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**AN INVESTIGATION INTO PALLADIUM – CATALYZED  
REDUCTION OF PERCHLORATE IN WATER**

Eric G. Barney, Captain, USAF, BSC

AFIT/GES/ENV/05M-01

**DEPARTMENT OF THE AIR FORCE  
AIR UNIVERSITY**

***AIR FORCE INSTITUTE OF TECHNOLOGY***

**Wright-Patterson Air Force Base, Ohio**

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AFIT/GES/ENV/05M-01

AN INVESTIGATION INTO PALLADIUM – CATALYZED REDUCTION OF  
PERCHLORATE IN WATER

THESIS

Presented to the Faculty

Department of Systems and Engineering Management

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Air University

Air Education and Training Command

In Partial Fulfillment of the Requirements for the  
Degree of Master of Science in Environmental Engineering and Science

Eric G. Barney, BS

Captain, USAF, BSC

March 2005

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PERCHLORATE IN WATER

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Abstract

Perchlorate is an emerging environmental contaminant which has been the focus of intense regulatory interest in recent years. As a major component in rocket and missile systems, perchlorate is also a critical national defense material. As such, effective and versatile treatment technologies for dealing with perchlorate contamination are needed.

In this study, application of a catalytic reactor to facilitate chemical reduction of perchlorate was investigated. Palladium-coated pellets were used as the catalyst, and formic acid was used as the reductant. Reactor performance was evaluated under a variety of operating conditions (influent pH, reductant concentration, residence time).

Very little perchlorate reduction was observed under any operating condition. At best, approximately 8% perchlorate reduction was observed. This small reduction efficiency is clearly not sufficient for environmental treatment applications. Perchlorate strongly adsorbed to the catalyst at low pH (3 – 3.3). At higher pH (4 – 10), little adsorption was observed. This pH behavior may be the result of dissociation of formic acid ( $pK_a \sim 3.75$ ). It is possible that perchlorate reduction was limited by the amount and speciation of formic acid in the system. Maximum perchlorate reduction was observed at high reductant concentration (10 millimolar formic acid) and low pH (minimized dissociation of formic acid to formate ion). Increasing the formic acid concentration and reducing the upward pH drift of the bulk fluid (via reduced residence time) may improve perchlorate reduction.

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Eric G. Barney

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# AN INVESTIGATION INTO PALLADIUM – CATALYZED REDUCTION OF PERCHLORATE IN WATER

## **1.0 Introduction**

### ***1.1 Motivation***

Perchlorate-contaminated water has become a major concern in the United States. In the last several years, the federal government has devoted a great deal of attention to assessing the scope and severity of perchlorate contamination. Most notably, perchlorate has been added to the Contaminant Candidate List, the Environmental Protection Agency (EPA) laundry list of substances which may require regulation under the Safe Drinking Water Act. If regulations are promulgated, effective remediation strategies that are capable of attaining regulatory standards will be required.

Perchlorate compounds have been used in a few common commercial products such as fireworks, flares, and matches. However, the major use for perchlorate salts has been as an oxidant in rocket boosters and missile systems. Much of the current perchlorate contamination is believed to be the result of legal (non-regulated) discharges from rocket fuel production activities (Urbansky, 1998). Other contamination is a result of accidental releases, such as the one which occurred during a 1988 explosion at a rocket fuel-

production factory near Henderson, Nevada (Hogue, 2003). These releases have impacted both groundwater and surface drinking water sources. Directly or indirectly, activities associated with defense projects and other federal aerospace programs are likely responsible for much of the perchlorate contamination in the environment.

According to EPA data from April 2003, perchlorate manufacturers or users are located in 40 states, and at least 25 states have had confirmed perchlorate releases (Mayer, 2003). The EPA has also collected information about detection of perchlorate in drinking water systems as part of their Unregulated Contaminant Monitoring Rule (UCMR) (USEPA, 2004c). As of December 2004, a total of 3,555 drinking water systems have performed analyses for perchlorate in accordance with the UCMR, and 147 of those systems detected perchlorate in their water at the EPA Minimum Reporting Level (four micrograms per liter) or higher. Though less than five percent of the water systems detected perchlorate, the vast majority of these systems were rated as “large” or “very large” suppliers. The total population served by the 147 systems detecting perchlorate was over 11 million people. Most small to medium-sized water systems are not subject to UCMR requirements, so many additional people who receive water from these untested systems may also be exposed to perchlorate-contaminated drinking water.

Some physiological effects of perchlorate exposure are well-known. The perchlorate ion is similar in size and electrical charge to the iodide ion, so the perchlorate ion can pass into the thyroid gland in place of iodide (Urbansky, 2002). This reduces the level of

iodide in the gland, which in turn reduces hormone production. Historically, perchlorate has been used medicinally for at least two purposes. First, it has been used to treat Graves' Disease, a condition where the thyroid produces excessive amounts of hormones. Second, it has been used to counteract a side-effect of amiodarone, a cardiac drug. Amiodarone produces free iodide when it degrades, and perchlorate is used to prevent the thyroid from taking up excessive levels of iodide (Urbansky, 2002).

The health effects associated with long-term, low-level perchlorate exposure are uncertain. In the last several years, much research has been conducted in order to fill data gaps which have frustrated efforts to develop realistic health and ecological risk assessments. In 2002, the EPA released an updated draft health risk assessment on perchlorate toxicity. The draft assessment applied a reference dose level of 0.00003 milligrams per kilogram per day, which would possibly translate into a drinking water standard of around 1 microgram per liter ( $\mu\text{g/L}$ ) (USEPA, 2004b). The Department of Defense (DoD), which supplied much of the data used by the EPA, strongly disagreed with the reference dose and several other aspects of the risk assessment. DoD argued that the scientific evidence indicated that human health would still be protected at a much higher perchlorate concentration (Rogers, 2003). On the other hand, at least one environmentalist group (EWG, 2004) advocates for a drinking water regulatory standard well below the proposed EPA level. Citing concerns about reproductive effects, the Environmental Working Group believes the perchlorate drinking water standard should be no higher than 0.1  $\mu\text{g/L}$ .

Because of the controversy surrounding the draft EPA risk assessment document, the National Academies of Science (NAS) has been asked to evaluate the scientific basis behind the 2002 EPA risk characterization. In 2003, the NAS Board of Environmental Studies and Toxicology (BEST) began the evaluation process. BEST was charged with determining whether the findings expressed in the EPA assessment were consistent with all available scientific evidence (NAS, 2005a). In their January 2005 report, BEST identified several flaws in the EPA risk characterization methodology, and recommended a reference dose approximately 23 times higher than the proposed EPA value (NAS, 2005b). It remains to be seen whether the BEST recommendation is accepted by EPA, or whether it will lead to additional delays in promulgating regulations. Conceivably, the perchlorate MCL may eventually be set somewhere in the range of 1 to 25  $\mu\text{g}/\text{L}$ .

Although the severity of the perchlorate health risk has been a matter of contention in recent years, federal regulations will almost certainly be promulgated at some point. In addition, some states are already moving toward regulatory standards. The California Department of Health Services has had a drinking water “action level” for perchlorate since 1997. Most recently, the action level has been revised to a value of 6  $\mu\text{g}/\text{L}$ . While the action level is not an official regulatory standard, it is being used as the basis for promulgating a regulatory maximum contaminant limit for perchlorate in California drinking water (CDHS, 2005).

DoD considers perchlorate to be an essential national defense material because of several special properties. Perchlorate is a highly efficient oxidizer, and is also relatively easy to handle (Rogers, 2003). With regulatory standards on the horizon, effective and versatile methods for dealing with contamination must be developed. Perchlorate contamination may be found in a variety of media, such as soil, groundwater, surface water, and industrial wastewater. Ideally, a perchlorate remediation technology should have excellent performance characteristics across a wide range of conditions (concentration, pH, temperature, *etc.*). Such versatility would potentially yield a treatment method with multiple applications including (i) *in situ* groundwater treatment, (ii) drinking water treatment (both for groundwater (*ex situ*) and surface water), and (iii) direct treatment of perchlorate-contaminated industrial process water. Unfortunately, perchlorate has unusual chemical properties that make treatment a difficult challenge.

First, perchlorate compounds have high solubilities. For example, at a temperature of 20 degrees celsius, 20.85 grams of ammonium perchlorate can be dissolved in just 100 cubic centimeters of water (Perry and Green, 1997). The perchlorate ion has poor sorption characteristics, so it can easily travel with the flow of groundwater or surface water. This high solubility and mobility means that perchlorate can easily migrate throughout the environment, potentially impacting drinking water sources located far from the initial release area.



Second, the perchlorate ion is remarkably stable in water. The ion consists of a chlorine atom bonded to four separate oxygen atoms. In this configuration, chlorine is in a highly oxidized state, with a charge of +7. Based on thermodynamics, the perchlorate ion should be easily reduced to chloride or chlorate (Urbansky, 1998). However, in reality, the perchlorate is essentially non-reactive in water. Urbansky (1998) suggests that reaction kinetics, not thermodynamics, is the limiting factor in perchlorate reduction. Urbansky and Schock (1999) suggest that the slow reduction reaction rate observed with perchlorate is caused by oxygen atoms shielding the chlorine atom from potential reducing agents (Urbansky and Schock, 1999).

Researchers have tried a variety of physical, chemical, and biological methods to treat perchlorate-contaminated waters (Urbansky, 1998). Currently, biological treatment is considered one of the most promising destruction mechanisms (Logan, 2001; Urbansky, 2002). However, the public may not accept biological treatment as a remediation method, particularly for drinking water supplies. Physical removal via ion exchange is also possible with perchlorate-contaminated water streams, and recent advances with ion exchange resins have improved their selectivity for perchlorate. Unfortunately, the ion exchange process does not destroy perchlorate; the contaminant is simply removed from the water, generating a secondary waste stream (perchlorate-contaminated resin and/or regeneration brine) which requires additional treatment or disposal.

As mentioned above, conventional chemical reduction is problematic due to slow reaction kinetics. However, another potential treatment strategy is to use catalytic reduction techniques. This process involves using a reductant (that is, a compound that can serve as an electron donor, such as hydrogen or formic acid) to degrade an oxidized contaminant (which serves as an electron acceptor) at the surface of a catalyst material. Catalytic reduction on palladium pellets has been shown to be effective in destroying chlorinated aliphatic hydrocarbons (CAHs) such as trichloroethylene (Welling, 2004). The process has also been shown to reduce nitrate ( $\text{NO}_3^-$ ) to nitrogen ( $\text{N}_2$ ) (Centi and Perathoner, 2003; Pallavi, 2003), though the transformation efficiency was found to be dependent on both pH and the physical properties of the catalyst. Perchlorate, like nitrate, is an inorganic anion that is an oxidized contaminant; therefore, catalytic reduction may be a viable treatment option. A study has evaluated perchlorate reduction on iron surfaces and reported relatively slow reaction rates (Moore *et al.*, 2003). To date, no studies investigating reduction of perchlorate via palladium catalysis have been identified. If viable, catalytic reduction could be used *in situ* to treat groundwater contamination, and also may potentially be used to treat surface water and wastewater streams (for example, a concentrated perchlorate waste stream from an existing ion exchange system). As such, catalytic reduction may be quite versatile compared to other proposed treatment methods. In addition, perhaps catalytic reduction could be used to simultaneously treat multiple contaminants.

As discussed earlier in this chapter, perchlorate is a potential contamination threat in at least 40 states. Also, groundwater aquifers and surface water sources across the U.S. have been contaminated with nitrate as a result of agricultural activities (USEPA, 2005b). Further, a review of the current EPA National Priorities List (<http://www.epa.gov/superfund/sites/npl/npl.htm>) clearly shows that CAHs such as trichloroethylene and tetrachloroethylene are very common on Superfund sites. Given the widespread occurrence of these different contaminants, some sites will inevitably be contaminated with a mixture of compounds, potentially requiring separate remediation technologies for each contaminant.

As an example, groundwater at the Aerojet facility near Rancho Cordova, California, is currently contaminated with CAHs, nitrate, and perchlorate. The current remediation plan for Aerojet Operable Unit 3 (OU-3) involves using a biological or ion exchange system to eliminate nitrate and perchlorate, while CAH contamination would be removed using a combination of ultraviolet light and air sparging technologies (USEPA, 2005a). As described earlier in this section, catalytic reduction is a promising remediation technology for treating CAH and nitrate contamination. If similar success can be demonstrated with perchlorate, perhaps catalytic reduction can serve as a unified solution for sites where CAHs, nitrate, and perchlorate are the primary contaminants of concern. At sites such as Aerojet, this would obviously simplify site operations, and may also lead to significant cost savings.

### ***1.2 Research Objective***

The main objective of this research is to assess the potential of palladium-catalysis to treat perchlorate-contaminated water. The experimental tasks include the following:

1. Determine how the rate and extent of perchlorate reduction is impacted by experimental conditions (*e.g.* pH, use of molecular hydrogen or formic acid as a reductant)
2. Investigate the formation of undesirable daughter compounds (*e.g.* chlorite) as a potential result of reduction
3. If the technology appears viable, develop a model of the reduction kinetics that can be used in technology design

### ***1.3 Research Methodology***

1. Perform a detailed literature search/review, with the goals of:
  - a. Ascertaining the current “state of science” with respect to catalytic reduction of anionic compounds (such as nitrate) in water.
  - b. Identifying models that have been applied to simulate catalytic reduction of anionic or organic compounds in water.
2. Using the existing palladium catalyst reactor at Wright State University, conduct flow-through column experiments to ascertain the rate and extent of perchlorate

reduction for varying operating parameters such as influent concentration, ambient pH, reactor residence time, and type of reductant.

3. Investigate whether the rate data obtained in the column experiments can be simulated using simple kinetic models (*e.g.* first-order, Michaelis-Menten, Langmuir-Hinshelwood, *etc.*)
4. Investigate the potential for formation of undesirable byproducts as a result of reduction.

## **2.0 Literature Review**

### ***2.1 Introduction***

This chapter summarizes research into perchlorate remediation that is relevant to this study. Background topics include sources of perchlorate contamination as well as health effects and regulatory issues. Following these sections, a brief discussion of “conventional” chemical, physical, and biological perchlorate remediation technologies will be presented. Finally, research in palladium-catalyzed reduction systems will be described.

### ***2.2 Sources of Perchlorate Contamination***

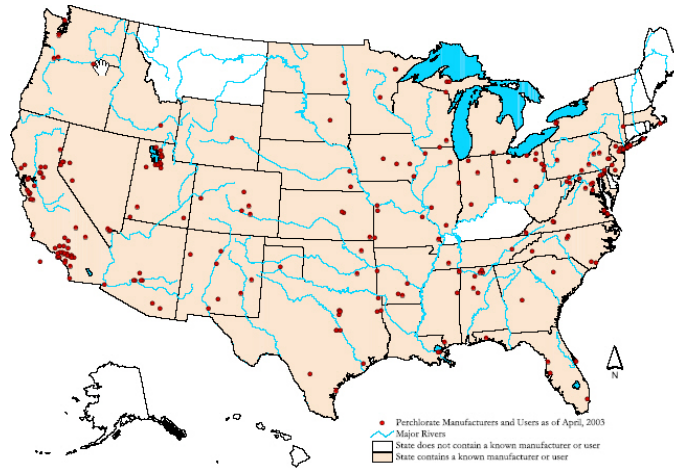
As mentioned in the previous chapter, DoD is the major consumer of perchlorate compounds within the United States. Perchlorate compounds have been produced in large quantities since the 1940s (Pontius *et al.*, 2000). Much of the perchlorate produced in the U.S. is used in solid rocket engines as the oxidizing component of the propellant. These propellants have finite shelf lives and must be periodically changed out (engine drained and refilled with fresh propellant) to ensure operational readiness of the rocket. Both the industrial manufacturing process and the rocket maintenance activities have generated large quantities of perchlorate waste. In the past, the lack of applicable discharge regulations led to the direct release of perchlorate-containing waste to the environment.

While DoD is the major user of perchlorate, several other small-scale uses exist. A variety of perchlorate salts are commercially available. The perchlorate salt used in rocket propellants, ammonium perchlorate, is also used in fireworks. Sodium perchlorate and perchloric acid have laboratory research applications, while potassium perchlorate is used in safety devices such as road flares and vehicle airbags (Clark, 2000). These commercial/research activities may result in some low-level environmental releases.

A third potential source of perchlorate contamination is related to agricultural activities. Though perchlorate contamination is generally considered to be the result of human activities, at least one naturally-occurring deposit of perchlorate exists. Chilean “caliche” ore is known to have relatively high concentrations of perchlorate. This ore is refined to make saltpeter (sodium nitrate), which may contain residual perchlorate concentrations on the order of around one gram per kilogram of saltpeter (Urbansky, 2000). Chilean saltpeter has been used as fertilizer in the U.S. for decades, though it tends to be used for specialty crops (e.g., tobacco) and constitutes just 0.1% of the overall fertilizer used in U.S. agriculture (Urbansky, 2002). Historical data on saltpeter application is extremely limited (Urbansky, 2002) and thus the contribution of Chilean saltpeter to the overall perchlorate contamination problem is largely unknown.

As mentioned in the previous chapter, at least 40 states have perchlorate users or manufacturers located within their borders, and at least 25 of those states have reported

perchlorate releases. Two maps (Figures 2.1 and 2.2) are presented below to illustrate the geographical distribution of the perchlorate problem.



**Figure 2.1 Map of perchlorate users and manufacturers. Shading indicates states with perchlorate users and/or manufacturers. Dots indicate specific locations of users and/or manufacturers (Mayer, 2004a)**



**Figure 2.2 Map of perchlorate releases. Shading indicates states with reported perchlorate releases. Dots indicate specific release locations (Mayer, 2004b)**



The two figures clearly show that perchlorate is a potential problem throughout the U.S, although the southwestern and northeastern regions appear to be at most risk. In terms of groundwater contamination, EPA Unregulated Contaminant Monitoring Rule (UCMR) data show that California is most affected, with 56 separate public water systems reporting perchlorate contamination at 4 micrograms per liter ( $\mu\text{g/L}$ ) or higher (USEPA, 2004c). These 56 water systems account for 38% of the total number of water systems nationwide reporting perchlorate contamination under the UCMR. Much of the perchlorate identified in California water systems is thought to originate from Lake Mead, which has been contaminated by discharges from manufacturing plants near Henderson, Nevada (Hogue, 2003). Lake Mead feeds into the lower Colorado River, which in turn serves as the drinking water source for millions of Californians. Each day, hundreds of pounds of perchlorate from existing contamination plumes feed into Lake Mead, so perchlorate will continue to be a particularly serious problem for those who obtain their drinking water from the lower Colorado River.

### ***2.3 Health Effects***

As described in the introduction chapter, perchlorate is similar in shape and charge to the iodide anion, and can therefore concentrate within the thyroid gland. Iodide is accumulated in the thyroid gland for use in hormone production (Clark, 2000). Hormone production is controlled via “stimulating” hormones produced in the hypothalamus. As the thyroid produces hormones, they are released to the bloodstream and travel to cells throughout the body, affecting cell respiration, metabolism, and protein production (Fox,

2004). Human physiology incorporates a negative feedback loop between the concentration of thyroid hormones in the bloodstream and the quantity of thyroid-stimulating hormones produced in the hypothalamus. As the thyroid produces more hormones, the hypothalamus senses the change and decreases production of stimulating hormones. This control loop maintains appropriate concentrations of thyroid hormones throughout the body and is essential to normal metabolic functioning.

The interaction of perchlorate with the thyroid gland is believed to be based on ion exchange principles (Wolff, 1998). As perchlorate interacts with the thyroid, it blocks uptake of iodide anions and also causes the thyroid to release any accumulated iodide (Clark, 2000). Lacking iodide, the thyroid is unable to synthesize hormones, which leads to reduced metabolic action throughout the body. Reduced metabolic activity results in symptoms such as fatigue and excessive weight gain.

In addition to direct metabolic effects, perchlorate has a secondary effect on the hormone control loop (described above). As perchlorate blocks iodide uptake, thyroid hormone levels decrease. This causes the hypothalamus to release additional stimulating hormones. Since the lack of iodide prevents the thyroid from producing additional hormones, the feedback loop is interrupted and there is no mechanism to stop the production of stimulating hormones. The stimulating hormones direct the thyroid to produce hormones, but they also have the secondary effect of stimulating thyroid growth

(Fox, 2004). As the thyroid is bombarded with stimulating hormones, excessive growth (thyroid goiter) occurs.

The effect of perchlorate on the thyroid gland is considered reversible. Once perchlorate ingestion ceases, iodide uptake resumes within a few hours. As the thyroid absorbs iodide, hormone production resumes and levels are controlled within normal limits via the feedback loop. Perchlorate is excreted, unmetabolized, through urine (Wolff, 1998).

Historically, perchlorate has been used as a therapeutic treatment for abnormal thyroid conditions. Graves' disease, an autoimmune condition where antibodies mimic the behavior of the stimulating hormones released from the hypothalamus, is characterized by excessive production of thyroid hormones. There are a variety of symptoms associated with this condition, including weight loss, irritability, goiter, and bulging eyes (Fox, 2004). Since the stimulating action is caused by antibodies instead of the hypothalamus, the normal control loop is bypassed and the thyroid produces hormones unchecked. Perchlorate has been administered to patients suffering from Graves' disease (Clark, 2000) in order to block iodide uptake, preventing the excessive buildup of thyroid hormones. However, during the 1960s, several Graves' disease patients developed lethal cases of aplastic anemia after being treated with perchlorate (Clark, 2000). After this event, administration of perchlorate for treatment of Graves' disease was halted.

In recent years, medical science has found another therapeutic application for perchlorate. Perchlorate is now used to counter a side-effect of amiodarone, a drug used to treat cardiac arrhythmia. The large quantities of iodide released when amiodarone is metabolized can have a toxic effect on the thyroid gland (Urbansky, 2002). In addition, amiodarone can lead to high concentrations of thyroid hormones in the bloodstream, which can have toxic effects on exposed tissue (Clark, 2000). Perchlorate has been used to inhibit iodide uptake, shielding the thyroid from the direct toxic effect and preventing high concentrations of hormones in the bloodstream. Perchlorate has been found to be more effective than other potential treatments (e.g., thioamides) when particularly high iodide loads are present (Wolff, 1998).

