rate constant (k). Values of these parameters were calculated to best fit the experimental data by least-square non-linear regressions using the MATLAB function “nlinfit”. Solutions to the equations (5.16), (5.18), (5.19), (5.21) and (5.23) were determined using the MATLAB function “ode15s”.

5.3 Results and Discussion

5.3.1 Preliminary experiment for perchlorate transport

To investigate the transport behavior of perchlorate, concentrations of perchlorate on each side of the membrane were measured at several time intervals. Before installing the ion exchange membrane into the reactor cell, the membrane was soaked in a solution of 1 M sodium chloride for 1 hour to prevent wrinkling. Typically, regeneration of perchlorate selective resins uses 1 M NaCl (5.8%) at 20°C. Thus, a solution with 1M NaCl and 1 mM perchlorate is used throughout this study as surrogate for a regenerant solution from an ion exchange treatment system. To investigate the transport of perchlorate from the contaminated zone to the degradation zone (in this case, without any reductants) through an ion exchange membrane, 1 M NaCl was injected into each zone and 1 mM perchlorate was injected into the contaminated zone. No acid or Ti(III) were placed in the degradation zone. The concentrations of perchlorate at each zone were measured until 168 hours had passed. Figure 5.3 shows the results of this experiment and it indicates that perchlorate ions are adsorbed rapidly to the membrane and then transported to the degradation zone. The system equilibrated in less than 24 hours with a perchlorate concentration of 0.04 mM both zones.

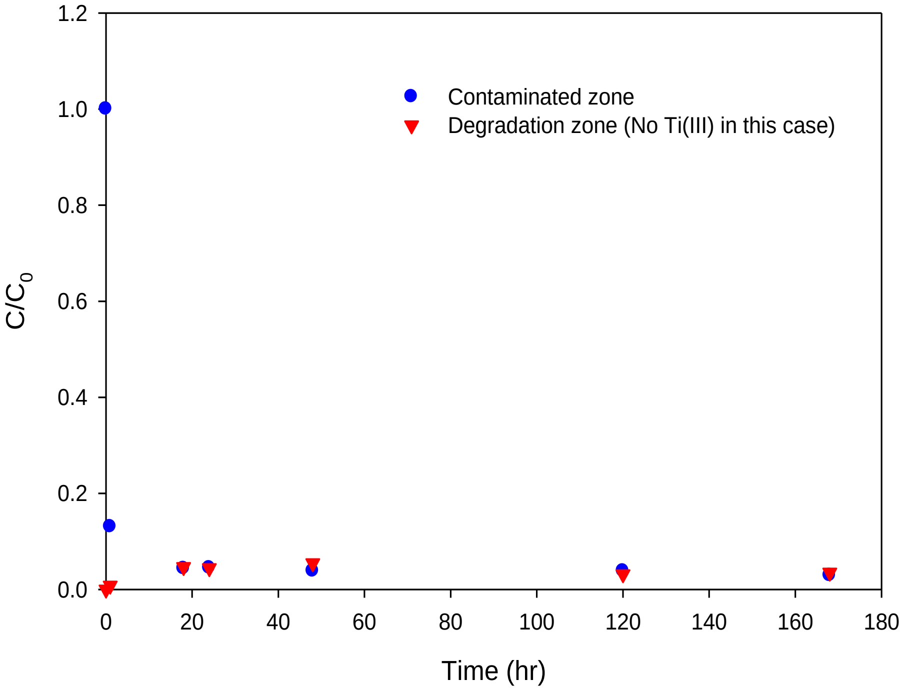


Figure 5.3. Perchlorate concentrations in each zone. Initial concentration of ClO_4^- in the contaminated zone is 1.0 mM

5.3.2 Adsorption equilibrium experiment

To further investigate the mechanisms of perchlorate behavior in the TMH system, basic characteristics of the ion exchange membrane were evaluated. The adsorption behavior of perchlorate onto different types of membranes was an important characteristic. Thus, isotherm equilibrium experiments were conducted for perchlorate adsorption on three types of ion exchange membranes (AMX, ACS, ACM). According to the manufacturer's handling manual, the AMX and ACS membranes were immersed for one hour in a solution of 1 M NaCl and the ACM membrane was immersed for one hour in a solution of 1 M HCl in order to prevent wrinkling. After that, the membranes were installed into a dialysis cell and a 1M NaCl solution containing various concentrations of $NaClO_4$ were injected into both zones of the system. The reaction time of 24 hours was used for each experiment, because a previous kinetic experiment (Figure 5.3) showed that equilibrium was achieved in less than 24 hours. Twenty seven sets of experiments were conducted for nine different perchlorate concentrations and three types of membranes and the results are shown in Figure 5.4.

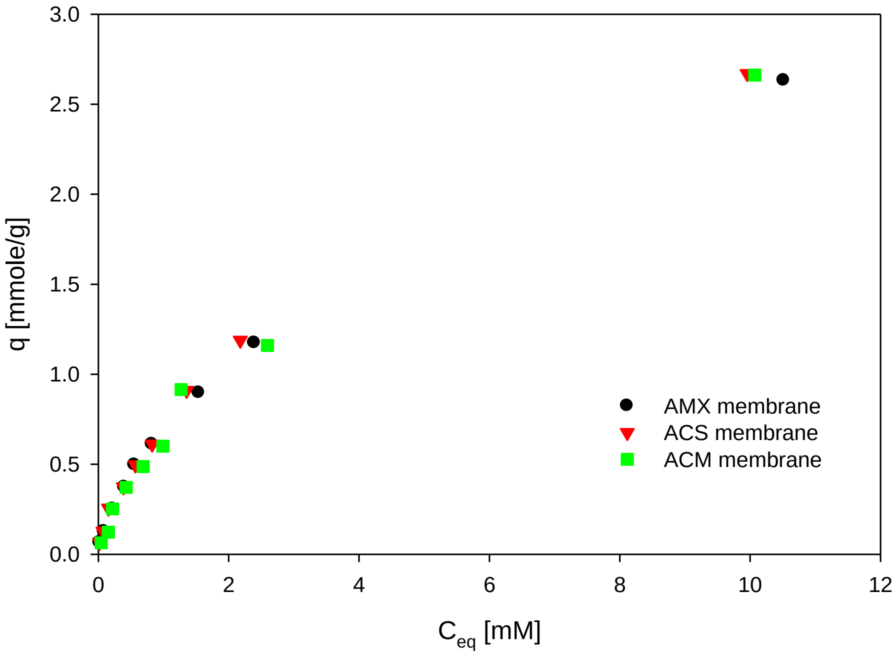


Figure 5.4. Perchlorate adsorption isotherms on AMX, ACS and ACM membranes.

Figure 5.4 shows that each membrane's adsorption behavior is similar. The three membranes' perchlorate adsorption capacities seem to be comparable. Freundlich and Langmuir models were used to find the best fitting model to describe perchlorate adsorption onto membranes.

$$q = K_f C_e^{\frac{1}{N}} \tag{5.24}$$

$$q = \frac{Q_0 b C_e}{1 + b C_e} \tag{5.25}$$

where, q [mmole/g], K_f [$(\text{mmole}^{N\text{-}1}\text{L})^{1/N}$/g], C_e [mmole/L], Q_o [mmole/g], b [L/mmole].

The isotherm parameters for each membrane were calculated by nonlinear regression and the results are shown in Table 5.2. This procedure chooses parameters to minimize the sum of squared residuals (SSR). A relative fitting error parameter (RFEP) was calculated using SSR in order to numerically compare the fits among different data sets. It is the ratio of the standard deviation of the points about regression line divided by the average value of the data (Equation 5.26). As such, it represents the ratio of an average error to the average value. Smaller values represent better fits of the model to the data.

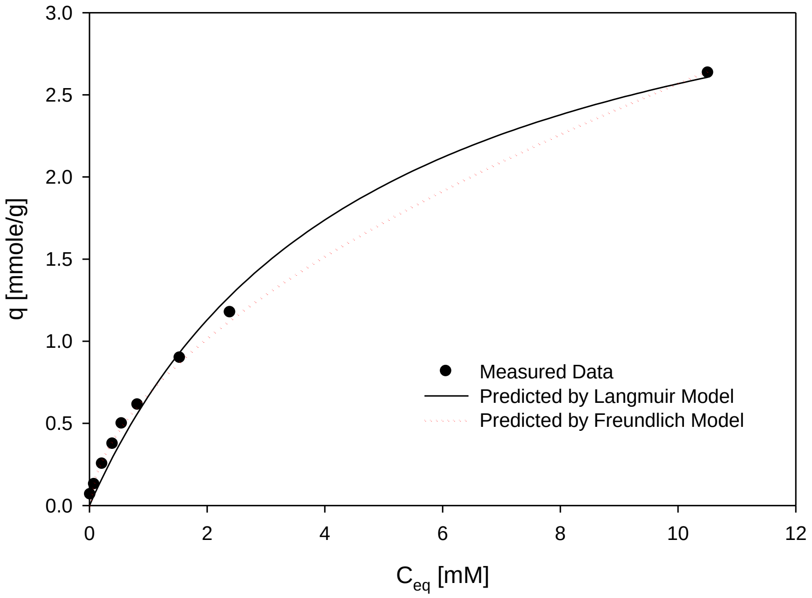
$$RFPE = \frac{\sqrt{\frac{SSR}{n-2}}}{\bar{q}} \quad (5.26)$$

where, SSR : Sum of Squared Residuals, n : number of data points, $\bar{q}$: average value of data.

Figure 5.5 shows the results for the experiment and predictions by both models. Both models describe the experimental data well with RFEP values less than 0.05, but the Freundlich model was better than the Langmuir model, as indicated by smaller RFEP values (Table 5.2). However, basic assumptions for the Langmuir model are closer to the conditions found in the TMH system.

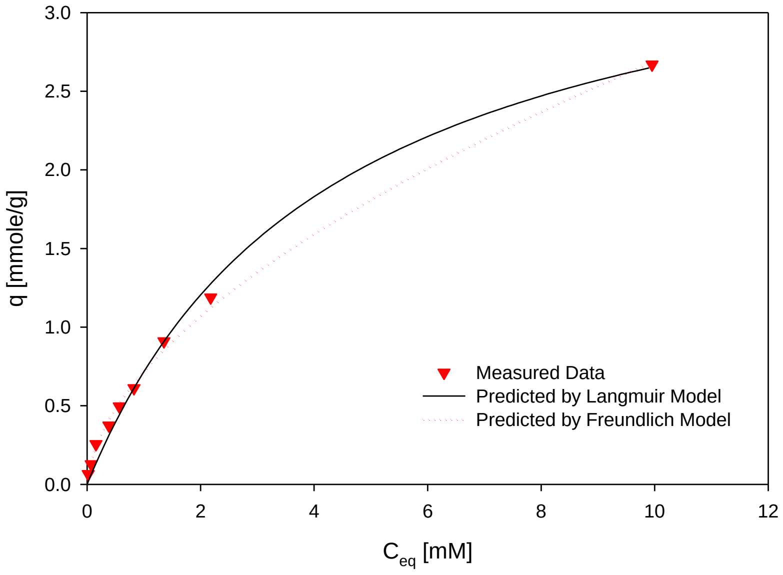
Table 5.2. Results of regressions for isotherm models. Parameters are shown with their relative 95% confidence intervals.

Models	**Parameters**	**AMX**	**ACS**	**ACM**
Freundlich	K_f [L/g]	6.84 E-01±4.52%	7.23 E-01±5.90%	6.53 E-01±11.3%
	N	1.74 E00±3.89%	1.75 E00±5.23%	1.64 E00±9.26%
	SSR $(mmole/g)^2$	6.40 E-03	1.20 E-02	3.79 E-01
	RFEP	1.65 E-02	2.40 E-02	4.02 E-02
Langmuir	Q_o [mmole/g]	3.76 E00±14.0%	3.80 E00±12.5%	4.02 E00±18.6%
	b $[mM^{-1}]$	2.15 E-01±29.0%	2.32 E-01±26.0%	1.88 E-01±36.7%
	SSR $(mmole/g)^2$	4.23 E-02	3.63 E-02	6.19 E-02
	RFEP	4.22 E-02	4.18 E-02	5.14 E-02

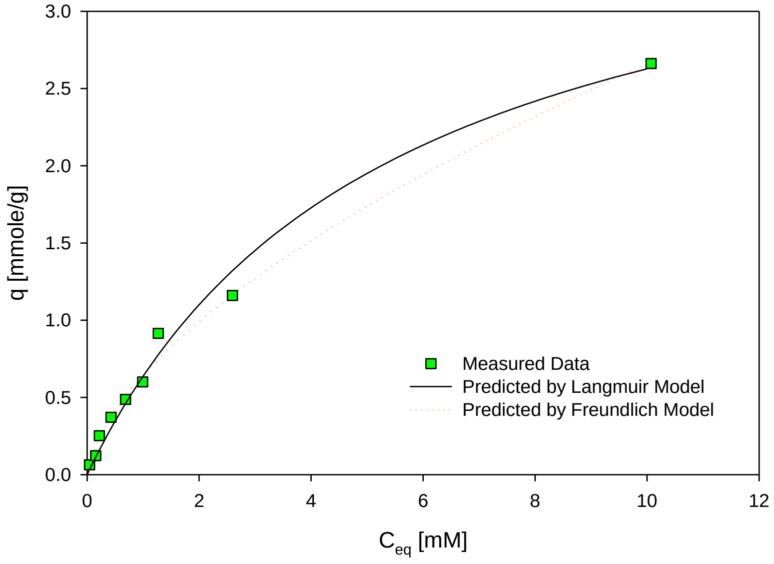


(a) AMX Membrane

Figure 5.5. Perchlorate adsorption isotherms and predictions of the Langmuir and Freundlich Models.



(b) ACS Membrane



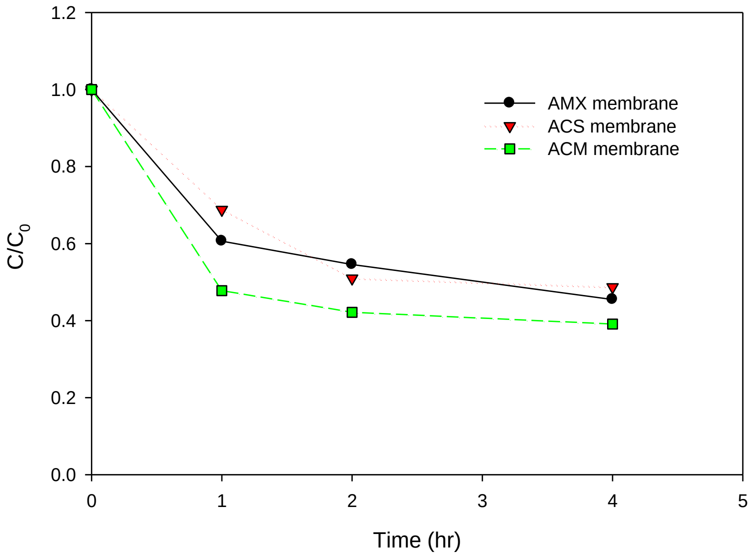
(c) ACM Membrane

Figure 5.5 Continued.