Though previous research suggests that the effects of perchlorate appear to be largely reversible and can have therapeutic benefits in certain cases (described above), serious concerns exist. Most human data on the toxicological effects of perchlorate are derived from clinical studies related to medical administration of perchlorate. Therapeutic applications have involved relatively large doses of perchlorate (200 milligrams or more per day), and toxicology data from these studies may not adequately quantify effects from chronic exposure to low perchlorate concentrations (as may be found in drinking water supplies). In addition, the clinical data are tied to a fairly small segment of the population, specifically those requiring treatment for thyroid and/or heart problems.

Greer *et al.* (2002) investigated the effects of low-level perchlorate exposure on “normal” adult subjects. In this study, 37 healthy adult volunteers (both male and female) ingested drinking water which had been doped with perchlorate. The perchlorate dosage for each volunteer ranged from 0.007 mg/kg-day to 0.5 mg/kg-day. The perchlorate solution was administered (on a daily basis) for a total of 14 days. During the study, iodide uptake was monitored in each volunteer, both during the 14-day exposure period and also 15 days after exposure ceased. In this study, the 0.007 mg/kg-day dose was found to be a No Observed Effect Level (NOEL). Additional statistical evaluation of the iodide uptake data led the researchers to conclude that the “true” No Effect Level (NEL) would be between 0.0052 and 0.0064 mg/kg-day. Using standard values for body weight and daily water ingestion (70 kg and 2 L/day, respectively), the NEL values translate to an equivalent drinking water concentration range of 182 – 224 µg/L. In summary, the Greer *et al.* (2002) study indicates that drinking water containing perchlorate at around 180 µg/L should have no impact on iodide uptake in typical healthy adults.

The Greer *et al.* (2002) work clearly applies to a much larger segment of the population than the previously mentioned therapeutic studies. However it still does not address the potential effects of perchlorate exposure on two key receptor groups, specifically pregnant mothers and young children.

Much of the concern over perchlorate exposure centers around the effects on pregnant mothers and infants. As described above, perchlorate affects hormone levels and can

disrupt metabolism and protein synthesis. These effects are extremely important during the early growth and development of the fetus and newborn infant, particularly from the end of the first trimester of pregnancy until about six months after birth (Fox, 2004). During this critical time, insufficient thyroid hormone levels (specifically thyroxine) can cause the infants to develop a condition called cretinism, which is characterized by mental retardation. While the mental retardation may be reversed by supplemental treatment with thyroxine shortly after birth, full recovery is not guaranteed.

Although there is little direct human toxicology data on the effects of low-level perchlorate exposure on pregnant mothers and newborn infants, several researchers have used statistical techniques to evaluate the potential effects. In one study (Lamm and Doemland, 1999), the researchers used neonatal screening data from 700,000 infants in several California and Nevada counties to determine whether perchlorate contamination in the drinking water supplies resulted in increased rates of hypothyroidism in newborns. At the time of the study, the water supplies in the counties studied had documented perchlorate concentrations between 4 and 16  $\mu\text{g/L}$ . Based on a statistical evaluation of statewide incidence rates, 243 cases of congenital hypothyroidism were expected in the counties studied, and 249 cases actually occurred. This slight increase was not statistically significant and the authors determined that the low-level water contamination did not lead to increased risk for congenital hypothyroidism.

In another study, Brechner *et al.* (2000) use neonatal screening data to compare thyroid function in infants born in two Arizona cities. The water supply for one city was contaminated with perchlorate (concentration of around 6 µg/L), while the other city did not have detectable levels of perchlorate in the water. The authors found that newborns in the city with the contaminated water supply had significantly higher levels of thyroid stimulating hormone, indicating that low concentrations of perchlorate in the drinking water may have an adverse effect on thyroid function in newborns. However, Crump and Weiss (2001) disputed the conclusions from the Brechner *et al.* (2000) study, pointing out that differences in age at time of neonatal screening (as well as other social and reproductive factors) may have confounded the comparison between the two cities.

A third study (Crump and Weiss, 2001) evaluated thyroid function in infants and school-age children (6 to 8 years old) from three cities in Chile. The three cities had high (~120 µg/L), low (5 to 7 µg/L) and non-detectable (< 4 µg/L) concentrations of perchlorate in the drinking water. Results showed that neither infants nor school-age children in the cities with perchlorate contamination had higher incidences of thyroid disorders compared to the control city, suggesting that perchlorate concentrations as high as 120 µg/L in drinking water do not have a substantial effect on thyroid function.

Perchlorate clearly affects thyroid function, though it is still unclear whether the relatively small concentrations found in contaminated drinking water supplies lead to adverse effects. Relatively few epidemiological studies have been performed on the most critical

target group (pregnant mothers and infants), and conflicting results from existing studies highlight the need for additional toxicological testing.

#### ***2.4 Regulatory Issues***

At the present time, the National Primary Drinking Water Regulations do not establish a Maximum Contaminant Level (MCL) for perchlorate. However, EPA does consider perchlorate to be a chemical of concern. In 1998, EPA included perchlorate in the Contaminant Candidate List (CCL), which is a group of contaminants which may require future regulation under the Safe Drinking Water Act (USEPA, 1998). In 2004, EPA published a (draft) revised CCL. Several contaminants from the original list were eliminated, but perchlorate was retained in the new version (USEPA, 2004a). EPA expects to reach a final decision on whether to regulate the current CCL contaminants sometime in 2006.

The 1999 revisions to the Unregulated Contaminant Monitoring Rule (UCMR) established monitoring and reporting requirements for CCL contaminants, including perchlorate. Large water systems (those serving a population greater than 10,000) and selected small water systems must monitor for perchlorate and report results to EPA (USEPA, 2001). The main thrust of the UCMR monitoring requirement is to provide EPA with data on CCL contaminant concentrations in water systems throughout the country. When deciding whether to regulate a given contaminant, EPA considers both



toxicological evidence and “prevalence” results from UCMR monitoring in the overall risk characterization process.

Since 1997, EPA has been working on a risk characterization document for perchlorate with the goal of quantifying the dose-response relationship. EPA released an initial draft characterization document in 1998 along with a revised draft in 2002. The 2002 version proposed a reference dose of 0.00003 mg/kg-day, which corresponds to a drinking water equivalent limit (DWEL) of 1 µg/L (USEPA, 2002). If perchlorate is eventually regulated, the DWEL may become a MCL. The EPA reference dose was based largely on toxicology studies performed on rats (NAS, 2005b), and included an overall uncertainty factor of 300 (USEPA, 2002). DoD strongly objected to many aspects of the EPA characterization document, believing EPA ignored key results from existing toxicology studies and also used excessive uncertainty factors in the derivation of the reference dose (DODPWG, 2002).

In light of the controversy described in the previous paragraph, the Interagency Working Group on Perchlorate (composed of members from DoD, EPA, NASA, and the Department of Energy) decided to refer the 2002 EPA characterization document to the National Academy of Sciences (NAS) for an objective evaluation of the scientific basis behind the characterization (Gilman, 2003). NAS agreed to determine whether the EPA report is truly consistent with the current state of the science and provide recommendations for fixing any identified deficiencies (NAS, 2005a).

In January 2005, the NAS review committee released a report detailing their findings. In short, the committee did not agree with the parameters EPA used to generate the reference dose. As mentioned in the previous section, the foundation of the EPA reference dose was derived from studies conducted on rats. NAS felt that a reference dose derived from existing human data would be more accurate and reliable (NAS, 2005b). Specifically, the committee felt that the NOEL of 0.007 mg/kg-day presented in the Greer *et al.* (2002) study should be used as the starting point in the reference dose derivation (NAS, 2005b).

NAS recognized the need to include an uncertainty factor in the reference dose calculation in order to protect sensitive population groups (recall from the previous section that the volunteers in the Greer *et al.* (2002) study were all healthy adults, while pregnant mothers and infants are potentially susceptible receptors). However, the review committee did not believe the available data supported EPA's uncertainty factor of 300; instead, they recommended using a total uncertainty factor of 10 (NAS, 2005b).

Combining the Greer *et al.* (2002) NOEL with the uncertainty factor, NAS recommended that the perchlorate reference dose should be set at 0.0007 mg/kg-day (NAS, 2005b). This is a 23-fold increase over EPA's proposed reference dose and (if adopted) would result in a DWEL of about 25 µg/L.

While the EPA and NAS have been attempting to characterize the perchlorate risk, the United States Congress has introduced several bills which, if passed, will require federal regulation of perchlorate. On 15 May 2003, the “Preventing Perchlorate Pollution Act of 2003” (H.R. 2123) was introduced to the U.S. House of Representatives (USHOR, 2003). This act (if passed) will require that EPA establish a MCL for perchlorate under the National Primary Drinking Water Standards. In addition, the act includes various requirements related to pollution prevention (e.g., generating a nationwide list of perchlorate storage facilities, mandating that perchlorate releases be reported to EPA, and creating a fund to be used in supporting local water suppliers that are impacted by high levels of perchlorate contamination). Shortly after H.R. 2123 was introduced to the House of Representatives, the “Perchlorate Community Right-to-Know Act of 2003” (S. 820) was introduced to the Senate (USS, 2003). The content of S.820 is basically the same as H.R. 2123 with the exception that it does not require that perchlorate be regulated under the National Primary Drinking Water Regulations. Both S.820 and H.R. 2123 were referred to subcommittees shortly after introduction. As of January 2005, no further action has been taken on either bill (as determined by a search on the <http://thomas.loc.gov/> website). A third bill, the “Safe Drinking Water for Healthy Communities Act of 2005” (H.R. 213) was introduced to the House of Representatives on 4 Jan 2005 (USHOR, 2005). H.R. 213 deals solely with promulgating perchlorate regulations under the National Primary Drinking Water Standards, essentially mandating that EPA promulgate proposed and final regulations in accordance with a specified

timetable. As with H.R. 2123 and S.280, H.R. 213 has been referred to a subcommittee for further evaluation.

As shown in the past few paragraphs, several agencies within the U.S. Government have initiated actions which may eventually lead to federal perchlorate regulations. In the interim, several states have taken preemptive steps to protect their citizens against the perceived perchlorate threat; for example, California has established a “notification level” of 6 µg/L for perchlorate in drinking water (CDHS, 2005). While notification levels are not enforceable as maximum contaminant limits (suppliers can still distribute water with perchlorate concentrations above the notification level), they do require that water suppliers provide notification to local and state government agencies when levels are exceeded. Other states such as Nevada, New Mexico, Arizona, Texas, and New York have established similar perchlorate standards, with “guidance” levels ranging from 1 µg/L to 18 µg/L depending on the state (USACHPPM, 2002).

Perchlorate has generated significant concern in the regulatory community. While efforts to promulgate federal regulations have been slowed by controversy over the true health risk, perchlorate will likely be regulated (at one level or another) in the near future.

### ***2.5 Fate and Transport***

Solubility and mobility are two key factors in the perchlorate contamination problem.

The solubility of a chemical dictates its maximum water concentration, which is

obviously a concern with potentially toxic compounds. Mobility affects transport of the chemical; a substantial release of a highly mobile compound can result in significant contamination far from the point of release. In the next two paragraphs, the solubility and mobility of perchlorate will be described.

As mentioned in the first chapter, perchlorate salts are extremely soluble. Potassium and ammonium perchlorate solutions at 20°C have solubility limits of about 18 g/L and 209 g/L, respectively (Perry and Green, 1997). Solubility values for other perchlorate salts (sodium, magnesium, calcium) are even higher than ammonium perchlorate (Flowers and Hunt, 2000). Since regulators are currently considering drinking water contaminant limits in the low  $\mu\text{g/L}$  range, it is obvious that groundwater concentrations can easily reach several orders of magnitude above “safe” limits.

Dissolved perchlorate is very mobile in both surface water and groundwater, and therefore travels readily with bulk water flow. Two factors are primarily responsible for this high degree of mobility. First, the perchlorate ion does not interact with other compounds which may be present in the water. As described in chapter one, perchlorate is essentially non-reactive in aqueous solutions under ambient conditions. Since perchlorate does not react with other compounds typically present in groundwater or surface water, it is recalcitrant. Second, as an anion, perchlorate does not easily sorb to the solid materials found in groundwater and surface water systems. As an example, breakthrough curves generated during biodegradation experiments (Tipton *et al.*, 2003)

showed that perchlorate does not significantly sorb to Columbia or Yolo loam soils.

Tipton *et al.* (2003) theorize that low pH perchlorate solutions may sorb to soils with high anion exchange capacities; however, these conditions are not likely to be typical in environmental water systems.

As a result of its recalcitrance and lack of sorption, perchlorate travels essentially unimpeded in groundwater and surface water, resulting in extremely long contaminant plume lengths. Plume length appears to be limited only by dilution. Natural attenuation may also theoretically limit plume length, although perchlorate-reducing organisms, anoxic reducing conditions, and suitable quantities of appropriate electron donors must be present (Cox *et al.*, 2000; Logan, 2000). This combination of conditions is not expected to occur in normal environmental water systems, so perchlorate contamination events typically require some form of human intervention.

Plant-mediated reduction may be an exception to the “intervention” requirement. There is some evidence that plants are capable of removing perchlorate from the subsurface.

Nzungung *et al.* (1999) evaluated removal of perchlorate using willow trees (*Salix nigra*).

In a series of hydroponic and sand bioreactor experiments, the researchers found that a substantial quantity of perchlorate was removed from the solution in which the willow roots were immersed. Much of the perchlorate taken into the plant was found to accumulate within the leaves, although the accumulated perchlorate appeared to be slowly destroyed via phytodegradation. Similar results were reported in sterile experiments

performed on poplar trees using a radio-labeled perchlorate compound ( $^{36}\text{ClO}_4^-$ ) (VanAken and Schnoor, 2002). Importantly, the non-sterile conditions used in the Nzungung *et al.* (1999) study showed that plant-mediated perchlorate destruction may occur through a second mechanism. After an initial lag period (about 20 to 50 days) where perchlorate concentrations in the bioreactor solution dropped relatively slowly, the concentrations rapidly decreased to non-detectable levels. The researchers attributed the rapid increase in reduction kinetics to rhizodegradation, and this theory was supported by a buildup of chloride in solution around the plant root zone. Further, once perchlorate concentrations in the bioreactor solution dropped below detectable levels, the researchers re-spiked the reactors with perchlorate. Perchlorate concentrations rapidly dropped to non-detectable levels within a few days (no lag period), indicating that once the bacteria in the root zone become acclimated to the presence of perchlorate, rhizodegradation may be the primary destruction mechanism.

The plant studies indicate that phytoremediation may help “naturally” reduce the spread of perchlorate in the environment. Rhizodegradation may be particularly effective for reducing perchlorate concentrations in shallow source zones, which in turn may reduce the size of a perchlorate plume. However, if the contamination occurred at a depth beyond the plant root zone, phytoremediation would not affect the transport of perchlorate. Also, once perchlorate is dispersed in a large groundwater plume, plant-mediated reduction would probably not be sufficient to limit the spread of the contaminant.

In groundwater systems, extremely large ammonium perchlorate releases may present an additional aquifer contamination problem. The density of a saturated ammonium perchlorate solution is around 1.11 g/mL, which is significantly higher than typical groundwater density (Flowers and Hunt, 2000). Flowers and Hunt suggest that once an ammonium perchlorate brine solution reaches an aquifer water table, the density difference will cause the brine to rapidly sink with very little dilution. Similar to Dense Non-Aqueous Phase Liquid (DNAPL) behavior, the brine will pool on (and penetrate into) lower-permeability aquifer layers, resulting in secondary source zones that may be very difficult to remediate. Modeling performed by Flowers and Hunt (2000) suggests that these pooled source zones release high concentrations of perchlorate to the aquifer for a very long time, perhaps on the order of 100 years. Removal of source contamination is mainly limited by slow diffusion of perchlorate which has penetrated into the lower-permeability layers, making source zone remediation even more difficult.

In summary, perchlorate's solubility and mobility characteristics make it a very potent environmental contaminant. With the exception of plant-mediated reduction, perchlorate does not "naturally" degrade under normal environmental conditions. Therefore, appropriate remediation technologies must be used to control perchlorate contamination.

## ***2.6 Existing Treatment Technologies***

In recent years, considerable research has been done in the area of perchlorate remediation. Remediation technologies can be broadly categorized as physical,



biological, and chemical treatment methods. The next few paragraphs will illustrate key features of several potential remediation technologies.

### *2.6.1 Ion Exchange*

Ion exchange (specifically, anion exchange) can be used to remove perchlorate from contaminated water streams. Perchlorate ions preferentially adsorb to the exchange resin as influent water passes through the system. Positively charged functional groups on the resin originally have relatively innocuous anions (such as chloride) weakly bound to them. As perchlorate ions pass through the resin, they sorb strongly to the receptor sites, releasing the weakly-bound ions to the effluent stream (hence the term anion exchange).

Selectivity is a key issue in the performance of ion exchange systems (Urbansky, 2002). In a contaminated water stream, the perchlorate concentration may be very low compared to other anions such as sulfate, nitrate, and bicarbonate. These ambient anions may compete for active sites on the exchange resin, potentially reducing the perchlorate removal efficiency and/or decreasing the effective lifespan of the resin. Further, removal of key anions such as bicarbonate may have secondary consequences. In the case of drinking water treatment, bicarbonate removal may lead to decrease in the pH of the effluent, potentially affecting compliance with other aspects of the Safe Drinking Water Act such as the Lead and Copper Rule (Guter, 2000). An ideal exchange resin would have a very high affinity for the perchlorate ion but very low affinity for other anions

typically found in water; this would result in optimal perchlorate removal without needless deactivation of the exchange media.

Early ion exchange systems had selectivity problems, but recent research has yielded specialized resins which efficiently remove perchlorate while leaving other anions in the water stream (Urbansky, 2002). Even with high selectivity, resins eventually become exhausted and must be regenerated or replaced. Regeneration usually involves flowing brine solution through the resin; the brine displaces adsorbed perchlorate from the resin, but large quantities of effluent with high perchlorate concentration may be generated during the process. Contaminated regeneration brine requires subsequent treatment or special disposal, increasing costs (Gu *et al.*, 2000). Certain highly selective resins (e.g., styrenic type strong-base resins) are difficult to regenerate (Batista *et al.*, 2000), leading to additional costs associated with disposing of the exhausted resin and replacing it with fresh media.

Overall, the fact that ion exchange systems do not directly destroy the perchlorate ion is a key limitation, mainly due to the costs of media regeneration/replacement. On the other hand, ion exchange is a relatively well-known technology and would likely be acceptable to regulatory agencies (Urbansky, 2002). Indeed, ion exchange has been approved by regulators in California for use in treating perchlorate-contaminated drinking water (AFCEE, 2002).

### 2.6.2 Biological Treatment

Biological reduction is another potential method for dealing with perchlorate contamination. Some microorganisms produce perchlorate reductase enzymes which (in the presence of a suitable electron donor) transform perchlorate into chlorite via the intermediate chlorate. Chlorite is subsequently biologically transformed to chloride via a dismutation reaction (Cox *et al.*, 2000). Thus, the overall process transforms perchlorate into chloride, with carbon dioxide, oxygen, and biomass as co-products. Recent research suggests that bacteria capable of reducing perchlorate are more prevalent in the environment than originally thought (Coates *et al.*, 1999).

Cox *et al.* (2000) studied the potential for *in situ* perchlorate bioremediation using microcosms from soil and groundwater at two contaminated field sites. Both sites were essentially perchlorate source areas with very high concentrations of perchlorate in the soil and groundwater. In these batch studies, various electron donors were added to the microcosms to evaluate the effectiveness of biostimulation. Large reductions in perchlorate were observed in all biostimulated microcosms, though significant acclimation lag time was observed for one site. Results indicated that stimulated *in situ* bioremediation may be a promising and cost-effective technique for cleaning up source areas.

*Ex situ* bioremediation techniques have also been studied. Logan (2000) presents a summary of several bioreactor configuration options. Both fluidized bed reactors (FBR)

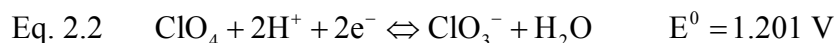
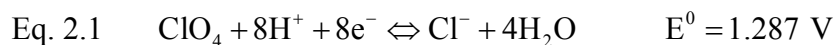
and packed bed reactors (PBR) show promise for reducing perchlorate concentrations to extremely low levels (essentially non-detect), while suspended cell reactors appear to require prohibitively long retention times. Though FBR and PBR systems have both been proven effective, Logan (2000) cautioned that much work remained in the area of optimizing performance.

Overall, bioremediation methods have a couple of advantages over ion exchange systems. First and foremost, the perchlorate ion is destroyed during treatment, eliminating the need to treat or dispose of secondary waste streams. Secondly, bioremediation is more versatile, with potential applications ranging from *in situ* destruction of highly contaminated source areas to *ex situ* drinking water pretreatment. Perhaps the most important limitation for this technology relates to public and regulatory acceptance, particularly with respect to drinking water applications. Microbiological drinking water treatment methods must be proven safe. Pilot-scale research at the Aerojet facility near Sacramento, California, indicates that contaminated groundwater can be treated to drinking water standards (Urbansky, 2002), and CDHS has issued “conditional approval” for the use of FBR technology in drinking water plants (CDHS, 2002). The CDHS approval means that FBR biological systems may theoretically be used in California drinking water plants; however, before a water supplier implements this treatment method, it must still obtain a CDHS permit. As of January 2005, no California water treatment plants have received FBR permits (Yamamoto, 2005).