5.3.3 Effect of membrane types in TMH system

The objective of this experiment was to investigate the effect of membrane types on perchlorate transport and degradation. Perchlorate (1 mM) and NaCl (1 M) were placed in the contaminated zone. For reduction of perchlorate, 200 mM of $TiCl_3$ and 1M of HCl were placed in the degradation zone.

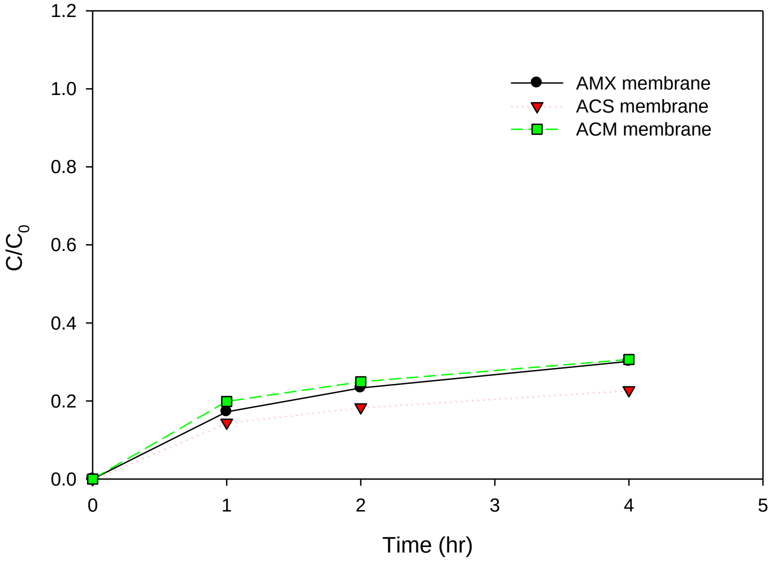
The effect of membrane types on perchlorate transport is shown in Figure 5.6. The effect is noticeable up to 4 hours. Figures 5.6 (a) and (b) show that ACM transports perchlorate ions more rapidly than ACS and AMX. However, the difference is negligible when the reaction time is over than 1 day, as shown in Figure 5.6 (c). The concentrations of perchlorate in each zone gradually decrease with time because perchlorate ions are reduced by reaction with Ti(III) in the degradation zone. However, the degradation rate is slow and 0.2 mM of perchlorate remained after 12 days.



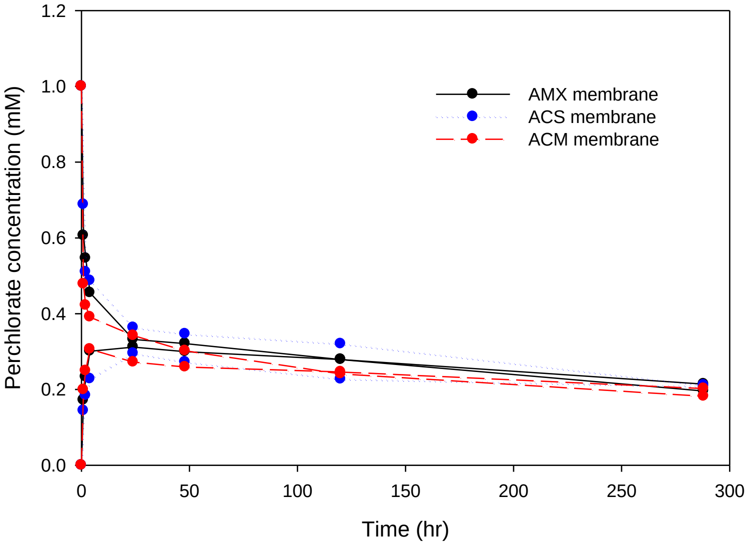
(a)

Figure 5.6. Perchlorate concentrations with 3 types of membranes.

(a) In contaminated zone (t<4 hr) (b) In degradation zone (t<4 hr) (c) in both zones for entire time range. Initial perchlorate concentration is 1 mM.



(b)



(c)

Figure 5.6 Continued.

5.3.4 Investigation of proton diffusion through three types of membranes

To determine which membrane will be the best option for perchlorate transport and degradation, it is important to know to what extent they are capable of hydrogen ion blocking. If hydrogen ions are blocked from diffusing through the membrane to the contamination zone, the reaction rate of reaction zone would be faster due to lower pH. Thus, the pH in the contaminated zone was measured initially and after 5 days.

Table 5.3 shows the measured pH in the contaminated zone and calculated values of the amount of hydrogen ions transported per volume of the contaminated zone, assuming that all of the hydrogen that were transported remain in solution as H^+ and that the activity coefficient for hydrogen ions is 1.0. The initial pH was 6.02 for all cases with different membranes, but the pH values are much lower after 5 days. Both ACS and ACM are better for proton blocking than AMX, because the concentrations of protons are lower by about 0.03 M. However, color of the solution in the contaminated zone changed to purple with the AMX membrane during the experiment, which means that Ti(III) ions were transported through the AMX membrane.

Table 5.3. pH of solution in contaminated zone.

	AMX membrane	**ACS membrane**	**ACM membrane**
$pH_{initial}$	6.02	6.02	6.02
pH_{5days}	0.75	0.84	0.84
$\Delta[H^{+}]=10^{-pH_{5days}}-10^{-pH_{i}}$ **(amount of diffused H^{+} ions per volume (M))**	0.178	0.145	0.145

5.3.5 Nonlinear regression for experimental data of TMH system with AMX membrane

The experimental data from Figure 5.6 (c) for perchlorate concentration as functions of time in both zones of the TMH system with an AMX membrane were analyzed by non-linear regressions to determine coefficients for the adsorption-diffusion-reaction model and to evaluate its ability to describe observed results. The material balance model was applied to a batch reactor to generate the differential equation that describes how the concentration of perchlorate should change during experiments. The dimensionless parameters p(1), p(2), p(3) and p(6) in the ODEs (18), (20), (21) and (25) were obtained by least-squares non-linear regression using the MATLAB (MathWorks Inc.) function “nlinfit”. Solutions to the model were determined using the MATLAB function “ode15s”, which solves equations numerically by backward differentiation formulas.

Figure 5.7 shows the result of measured and predicted perchlorate concentrations in the contaminated zone and the degradation zone. Figure 5.8 shows concentrations of perchlorate at different nodes at element boundaries in the membrane at various times. At time zero, the perchlorate concentration at node 1 is same as the initial concentration (1.0 mM). After 1 hour, the concentration decreases from 0.5 mM at node 1 (boundary with contaminated zone) to 0.2 mM at node n (boundary with degradation zone). After 24 hours, the concentration profile becomes flat for all nodes and the average concentration decreases with time until the final time simulated (280 hr).

Table 5.4 shows the calculated values for coefficients in the model. The values of dimensionless variables p(1), p(2), p(3) and p(6) were calculated by nonlinear regression with experimental data. The effective diffusivity (D_e), adsorption coefficients (Q_0 and K) and first-order reaction rate coefficients (k) were calculated from the dimensionless variables. The values of physical coefficients in the dimensionless variables that were used in the calculations are: standard effective diffusivity (D_e^0) 3.8 E-4 m^2/hr, bulk density of membrane (ρ_b) 840 g/L, porosity of membrane (ε) 0.4 [85], initial perchlorate concentration (C_0) 1.0 mM, and thickness of membrane (L) 0.17 mm. The effective diffusivity that was calculated (3.8 E-06±1.92% m^2/hr) is much higher than the diffusivity of perchlorate through NF and UF membranes (2.95 E-10 m^2/hr), but a little smaller than the diffusivity of perchlorate in water (6.44 E-6 m^2/hr)[57, 58]. The reaction rate coefficient has a large 95% confidence interval. This seems to be due to the small number of data points after 24 hours that were be used to estimate the reaction rate constants. Also, the concentration of perchlorate in degradation zone is varying because the degradation zone is receiving perchlorate ions from contaminated zone through the membrane. Thus, it makes difficult to calculate the reaction rate constant in degradation zone with small confidence interval.

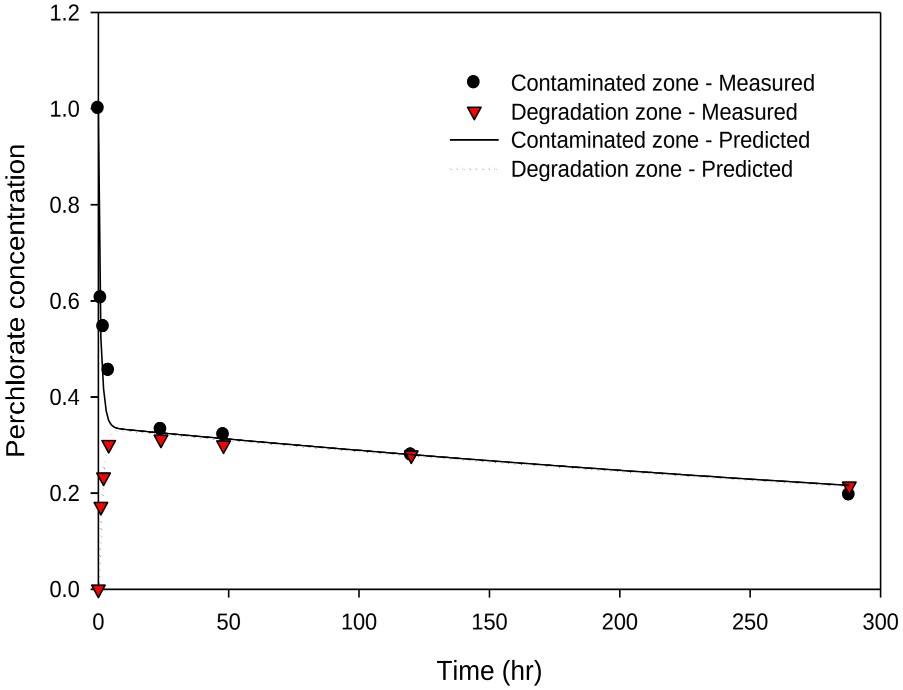


Figure 5.7. Measured and predicted perchlorate concentrations in both zones.

Table 5.4. Calculated values of coefficients Errors are 95% confidence intervals.

Dimensionless parameters	$p_1 = \frac{D_e}{D_e^0}$	$p_2 = \frac{\rho_b Q_0 K}{\epsilon (C^0)^2}$	$p_3 = \frac{K}{C^0}$	$p_6 = \frac{kL^2}{D_e^0}$
Coefficients	D_e (m^2/hr)	Q_0 (mmole/g)	K (mmole/L)	k (1/hr)
Calculated Values for coefficients	3.8×10^{-6} ± 1.92%	2.16×10^{-1} ± 2.06%	6.81 ± 1.43%	1.58×10^{-2} ± 424%

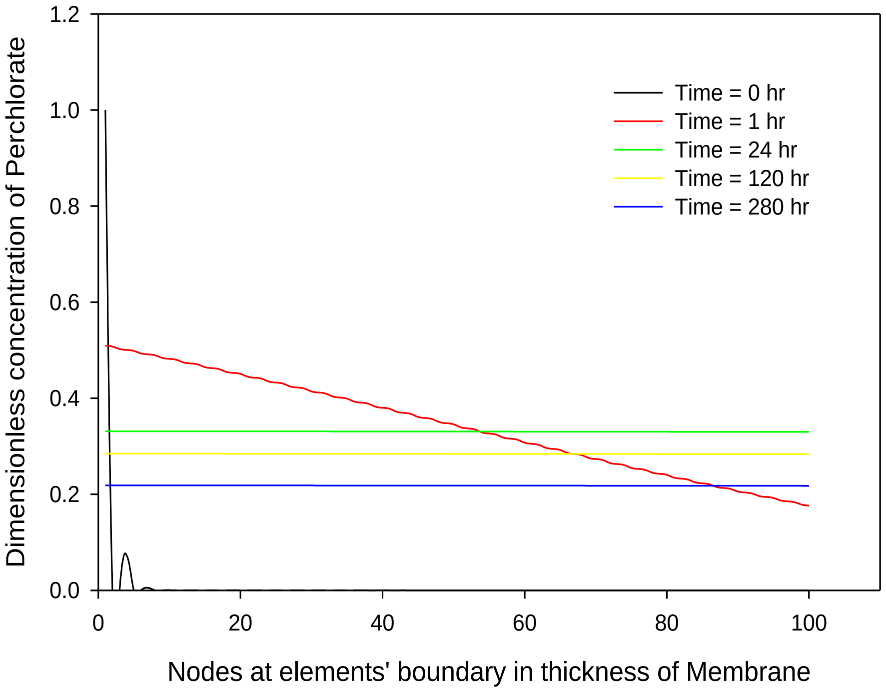


Figure 5.8. Concentration profile of perchlorate through the membrane at different times.

5.3.6 Predictions of perchlorate concentrations in TMH system under different conditions

The model can describe each coefficient's effects on physical and chemical behavior in the system. Figures 5.9, 5.10 and 5.11 show the effect of effective diffusivity, adsorption coefficient and reaction rate coefficient, respectively. Figure 5.9 shows that the higher effective diffusivity (D_e) enhances transport of perchlorate ions through the membrane to the degradation zone. Higher temperature can increase the effective diffusivity and it will also increase the reaction rate. The increased reaction rate will result in lower perchlorate concentration in degradation zone, which will increase the concentration gradient between contaminated zone and degradation zone, thereby increasing the rate of transport of perchlorate into the reaction zone. The adsorption coefficient (Q_0) describes the amount of perchlorate adsorbed per unit mass of ion exchange membrane at complete surface coverage [86]. Thus, the equilibrium concentration in solution would decrease with higher Q_0 values and this behavior is shown in Figure 5.10. Higher maximum surface coverages might be observed when pH is closer to the optimal pH for adsorption. Figure 5.11 shows that higher values of the rate constant (k) result in faster degradation. Higher concentrations of HCl can increase the reaction rate constant for perchlorate in the degradation zone as shown in chapter III, but additional experiments are needed to investigate side effects of higher acid concentrations, such as transfer of proton and Ti(III) ions. Also, higher temperature will result in an increase in the reaction rate constant.

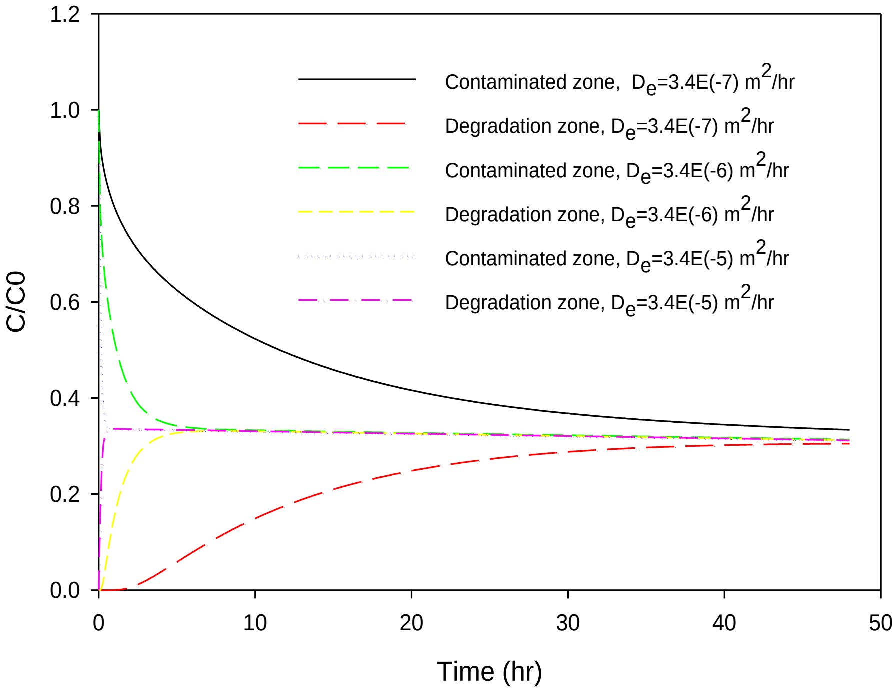


Figure 5.9. Predicted perchlorate concentration for different diffusivities.