### 2.6.3 Chemical Treatment

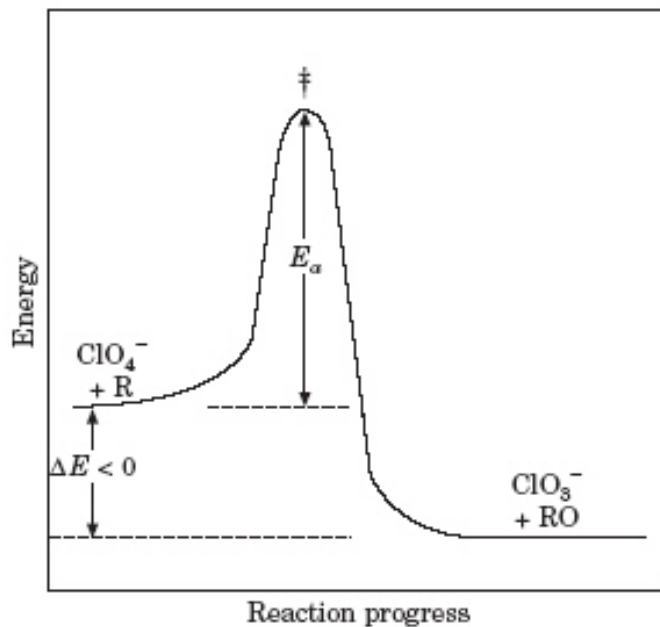
Chemical reduction is a third option for dealing with perchlorate contamination. Because of perchlorate's properties, direct chemical treatment methods are considered to be less promising than the physical and biological techniques described above.

The reader should recall from the first chapter that perchlorate consists of a highly oxidized chlorine atom (+7 charge) surrounded by four oxygen atoms in a tetrahedral arrangement. The following half-cell potentials (Urbansky, 1998) illustrate the thermodynamic properties of the perchlorate ion and molecular oxygen:



The highly positive reduction potential values (equations 2.1 and 2.2) indicate that the perchlorate ion should be a very strong oxidizing agent and therefore, very easily reduced. In fact, looking at equation 2.3, one can see that the perchlorate ion is an even stronger oxidant than molecular oxygen! Thus, strictly from a thermodynamics standpoint, one would expect an aqueous perchlorate solution would be able to spontaneously oxidize water to oxygen (Urbansky, 1998). However, as stated earlier in this chapter, this reaction does not occur. In reality, perchlorate ions are remarkably stable in water.

The explanation for this apparent paradox lies in reaction kinetics. Thermodynamics may predict that perchlorate should be easily reduced, but there are other chemical factors to consider. Two important factors cited by Urbansky and Schock (1999) are the strong chlorine-oxygen bonds (which inhibit direct abstraction of oxygen atoms) and also physical/electrical shielding of the central chlorine atom from potential reducing agents. The result is a kinetic barrier, which is depicted in Figure 2.3:



**Figure 2.3 Kinetic Limitation (Urbansky and Schock, 1999)**

In Figure 2.3, initial reactants are the perchlorate ion and a reducing agent “R”. Products are the chlorate ion along with a reducing agent-oxygen complex. Thermodynamic favorability is illustrated by the fact that the products have lower energy than the reactants ( $\Delta E < 0$ ). However, it is clear that the reactants must overcome a large energy “hump”

(shown by the activation energy,  $E^0$ ) before reacting. This activation energy inhibits the spontaneous reduction of perchlorate; additional energy must be provided before the reaction can occur.

For nearly 100 years, researchers have attempted to find ways to chemically overcome the perchlorate kinetic barrier. A variety of specialized reducing agents have been used in a variety of experimental conditions. For a short summary of important historical perchlorate reduction investigations, the reader is referred to Urbansky and Schock (1999). The few “successful” reductants that have been identified over the years all have critical limitations that prohibit their application to environmental water systems.

Reaction rates are sluggish under normal (environmental) pH and perchlorate concentration conditions, and the presence of molecular oxygen inhibits most reductants (Urbansky, 1998).

Recent work by Moore *et al.* (2003) evaluated the reduction of perchlorate in the presence of iron surfaces. Several types of iron preparations were used in both batch and column experiments. Significant perchlorate reduction was achieved at near-neutral pH values, though overall reaction rates were slow and buildup of the degradation product, chloride, tended to inhibit further perchlorate reduction. The exact reaction mechanism was not identified, although the researchers theorized that perchlorate sorbed to the iron surface and was subsequently reduced via interaction with the iron hydroxide surface layer.

While the study proved that perchlorate reduction can be achieved with iron surfaces, the

deactivation problem and slow kinetics dictate that additional research is required before this technology can be applied to remediate perchlorate-contaminated water.

Direct chemical reduction is not feasible for environmental water systems, but catalytic methods may provide a suitable alternative. Catalysts are widely used in chemical manufacturing applications as a means of decreasing the activation energy associated with non-spontaneous reactions; perhaps catalysts can also be used to overcome the perchlorate kinetic barrier. In particular, palladium may be a promising catalyst for reduction of perchlorate.

### ***2.7 Palladium-Catalyzed Reduction***

The noble metal palladium (Pd) has been used to destroy several types of common groundwater contaminants. To date, no studies have evaluated the potential for Pd-catalyzed perchlorate reduction. However, given the successful use of palladium with similar contaminants (*e.g.*, nitrate), application of this catalytic technology to the perchlorate problem has potential.

Nitrate ( $\text{NO}_3^-$ ) is similar to perchlorate in both charge and structure. In this section, the environmental threat posed by nitrate will be briefly described, and an overview of key results from Pd-catalyzed nitrate reduction studies will be presented.



Nitrate is a common groundwater contaminant which poses serious health hazards, particularly for infants. Bacteria present in the human digestive system can convert ingested nitrate to nitrite ( $\text{NO}_2^-$ ), which can interfere with the transport of oxygen within the body. This condition is called methemoglobinemia (also known as “blue baby syndrome”) and can be fatal. Infants less than six months old are particularly at risk because the pH in their digestive systems is higher, providing favorable conditions for the nitrate-reducing bacteria (Skipton and Hay, 1998). Nitrate is commonly found in fertilizer and is highly soluble, leading to widespread contamination of drinking water sources (USEPA, 2005b). According to the National Primary Drinking Water Regulations (CFR, 2005), the MCL for nitrate is 10 mg/L  $\text{NO}_3\text{-N}$  (nitrate as nitrogen), while the nitrite MCL is 1 mg/L  $\text{NO}_2\text{-N}$  (nitrite as nitrogen). The widespread occurrence of nitrate groundwater contamination has led to extensive efforts to identify cost-effective water treatment technologies for reducing nitrate and nitrite concentrations below MCL values.

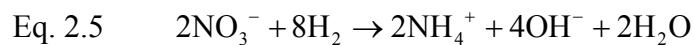
As discussed in Pallavi (2003), a number of studies have focused on using noble metal catalysts to reduce nitrate and nitrite to nitrogen gas ( $\text{N}_2$ ). These studies have explored the performance characteristics of various catalyst configurations, including both monometallic and bimetallic structures. With monometallic catalysts, a thin coating of noble metal (*e.g.*, Pd) is deposited on some form of support material, such as alumina ( $\text{Al}_2\text{O}_3$ ), carbon, silica, calcium carbonate, etc. With bimetallic versions, the noble metal is combined with a less active metal (*e.g.*, copper, tin) prior to deposition on the support.

Performance of the catalyst depends on the choice of noble metal, support material, and configuration (monometallic vs. bimetallic). With bimetallic catalysts, the choice of secondary metal along with the relative ratio of primary to secondary metal can also impact performance. With so many factors affecting catalytic activity, identifying an appropriate formulation for a given application can be difficult.

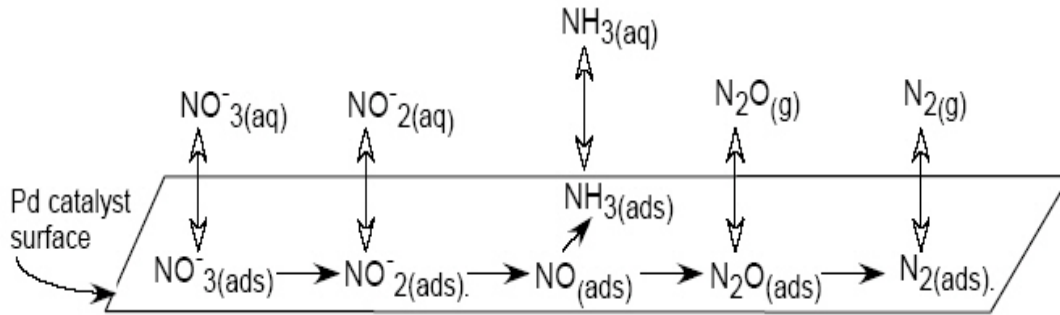
Fortunately, many researchers have investigated the degradation of nitrate and nitrite using a wide range of catalyst materials. In her M.S. thesis, Pallavi (2003) summarized results from several previous studies which had evaluated nitrate/nitrite reduction with various catalyst configurations. Overall, palladium was found to be more suitable for nitrate and nitrite reduction than other noble metals (the main nitrate/nitrite reduction product when using a Pd catalyst was  $N_2$ , while other noble metal catalysts tended to produce large amounts of ammonium, an undesirable contaminant in drinking water). Alumina was determined to be a good choice of support material, facilitating reasonable reduction rates while minimizing catalyst deactivation. Bimetallic Pd-Cu catalysts effectively reduced nitrate to nitrite, but subsequent conversion of nitrite to  $N_2$  was not as effective. On the other hand, monometallic catalysts successfully converted nitrite to  $N_2$ , but were less effective in directly reducing nitrate to nitrite than the Pd-Cu bimetallic version. Thus, efficient conversion of nitrate to  $N_2$  in drinking water may require a system incorporating both bimetallic (nitrate to nitrite reduction step) and monometallic (nitrite to  $N_2$  reduction step) catalysts. However, Pallavi (2003) performed flow-through column experiments investigating the reduction of nitrate using Pd/ $Al_2O_3$  monometallic

catalyst; results showed high conversion of nitrate to N<sub>2</sub> with minimal production of ammonia or nitrite, indicating that monometallic Pd/Al<sub>2</sub>O<sub>3</sub> may indeed be an effective catalyst for use in nitrate remediation technologies. This is quite important because the monometallic Pd catalyst used in Pallavi's study is commercially available, while production of a suitable bimetallic catalyst would require a series of preparation steps (Pintar *et al.*, 1998; Pintar and Batista, 1999; Ilinitich *et al.*, 2000; Pintar *et al.*, 2001; Palomares *et al.*, 2003).

Catalyzed reduction of nitrate is thought to occur through a hydrogenation reaction at the catalyst surface (Palomares *et al.*, 2003). This reaction requires a suitable electron donor. Hydrogen gas has been used as the electron donor in many of the catalyst studies described above. The overall nitrate conversion reactions are considered to be (Prusse *et al.*, 2000):



Equation 2.4 illustrates the conversion of nitrate to nitrogen gas, while equation 2.5 shows the (undesired) transformation to ammonium. A proposed representation of the sequence of reactions (including intermediates) at the catalyst surface is shown in Figure 2.4:



**Figure 2.4 Nitrate Reduction at Catalyst Surface (Pallavi, 2003)**

Investigators reported that as pH increases, nitrate reduction rates slow and ammonium production increases (Prusse *et al.*, 2000). As shown in equations 2.4 and 2.5, hydroxide ions are produced during the nitrate reduction reaction, potentially leading to a localized increase in pH at the catalyst surface, decreasing reduction efficiency. When hydrogen is used as the electron donor, rapid deactivation of the catalyst may occur. Fortunately, alternative electron donors such as formic acid may facilitate nitrate reduction while mitigating the deactivation effect associated with hydroxide buildup at the catalyst surface.

Formic acid (chemical formula:  $\text{HCOOH}$ ) can decompose into hydrogen gas and carbon dioxide at the catalyst surface (Prusse *et al.*, 2000). This decomposition is quite fortunate; hydrogen produced during the  $\text{HCOOH}$  decomposition can be used as the electron donor for the nitrate reduction, while the carbon dioxide can combine with nearby hydroxide molecules to form bicarbonate ( $\text{HCO}_3^-$ ), providing some degree of buffering capacity at the catalyst surface. This buffering can help prevent the localized

pH increase which can occur as nitrate reduction proceeds, thereby reducing catalyst deactivation. Prusse *et al.* (2000) performed experiments to test whether formic acid truly yields improved nitrate reduction compared to hydrogen gas. Results from hydrogen vs. formic acid comparison tests using several bimetallic palladium catalysts showed that formic acid yields improved nitrate reduction with less ammonium production. Pallavi's work with nitrate reduction using monometallic Pd catalyst in a flow-through column (Pallavi, 2003) also showed that formic acid performs better as a reductant than hydrogen alone. Beyond these performance enhancements, HCOOH is more soluble than hydrogen and also requires fewer safety measures. On all counts, formic acid appears to be the preferable reductant in Pd-catalyzed nitrate reduction.

Nitrate and perchlorate ions are physically similar (highly oxidized central atom surrounded by oxygen atoms) and both have a highly delocalized molecular charge of -1. Both ions are stable in aqueous solution in spite of the fact that (according to thermodynamics) they should readily oxidize other dissolved materials. Since research has shown that Pd catalysts can facilitate the reduction of nitrate, perhaps similar results can be achieved with perchlorate. Clearly, there are differences between perchlorate and nitrate that may inhibit Pd-catalyzed reduction. For example, perchlorate has an extra oxygen atom which may play an important role in reduction chemistry. Nonetheless, it seems reasonable to investigate the potential for perchlorate reduction in Pd-catalyzed reactor systems. If successful, a catalytic reduction method may provide an alternative to existing physical and biological perchlorate remediation techniques.

## **3.0 Experimental Materials and Methods**

### ***3.1 Introduction***

This section describes the materials and methods used in the course of this research project. A detailed listing of chemicals and equipment is presented, followed by an “overview” description of the reactor apparatus and basic experimental method. Next, the ion chromatography analytical procedure is described. This section concludes with a summary table which outlines the key operating conditions (pH, substrate concentration, residence time, *etc.*) for each experiment.

### ***3.2 Chemicals***

The chemicals used in this experiment were procured from commercial sources and no additional purification was attempted. Specific reagents are listed in the subsections below.

#### ***3.2.1 Perchlorate***

Two different perchlorate salts were used in the course of this research. In the first two experiments, a crystalline sodium perchlorate salt (Fisher Scientific, HPLC Grade, Catalog #S490-100) was used to make high-concentration (6 mg/L and 10 mg/L) feedstock solutions. The target concentration in experiments 3 through 13 was much lower (0.5 mg/L), so an ion chromatography standard (Alltech Associates, potassium perchlorate IC standard, certified concentration 994 mg/L +/- 3 mg/L, catalog #37048)

was used in these experiments. By using the ion chromatography standard for low-concentration experiments, the problems associated with measuring minute quantities of a pure (solid) perchlorate salt were avoided.

### *3.2.2 Reductants*

Concentrated formic acid was used as a reductant in most experiments (Fisher Scientific, 88% Formic Acid, Certified ACS, Catalog #A118<sup>P</sup>-500). In two experiments (#13 and #16), compressed hydrogen gas (Airgas Inc., Ultra High Purity/Zero Grade) was used instead of formic acid.

### *3.2.3 Catalyst*

Commercially available Pd/Al<sub>2</sub>O<sub>3</sub> catalyst pellets (Aldrich Chemical Company, catalog #205745-50G) were used in this research without modification. The catalyst pellet size was 3.2 millimeters and consisted of 0.5 wt% palladium deposited on alumina. The catalyst was directly added to the reactor vessel without any special precautions.

### *3.2.4 Ion Chromatography Calibration Standards*

Ion chromatography was the primary analytical method used in this research. Certified standards were used as “stock” solutions; serial dilution with DI water was performed in order to create a series of low-concentration instrument calibration standards. Table 3.1 lists each of the stock standards, along with the certified concentration and ordering information:

Analyte	Certified Concentration (mg/L)	Supplier	Catalog #
Perchlorate	994.0 +/- 3.0	Alltech	37048
Chlorate	999.5 +/- 3.0	SPEX CertiPrep	AS-CLO39-2Y
Chlorite	1001.0 +/- 3.0	SPEX CertiPrep	AS-CLO29-2Y
Chloride	99.82 +/- 0.3	SPEX CertiPrep	AS-CL9-1X

**Table 3.1 Ion Chromatography Stock Calibration Standards**

### *3.2.5 pH and Conductivity Probe Calibration Standards*

Effluent from the catalytic reactor was monitored for both pH and conductivity (described below in the experimental method section). A three-point calibration was accomplished for the pH probe. The buffer solutions used for pH calibration were obtained from Fisher Scientific and included pH 4 (catalog #SB101-500), pH 7 (catalog #SB107-500), and pH 10 (catalog #SB115-500) buffers. For conductivity, a one-point calibration was accomplished using a 1413  $\mu\text{S}$  standard (Oakton, 1413  $\mu\text{S}$  @ 25°C, catalog #WD-00653-18). Temperature compensation for both pH and conductivity was accomplished automatically by the electrode control unit.

### *3.2.6 Miscellaneous Chemicals*

Several experiments required adjustment of the feedstock pH. When formic acid was used as reductant, a sodium hydroxide solution (Fisher Scientific, 2 Normal/certified, catalog number SS264-1) was used to increase the pH to the desired value via manual titration. For experiments using hydrogen gas as reductant, a solution of crystalline MES (also known as 2-[N-Morpholino]ethanesulfonic acid Hydrate, minimum 99.5 %, Sigma-



Aldrich catalog #M-8250) in deionized water was added to the feedstock reservoir in order to decrease the pH on the influent fluid to the required level.

### *3.2.7 Deionized (DI) Water*

DI water was used for both the experimental feedstock and the ion chromatography eluent. This bench-scale investigation involved lab work in two geographically separated locations. The experiments were performed in the Geological Sciences Department at Wright State University, while effluent samples were analyzed in the Environmental Laboratory at the Air Force Institute of Technology. Each location had a different water purification system. DI water for the feedstock was obtained from a Barnstead NANOpure Infinity Ultrapure Water System; this unit generated DI water with a resistivity of 18.0 M $\Omega$ -cm. The DI water used for ion chromatography eluent was produced with a Millipore DirectQ-5 purification system. The Millipore unit consistently produced 18.2 M $\Omega$ -cm DI water.

## **3.3 Equipment**

### *3.3.1 Reactor Vessel – Specifications and Construction*

The catalytic reactor was constructed using a 316-gauge cylindrical steel tube (Mainline Supply, Dayton, Ohio). The tube was approximately 13 cm long with an internal diameter of about 4 cm. Steel endcaps were screwed onto each end of the cylinder to seal the chamber (Teflon tape was applied to the threads to ensure a watertight seal). A ¼ inch hole was drilled in the center of each endcap to facilitate influent and effluent tubing

lines (see “pump and tubing” section for tubing specifications). The empty volume of the reactor vessel was measured to be 133.4 milliliters (mL).

After determining the empty volume of the reactor, both endcaps were removed. A thin layer of pesticide-grade glass wool was placed inside the bottom (influent) endcap to prevent catalyst pellets from clogging the inlet port. After reapplying Teflon tape to the tube threads, the bottom endcap was screwed back on. Next, the reactor vessel was filled with the Pd/Al<sub>2</sub>O<sub>3</sub> pellets described previously. As the catalyst was added, the vessel was repeatedly tapped with a wrench in order to maximize settling and remove unintentional void space. The reactor was able to accommodate a total of 158.69 grams of catalyst pellets. After the steel tube was filled with catalyst pellets, the top (effluent) endcap was fitted with a layer of glass wool and reattached. Each endcap was tightened using a pipe wrench. The reactor was positioned vertically, with the influent line at the bottom and the effluent line at the top. Once constructed, the reactor was not opened or repositioned.

In an attempt to determine the residence time and the pore volume within the reactor, two tracer studies were performed. A sodium bromide solution was used as the tracer in each experiment. The first study used a “step” injection of the tracer solution, while the second involved an impulse injection. Unfortunately, neither tracer study yielded suitable data, mainly due to strong sorption of the bromide tracer to the catalyst pellets. In the end, the reactor pore volume was estimated by injecting water into the vessel. First, the reactor was drained of bulk fluid through gravity flow. Next, air was forced through the

system (using a syringe) in order to help remove residual fluid from the pore spaces. The influent port was then closed and water was injected through the effluent port. The quantity of water required to fill the reactor to overflow was measured. This procedure was performed a total of four times, yielding an average pore volume of 57.7 ml (standard deviation 0.4 mL).

### *3.3.2 Pump and Tubing*

The pump used in this experiment consisted of a Masterflex L/S Digital Standard Drive (Cole-Parmer, model 7523-70) equipped with a PTFE Diaphragm Pump (Cole-Parmer, model 7090-62). Two types of tubing were used. The influent and effluent lines were 5/64"ID x 1/8"OD polyethylene tubing (Cole-Parmer, catalog #95626-00). For other portions of the fluid flow train, 1/8"ID x 1/4"OD Tygon FEP-lined tubing was used (Cole-Parmer, catalog #95711-00).

### *3.3.3 pH/Conductivity Meter*

The pH probe, conductivity probe, and base unit were obtained from Denver Instrument Co. For pH measurements, a pH/ATC electrode (catalog #300729.1) was used. Conductivity measurements were accomplished using a conductivity/ATC electrode (4-band,  $c = 1\text{cm}^{-1}$ , catalog #301047.1). The signal from each electrode was displayed on a Model 200 pH/Conductivity Meter. Both probes had integrated temperature sensors, and the Model 200 control unit automatically adjusted the displayed pH and conductivity readings for temperature changes.

### *3.3.4 Feedstock Containers*

Two types of containers were used for feedstock. For experiments where formic acid was used as the reductant, a four-liter Pyrex #4980 Erlenmeyer flask was used. For experiments with H<sub>2</sub> as the reductant, the feedstock was contained in a 19-liter Pyrex #1596 jug. Pre- and post-experiment column flushing was accomplished using a two-liter Pyrex #4980 Erlenmeyer flask.

### *3.3.5 Pipette*

For most experiments, the feedstock solution was created by adding small volumes of perchlorate and formic acid solutions to a large quantity of DI water. In some experiments, small quantities of sodium hydroxide solution were added in order to adjust the feedstock pH. In order to maximize repeatability, a Repeater Plus® pipette (Eppendorf, catalog #022260201) was used. The Repeater Plus® incorporates a dispensing trigger along with a rotating dial which controls the stroke length of the trigger mechanism. Highly repeatable volume additions were accomplished by selecting an appropriate pipette tip and dial position. For very small volume additions, a 1.0 mL Combitip® (Eppendorf, catalog #022266209) was used. This tip dispensed between 0.01 and 0.2 mL of liquid with each trigger depression, depending on the dial setting. For larger liquid additions, a 10.0 mL Combitip® (Eppendorf, catalog #022266501) was used. This larger tip was capable of adding between 0.1 and 2.0 mL of liquid with each trigger depression.

### 3.3.6 Ion Chromatograph

Sample analysis was accomplished using a Dionex DX-600 ion chromatography system. This fully automated system executed all aspects of sample analysis, including sample injection, eluent generation, signal measurement, and data analysis (peak identification, quantification, *etc.*). Effluent samples were collected in 10 mL plastic vials (Dionex, part #055058). Key components of the DX-600 system are listed in Table 3.2 (all parts manufactured by Dionex):

<b>Model #</b>	<b>Name</b>	<b>Function</b>
AS-50	Autosampler	Automatic sample injection
GP-50	Gradient Pump	Fluid transport
ATC-3	Anion Trap Column	Removal of trace anions from DI water
AS-16	Analytical Column	Chromatographic separation
AG-16	Guard Column	Protects analytical column
EG-40	Eluent Generator	Electrolytically generates high-purity potassium hydroxide eluent from DI water and EGC-II cartridge
EluGen EGC-II KOH	Potassium Hydroxide Cartridge	Used with EG-40 to generate potassium hydroxide eluent
ASRS Ultra II	Automatic Self-Regenerating Suppressor	Decreases conductivity of eluent and increases analyte conductivity (improves signal-to-noise ratio)
CD-25	Conductivity Detector	Measures analytical signal
Chromleon version 6.3	Data Management Software	Controls all system operating parameters; records analytical signal; identifies peaks and quantifies results

**Table 3.2 Dionex DX-600 System Components**

All operating conditions were programmed using the Chromleon software. Additional analytical method details will be presented later in this chapter.

### ***3.4 Experimental Apparatus***

The apparatus used in this experiment was fairly simple. Major components included the feedstock reservoir, pump, catalytic reactor, and effluent drainage reservoirs (Figure 3.1).

The feedstock reservoir contained the influent solution along with a magnetic stir bar.

The container was placed on a magnetic stir plate, ensuring continuous mixing. One end of a Tygon FEP tubing section was placed in the feedstock solution, and the other end was connected to the inlet port of the diaphragm pump. Another section of Tygon FEP tubing was used to connect the pump outlet to a two-position splitter valve. One of the valve outlet ports was left exposed to the atmosphere, while the other was connected to the inlet (bottom) port on the catalytic reactor.

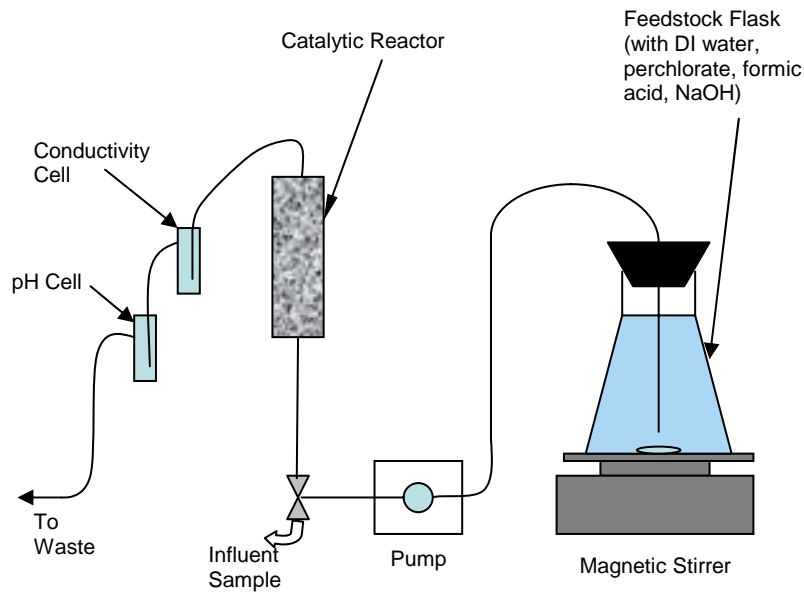
Influent samples were obtained by closing the port leading to the reactor, which directed all fluid flow through the “exposed” valve outlet into a 10 mL plastic sample vial.

Influent samples were collected before and after the main experimental run; at all other times, the “exposed” valve outlet was completely closed and all fluid flowed directly to the reactor.

A small section of polyethylene tubing was connected to the outlet (top) port on the reactor. Effluent samples for ion chromatography analysis were collected at various intervals by placing the free end of this tubing directly into a 10 mL sample vial. At all other times, the free end of the effluent tubing was placed in a 20 mL plastic vial which held a conductivity probe. A small section of FEP tubing was used to connect a drainage

hole drilled near the top of the vial to a second 20 mL plastic vial which held a pH electrode. A final section of FEP tubing served as a drain line running from the pH vial to a 40-liter waste storage jug. This sequence of effluent drainage containers facilitated continuous measurement of effluent pH and conductivity.

Figure 3.1 depicts the major components of the experimental apparatus:

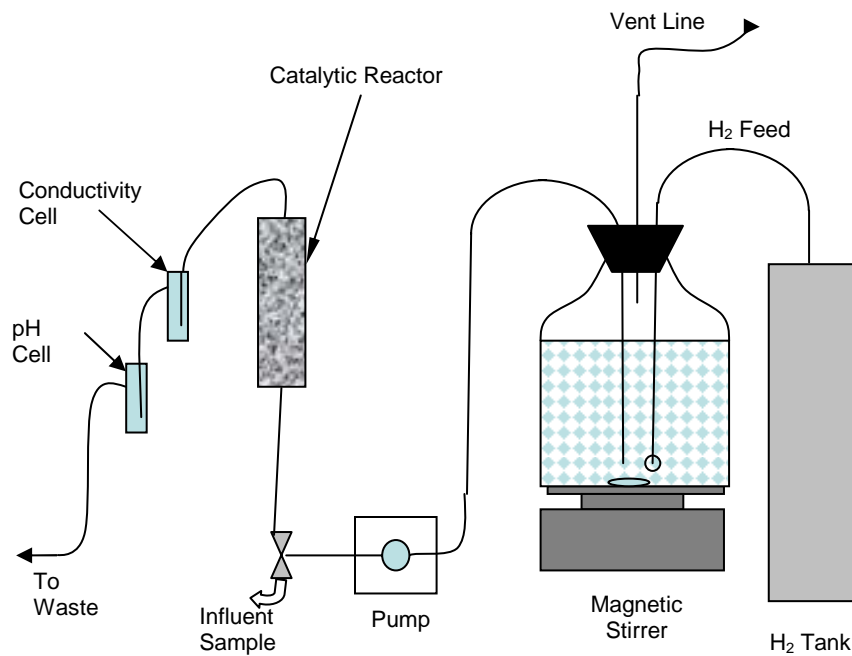


**Figure 3.1 Basic Experimental Apparatus**

Note that Figure 3.1 applies only to experiments where formic acid was used as the reductant. Experiments using hydrogen as reductant had a slightly different configuration (Figure 3.2). In these experiments, a length of FEP tubing connected a cylinder of compressed hydrogen to a submerged diffuser located near the bottom (well below the liquid line) of a 19-liter feedstock container. The regulator on the hydrogen tank was set at a point where vigorous bubbling was visible within the feedstock reservoir. One end of

another FEP tubing section was positioned in the headspace above the feedstock solution, with the other end placed outside a window near the apparatus. This line served as a safety vent, transferring gaseous hydrogen from the feed reservoir to the exterior of the building. A final section of FEP tubing was used as the liquid transfer line, with one end submerged in the feed solution and the other attached to the pump inlet (configuration downstream of the pump was identical to the description provided in the previous paragraphs). Note that the hydrogen feed, vent, and liquid transfer lines all passed through holes which had been drilled through the feedstock container's rubber stopper.

Once the tubing lines were in place, the stopper holes were filled with liberal amounts of glue to ensure the system was completely sealed.



**Figure 3.2 Modified Experimental Apparatus (Hydrogen Experiments Only)**



### ***3.5 Experimental Method***

#### *3.5.1 General Method*

The basic procedure in each experiment involved pumping the feedstock solution through the catalytic reactor at a specified flowrate. The flowrate was used to calculate the hydraulic residence time (HRT) for the reactor. HRT, defined as the reactor pore volume divided by the fluid flowrate, is the average amount of time a water molecule spends in the reactor. Assuming the perchlorate ion travels with the bulk water flow, the HRT may affect the extent of perchlorate reduction. With a low HRT, the time that the perchlorate interacts with the reductant and catalyst material is reduced, potentially resulting in decreased perchlorate degradation. At higher HRT values, the situation is reversed; potentially resulting in increased reduction of perchlorate.

In a given experiment, the formic acid and perchlorate concentrations in the feedstock remained constant. Over the course of this research project, various combinations of perchlorate concentration, formic acid concentration, and HRT were tested in order to determine reactor performance across a range of conditions. In experiments 13, hydrogen was used as the reductant instead of formic acid. In this experiment, the influent was assumed to be saturated with hydrogen.

In each experiment, samples were collected for ion chromatography analysis. Influent samples were collected immediately before and immediately after the main experimental

run. These samples were analyzed for perchlorate, and results were averaged in order to quantify the mean influent perchlorate concentration.

During the main run, effluent samples were collected at periodic intervals. All effluent samples were analyzed for perchlorate. In some experiments, selected effluent samples were also analyzed for potential reduction byproducts (chlorate, chlorite, chloride). The time interval between effluent samples varied from experiment to experiment, depending largely on the fluid flowrate. For example, in a 120-minute experiment with a flowrate of about 20 mL/min (HRT ~3 min), effluent samples were typically collected at  $t = 0, 2.5, 5, 7.5, 10, 15, 20, 30, 45, 60, 80, 100,$  and 120 minutes.

As described previously, effluent pH and conductivity were also monitored. The purpose of these measurements was to track general changes in effluent water quality; they were not intended to provide any direct information on the amount of perchlorate in the effluent. In general, pH and conductivity readings were recorded whenever an effluent sample was collected.

### *3.5.2 pH and Conductivity Electrode Calibration*

Prior to each experiment, calibration checks were performed on the pH and conductivity electrodes. For the pH electrode, performance was verified at both pH 4 and pH 7 by immersing the electrode in the corresponding buffer solution. If either of the measured responses differed from the proper values by more than 0.05 pH units, a new three-point

calibration was performed. The conductivity probe was checked against the conductivity calibration solution, which had a certified value of 1413  $\mu\text{S}$ . If the response was between 1403 – 1423  $\mu\text{S}$ , no action was taken; otherwise, a new conductivity calibration was performed.

### *3.5.3 Feedstock Preparation*

The influent feedstock for each experiment had a predetermined “desired” concentration of formic acid and perchlorate. To achieve these target values, feedstock was prepared by adding calculated quantities of formic acid and perchlorate to a known volume of DI water. In some experiments, sodium hydroxide was also added in order to adjust the solution pH to a desired level. An example of the preparation calculations used to determine the required amounts of perchlorate, formic acid, and sodium hydroxide is provided in Appendix B.

When hydrogen was used as reductant (instead of formic acid), a known volume of DI water was placed in a 19-L jug. The required (calculated) volume of perchlorate was then added to the solution to achieve the target perchlorate concentration. Next, MES was added to reduce the influent pH to around 4.0. Finally, the hydrogen gas feed was switched on and the regulator was adjusted so that vigorous bubbling was achieved. The solution was equilibrated for about 30 minutes before being used in the experimental run.

A few experiments were conducted with chlorate as substrate. Feedstock preparation steps for these experiments were identical to those described above, except that a calculated volume of chlorate stock solution was added to the mixture instead of perchlorate.

#### *3.5.4 Reactor Flushing*

In each experiment, the catalytic column was flushed both before and after the main experimental runs. Hereafter, these sessions will be referred to as “pre-experiment flush” and “post-experiment flush”.

The purpose of the pre-experiment flush was to (1) remove stagnant fluid from the column, and (2) activate the catalyst surface. No effluent samples were collected during the pre-experiment flush. Flush solution was prepared in a dedicated two-liter Pyrex Erlenmeyer flask. The pre-experiment flush solution used in a given experiment was identical to the feedstock except it did not contain any perchlorate (in other words, the flush solution had the same reductant concentration and pH as the experimental feedstock). Flush solution was pumped through the reactor at the flowrate selected for the main experiment. The pre-experiment flush session lasted until effluent pH and conductivity readings stabilized, typically 30 to 60 minutes. Once the pH and conductivity readings stabilized, the valve leading to the reactor inlet was closed and the flush solution container was replaced with the feedstock reservoir. After the tubing lines

were re-primed and influent samples were collected, the valve leading to the reactor inlet was reopened and the main experimental run was initiated.

Once the main experimental run was completed, a post-flush was performed in order to clear residual perchlorate from the reactor. In the first six experiments, the solution used in the post-experiment flush session was identical to that used during the pre-experiment flush. In all subsequent experiments, the pH of the post-experiment flush solution was increased in order to speed removal of sorbed perchlorate from the catalyst surface (this will be discussed further in chapter 4). Formic acid was always used in the post-experiment flush solution, even when hydrogen was used as the reductant in the main experiment. In early experiments, effluent samples were not collected during the post-experiment flush sessions. However, once it became clear that perchlorate was sorbing to the catalyst surface during the main experimental run (see chapter 4), we began collecting post-experiment flush effluent samples at periodic intervals for ion chromatography analysis. In most experiments, post-experiment flush sessions lasted between 60 and 90 minutes.

### ***3.6 Ion Chromatography Analysis Method***

Ion chromatography was the sole method used to quantify perchlorate concentrations in the reactor influent and effluent samples. In addition, ion chromatography was used to identify/quantify perchlorate reduction byproducts in selected effluent samples.

As described earlier, the instrument used was a Dionex DX-600 ion chromatography system equipped with an AS-16 analytical column. Injection volume for all samples was 800  $\mu\text{L}$ .

### *3.6.1 Analysis Programs*

Chromeleon data management software was used to program the instrument operating parameters. Separate programs were used for perchlorate and byproduct analyses. Operating conditions for perchlorate analysis (eluent concentration, flowrate, *etc.*) were identical to those listed in Dionex Application Note 134 (Dionex, 2004). In these analyses, distinct perchlorate peaks were observed at approximately 9.3 minutes. This isocratic method was specifically designed for rapid identification of perchlorate in drinking water. All other anions eluted in an indistinguishable cluster very early in the program runtime. Since individual reduction byproduct peaks could not be identified using the isocratic perchlorate method, a separate program was developed.

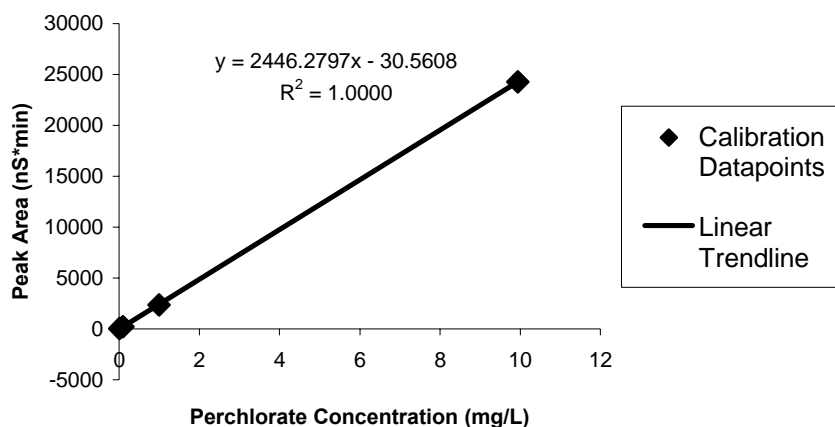
A gradient program with 30-minute total runtime was developed for byproduct analysis. In this program, suppressor current was set at 210 milliamps, oven temperature was 30  $^{\circ}\text{C}$ , and eluent flowrate was 1.5 mL/min. For the first 8.3 minutes of the program, the potassium hydroxide eluent concentration was held at 1.5 millimolar (mM). From 8.3 minutes to 14.3 minutes, eluent concentration was ramped up from 1.5 mM to 10 mM. In the remaining 15.7 minutes of the program, eluent concentration was ramped up from 10 mM to 55 mM. This analytical program yielded distinct peaks for chlorite ( $t \sim 9.5$  min),

chloride ( $t \sim 12.4$  min), chlorate ( $t \sim 15.6$  min), and perchlorate ( $t \sim 26.5$  min). Note that while this gradient program yielded distinct perchlorate peaks, the required analytical time per sample was triple that of the isocratic method. Because of this, the isocratic program was the primary method for quantification of perchlorate.

### *3.6.2 Calibration Quantification*

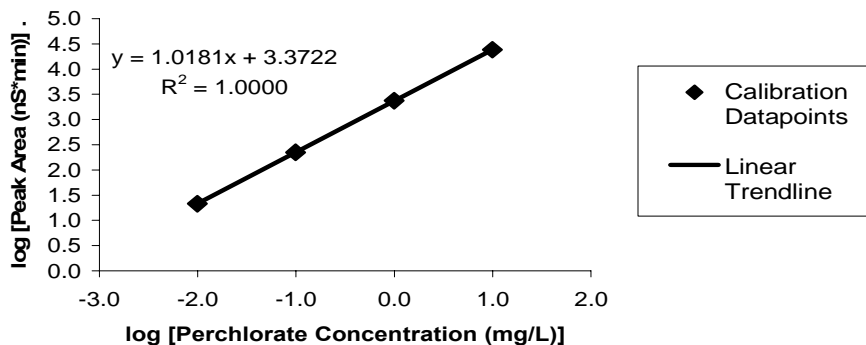
Instrument calibration was achieved by analyzing a series of samples with known analyte concentrations. Separate standards were prepared for each analyte. For a given analyte, the series of calibration standards was prepared through serial dilution of aliquots extracted from the applicable stock standard (listed above in the “ion chromatography calibration standards” section). For perchlorate analysis, a four-point calibration was performed using standards with concentrations of 0.00994 mg/L, 0.0994 mg/L, 0.994 mg/L, and 9.94 mg/L. For the remaining analytes (chlorate, chlorite, and chloride), three-point calibrations were performed at concentrations of 0.1 mg/L, 1.0 mg/L, and 10.0 mg/L.

During the calibration procedure, the concentrations of the known standards were entered into the Chromeleon software program. All samples were analyzed as usual. After measuring the analyte peak area in each sample, Chromeleon created a linear calibration curve which was then applied to subsequent unknown samples. An example of the perchlorate calibration curve (isocratic method) is provided in Figure 3.3:



**Figure 3.3 Perchlorate Calibration Curve (Normal Scale)**

In Figure 3.3, the two datapoints at the low end of the x-axis are difficult to distinguish. For the reader's convenience, Figure 3.4 presents a log-log plot of the calibration data in order to more clearly illustrate the overall linearity:



**Figure 3.4 Perchlorate Calibration Curve (log-log Scale)**

Chromeleon created similar calibration curves for chloride, chlorite, and chlorate.

Instrument response was highly linear for each analyte and remained stable throughout



the entire research project. In many experimental runs, known standards were inserted in the analysis queue to verify calibration stability. Qualitatively, the observed results were very close to those obtained during the initial calibration sequence, verifying instrument accuracy. Unfortunately, data from these calibration checks were inadvertently deleted in the course of data analysis.

Deletion of calibration check data is recognized as a major quality control shortcoming in this project. However, we do have data that may serve as an alternative indicator of calibration stability. In most experiments, the target concentration of perchlorate in the feedstock was 0.5 mg/L. In these experiments, the feedstock solution was created by adding small quantities of concentrated perchlorate calibration standard to a known volume of DI water. A high degree of repeatability (from experiment to experiment) was achieved by using the Eppendorf Repeater Plus® pipette to dispense the perchlorate solution into the feedstock water. Influent samples were collected during the experiments in order to quantify the true perchlorate concentration in the feedstock. Typically, two influent samples were collected before the main experimental run, and two more collected after the run. Results from all experiments which had a target feedstock concentration of 0.5 mg/L are shown in the Table 3.3:

Experiment #	Number of Influent Samples	Mean ClO <sub>4</sub> Concentration (mg/L)	Feedstock Volume (L)	Notes
3	4	0.5237 +/- 0.0039	3	
5	4	0.5279 +/- 0.0016	4	
6	4	0.5228 +/- 0.0039	4	
8	2	0.5032 +/- 0.0080	3	Both influent samples collected prior to main experiment
9	4	0.5265 +/- 0.0148	2.5	
10	4	0.5284 +/- 0.0127	2	
11	4	0.5254 +/- 0.0178	2	
12	4	0.5228 +/- 0.0041	2	
13	4	0.5048 +/- 0.0156	11	Hydrogen experiment
16	4	0.5234 +/- 0.0185		

\* ClO<sub>4</sub> concentration data reported as mean value +/- standard deviation

**Table 3.3 Influent Analysis Results for Experiments where Target Perchlorate Concentration was 0.5 mg/ L**

As shown in Table 3.3, the measured perchlorate concentrations in the feedstock were very consistent during a single experiment. The Relative Standard Deviation (RSD) values, calculated by dividing the standard deviation by the mean, ranged from 0.74% (experiment 6) to 3.38% (experiment 11). The EPA method for analysis of perchlorate in drinking water specifies a maximum RSD of 10% for a series of replicate analyses on a 0.025 mg/L sample (USEPA, 1999). Granted, the perchlorate concentrations shown in Table 3.3 were substantially higher than 0.025 mg/L, and the values used to calculate the mean influent concentration were from analyses on separate samples, not replicate analyses on a single sample. However, given (1) the extremely linear instrument response across a concentration range from 0.00994 mg/L to 9.94 mg/L, and (2) the fact that all calculated RSD values were well below the maximum limit, it seems reasonable to conclude that the instrument was performing within acceptable parameters.