Q_0=2.2 E-01 mmole/g, k=1.58 E-02 1/hr

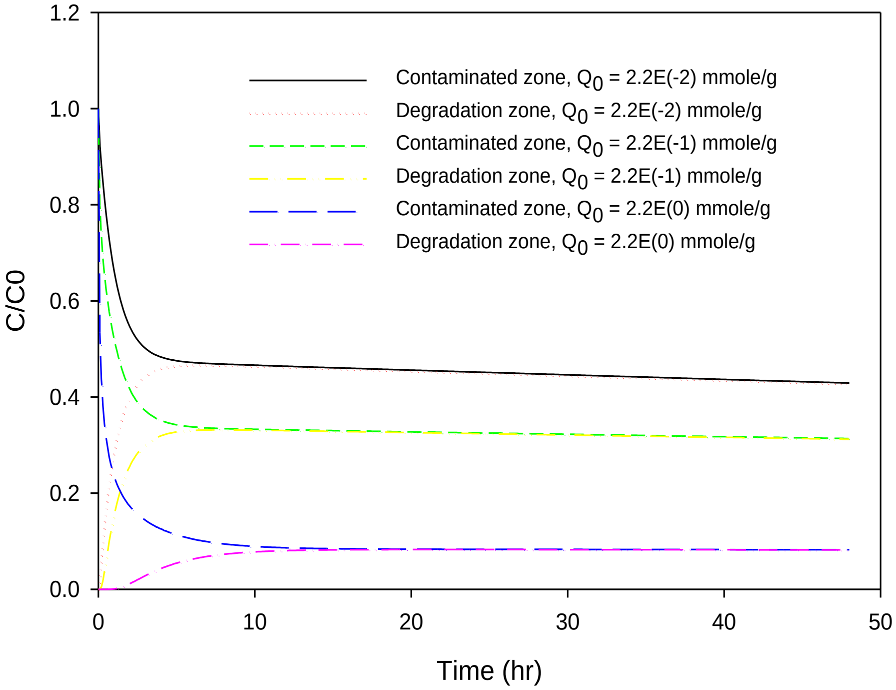


Figure 5.10. Predicted perchlorate concentration for different adsorption coefficients.

D_e=3.8 E-06 m^2/hr, k=1.58 E-02 1/hr

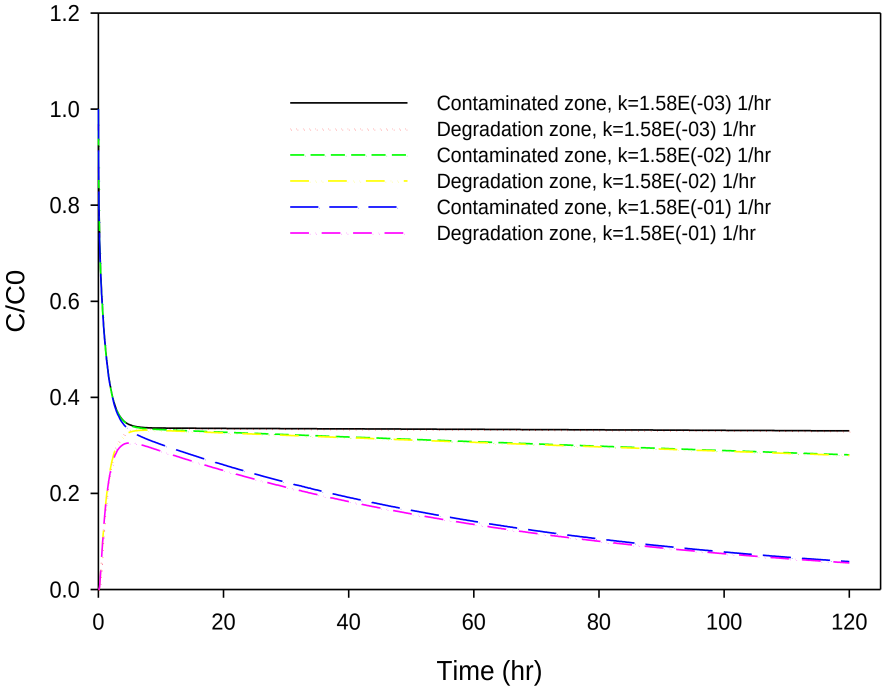


Figure 5.11. Predicted perchlorate concentration for different reaction rate coefficients.

D_e=3.8 E-06 m^2/hr, Q_0=2.2 E-01 mmole/g

5.4 Conclusions

The present study demonstrated the feasibility of a treatment system (TMH) that combines an ion exchange membrane and titanium ions for perchlorate reduction. To evaluate the TMH system, batch experiments were conducted to characterize perchlorate transport and reduction. The perchlorate ions were rapidly adsorbed onto the ion exchange membrane and diffused through it, but were reduced by Ti(III) ions in degradation zone relatively slowly. To enhance the overall rate of reaction, high concentrations of acid and Ti(III) are needed, but transport of hydrogen ions through the anion permeable membrane was observed and would be greater at higher acid concentrations. To apply the TMH system as a treatment method, membranes that can block hydrogen ions more effectively are needed.

The proposed mathematical model predicts the performance and behavior of the TMH system for different physical and chemical conditions. It successfully described adsorption, diffusion and reduction of perchlorate in the system. This model could be used as an important tool for process design and optimization.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The results shown in this research demonstrate the feasibility of using partially oxidized titanium ions with an ion exchange membrane to treat perchlorate and they also demonstrate the potential for treating other oxidized contaminants. The results of this research: 1) provide basic knowledge about methods for producing solutions of Ti(II) that are effective in degrading perchlorate, 2) characterize destruction of perchlorate by Ti(II) and Ti(III), and 3) evaluate the ability of a Titanium Membrane Hybrid System to provide for perchlorate treatment. This knowledge could be used to provide a novel method of destroying perchlorate in contaminated ground and surface waters, ion exchange regenerant solutions and other contaminated media.

The specific conclusions obtained from the research are as follows:

1) The amounts of Ti(II) produced using HCl and H_2SO_4 are similar when equivalent concentrations are used. The concentrations of Ti(II) produced with HCl and H_2SO_4 have a maximum difference of 21% when Ti(0) concentration is the same.

2) However, HCl was more effective than H_2SO_4 in promoting the ability of those solutions to degrade perchlorate when the concentration of acid was high. The reaction rate constants with H_2SO_4 are significantly smaller than those with HCl when 5 N acid was used at the same Ti(0) concentrations.

3) Higher concentrations of Ti(0) produced higher concentrations of Ti(II), which resulted in more rapid perchlorate destruction. The highest reaction rate constant achieved was 0.198±12.1% $mM^{-1}day^{-1}$ and half of initial perchlorate was degraded in less than one hour when 200 mM of Ti(0) and 10 N of HCl were used.