Table 3.3 also shows that the perchlorate concentration was consistent from experiment to experiment. In two experiments (8 and 13), the measured concentration was somewhat lower than in the other experiments; however, both of these experiments had mitigating factors which may have impacted the results. In experiment 8, no post-experiment influent samples were collected. In general, results from post-experiment influent samples tended to have higher perchlorate concentrations than their pre-experiment counterparts (in other words, the perchlorate concentration in the feedstock container increased slightly as the experiment progressed). Since the influent samples for experiment 8 were collected at the beginning the experimental run, the calculated result may underestimate the true average influent concentration. In experiment 13, the low influent concentration was almost certainly due to an error in the feedstock volume. The DI water used to generate the feedstock solution was measured in 500 mL increments using a graduated cylinder. Some degree of error is inherent in this process because it was difficult to accurately judge the meniscus level, leading to a potential error of several milliliters per 500 mL addition. Since the feedstock volume was much higher in experiment 13, the measurement error was compounded several-fold over other experiments. Thus, the relatively low perchlorate concentration in the experiment 13 feedstock is likely due to an error in the solution volume, not an instrument calibration problem.

Overall, the small RSD values calculated from influent analyses during a single experiment indicate a high degree of analytical precision. Further, the relative consistency in mean influent concentration from experiment to experiment is indicative of both a highly stable instrument, as well as reliable calibration and feedstock preparation techniques. The consistency of these influent measurements gives us confidence in the ion chromatography measurements.

*3.6.3 Method Detection and Quantification Limits*

The Method Detection Limit (MDL) and Method Reporting Limit (MRL) were calculated using the procedures outlined in sections 9.2.6 and 9.2.7 in EPA Method 314 (USEPA, 1999). Seven replicate analyses were performed on a sample containing 0.00994 mg/L of perchlorate. Using results from these analyses, the perchlorate MDL and MRL were calculated (Table 3.4):

Replicate #	Reported Concentration (mg/L) *	
1	0.0085	
2	0.0072	
3	0.0085	
4	0.0087	
5	0.0076	
6	0.0079	
7	0.0072	
* True concentration 0.00994 mg/L		
Standard Deviation (mg/L):		0.00063471
Student t (99% Confidence, n-1 = 6):		3.14
<b>MDL - from EPA 314, MDL = [ (t) (st dev) ]</b>		
MDL (mg/L):		0.00199
<b>MRL - from EPA 314, MRL = [ (3) (MDL) ]</b>		
MRL (mg/L):		0.00598

**Table 3.4 MDL and MRL Calculation**

The calculations resulted in a MDL of 0.00199 mg/L and a MRL of 0.00598 mg/L. The MRL was used as the quantification limit for the method; if the Chromeleon software reported a concentration below 0.00598 mg/L, the sample was assigned a concentration of zero.

Note that the MRL was slightly lower than the lowest concentration used for instrument calibration. This conflicts with the MRL criteria in EPA Method 314. However, given the extremely linear nature of the calibration curve, we feel it is reasonable to use the calculated MRL despite the fact that it is just below the low end of the calibration range.

### ***3.7 Experimental Schedule***

Control variables in this research project included substrate concentration, reductant type and concentration, feedstock pH, and HRT. Reactor performance was explored by varying the control variable values from experiment to experiment (results will be provided in the next chapter). Table 3.5 lists the control variable combinations that were studied in this project:

Exp #	Substrate	[Substrate] (mg/L)	[HCOOH]	Feed pH	HRT (min)	Notes
1	Perchlorate	9.1511	2	4.11	6.42	
2	Perchlorate	5.5974	2	4.01	2.90	
3	Perchlorate	0.5237	2	3.24	12.00	
4	None	--	2	Varied	Varied	Qualitative experiment examining effluent conductivity at various pH and HRT
5	Perchlorate	0.5279	2	3.27	2.84	
6	Perchlorate	0.5228	1	3.47	2.90	
7	None	--	1	~3.50	2.87	Flushing only (clearing out sorbed perchlorate mass)
8	Perchlorate	0.5032	2	3.30	2.87	
9	Perchlorate	0.5265	10	3.08	2.89	
10	Perchlorate	0.5284	10	3.00	12.36	
11	Perchlorate	0.5254	10	2.98	7.61	
12	Perchlorate	0.5228	10	10.58	7.51	
13	Perchlorate	0.5048	N/A	4.21	3.21	Hydrogen was reductant
14	Chlorate	1.0758	10	2.96	7.98	
15	Chlorate	0.9400	1	3.47	7.68	
16	Perchlorate	0.5234	10	2.96	3.02	24 hours between main experiment and postflush

**Table 3.5 Experimental Schedule**

## 4.0 Results and Discussion

### *4.1 Introduction*

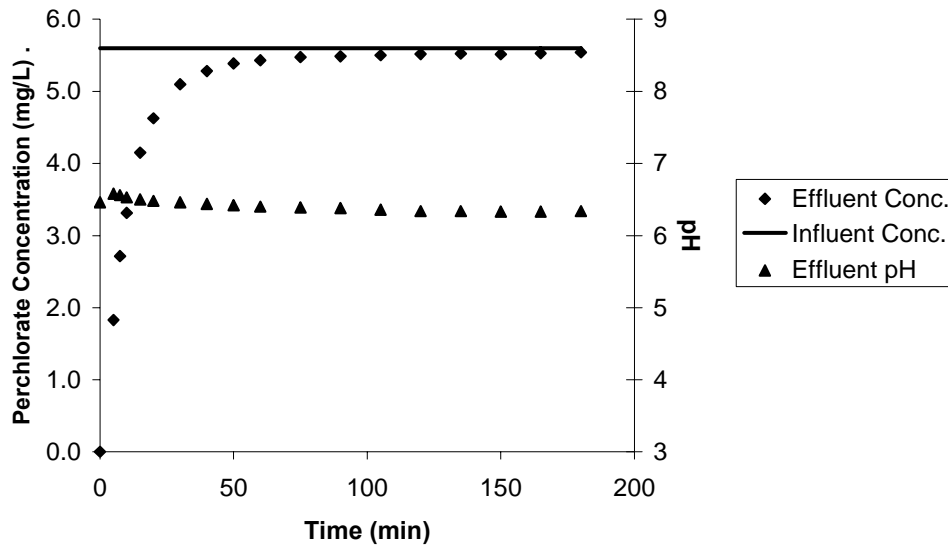
This chapter summarizes key experimental results and observations. Where appropriate, figures and tables are used to illustrate the points described in the text. For more details, the reader is referred to Appendix A, which presents the raw analytical data for each experiment.

The latter portion of this chapter is devoted to a discussion of overall perchlorate reduction and the effects of individual control variables (pH, HRT, reductant concentration, etc.) on reactor performance. However, before discussing the control variables, it is important to highlight the overarching result obtained in these experiments: specifically, very little (if any) verifiable perchlorate reduction was observed. In many experiments, the effluent perchlorate concentrations were much lower than those in the influent, implying that a substantial portion of the perchlorate fed to the reactor was being destroyed. However, further examination showed that adsorption, not reduction, was responsible for the low perchlorate concentrations in the effluent. This resulted in data analysis problems in the first seven experiments. In the next section, the perchlorate adsorption effect is described.

## 4.2 Perchlorate Adsorption – An Unforeseen Experimental Challenge

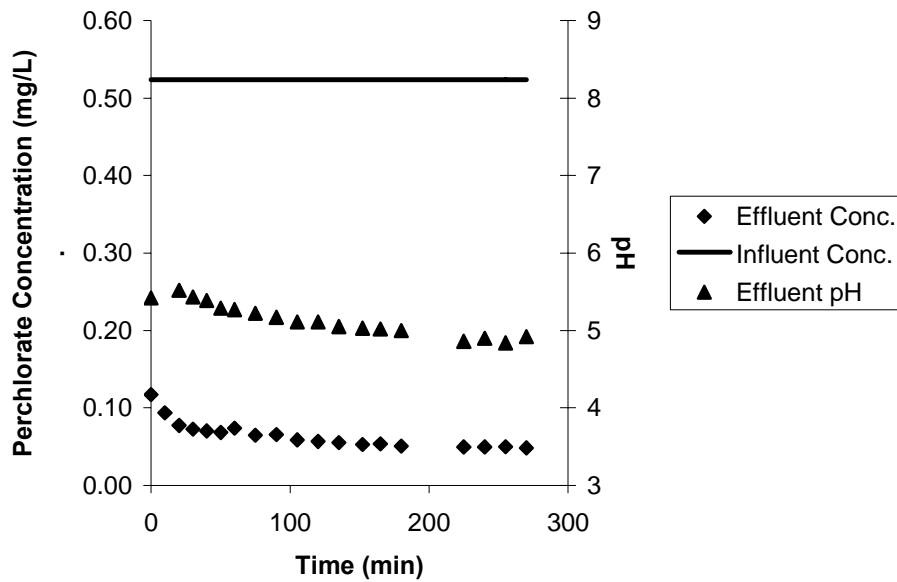
### 4.2.1 Evolution of the Problem

Initially, perchlorate that adsorbed to the catalyst surface was expected to either (i) desorb without any chemical change, or (ii) undergo a reduction reaction. These effects were expected to occur within a relatively short time after adsorption. Initially, the possibility that perchlorate may remain adsorbed to the catalyst surface for extended periods of time was not considered. Thus, in the first few experiments, the difference between the influent and effluent concentration was attributed to catalytic reduction. As an example, Figures 4.1 and 4.2 show the effluent and influent concentration data for experiments 2 and 3, respectively:



**Figure 4.1 Effluent pH and Perchlorate Concentrations in Experiment 2;  
Feedstock pH = 4.01, [HCOOH] = 2mM, HRT = 2.90 min**





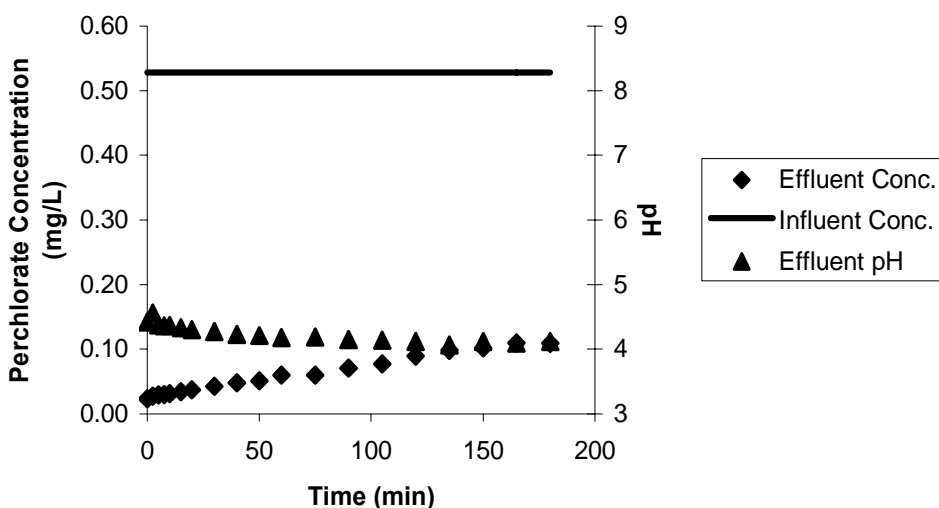
**Figure 4.2 Effluent pH and Perchlorate Concentrations in Experiment 3; Feedstock pH = 3.24, [HCOOH] = 2mM, HRT = 12.0 min**

Figure 4.1 shows that the effluent concentration in experiment 2 rapidly increased, eventually approaching the influent concentration. On the other hand, the effluent concentrations in experiment 3 (Figure 4.2) were quite low during the entire run. Based on these results, one logical conclusion is that the relatively low effluent perchlorate concentrations observed in experiment 3 were the result of its catalytic reduction within the reactor, and that such reduction did not occur in experiment 2 (perhaps because of the different operating conditions). However, further analysis of the experiment 3 data shows that another factor may be at work.

In particular, note that the effluent perchlorate concentration at the beginning of experiment 3 ( $t = 0$ , first effluent datapoint in Figure 4.2) was approximately 0.12 mg/L.

This was alarming, since the pre-experiment flush and post-experiment flush sessions should have removed any residual perchlorate from the reactor; there should not have been detectable levels of perchlorate in the effluent at the beginning of experiment 3. Initially, the perchlorate found in the effluent sample at t=0 in experiment 3 was attributed to inadequate flushing.

Unfortunately, the problem was seen again in the results from experiment 5 (Figure 4.3):



**Figure 4.3 Effluent pH and Perchlorate Concentrations in Experiment 5; Feedstock pH = 3.27, [HCOOH] = 2mM, HRT = 2.84 min**

As shown in Figure 4.3, the effluent sample at t=0 in experiment 5 had a detectable concentration of perchlorate. In this case, the concentration was about 0.02 mg/L, a value substantially lower than the corresponding sample in experiment 3, yet well above the minimum quantification limit (recall MRL = 0.00598 mg/L, discussed in chapter 3..

The detectable perchlorate at  $t=0$  in experiment 5 was particularly troubling in the context of the previous experiment (experiment 4), which consisted of flushing the column with formic acid solution at different flowrates and pH values; no perchlorate was added to the system during this experiment. The purpose of experiment 4 was to evaluate the effects of different combinations of two control variables (influent pH and fluid flowrate) on the effluent pH and conductivity values. In the course of this experiment, an estimated 3370 mL of flush solution flowed through the reactor (an equivalent of roughly 58 pore volumes). Considering that additional flushing was performed immediately after experiment 3 and immediately before experiment 5, the extensive flushing should have easily cleared any dissolved perchlorate from the reactor. Thus, it appeared that insufficient flushing was not an adequate explanation for the presence of detectable perchlorate in the  $t=0$  effluent samples in experiments 3 and 5.

In response to this observation, the analytical protocol for experiment 6 was modified slightly. Several effluent samples were collected during the pre-experiment flush and post-experiment flush sessions in order to verify the presence of perchlorate during flushing. Results from the pre-experiment flush, main experimental run, and post-experiment flush are shown in Figures 4.4, 4.5, and 4.6 respectively (below):

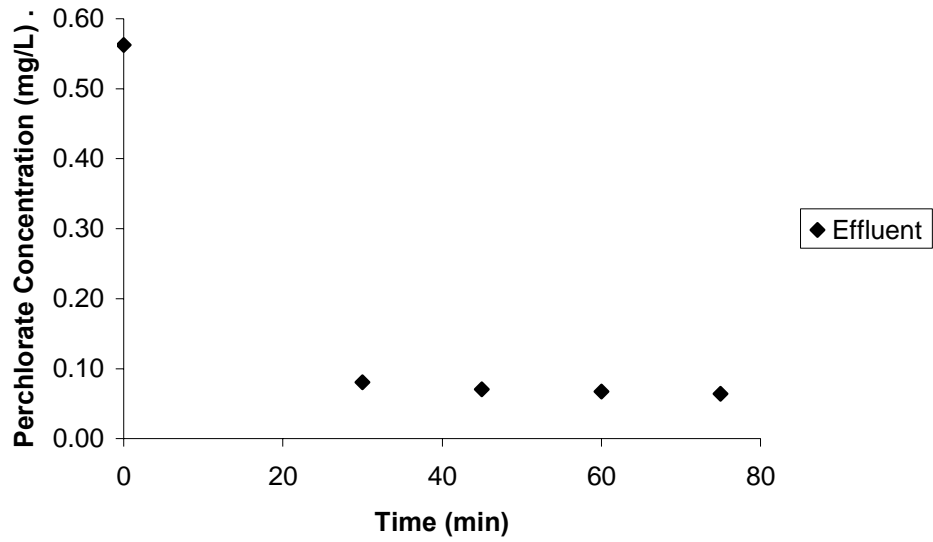


Figure 4.4 Perchlorate Concentrations in Experiment 6 Pre-Experiment Flush; Flush Solution pH ~ 3.5, [HCOOH] = 1mM, HRT = 2.90 min

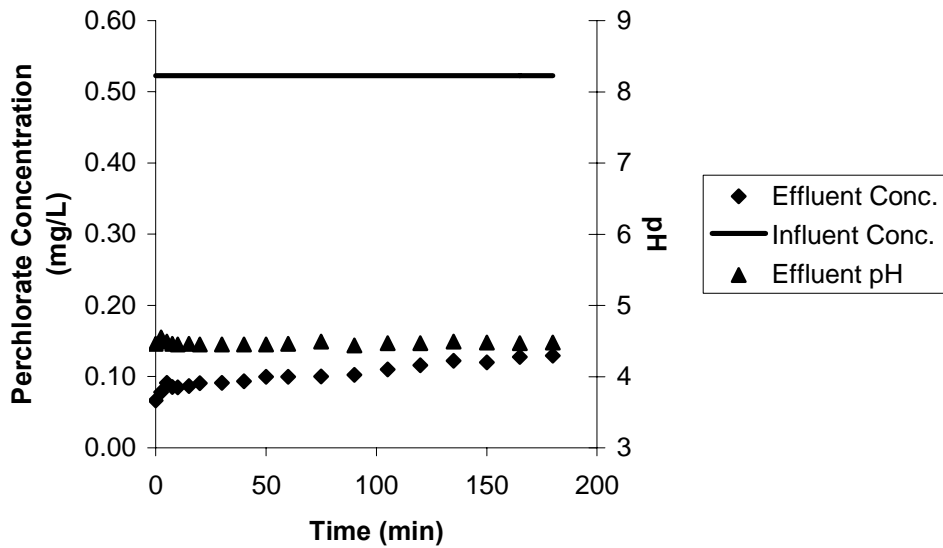
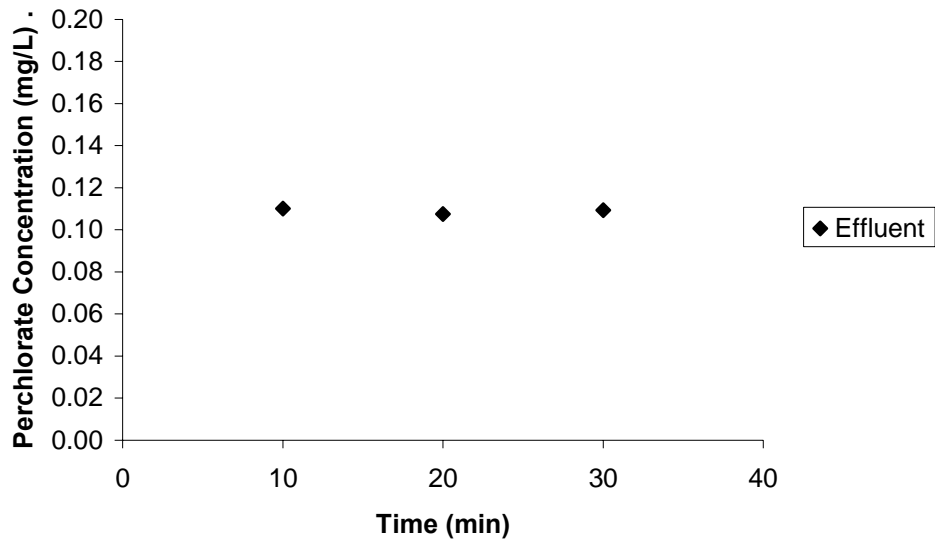


Figure 4.5 Effluent pH and Perchlorate Concentrations in Experiment 6 Main Run; Feedstock pH = 3.47, [HCOOH] = 1mM, HRT = 2.90 min



**Figure 4.6 Perchlorate Concentrations in Experiment 6 Post-Experiment Flush;**  
**Flush Solution pH ~ 3.5, [HCOOH] = 1mM, HRT = 2.90 min**

Close examination of the experiment 6 data reveals a series of interesting trends. Figure 4.4 shows that during the pre-experiment flush, the perchlorate concentration was initially quite high (~ 0.56 mg/L). In the first 30 minutes of the pre-experiment flush, the concentration dropped to about 0.08 mg/L, and then slowly declined to a final value of 0.06 mg/L during the remaining 45 minutes of the session. During the main experiment (Figure 4.5), however, the effluent perchlorate concentration slowly increased from 0.07 mg/L (t=0) to 0.13 mg/L (t=180). The three samples collected during the post-experiment flush (Figure 4.6) all had concentrations of approximately 0.11 mg/L.

Essentially, the data from experiment 6 show that pre-experiment flush effluent initially contained a large quantity of perchlorate, but the concentration rapidly decreased and

“tailed off” within 30 minutes. During the main experiment, the concentration slowly increased in a nearly linear fashion. Finally, during the post-experiment flush, the effluent perchlorate concentration remained surprisingly stable. These trends do not seem to be consistent with removal of perchlorate that is entrained with the bulk fluid. In particular, the results in Figure 4.6 rule out this possibility; if perchlorate was simply dissolved in the bulk fluid, a significant concentration decrease should have been observed over the course of the post-experiment flush. The observed results clearly indicate that another factor is responsible for the persistent presence of perchlorate within the reactor.

Slow desorption of perchlorate from the catalyst surface was considered as an explanation for the behavior observed in experiment 6. During the pre-experiment flush, the large quantity of perchlorate initially present may have been the result of perchlorate slowly desorbing into the bulk fluid (*i.e.* slowly approaching equilibrium) between experiments 5 and 6. As the equilibrated fluid was flushed from the column during the pre-experiment flush, the concentration rapidly decreased and stabilized. During the main run, effluent perchlorate concentrations were much lower than the influent concentration; however, the slow increase in effluent concentration as the main run progressed may be consistent with adsorption. As perchlorate ions became adsorbed to the catalyst surface, fewer vacant sites were available on the catalyst, so more perchlorate exited the reactor with the bulk fluid. Finally, as described in the last paragraph, the stable post-experiment flush

concentrations appear to be consistent with slow desorption of perchlorate from the catalyst.