4) Rate constants for perchlorate degradation by Ti(II) increased with HCl concentrations. The highest reaction rate constant was 0.199±13.5% $mM^{-1}day^{-1}$ and half of the initial perchlorate was degraded in less than 1 hour when 300 mM of Ti(0) and 8.2 N of HCl were used.

5) Lower molar ratios of F/Ti(0) enhanced the production of Ti(II), which resulted in more effective reduction of perchlorate. This is an important result concerning production of Ti(II) solutions. Fluoride ions have critical effect on production of Ti(II).

6) Most of the metals that were tested showed no catalytic effect on the rate of perchlorate reduction, but rhenium (Re) increased the degradation rate to a small degree.

7) Absorption spectra of the Ti(II) solutions formed by reaction of Ti(0) in the presence of acid and fluoride showed that as F/Ti(0) molar ratio decreased, the absorbance spectra shifted to become similar to that of Ti(III) solutions. This implies that Ti(III) might be present in these solutions.

8) Higher concentration of HCl increased the reaction rate and its rate constant of perchlorate reduction by Ti(III).
9) High ionic strength does not enhance the perchlorate-Ti(III) reaction, but high acid concentration does.
10) Sodium or chloride ions do not seem to inhibit perchlorate reduction by Ti(III).
11) Metals (Mo, Cu, Ni, Re, W) do not have catalytic effects on the perchlorate-Ti(III) reaction.
12) The solid acid catalyst decreased the reaction rate between perchlorate and Ti(III), possibly due to the reduction in the concentration of Ti(III) ions caused by removal by cation exchange resins.

These conclusions show that perchlorate can be reduced by Ti(II) or Ti(III) in solutions with high concentrations of acid and titanium. However, the high acid concentration makes it difficult to practically apply the method to a treatment process. To overcome this weakness, a Titanium Membrane Hybrid System (TMH System) was developed and a physicochemical model was built to describe transport and degradation of perchlorate in this system. The specific conclusions for the TMH System are as follows :

13) The perchlorate ions were rapidly adsorbed onto the ion exchange membrane and diffused through it, but were reduced by Ti(III) ions in the degradation zone relatively slowly.

14) To enhance the overall rate of reaction, high concentrations of acid and Ti(III) are needed, but transport of hydrogen ions through the anion permeable membrane was observed and would be greater at higher acid concentrations. To apply the TMH system as a treatment method, membranes that can block hydrogen ions more effectively are needed.

15) The proposed mathematical model predicts the performance and behavior of the TMH system for different physical and chemical conditions. It successfully described adsorption, diffusion and reduction of perchlorate in the system. This model could be used as an important tool for process design and optimization.

6.2 Recommendations

The results described in this research propose some relevant research topics for future work in similar experimental systems. The specific research topics for future research are as follows.

1) Determination of the ability of Ti(II) and Ti(III) to reduce a variety of contaminants. The solutions of Ti(II) and Ti(III) could be used to reduce other specific environmental contaminants such as nitrate, chromate, arsenate, selenate, mercury and PCE. Therefore, more sets of batch kinetic experiments with various contaminants would be useful to develop Ti(II) and Ti(III) as reducing agents. Also, these contaminants' effects on perchlorate reduction should be evaluated.

2) Improvement of a kinetic model: The kinetic model developed in this research only considered concentrations of perchlorate and titanium ions to predict their

concentrations as functions of time. The model needs to be modified and improved to describe effects of concentrations of hydrogen ion and fluoride.

3) Enhancement of perchlorate removal rate in TMH System: As predicted from physicochemical modeling, the effective diffusivity and reaction rate constant influence the system's behavior very much. Higher temperature and higher concentrations of HCl and titanium ions could result in faster transport and degradation of perchlorate ions. More sets of experiment will be useful for development of TMH System as a practical treatment method.

4) Investigation of cation transfer through an ion exchange membrane: The transfer of cations such as hydrogen and oxidized titanium ions in TMH System through an anion exchange membrane is critical problem because it decreases system's efficiency and makes another contamination to target water.

5) Estimation of various ion exchange membranes: ACS, AMX and ACM were used in this research, but various ion exchange membranes from other manufacturer could be tested for best efficiency of TMH System to enhance perchlorate ions adsorption and transport and to prevent the transport of cations.

6) Application of TMH System to continuous flow reactor: In this research, TMH System was used as a batch reactor. To apply it for practical treatment process, its performance in continuous flow systems should be evaluated.

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APPENDIX A

NOMENCLATURE

Abbreviations

BAT	Best Available Technology
DOD	Department of Defense
DWEL	Drinking Water Equivalent Level
NRC	National Research Council
RFEP	Relative Fitting Error Parameter
SSR	Sum of Squared Residuals
TMHS	Titanium and Membrane Hybrid System

Chemicals

Bzqn	Benzoquinone
CHBzqn	2,5-Dichloro-3,6-dihydroxybenzoquinone
Cl^-	Chloride
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate
Cu	Copper
F^-	Fluoride
HCl	Hydrochloric acid

HF	Hydrofluoric acid
H_2SO_4	Sulfuric acid
Mo	Molybdenum
NDS	Nitrosodisulfonate
Ni	Nickel
Re	Rhenium
Ti	Titanium
Ti(II)	Divalent titanium (Ti^{2+})
Ti(III)	Trivalent titanium (Ti^{3+})
Ti(IV)	Tetravalent titanium (Ti^{4+})
W	Tungsten
ZVI	Zero Valent Iron

Symbols

C	Perchlorate concentration on liquid volume basis
C_a	Concentration of perchlorate in the contaminated zone
C_b	Concentration of perchlorate in the degradation zone
C_c	Concentration of the competing ion
C_e	Equilibrium concentration of perchlorate in solution
C^0	Standard concentration (initial concentration)
D_e	Effective diffusivity (L^2/T)
D_e^0	Standard effective diffusivity (L^2/T)

ε	Porosity of film (membrane)
h_e	Width of element
L	Thickness of film
q	Mass of perchlorate in membrane [M/M]
Q_o	Maximum concentration of perchlorate in membrane
ρ_b	Bulk density of film (M/L^3)
V_a	Volume of solution in the contaminated zone
V_b	Volume of solution in the degradation zone
x	Distance into the membrane

APPENDIX B

COMPUTER PROGRAM (MATLAB) TO PREDICT PERCHLORATE DEGRADATION BY AQUEOUS TITANIUM IONS

B1. This program calculates perchlorate reaction rate constant with Ti(II) and initial Ti(II) concentration by nonlinear regression

```
clc
clear all
global Ti0 ClO40       %Ti0 = initial Ti(II) concentration
data=load('exp7_1.txt') % call data file
t_data=data(:,1)       % assign time data
c_data=data(:,2)       % assign conc. data
ClO40=c_data(1)        % initial perchlorate conc.
n=length(c_data);
Ti0=4*(c_data(1)-c_data(length(c_data)))     % initial guess of initial [Ti(II)]

[beta,resid,j]=nlinfit(t_data,c_data,@callode_1,[0.001 Ti0]);
k=beta(1)              % determine k and initial Ti2+ using nonlinear regression

Ti_initial=beta(2)
betaci=nlparci(beta,resid,j)   %  call function to calculate confidence intervals

percenterror1=(beta(1)-betaci(1))/beta(1)*100        % Calculate percentage error of k
percenterror2=(beta(2)-betaci(2))/beta(2)*100        % Calculate percentage error of
Ti(II)

[tout,cout]= ode45(@matbalance2k, t_data, [c_data(1), beta(2)],[],beta(1));
%for detailed data use [0:0.1:t_data(length(t_data)) instead of t_data
% run ODE to obtain model concentration

plot(t_data, c_data,'o',tout, cout(:,1), '-')
xlabel('Time (day)')
ylabel('[ClO_4^-] (mM)')
legend('Experiment','Model')

hold on
out=[tout cout];
```

```
SR=(c_data-cout(:,1)).^2
SSR=sum(SR)
half_perchlorate=cout(1,1)/2
out(find(abs(max(out(:,2))/2-out(:,2)) == min(abs(max(out(:,2))/2-out(:,2)))),:)
% Find half life of perchlorate

GFP=sqrt(SSR/(n-2))/mean(c_data)   % Calculate Relative Fitting Error Parameter
percenterror1
percenterror2

----------------
function c=callode_1(k,t_data)
global ClO40
    [tout,cout]= ode45(@matbalance2k, t_data, [ClO40 k(2)],[],k(1));
    c=cout(:,1);
----------------

function dcdt=matbalance2k(t,c,k,Ti0)
c(2)=Ti0
r=k*c(1)*c(2);
dcdt(1)=-r;
dcdt(2)=-4*r;
dcdt=dcdt';
```

B2. **This program calculates perchlorate reaction rate constant with Ti(II) by nonlinear regression**

```
clc
clear all
global Ti2 ClO40
data=load('exp8_1.txt');        % call data file
t_data=data(:,1)                 % assign time data
c_data=data(:,2)                % assign conc. data
ClO40=c_data(1);                % initial perchlorate conc.

plot(t_data,c_data,'o')
hold on

Ti2=100;                        % This is initial Ti(II) concentration

[beta,r,j]=nlinfit(t_data,c_data,@callode_2,[0.005]);
k=beta                          % determine k using nonlinear regression
betaci=nlparci(beta,r,j)        %95% confident interval

percenterror=(beta(1)-betaci(1))/beta(1)*100
[tout,cout]= ode45(@matbalance2k, t_data, [c_data(1), Ti2],[],beta);

% run ODE to obtain model concentration

plot(t_data, c_data,'o',tout, cout(:,1))
xlabel('Time (day)')
ylabel('[ClO_4^-] (mM)')
legend('Experiment','Model')
gtext('exp15-2')
hold on

out=[tout cout];

SR=(c_data-cout(:,1)).^2
SSR=sum(SR)

half_perchlorate=cout(1,1)/2
out(find(abs(max(out(:,2))/2-out(:,2)) == min(abs(max(out(:,2))/2-out(:,2)))),:)

[tout_whole,cout_whole]=         ode45(@matbalance2k,[0:0.01:t_data(length(t_data))],
[c_data(1), Ti2],[],beta);  %[0:0.01:t_data(length(t_data))]
plot(tout_whole, cout_whole(:,1),'r')
```

```
----------------
function c=callode_2(k,tt)
global Ti0 ClO40
%if(size(t,1)==1)
   tspan=tt;
   [tout,cout]= ode45(@matbalance2k, tspan, [ClO40 Ti0],[],k,Ti0);
   c=cout(:,1);
----------------

function dcdt=matbalance2k(t,c,k,Ti0)

c(2)=Ti0
r=k*c(1)*c(2);
dcdt(1)=-r;
dcdt(2)=-4*r;
dcdt=dcdt';
```

B3. This program calculates initial Ti(II) concentration with constant reaction rate constant by nonlinear regression

```
clc
clear all
global Ti0 ClO40 fk             %fk = fixed rate constant k
data=load('exp7_1.txt')         % call data file
t_data=data(:,1)                % assign time data
c_data=data(:,2)                % assign conc. data
ClO40=c_data(1)                 % initial perchlorate conc.
n=length(c_data);
Ti0=4*(c_data(1)-c_data(length(c_data)))     % initial guess of initial [Ti2+]
fk=0.00696 ;


[beta,resid,j] = nlinfit(t_data,c_data,@callode_fixedk,Ti0)
% determine k and initial Ti2+ using nonlinear regression
Ti_initial=beta

betaci=nlparci(beta,resid,j)     %  call function to calculate confidence intervals
percenterror1=(beta(1)-betaci(1))/beta(1)*100

[tout,cout]= ode45(@matbalance2fixedk, t_data, [ClO40 beta])
% run ODE to obtain model concentration

plot(t_data, c_data,'o',tout, cout(:,1), '-')
xlabel('Time (day)')
ylabel('[ClO_4^-] (mM)')
legend('Experiment','Model')

hold on
out=[tout cout];

SR=(c_data-cout(:,1)).^2
SSR=sum(SR)
half_perchlorate=cout(1,1)/2
out(find(abs(max(out(:,2))/2-out(:,2)) == min(abs(max(out(:,2))/2-out(:,2)))),:)

[tout_whole,cout_whole]=   ode45(@matbalance2fixedk,   [0:0.1:t_data(length(t_data))],
[ClO40 beta]);  %for detailed data use [0:0.1:t_data(length(t_data))] instead of t_data
```

```
GFP=sqrt(SSR/(n-2))/mean(c_data)
percenterror1

----------------
function c=callode_fixedk(beta,t_data)
global ClO40
   [tout,cout]= ode45(@matbalance2fixedk, t_data, [ClO40 beta]) %,[],beta)
   c=cout(:,1);
----------------

function c=callode_fixedk(beta,t_data)
global ClO40
   [tout,cout]= ode45(@matbalance2fixedk, t_data, [ClO40 beta]) %,[],beta)
   c=cout(:,1);
```

B4. This program calculates perchlorate reaction rate constants with Ti(III) by nonlinear regression

```
clc  % with fixed Ti(III) condition
clear all
global Ti3 ClO40                  % Ti3=conc.of Ti(III)
data=load('exp14_1.txt');        % call data file
t_data=data(:,1);                % assign time data
c_data=data(:,2);                % assign conc. data
ClO40=c_data(1);                 % initial perchlorate conc.

Ti3=100;                         % Concentration of Ti(III)

[beta,r,j]=nlinfit(t_data,c_data,@callode_3,[0.005]);
k=beta                           % determine k using nonlinear regression
ci=nlparci(beta,r,j)             %95% confident interval

[tout,cout]= ode45(@matbalance3k, [0 t_data(length(t_data))], [c_data(1), Ti3],[],beta);
% run ODE to obtain model concentration

plot(t_data, c_data,'o',tout, cout(:,1), '-')
xlabel('Time (day)')
ylabel('[ClO_4^-] (mM)')
legend('Experiment','Model')
%gtext('exp4-2')
hold on

----------------
function c=callode_3(k,t) % with fixed Ti(II) condition
global ClO40 Ti3
%if(size(t,1)==1)
   tspan=t
   [tout,cout]= ode45(@matbalance3k, tspan, [ClO40 Ti3],[],k)
   c=cout(:,1);
----------------

function dcdt=matbalance3k(t,c,k)
r=k*c(1)*c(2);
dcdt(1)=-r;
dcdt(2)=-8*r;
dcdt=dcdt';
```