To test the adsorption theory, experiment 7 consisted of two discreet flushing sessions. No perchlorate was fed to the column, but effluent samples were periodically collected just as in a “normal” experimental run. The purpose of the experiment was to (i) clear the reactor of all perchlorate, and (ii) calculate the mass of perchlorate that was left in the reactor at the end of experiment 6. The analytical data and mass-balance calculations from experiment 7 are presented in Table 6.8, which is located in Appendix A.

Results from experiment 7 revealed two important points. First, removal of perchlorate from the column was extremely slow. Perchlorate was still present in the last sample although roughly 167 pore volumes of flush solution had been run through the column to that point. Interestingly, the pH and formic acid concentration of the flush solution appeared to have an impact on perchlorate removal. The mass removed in the first flush session (influent pH ~ 3.5, [HCOOH] = 1mM, runtime 480 minutes) was almost identical to the mass removed in the first 30 minutes of the second session (influent pH ~4, [HCOOH] = 2mM). Clearly, the pH and/or formic acid concentration of the solution had a substantial impact on perchlorate removal. Second, a very large quantity of perchlorate (~ 2.04 mg) was recovered in experiment 7. For comparison purposes, the total perchlorate mass fed to the reactor during experiment 6 was just 1.88 mg. Essentially,

mass recovery exceeded 100%, indicating that some of the perchlorate removed in experiment 7 had originally been fed during experiment 5.

The implication of this mass balance analysis was clear; the perchlorate recovered during experiment 7 had been building in the reactor for some time. The logical explanation for this effect is adsorption. Given the large amount of mass recovered, very little (if any) of the perchlorate in previous experiments could be attributed to catalytic reduction; the mass was simply flowing out of the reactor during the flush sessions, albeit at a relatively slow rate. Based on the differences in mass removal between the two flush sessions in experiment 7, it appears that the pH and/or formic acid concentration of the flush solution accelerated the desorption rate.

#### *4.2.2 Experimental Method Modifications*

In the original research plan, the degree of perchlorate reduction in a given experiment was to be determined by comparing the concentration of perchlorate in the effluent samples to the influent feed concentration. For example, if the influent concentration was 0.5 mg/L and the effluent concentration was 0.1 mg/L, an overall reduction of 0.4 mg/L (80%) would be assumed. Further, since the influent concentration remained constant in each experiment, reactor performance over time would be evaluated by examining the trend in effluent concentration. As an example, an increasing trend in effluent concentration within a given experiment would indicate decreasing reactor efficiency, possibly because of catalyst deactivation. The “presumptive” reduction determined



through comparison of influent and effluent concentrations would be verified by analyzing selected samples for potential degradation byproducts such as chlorate, chlorite, and chloride.

Unfortunately, since perchlorate adsorption within the column was found to be significant, the rather straightforward analysis procedure described above was not applicable. Low concentrations of perchlorate in the effluent could not be directly attributed to catalytic reduction; a substantial quantity of the perchlorate may have simply adsorbed to catalyst without undergoing any subsequent reaction.

To account for the adsorption effect, a new data analysis method (based on mass balance) was used to estimate perchlorate reduction. Beginning with experiment 8, effluent samples were collected during all post-experiment flush sessions. The mass recovered in the effluent from the main experimental run and post-experiment flush was compared to the mass fed to the system during the experiment. The perchlorate mass recovery percentage (MRP) was calculated using Equation 4.1:

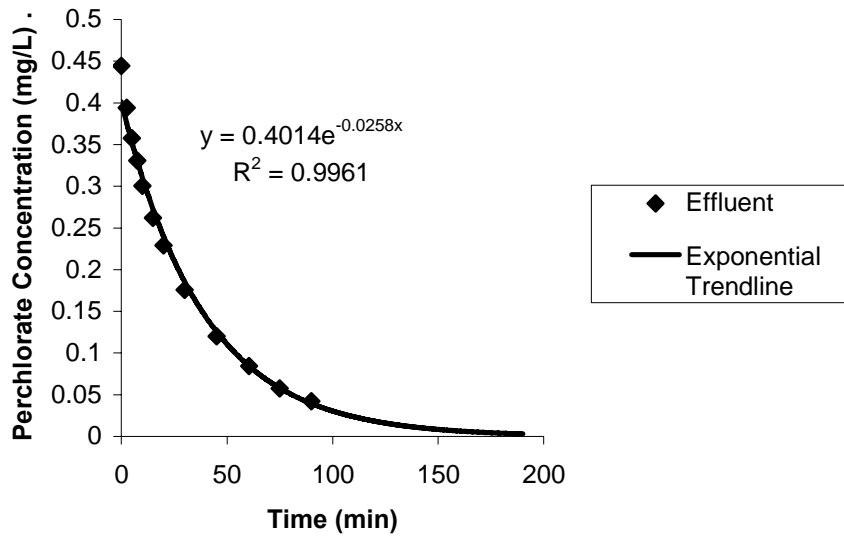
$$\text{Eq. 4.1} \quad \text{MRP} = \frac{\text{Total Effluent Mass}}{\text{Total Influent Mass}} \times 100$$

The MRP value provided a more accurate estimate of the quantity of perchlorate which may have underwent reduction within the reactor. If the MRP value approached 100%, perchlorate fed to the reactor during the experiment clearly was not destroyed, regardless

of the distribution pattern of effluent concentration values. On the other hand, an MRP value of less than 90% was considered to be an indicator that substantial perchlorate reduction may have occurred. When the MRP was less than 90%, effluent samples from the main experimental run were analyzed for degradation byproducts in order to verify perchlorate reduction.

A final note on the revised data analysis procedure is warranted. The post-experiment flush was not always sufficient to completely clear all adsorbed perchlorate from the reactor. With the exception of experiments 10 and 12, perchlorate was present in the final post-experiment flush sample. This “residual” mass (the mass left in the reactor at the end of an experiment’s post-experiment flush) was cleared out during the next experiment’s pre-experiment flush; however, since samples were not collected during pre-experiment flush sessions, the residual mass could not be directly calculated.

Fortunately, in most cases, the post-experiment flush effluent concentrations were found to decrease exponentially (Figure 4.7). The strong correlation between the individual datapoints and the exponential trendline ( $R^2 > 0.99$ ) provided a means for estimating the residual perchlorate mass.



**Figure 4.7 Perchlorate Concentration Data and Trendline for Experiment 8 Post-Experiment Flush (post-experiment flush duration was 90 minutes)**

An estimate of the residual mass was obtained by integrating the trendline equation across an appropriate time domain (beginning with the time the last post-experiment flush sample was collected and ending at a point where the perchlorate concentration should be effectively zero), then multiplying the integrated result by the fluid flowrate. Equation 4.2 illustrates this calculation for experiment 8:

$$\text{Eq. 4.2} \quad \text{Mass}_{\text{residual}} = 0.02 \cdot \frac{\text{L}}{\text{min}} \left[ \int_{90\text{min}}^{300\text{min}} 0.4015 \cdot e^{-0.0258 \cdot t} \left( \frac{\text{mg}}{\text{L}} \right) dt \right] = 0.0304\text{mg}$$

Note that the values shown in Eq 4.2 are experiment-specific and only apply to experiment 8. The resulting estimate of the residual perchlorate mass was combined with

the mass calculated through analysis of the effluent samples (described previously in the discussion of Table 4.1) to form the “total effluent mass” used in the numerator of Equation 4.1. In essence, calculation of the residual mass improved the accuracy of the MRP calculation by accounting for perchlorate which had remained in the reactor after the conclusion of the post-experiment flush.

Note that the residual mass was only estimated when there was an excellent fit ( $R^2 > 0.99$ ) between the post-experiment flush data and the exponential trendline. In experiment 13, the correlation coefficient was less than 0.99, so residual mass was not taken into account during calculation of the perchlorate MRP value for this experiment.

#### *4.2.3 Section Summary*

It should be clear from the extensive discussion above that adsorption of perchlorate to the catalyst surface was a confounding factor in the initial experiments. Since the magnitude of the problem was not fully understood until the end of experiment 7, the data from the first seven experiments were incomplete; retention of perchlorate within the reactor from experiment to experiment interfered with the reactor performance evaluation.

Beginning with experiment 8, the experimental method was modified to include post-experiment flush samples, and a mass-balance approach (centered around the MRP

calculation) was used to estimate perchlorate reduction. In the next section, MRP results from the remaining perchlorate experiments (8-13, 16) are presented.

### ***4.3 Perchlorate Reduction – MRP***

Once the perchlorate adsorption effect was recognized, calculation of the mass recovery percentage became the primary tool for evaluating perchlorate reduction. By using the MRP approach to estimate perchlorate reduction, slow desorption of perchlorate from the catalyst did not affect the results (as long as perchlorate was eventually removed from the reactor).

The MRP could not be calculated for experiments 1 through 7 (due to insufficient data on effluent mass during flush sessions, and the fact that perchlorate was retained in the reactor across multiple experiments). Beginning with experiment 8, the experimental protocol was modified to incorporate analysis of post-experiment flush samples, facilitating calculation of the MRP. Results are presented in Table 4.1:

Exp #	Feed pH	Average Effluent pH	[HCOOH] (mM)	HRT (min)	TIM (mg)	TEM (mg)	MRP	Notes
8	3.3	4.15	2	2.87	1.2118	1.1966	98.75%	
9	3.08	3.41	10	2.89	0.9477	0.8750	92.32%	
10	3	4.58	10	12.36	0.4442	0.0160	3.61%	No HCOOH used in flush solution.
11	2.98	3.86	10	7.61	0.7169	1.1010	153.59%	[ClO <sub>4</sub> ] = 0.0558 mg/L @ t=0
12	10.58	6.62	10	7.51	0.7227	0.7107	98.34%	[ClO <sub>4</sub> ] = 0.0136 mg/L @ t=0
13	4.21	4.36	N/A	3.21	0.9086	0.8366	92.07%	H <sub>2</sub> gas used as reductant. Residual mass not calculated
16	2.96	3.59	10	3.02	1.2003	1.1235	93.60%	24 hours between main experiment and postflush

**Table 4.1 Mass Recovery Percentage Summary for Experiments 8 - 13, 16**

In Table 4.1, “TIM” is the Total Influent Mass, defined as the amount of perchlorate mass fed to the reactor over the course of the experiment. TEM is the Total Effluent Mass, calculated from the ion chromatography analyses performed on samples collected during the main experimental run and the post-experiment flush. For experiments where the perchlorate concentration in the final post-experiment flush sample was nonzero and the data could be fit with an exponential trendline, the TEM also included the residual mass left in the reactor at the conclusion of the post-experiment flush (calculated by integrating the exponential trendline, as described in the previous section).

MRP values for experiments 8 and 9 were 98.75% and 92.32%, respectively. The only difference between these experiments was the formic acid concentration. The higher formic acid concentration yielded the lower MRP value, indicating that high levels of formic acid may lead to increased perchlorate reduction.

The MRP for experiment 10 was 3.97%. At first glance, this implies substantial perchlorate reduction. In an attempt to verify that perchlorate was destroyed, several of the samples collected during the main experimental run were analyzed for reduction byproducts. Results are shown in Table 4.2:

Sample #	Experiment Phase	Time (min)	Chlorate (mg/L)	Chlorite (mg/L)	Chloride (mg/L)
E10-008	Main Run	30	ND	ND	0.003
E10-010	Main Run	60	ND	ND	0.004
E10-012	Main Run	100	ND	ND	0.003
E10-014	Main Run	140	ND	ND	0.002
E10-016	Main Run	180	ND	ND	0.002
E10-021	Postflush	5	ND	ND	0.008
E10-023	Postflush	10	ND	ND	0.003
E10-025	Postflush	20	ND	ND	0.002
E10-027	Postflush	45	ND	ND	0.007
ND = Not Detected					

**Table 4.2 Byproduct Analysis Results for Experiment 10**

The results shown in Table 4.2 are not consistent with a significant reduction of perchlorate. No chlorate or chlorite was found in any of the samples, and chloride concentrations were barely detectable. If substantial perchlorate reduction had occurred, higher concentrations of byproducts should have been observed.

The reason for the low MRP in experiment 10 can be explained when the results from experiment 11 are taken into account (Table 4.1). Perchlorate was detected in the  $t=0$  sample for experiment 11, and the MRP was over 153%. Clearly, a large portion of the mass from experiment 10 was carried over into experiment 11. Fortunately, the data allow for calculation of a “combined” MRP for these two experiments (Table 4.3):

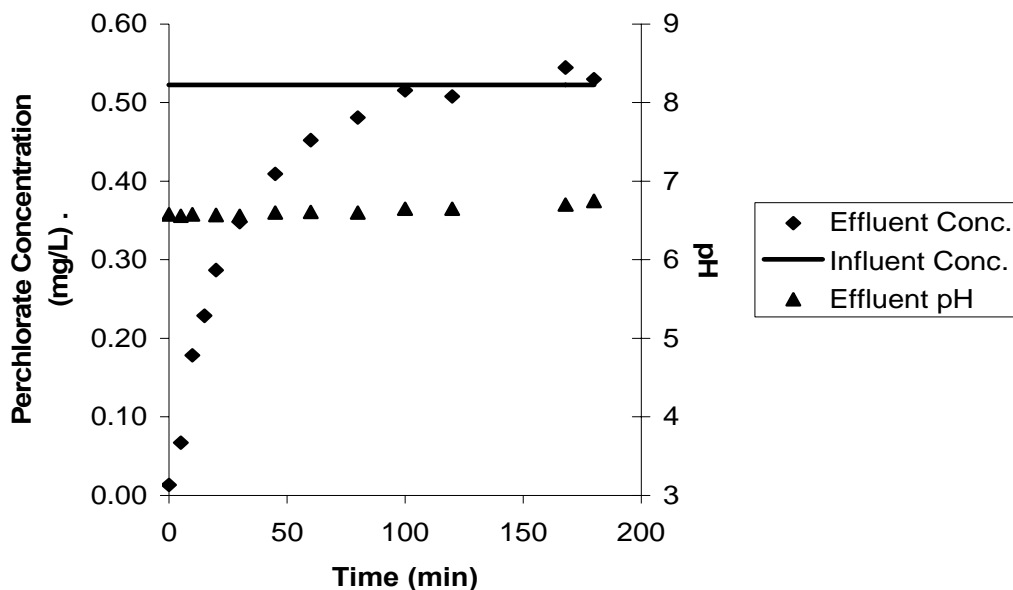
Exp #	TIM (mg)	TEM (mg)	MRP
10	0.4442	0.0160	3.61%
11	0.7169	1.1010	153.59%
<b>Combined</b>	<b>1.1610</b>	<b>1.1170</b>	<b>96.21%</b>

**Table 4.3 Combined MRP for Experiments 10 and 11**

The combined MRP in Table 4.3 shows that just 3.79% of the mass fed to the reactor during experiments 10 and 11 remained unaccounted for. Obviously, very little perchlorate reduction occurred in these experiments. The logical explanation for the low MRP in experiment 10 is that perchlorate did not desorb from the catalyst surface during the post-experiment flush. Note that the post-experiment flush solution used in experiment 10 was pure DI water (pH ~ 5.7); no formic acid was added to the solution. During the discussion of the results from experiment 7 (earlier in this chapter), it was mentioned that high formic acid concentration and high pH appeared to result in faster removal of perchlorate from the reactor. Results from experiment 10 appear to verify that formic acid is a major factor in facilitating perchlorate desorption.



Experiment 12 did not yield substantial perchlorate reduction (MRP = 98.34%, shown in Table 4.1). This experiment was conducted at a pH of about 10.6, and the effluent concentration trend during the main experimental run is shown in Figure 4.8:



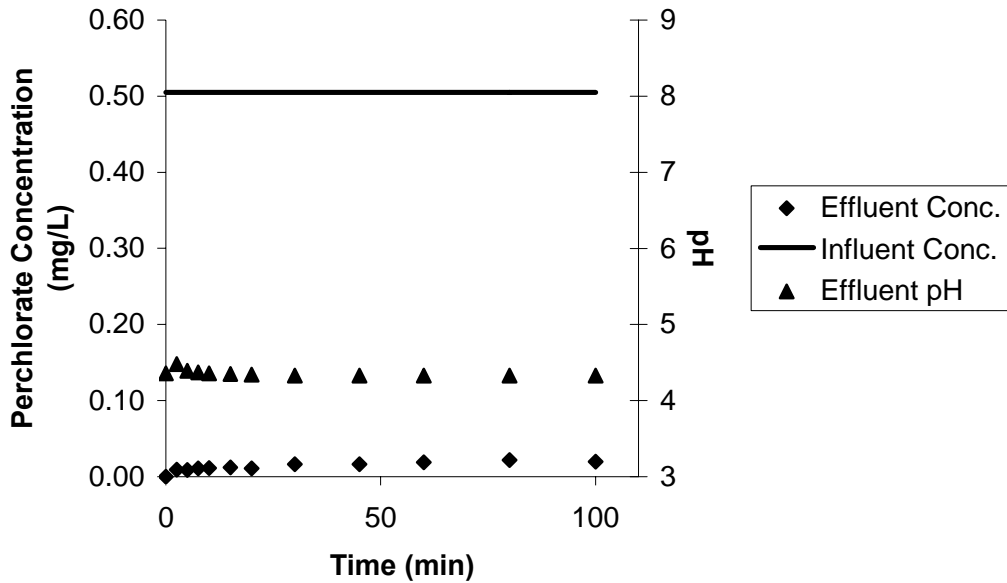
**Figure 4.8 Effluent pH and Perchlorate Concentrations in Experiment 12 Main Run; Feedstock pH = 10.58, [HCOOH] = 10mM, HRT = 7.51 min**

The effluent concentration in experiment 12 rapidly increased and approached the average influent concentration. This behavior was seen earlier in experiment 2 (Figure 4.1), where the pH was about 4. These results indicate that when formic acid is used as the reductant and the feedstock pH is 4 or above, perchlorate does not adsorb/remain adsorbed to the catalyst surface.

After experiment 12, it was clear that formic acid was not facilitating the reduction of perchlorate at the catalyst surface. Therefore, in experiment 13, hydrogen was used as

alternative reductant. Unfortunately, performance did not improve with hydrogen. As shown in Table 4.1, the MRP for experiment 13 was 92.07%. Note that the MRP was calculated without accounting for the residual mass because post-experiment flush data could not be adequately fit with an exponential trendline. The final post-experiment flush sample had a high perchlorate concentration (0.2543 mg/L), indicating there was a significant amount of mass left in the reactor. Thus, the MRP calculated for experiment 13 is lower than the actual MRP.

The pH of the feedstock in experiment 13 was approximately 4.2. The effluent concentration distribution is presented in Figure 4.9:



**Figure 4.9 Effluent pH and Perchlorate Concentrations in Experiment 13 Main Run; Feedstock pH = 4.21, Hydrogen Reductant, HRT = 3.21 min**

The low effluent concentrations in Figure 4.9 indicate strong adsorption of perchlorate within the reactor, even at pH 4. In formic acid experiments conducted at similar pH (see Figure 4.1), effluent concentrations were much higher, indicating the perchlorate flowed through the column without significant sorption. The low effluent concentrations observed during the hydrogen experiment appear to be yet another indicator that formic acid plays a role in facilitating perchlorate desorption (this will be discussed further in a later section).

In experiment 16, the flowrate, pH, influent perchlorate concentration and HRT were identical to those used in experiment 9. Essentially, the only difference in experiment 16 was that 24 hours elapsed between the main experimental run and the post-experiment flush. The purpose of this experiment was to evaluate whether reduction would occur in the time between the main run and post-experiment flush. The resulting MRP for experiment 16 was 93.60% (Table 4.1), which is close to the result from experiment 9. Thus, increasing the reaction time by delaying the flush session does not appear to lead to increased reduction.

Overall, very little perchlorate reduction was observed in any of the experiments. The MRP values for experiments 8, 9, 12, and 13, and 16 were all greater than 92%. For experiments 10 and 11, the combined MRP was over 96%. Thus, the vast majority of the perchlorate passed through the column without reacting.

While efforts to reduce perchlorate were largely unsuccessful, some interesting trends were observed. In the next section, the effects of individual control variables on experiments results will be discussed.

#### ***4.4 Effects of Control Variables***

##### *4.4.1 Effect of Formic Acid Concentration*

Data from experiments 8 and 9 (Table 4.1) indicate that slightly improved perchlorate reduction may occur at higher formic acid concentrations. HRT and feedstock pH were roughly the same in these two experiments; the formic acid concentration was the only substantial difference. A formic acid concentration of 10mM (experiment 9) yielded a MRP approximately 6% lower than the 2mM result (experiment 8). Thus, with all other variables similar, higher formic acid concentration may slightly improve reduction. However, it should be noted that a high formic acid concentration, by itself, does not necessarily lead to substantial reduction; the pH of the fluid may also be an important factor.

##### *4.4.2 Effect of pH*

When formic acid was used as the reductant, the feedstock pH affected the adsorption of perchlorate to the catalyst surface. As shown earlier (Figures 4.1 and 4.8), when the feedstock pH was 4 or higher, the effluent perchlorate concentrations were quite high, indicating that very little perchlorate adsorbed to the catalyst surface. On the other hand, when the feedstock pH was lower than 4, the effluent concentrations were quite small

compared to the influent concentration (representative examples shown in Figures 4.2, 4.3, and 4.5), suggesting significant adsorption of perchlorate.

Interestingly, different behavior was observed in the experiment where hydrogen was used as the reductant. In experiment 13, the feedstock pH was 4.21, yet the effluent concentrations were barely detectable (Figure 4.9).

Formic acid chemistry may yield an important clue on the effect of pH on perchlorate adsorption. When dissolved in water, formic acid (HCOOH) exists in equilibrium with its conjugate base, the formate ion (HCOO<sup>-</sup>). The dissociation reaction for formic acid is shown in Equation 4.3:



As with other acids, the equilibrium constant (acidity constant, or  $K_a$ ) for the reaction in Equation 4.3 can be calculated by dividing the concentration of the products by the concentration of the reactants (Equation 4.4):

$$\text{Eq.4.4} \quad K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

At a given temperature,  $K_a$  is constant. Therefore, the speciation between formic acid and the formate ion is strictly a function of pH (pH is defined as the negative log of the

hydrogen ion concentration, or  $-\log[\text{H}^+]$ ). Algebraic rearrangement of Eq 4.4 yields the following relationship (Equation 4.5):

$$\text{Eq. 4.5} \quad \frac{[\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{[\text{H}^+]}{K_a}$$

At 25 °C, the  $K_a$  for formic acid is approximately  $1.8 \times 10^{-4}$  (or  $\text{p}K_a = 3.75$ ). By varying the pH, we can easily calculate the ratio of formic acid to formate ion under different conditions. This ration can be used to calculate the percentages of each species in the solution. Table 4.4 shows the speciation between pH 3 and pH 5:

pH	HCOOH	HCOO <sup>-</sup>
3.0	84.7%	15.3%
3.1	81.5%	18.5%
3.2	77.8%	22.2%
3.3	73.6%	26.4%
3.4	68.9%	31.1%
3.5	63.7%	36.3%
3.6	58.3%	41.7%
3.7	52.6%	47.4%
3.8	46.8%	53.2%
3.9	41.2%	58.8%
4.0	35.7%	64.3%
4.1	30.6%	69.4%
4.2	26.0%	74.0%
4.3	21.8%	78.2%
4.4	18.1%	81.9%
4.5	14.9%	85.1%
4.6	12.2%	87.8%
4.7	10.0%	90.0%
4.8	8.1%	91.9%
4.9	6.5%	93.5%
5.0	5.3%	94.7%

**Table 4.4 Formic Acid Speciation from pH 3 to pH 5**

The speciation results in Table 4.4 follow a distinct pattern. At pH 3, formic acid is clearly the dominant species; the formic acid concentration is much higher than the formate concentration. As pH rises, formic acid dissociates and the formate ion concentration increases. At a pH of about 3.75, the formic acid and formate concentrations are approximately equal. Above pH 3.75, formate becomes the dominant species, and the concentration of formic acid rapidly diminishes.

It appears that the presence of the formate ion plays a key role in the adsorption/desorption behavior of perchlorate to/from the catalyst surface. In formic acid experiments where the feedstock pH was low (below 4), little formate was present and significant perchlorate adsorption was observed. On the other hand, when the pH was 4 or above, formate was the dominant species, and less adsorption occurred. The formate ion may interfere with perchlorate adsorption (perhaps through electrostatic repulsion of the negatively charged perchlorate ions), and it certainly helps dislodge perchlorate ions that have already adsorbed to the catalyst surface (most likely via competitive adsorption), as evidenced by the rapid removal observed while flushing the column with high-pH formic acid solution. This theory seems consistent with the results from the hydrogen experiment; although the hydrogen feedstock had a relatively high pH, there were no formate ions in the solution, and therefore the perchlorate ions remained adsorbed to the catalyst surface.

In terms of perchlorate reduction, it appears that a low pH (below 3.75) is required. Simply put, low pH maximizes the concentration of the HCOOH molecule (greater adsorption potential) and therefore maximizes the potential for perchlorate reduction.

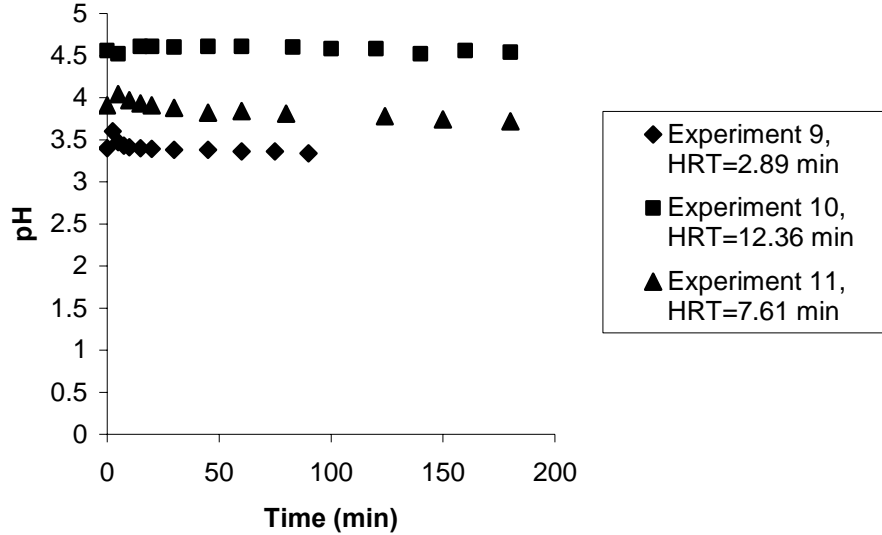
#### *4.4.3 Effect of HRT*

Experiments 9, 10, and 11 were carried out at HRT values of 2.89 min, 12.36 min, and 7.61 min, respectively. In all three experiments, the formic acid concentration was 10mM and the feedstock pH was approximately 3. As shown in Table 4.1, the MRP for experiment 9 was 92.32%. The individual MRP values for experiments 10 and 11 were not considered accurate (due to inadequate flushing after experiment 10), but the combined MRP for these two experiments was found to be 96.21% (Table 4.3). Since the lowest MRP occurred when the HRT was short, it appears that the flowrate of the bulk fluid influences perchlorate reduction.

These results seem counterintuitive. At the low (feedstock) pH values studied in experiments 9 through 11, perchlorate rapidly adsorbs to the catalyst surface. Because of this, the perchlorate remains in the reactor for a long time, regardless of the bulk fluid flowrate. One would expect that a longer HRT would increase the opportunity for formic acid to interact with the adsorbed perchlorate, yielding improved reduction. However, the MRP results described in the last paragraph imply that the opposite is true; as the HRT increases, perchlorate reduction decreases. The reason for this is not entirely clear,



although the pH of the bulk fluid appears to play a role (see effluent pH for the three experiments in Figure 4.10):



**Figure 4.10 Effluent pH in Experiments 9, 10, and 11**

**Experiment 9:** Feedstock pH = 3.08, [HCOOH] = 10 mM,  
**Experiment 10:** Feedstock pH = 3.00, [HCOOH] = 10 mM,  
**Experiment 11:** Feedstock pH = 2.98, [HCOOH] = 10mM

Figure 4.10 shows that effluent pH was relatively stable in each experiment. The effluent pH was higher than the influent (feedstock) value, and the degree of pH elevation appears to be proportional to the HRT. As the HRT increased, the effluent pH increased. Note that the effluent pH associated with a HRT of 2.89 minutes was less than 3.75, while the longer HRTs yielded effluent pH values above 3.75 (presumably due to greater loss of carbonic acid ( $H_2CO_3$ ) driven by volatilization of  $CO_2$  at larger HRT). As discussed in the previous section, the pH of the bulk fluid influences the speciation of formic acid.

Table 4.5 illustrates the speciation for experiments 9, 10, and 11:

Exp #	HRT	Effluent pH (average)	[HCOOH]/[COOH] Ratio
9	2.89	3.41	~ 2.21
10	12.36	4.58	~ 0.14
11	7.61	3.86	~ 0.7

**Table 4.5 Formic Acid Speciation for Experiments 9, 10, and 11**

If the protonated form of formic acid (HCOOH) is responsible for perchlorate reduction, the data in Table 4.5 may explain why slightly more perchlorate reduction was observed in experiment 9 (recall that the MRP for experiment 9 was 92.32% (Table 4.1), while the combined MRP for experiments 10 and 11 (Table 4.3) was 96.21%). While the feedstock formic acid concentration was 10 mM in all three experiments, the long HRT used in experiments 10 and 11 yielded substantial increases in the pH of the bulk fluid (presumably due to catalytic destruction of formic acid into H<sub>2</sub> and CO<sub>2</sub>). In response to the pH increase, the remaining formic acid dissociated and the formate ion became the dominant species. In a sense, the catalyst may have been “starved” for the protonated HCOOH species due to the increase in the ambient pH, leading to a decrease in perchlorate reduction. On the other hand, in experiment 9, the pH of the bulk fluid did not exceed 3.75 (presumably due to a short contact time of formic acid with the Pd catalyst), so HCOOH remained the dominant species. The resulting (relative) abundance of HCOOH may have favored perchlorate reduction despite a shorter contact time period of perchlorate with the catalyst surface.

In summary, HRT appears to be a significant factor in perchlorate reduction. Longer HRT leads to a pH increase in the bulk fluid due to loss of acidity via CO<sub>2</sub> volatilization. This pH increase drives the formic acid speciation toward the formate ion, reducing the availability of the HCOOH and therefore decreasing perchlorate reduction.

#### *4.4.4 Effects of Control Variables – Summary*

Experimental results indicate that perchlorate reduction increases when a high concentration of formic acid is present. However, it appears that the formic acid must remain in the protonated form to favor perchlorate adsorption and reduction. Ideally, the reactor pH should be maintained well below 3.75 in order to enhance perchlorate adsorption and its subsequent catalytic degradation by formic acid. However, in order to minimize the pH increase caused by the breakdown of formic acid, the HRT should not exceed 3 minutes.

#### ***4.5 Hypothesis on Low Perchlorate Removal***

Very little perchlorate reduction was observed in this study. The best reduction was observed in experiment 9, where the MRP was 92%.

The reason for the poor performance is not clear. At low pH (3 – 3.3), adsorption of perchlorate to the catalyst surface is clearly not a problem. Given the available data, the most logical explanation is that the conditions at the catalyst surface were not suitable for transfer of electrons to the perchlorate ion.

In the perchlorate ion, the central chlorine atom has an oxidation number of +7.

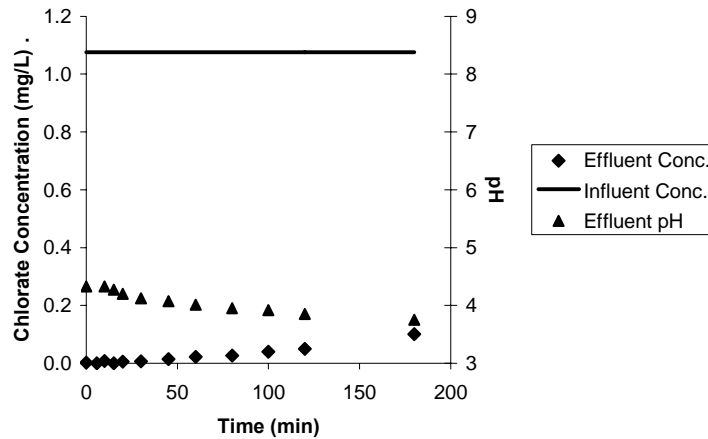
Reduction of perchlorate yields the chlorate ion ( $\text{ClO}_3^-$ ). In chlorate, the chlorine atom has an oxidation number of +5. Thus, for reduction to occur, two electrons must be transferred to the perchlorate ion.

As discussed in chapter 2, perchlorate does not readily favor electrons from reducing agents, possibly because the tetrahedral arrangement of oxygen atoms shields the highly oxidized chlorine atom. Use of a palladium catalyst was hoped to facilitate the reduction of the central chlorine atom. Decomposition of the formic acid into  $\text{H}_2$  (and  $\text{CO}_2$ ) at the Pd surface creates a strongly reducing environment. However, when perchlorate adsorbs to the catalyst surface, the tetrahedral arrangement of oxygen atoms may not favor electron transfer to the central chlorine atom.

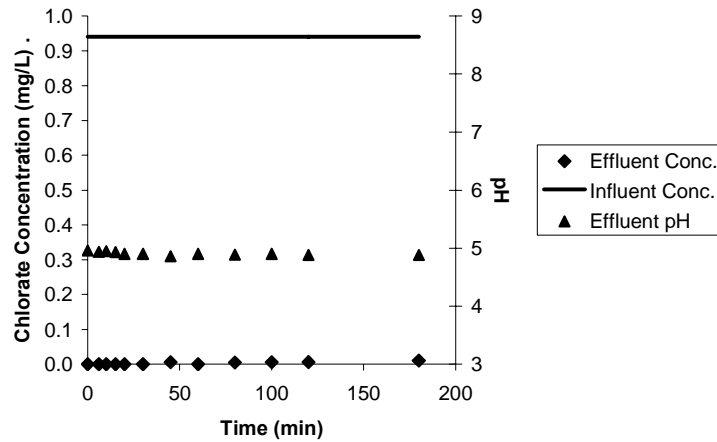
The available data seem to support the above hypothesis. Recall that more reduction was observed when the formic acid concentration was 10mM than when it was 2mM (with no differences between the other control variables). The 5-fold increase in the reductant (formic acid) concentration favors increased reduction. However, given the fact that the observed reduction with 10mM formic acid was still very small, it is likely that the perchlorate ion remains inherently resistant to reduction, even when adsorbed to the catalyst.

#### 4.6 Supplemental Experiments - Chlorate Reduction

Two experiments were performed using chlorate as the substrate instead of perchlorate. The purpose of these experiments was, essentially, to examine the role of the shape of perchlorate and chlorate species on their catalytic reduction. Since chlorate has one less oxygen, the shielding effect due to the negative charge of the oxygen atoms may be less than perchlorate. Further, the oxygen atoms in the chlorate molecule are arranged in a planar configuration (as opposed to the tetrahedral array found in the perchlorate ion), which may make it easier for the reductant to attack the central chlorine atom. For these reasons, chlorate may be more susceptible to reduction than perchlorate. Effluent pH and chlorate concentration results from the two chlorate experiments are shown in Figures 4.11 and 4.12:

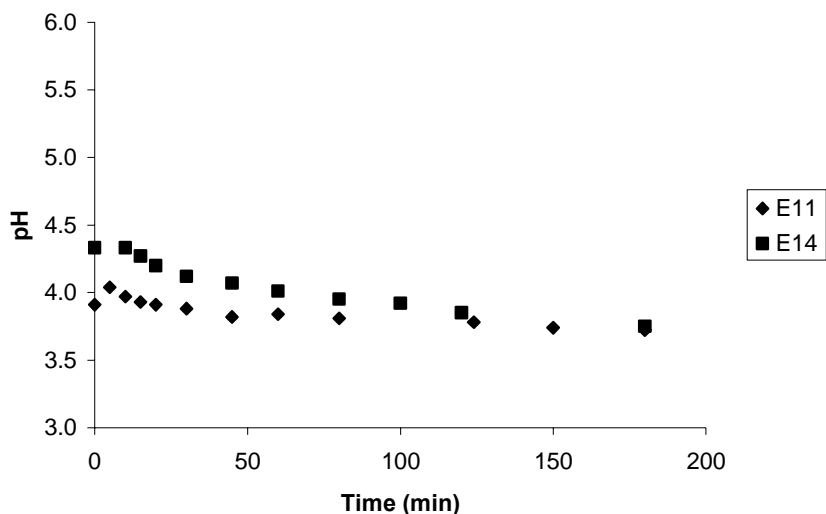


**Figure 4.11 Effluent pH and Chlorate Concentrations in Experiment 14 Main Run; Feedstock pH = 2.96, [HCOOH] = 10mM, HRT = 7.98 min**



**Figure 4.12 Effluent pH and Chlorate Concentrations in Experiment 15 Main Run; Feedstock pH = 3.47, [HCOOH] = 1mM, HRT = 7.68 min**

As shown in Figure 4.11, the effluent chlorate concentration in experiment 14 slowly increased throughout the experiment, although it remained well below the influent concentration. This is consistent with observations from perchlorate experiments performed under similar conditions. Interestingly, the effluent pH in experiment 14 clearly *decreased* throughout the experiment. This behavior is not consistent with the perchlorate experiments, where the effluent pH either remained relatively stable or increased as the experiment progressed. Most likely, the decreasing pH was the result of incomplete catalyst stabilization during the pre-experiment flush for experiment 14. Comparing the pH results for experiment 14 with a similar perchlorate experiment (experiment 11) shows that the effluent pH eventually approached the same value (Figure 4.13):



**Figure 4.13 Comparison of Effluent pH in Experiments 11 and 14; Experiment 11 (Perchlorate): Influent pH = 2.98, [HCOOH] = 10mM, HRT = 7.61 min; Experiment 14 (Chlorate): Influent pH = 2.96, [HCOOH] = 10mM, HRT = 7.98 min**

Since the effluent pH in experiments 11 and 14 eventually approached a value of approximately 3.7, it appears that the decreasing effluent pH in experiment 14 was the result of an unusually high pH in the reactor at the beginning of the experiment, which was probably the result of an insufficient pre-experiment flush.

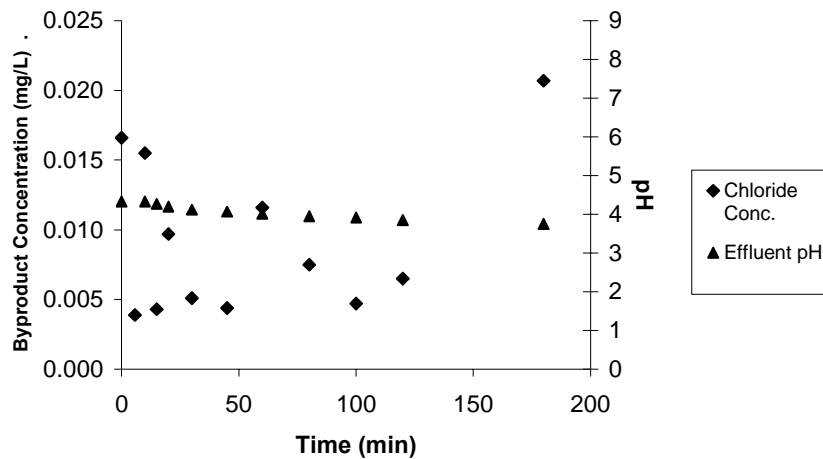
In experiment 15 (Figure 4.12), the effluent pH remained stable throughout the experiment. Also, effluent concentrations were very low throughout the experiment (this was the result of adsorption, as discussed in the next section).

As with perchlorate experiments, MRP calculations were performed on the data from experiments 14 and 15 in order to estimate chlorate reduction. Results are summarized in Table 4.6:

Exp #	Chlorate Concentration (mg/L)	Feed pH	[HCOOH] (mM)	HRT (min)	MRP	Byproducts Detected?
14	1.0758	2.96	10	7.98	85.35%	Yes (chloride only)
15	0.9400	3.47	1	7.68	102.48%	No

**Table 4.6 Chlorate Experiment Results (Summary)**

In experiment 14, a 10mM formic acid concentration yielded about 15% reduction. Small amounts of chloride were measured in the effluent, confirming that some reduction had occurred (Figure 4.14):



**Figure 4.14 Experiment 14 Effluent pH and Byproduct Concentration Results**

Chloride was the only byproduct detected. As shown in Figure 4.14, the concentrations were fairly low and quite erratic. Unfortunately, the presence of byproducts in the post-experiment flush samples could not be evaluated. The high pH of the post-experiment flush solution resulted in a high concentration of formate ions in the effluent. During the



ion chromatography analysis, the formate ions yielded a massive peak which overwhelmed any potential chlorite or chloride peaks. Thus, it is not possible to confirm (via mass balance) that all of the “missing” chlorate mass was transformed into chloride.

In contrast to the experiment 14 results, essentially all of the mass in experiment 15 was accounted for. Also, no byproducts were detected in the experiment 15 samples, confirming that no reduction occurred. The extremely low effluent concentrations in experiment 15 were the result of chlorate adsorption, not reduction.

Assuming the MRP values for experiments 14 and 15 are reasonably accurate, we have some reduction at high (10mM) formic acid concentration and feed pH = 2.96, and essentially no reduction at 1mM formic acid and feed pH = 3.47. This is consistent with the observations in the perchlorate reduction experiments. However, the overall amount of chlorate reduction in the 10mM experiment was greater than for perchlorate at the same formic acid concentration. One reason for this behavior may be that chlorate is indeed more susceptible to catalytic reduction than perchlorate. Even though much of the formic acid fed to the system in experiment 14 was transformed to formate ion (average effluent pH = 4.07, formate was dominant species), approximately 15% of the influent chlorate was reduced at the catalyst surface. This indicates that chlorate reduction can be achieved under less severe reducing conditions than with the perchlorate ion. Also, the influent substrate concentration may be another factor in the higher reduction observed with chlorate. Note that the influent chlorate concentration in experiment 14 was 1.08

mg/L, while the perchlorate experiments were run at 0.5 mg/L. With the higher influent concentration, more chlorate ions adsorbed to the catalyst, and this may have increased the probability of electron transfer to a chlorate species.

## 5.0 Conclusions

### *5.1 Summary*

The potential for palladium-catalyzed reduction of perchlorate was investigated in a flow-through column reactor. Formic acid was used as the primary reductant. Experiments were performed using different combinations of influent pH, hydraulic residence time (HRT), and reductant concentration.

In initial experiments, efforts to characterize reduction were hampered by slow desorption of perchlorate from the catalyst, which resulted in an overestimation of the amount of perchlorate destroyed. Once the adsorption problem was recognized, the experimental procedure was modified to estimate perchlorate reduction using a mass-balance approach that compared the mass of perchlorate that entered and exited the reactor. The Mass Recovery Percentage (MRP) served as an indicator for the amount of perchlorate mass destroyed in the reactor. A MRP of 100% indicated all influent perchlorate was accounted for in the reactor effluent (in other words, no reduction occurred). MRP values less than 100% indicated that some influent mass was destroyed within the reactor. The MRP values for each experiment were compared in order to establish the effects of control variables (pH, HRT, reductant concentration) on reactor performance.

## 5.2 Conclusions

In this section, conclusions for each of the three research objectives outlined in section 1.2 will be presented.

- 1) Determine how the rate and extent of perchlorate reduction is impacted by experimental conditions (*e.g.* pH, use of molecular hydrogen or formic acid as a reductant)
  - **In all experiments, very little perchlorate reduction occurred.** The smallest MRP was observed in experiment 8 (92.32%), corresponding to a perchlorate reduction of just 7.68%. This small reduction is not sufficient for water treatment or environmental remediation applications.
  - **High formic acid concentrations are required for reduction.** Maximum reduction occurred at the highest formic acid concentration studied (10mM). In experiments with lower formic acid concentrations, perchlorate reduction was negligible.
  - **Influent pH indirectly affects reduction.** Maximum reduction occurred at low pH (~ 3), presumably because most of the formic acid remained in the protonated (HCOOH) form. Above pH 3.75, formic acid's conjugate base (formate ion, COO<sup>-</sup>) dominates, reducing the amount of "active" reductant in the system. Formate ion also appears to affect the adsorption of perchlorate to the catalyst; high formate concentrations led to rapid desorption of perchlorate from the catalyst surface.