APPENDIX C

COMPUTER PROGRAM (MATLAB) TO PREDICT PERCHLORATE ADSORPTION, DIFFUSION AND REACTION IN A TITANIUM MEMBRANE HYBRID SYSTEM

```
clc
clear all
global cout n c tout p rout

data=load('amxdata_all.txt')             % call data file
data2=load('amxdata.txt')

t_all_data=data(:,1)    % assign time data
all_data=data(:,2);
% assign concentration of perchlorate data in contaminated zone and degradation zone
together

t_data=data2(:,1);      % assign time data
c_data=data2(:,2);      % assign conc. of contaminated zone data
r_data=data2(:,3);      % assign conc. of degradation zone data

plot(t_data,c_data,'r*')
hold on
plot(t_data,r_data,'o')

beta0 = [32 5.6 21 15]          % assign initial guess for beta
[beta,r,j]=nlinfit(t_all_data,all_data,@diffads_psh,beta0)
betaci=nlparci(beta,r,j)

Depercenterror=(beta(1)-betaci(1))/beta(1)*100
Qopercenterror=(beta(2)-betaci(3))/beta(2)*100
Kpercenterror=(beta(3)-betaci(5))/beta(3)*100
kpercenterror=(beta(4)-betaci(7))/beta(4)*100
% Calculate percentage errors of De, Q0, K and k

plot(tout,cout(:,1),'r')
plot(tout,cout(:,n),'b')
xlabel('time(hr)')
ylabel('C/C0')
```

```
----------------
function c=diffads_psh(beta,t)
% This function similates diffusion and Langmuir adsorption through a film
% It assumes that two solutions of known volume exist on each side of the
% film.  While diffusing through the film, a compound adsorbs/desorbes to
% the film and the adsorption/desorption achieves local equilibrium as
% described by the Langmuir isotherm equation.  The dynamic material
% balance equations are converted to ODEs by applying orthogonal
% collocation on finite elements, using elements with two internal nodes.
% The ODEs and algebraic equations are solved with a call to ode15s.
% The options used by the ode solver can in the statement that calls
% odeset, which is near the bottom of the program.

global cout n c tout p rout

% User adjusted values:
n=100 ;                 % number of nodes
                 % check to see if n is appropriate value for OC with two internal nodes
                 % (check for when different values of n are specified)
   if (rem((n-1),3)+0.01 > 0.10)
      error('The value of n is not compatable with this type of orthogonal collocation on
finite elements.  (n-1)/3 should be an integer.')
   end

% define c0, dimensionless concentrations
c0=zeros(1,n);
c0(1)=1;
% dimensionless concentration in solution A and at node 1 assuming standard
concentration set at initial C_a

% Define dimensionless parameters

Q0 = 4.52/1000 ;        % assign Q0 value     [mmole/g]
K  = 2.78 ;             % assign K value      [mmole/L]
A = 2.1*10^(-3);        % contact area of membrane  [m2]
L = 1.7*10^(-4);        % thickness of membrane     [m]
V = 10^(-5);            % volume of zones           [m3]
m = 0.3;                         % mass of membrane          [g]
rho_b = m/(A*L)/1000;            % density of membrane       [g/L]
epsilon=0.4;                     % porosity of membrane
C0=1;                            % initial concentration of perchlorate
De0 = 10^(-7);                   % standard effective diffusivity [m2/hr]
```

```
p=zeros(1,6);
p(1)= beta(1) ;
p(2)= rho_b * beta(2)*beta(3) /(epsilon *C0^2);
p(3)=beta(3)/C0;
p(4)=epsilon*A*L/V;
p(5)=epsilon*A*L/V;
p(6)=10^(-3)*beta(4)*L^2/De0;
p;
beta;
% end of parameter specification section

ne=(n-1)/3 ;    % calculate number of elements

% specify roots of polynomials on each element, i.e. location of node on each element
%  x= [0.0 0.211324865 0.788675135 1.0];

% specify A matrix (alpha=0, beta=0 as per Villadsen; non-symetric, planar, W=1 as per
Finlayson)
% roots at x = 0.0 0.211324865 0.788675135 1.0
A=[-6.999999987004  8.19615248704 -0.196152469502  .9999999694669;
-2.732050422526578  1.73205025788307  1.732051036984493 -.7320508723409855;
 .73205086956148 -1.732051032170222 -1.732050262697411  2.732050425306153;
 -1.000000903425764  2.196153747076371 -8.196152835469297  6.99999999181869];
%
% specify B matrix(alpha=0, beta=0 as per Villadsen; non-symetric, planar, W=1 as per
Finlayson)
B = [24.000001754868 -37.176917442313  25.17691554894949 -11.99999986150519 ;
 16.39230528473852 -24.00000082220009  12.00000010694436 -4.3923045694828 ;
-4.392307832837197  12.00000458113203 -24.00000207773684  16.39230532944201 ;
-12.00000358771175  25.17691996238572 -37.17691628088263  23.99999990620866];

% define mass matrix used by ode solver (ode15s)
md=ones(1,n);
md(4:3:n-3)=0;
%solidzero=ones(1,ns);
%solidzero(1:3:ns)=zeros(1,(nes+1));
%for i=1:2*ne
%md=[md solidzero];
%end
M=diag(md);

options=odeset('Mass', M);
```

```
% Call ode solver

[tout,cout]=ode15s(@deriv_diffads_psh,t,c0,options,A,B,n,p);

z=zeros(16,1);
for i=1:2:15
   z(i)=cout(i,1);
end
for i=2:2:16
   z(i)=cout(i/2,n) ;
end
c=z;
% plot(t,c,'*')
----------------
function dcdt=deriv_diffads_psh(t,c,A,B,n,p)
% Function to calculate derivatives of concentration with time.  Called by ode solver.

% calculate thickness of element
he=3/(n-1);

%Calculate derivatives
dcdt=zeros(n,1);
dcdt(1)=p(1)*p(4)*(A(1,:)*c(1:4))./he; % node at boundary with solution A
for k=3:3:n-4
   dcdt(k-1) = p(1)*(B(2,:)*c(k-2:k+1))./(1+p(2)/(p(3)+c(k-1))^2)./he^2; % internal node
   dcdt(k) = p(1)*(B(3,:)*c(k-2:k+1))./(1+p(2)/(p(3)+c(k))^2)./he^2; % internal node
   dcdt(k+1)=A(4,:)*c(k-2:k+1)-A(1,:)*c(k+1:k+4); % node at element boundary
end
dcdt(n-2)=p(1)*(B(2,:)*c(n-3:n))./(1+p(2)/(p(3)+c(n-2))^2)./he^2; % internal node
dcdt(n-1)=p(1)*(B(3,:)*c(n-3:n))./(1+p(2)/(p(3)+c(n-1))^2)./he^2; % internal node
dcdt(n)=-p(1)*p(5)*A(4,:)*c(n-3:n)/he-p(6)*c(n); % node at boundary with solution B
------------------
```

% amxdata.txt
(time, concentration in contaminated zone,
concentration in degradation zone)

```
0 1.000 0.000

1 0.606 0.172

2 0.546 0.233

4 0.455 0.301

24 0.332 0.312

48 0.321 0.300

120 0.279 0.279

288 0.196 0.214
```

% amxdata_all.txt
(time, concentration in both zones)

```
0 1.000

0.0001 0.000

1 0.606

1.0001 0.172

2 0.546

2.0001 0.233

4 0.455

4.0001 0.301

24 0.332

24.0001 0.312

48 0.321

48.0001 0.300

120 0.279

120.0001 0.279

288 0.196

288.0001 0.214
```

VITA

Sung Hyuk Park was born in Daejeon, Korea. He received his B.S. degree in civil engineering from Hanyang University in Korea in 1999. After receiving his B.S. degree, he served in the Korean Army for three years and finished in 2002 as a first lieutenant. He joined the civil and environmental engineering program in KAIST (Korea Advanced Institute of Science and Technology) and received his M.S. degree while majoring in environmental engineering in 2005. Since joining the environmental engineering program in the Civil Engineering Department at Texas A&M University for his Ph.D. degree, his research has focused on the reduction of perchlorate by titanium ions and ion exchange membrane. His interests include environmental chemistry and engineering for water supply, serving people who are lacking clean water internationally, and making environmental policy. He can be reached at Zachry Department of Civil Engineering, Texas A&M University, 3136 TAMU, College Station, TX 77843-3136 (Dr. Bill Batchelor).