- **Long HRT decreases reduction.** Best reduction occurred at the shortest HRT studied (~ 3 minutes). At this HRT, the pH of the bulk fluid remained below 3.75, minimizing the formation of formate ion. At longer HRT, the pH of the bulk fluid increased above 3.75 (presumably due to decomposition of formic acid at the catalyst surface), which decreased the concentration of protonated formic acid (HCOOH) species in the system.
- **Use of hydrogen as reductant did not improve performance.** Hydrogen was used as reductant in just one experiment (experiment 13). The MRP of experiment 13 was 92.07%, but this value does not take into account residual perchlorate mass that was in the reactor at the conclusion of column flushing. Given the high concentration of perchlorate in the last sample collected during the post-experiment flush (~ 0.25 mg/L), the calculated MRP is a low estimate, and much less reduction than is indicated by the MRP appears to have occurred.

2) Investigate the formation of undesirable daughter compounds (*e.g.* chlorite) as a potential result of reduction

- **Perchlorate reduction was too low to explore the formation of byproducts.** Since very little perchlorate mass degraded in the system (< 8%), the reduction byproducts could not be detected or quantified.
- **Limited evidence suggests chloride is the main reduction byproduct.** In an experiment where chlorate was used as substrate instead of

perchlorate, approximately 15% reduction was observed. Small concentrations of chloride were detected in the effluent, but no chlorite was found in any of the samples. This indicates that when chlorate is reduced, the chlorite formed is rapidly reduced to chloride.

3) If the technology appears viable, develop a model of the reduction kinetics that can be used in technology design

- **Reduction was not sufficient for modeling purposes.** Since reduction was extremely small, kinetic parameters could not be ascertained.

### ***5.3 Future Research***

Based on the very small reduction efficiencies observed in the above experimental design, palladium-catalyzed reduction may not be a promising technology for remediation of perchlorate-contaminated water. However, the following four observations may warrant additional investigation:

- **Investigate the effect of formic acid speciation on chlorate reduction.**  
Two experiments were performed to evaluate chlorate reduction; however, both experiments were performed at the same influent pH and HRT. Since pH and HRT were very important variables in perchlorate reduction, it may be worthwhile to study their effect on chlorate reduction. The data obtained may reveal additional details on the chlorate and perchlorate

reduction mechanisms. Further, if formic acid speciation proves to be an important factor in chlorate reduction (as with perchlorate), this effect may need to be considered in the experimental design for future palladium catalysis studies (for other contaminants) where formic acid is used as the reductant.

- **Evaluate perchlorate reduction at higher formic acid concentrations.**

In this project, increased reduction was observed at the maximum formic acid concentration studied. Reduction of perchlorate may be limited by the distribution of free electrons at the catalyst surface, and it is possible that 10mM formic acid did not create a sufficient quantity of electrons. Increasing the formic acid concentration above 10mM may result in a higher density of free electrons at the catalyst surface, potentially increasing perchlorate reduction.

- **Evaluate perchlorate reduction at shorter HRT.** Maximum performance was observed at a HRT of 3 minutes due to the relatively small increase in reactor pH (longer HRT led to larger reactor pH increases, reducing the availability of the HCOOH species). However, even with a HRT of 3 minutes, the pH increased ~ 0.5 units as the fluid flowed through the reactor. This relatively small pH increase can have a large effect (20% or more) on the concentration of the HCOOH species. If the HRT is shorter than 3 minutes, the pH increase of the bulk fluid may

be reduced, maximizing the concentration of the HCOOH species and potentially improving reduction.

- **Study reactor performance at higher perchlorate concentrations.** In this project, the influent perchlorate concentration was relatively low (0.5 mg/L). If higher concentrations of perchlorate are fed to the reactor, more perchlorate may adsorb to the catalyst surface, potentially increasing the probability of a perchlorate ion interacting with nearby electrons. Thus, reduction efficiency may increase at higher perchlorate concentrations. If higher performance is observed at larger perchlorate concentrations, catalytic reduction may be an appropriate technology for specialized applications (*e.g.* treatment of concentrated perchlorate created during regeneration of ion exchange resin).



## **6.0 Appendices**

### 6.1 Appendix A: Experimental Result Data

<b>Experiment 1:</b>				
[HCOOH] = 2mM				
Source pH = 4.11 (amended w/ NaOH)				
Target Perchlorate Concentration: 10 mg/L				
Flowrate = 8.995 ml/min (average of 2 measurements - before/after)				
HRT = 6.42 min (based on flow and pore volume of 57.7 mL)				
<b>Influent Results:</b>				
Sample	Time	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E1-001	Before Exp	9.1434	4.11	210.7
E1-022	After Exp	9.1373	4.10	204.4
E1-023	After Exp	9.1727	4.10	204.4
<b>Effluent Results:</b>				
Sample	Time (min)	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E1-004	0	0.0000	6.70	181.7
E1-005	5	0.8219	7.41	156.3
E1-006	10	4.0100	7.50	153.9
E1-007	15	6.0378	7.47	151.4
E1-008	20	7.1272	7.43	150.2
E1-009	30	8.1904	7.40	150.3
E1-010	35	8.4689	7.41	150.5
E1-011	41.5	8.7311	7.41	150.3
E1-012	50	8.9251	7.39	150.0
E1-013	60	9.0734	7.37	150.4
E1-014	75	9.1515	7.39	150.5
E1-015	90	9.1532	7.34	151.9
E1-016	105	9.1238	7.32	152.7
E1-017	120	9.0871	7.30	153.1
E1-018	135	9.0467	7.29	153.8
E1-019	150	9.0424		155.2
E1-020	165	9.0397		157.8
E1-021	180	9.0125	7.27	155.8

**Table 6.1 Experiment 1 Results**

### E1 - Effluent pH and Conductivity

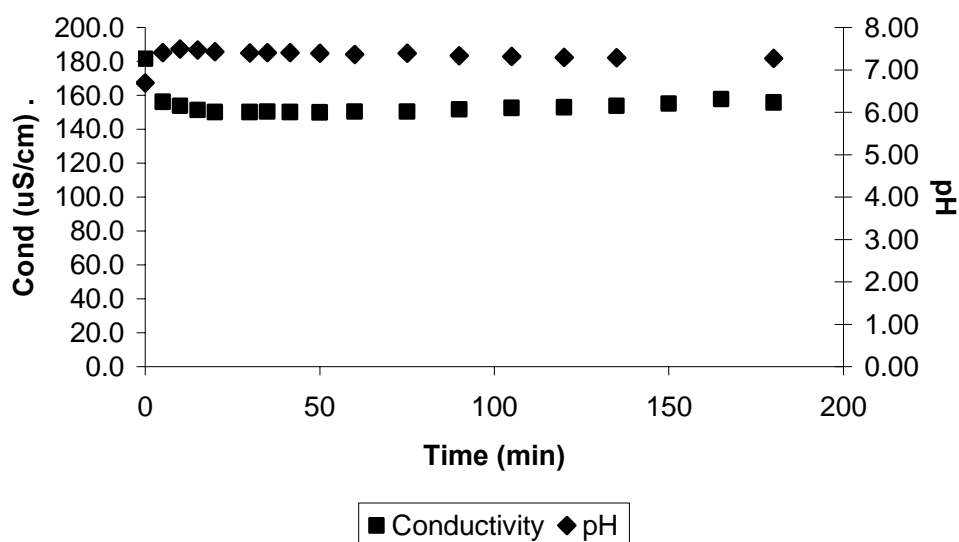


Figure 6.1 Experiment 1 pH and Conductivity Data;  
 Influent pH = 4.11, Influent Conductivity = 210.7  $\mu$ S/cm

### E1 - Concentrations

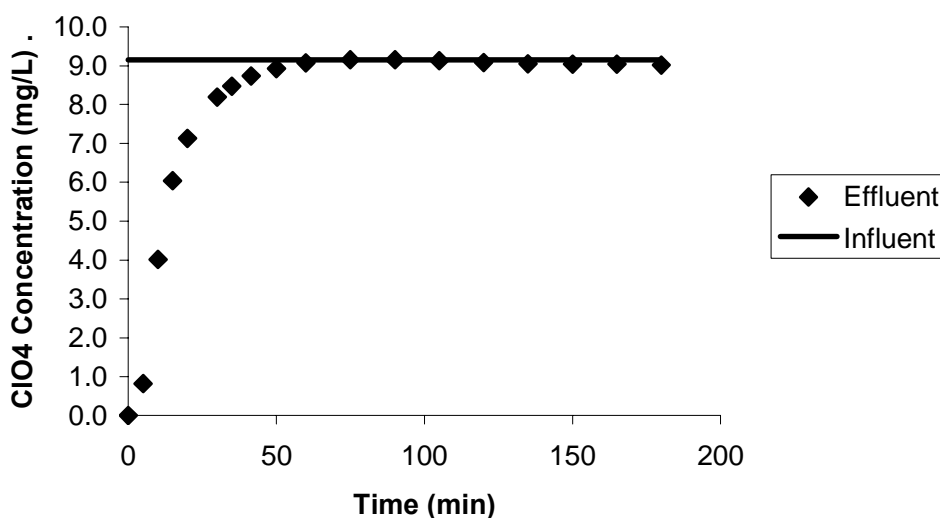


Figure 6.2 Experiment 1 Perchlorate Concentration Data;  
 [HCOOH] = 2mM, pH = 4.11, HRT = 6.42 min

<b>Experiment 2:</b>				
[HCOOH] = 2mM				
Source pH = 4.01 (amended w/NaOH)				
Target Perchlorate Concentration: 5 mg/L				
Flowrate = 19.9 ml/min (average of 2 measurements - before/after)				
HRT = 2.90 min (based on flow and pore volume of 57.7 mL)				
<b>Influent Results:</b>				
Sample	Time	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E2-001	Before Exp	5.5162	4.01	200.2
E2-002	Before Exp	5.5387	4.01	200.2
E2-021	After Exp	5.6750	---	---
E2-022	After Exp	5.6598	---	---
<b>Effluent Results:</b>				
Sample	Time (min)	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E2-003	0	0.0000	6.46	137.4
E2-004	5	1.8304	6.58	138.1
E2-005	7.5	2.7121	6.56	139.4
E2-006	10	3.3154	6.53	140.0
E2-007	15	4.1488	6.50	140.5
E2-008	20	4.6258	6.48	140.2
E2-009	30	5.0994	6.46	140.1
E2-010	40	5.2814	6.44	139.8
E2-011	50	5.3854	6.42	139.2
E2-012	60	5.4326	6.40	139.4
E2-013	75	5.4768	6.39	138.9
E2-014	90	5.4869	6.38	138.0
E2-015	105	5.5008	6.36	137.5
E2-016	120	5.5160	6.34	137.8
E2-017	135	5.5260	6.34	136.6
E2-018	150	5.5132	6.33	136.0
E2-019	165	5.5273	6.33	135.0
E2-020	180	5.5429	6.34	137.5

**Table 6.2 Experiment 2 Results**

### E2 - Effluent pH and Conductivity

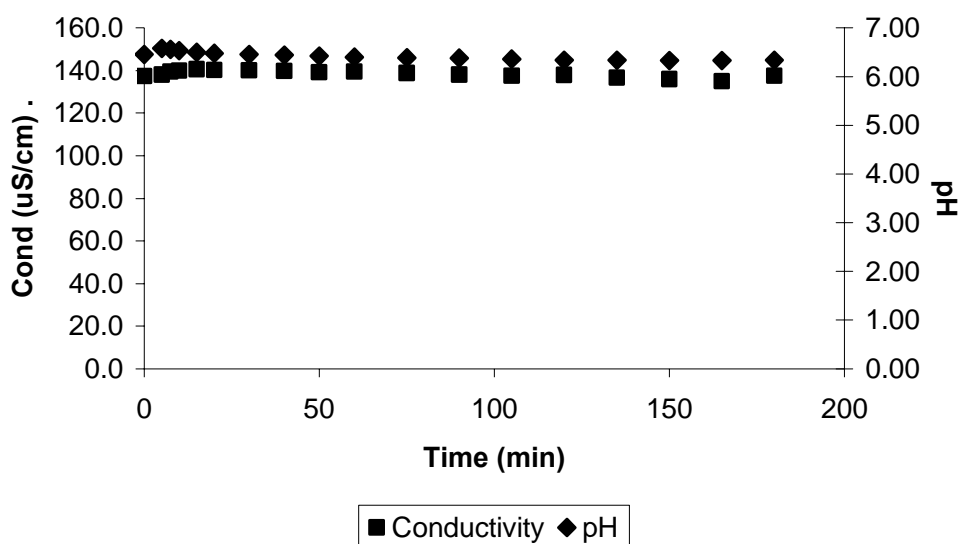


Figure 6.3 Experiment 2 pH and Conductivity Data;  
Influent pH = 4.01, Influent conductivity = 200.2  $\mu\text{S}/\text{cm}$

### E2 - Concentrations

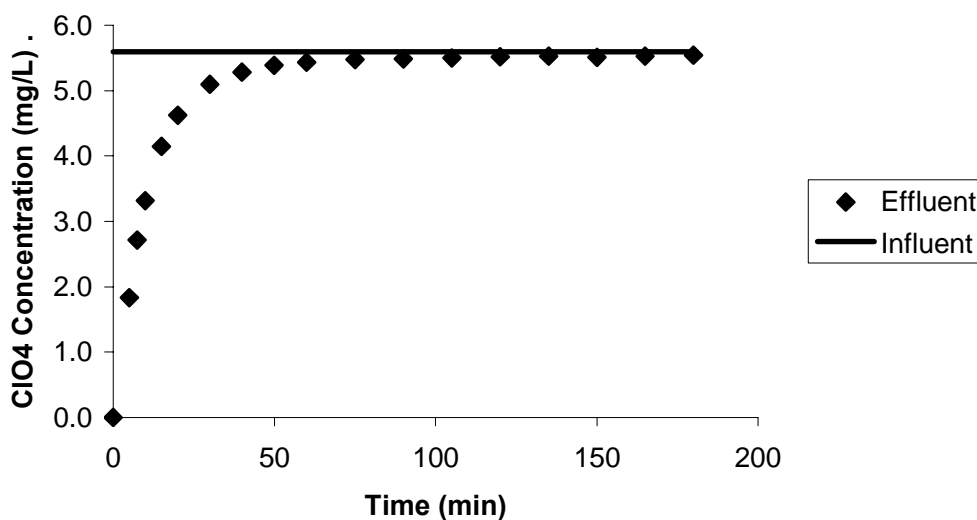


Figure 6.4 Experiment 2 Perchlorate Concentration Data;  
[HCOOH] = 2mM, pH = 4.01, HRT = 2.90 min

<b>Experiment 3:</b>				
[HCOOH] = 2mM				
Source pH = 3.24 (no NaOH added)				
Target Perchlorate Concentration: 0.5 mg/L				
Flow = 4.81 ml/min (average of 2 measurements - before/after)				
HRT = 12.00 min (based on flow and pore volume of 57.7 mL)				
<b>Influent Results:</b>				
Sample	Time	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E3-001	Before Exp	0.5213	3.24	270.7
E3-002	Before Exp	0.5195	3.24	270.7
E3-022	After Exp	0.5279	3.27	255.8
E3-023	After Exp	0.5262	3.27	255.8
<b>Effluent Results:</b>				
Sample	Time (min)	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E3-003	0	0.1170	5.42	14.26
E3-004	10	0.0936		
E3-005	20	0.0775	5.52	13.78
E3-006	30	0.0725	5.43	13.69
E3-007	40	0.0702	5.39	13.38
E3-008	50	0.0682	5.29	13.53
E3-009	60	0.0738	5.27	13.57
E3-010	75	0.0647	5.22	13.61
E3-011	90	0.0657	5.17	13.88
E3-012	105	0.0588	5.11	13.73
E3-013	120	0.0570	5.11	13.75
E3-014	135	0.0551	5.05	13.86
E3-015	152	0.0529	5.03	13.99
E3-016	165	0.0535	5.02	14.17
E3-017	180	0.0508	5.00	14.20
E3-018	225	0.0496	4.86	14.60
E3-019	240	0.0498	4.90	14.95
E3-020	255	0.0502	4.84	14.94
E3-021	270	0.0486	4.92	14.93

**Table 6.3 Experiment 3 Results**

### E3 - Effluent pH and Conductivity

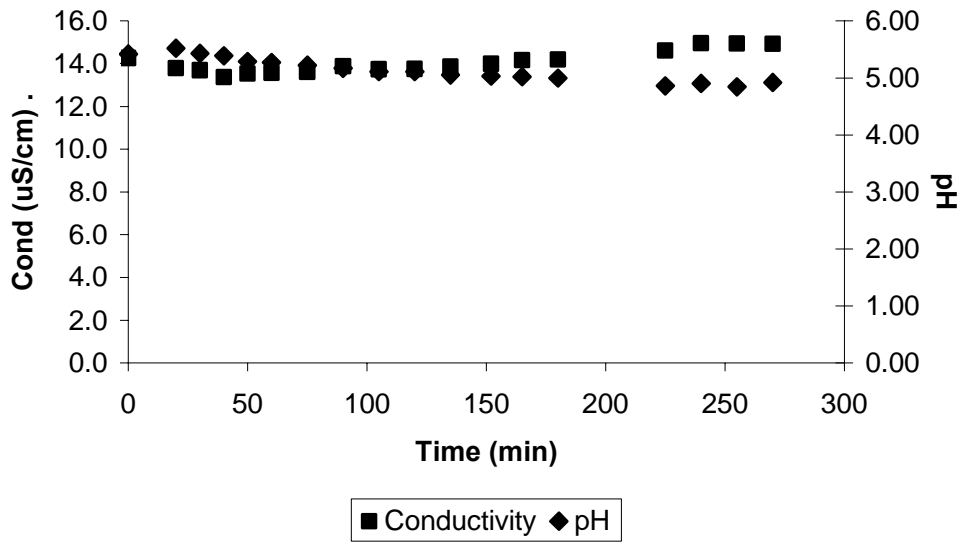


Figure 6.5 Experiment 3 pH and Conductivity Data;  
Influent pH = 3.24, Influent Conductivity = 270.7  $\mu\text{S}/\text{cm}$

### E3 - Concentrations

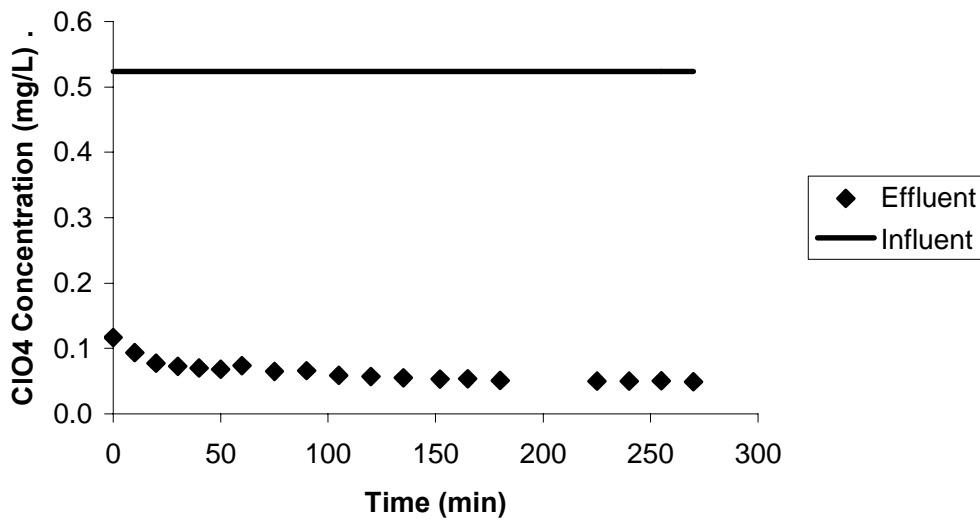


Figure 6.6 Experiment 3 Perchlorate Concentration Data;  
[HCOOH] = 2mM, pH = 3.24, HRT = 12.00 min

<b>Experiment 5:</b>				
[HCOOH] = 2mM				
Source pH = 3.27 (no NaOH added)				
Target Perchlorate Concentration: 0.5 mg/L				
Flow = 20.34 ml/min (average of 2 measurements - before/after)				
HRT = 2.84 min (based on flow and pore volume of 57.7 mL)				
<b>Influent Results:</b>				
Sample	Time	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E5-001	Before Exp	0.5265	3.27	232.7
E5-002	Before Exp	0.5271	3.27	232.7
E5-022	After Exp	0.5302	3.29	220.1
E5-023	After Exp	0.5277	3.29	220.1
<b>Effluent Results:</b>				
Sample	Time (min)	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E5-003	0	0.0231	4.42	20.76
E5-004	2.5	0.0276	4.56	21.17
E5-005	5	0.0291	4.38	20.12
E5-006	7.5	0.0300	4.36	23.50
E5-007	10	0.0313	4.37	24.97
E5-008	15	0.0342	4.33	25.57
E5-009	20	0.0375	4.30	26.93
E5-010	30	0.0428	4.27	28.75
E5-011	40	0.0482	4.23	30.07
E5-012	50	0.0509	4.21	31.10
E5-013	60	0.0601	4.18	33.85
E5-014	75	0.0603	4.19	33.75
E5-015	90	0.0710	4.15	34.83
E5-016	105	0.0775	4.14	34.92
E5-017	120	0.0893	4.12	36.45
E5-018	135	0.0985	4.07	40.33
E5-019	150	0.1018	4.12	36.55
E5-020	165	0.1099	4.10	38.23
E5-021	180	0.1094	4.12	36.30

**Table 6.4 Experiment 5 Results**



### E5 - Effluent pH and Conductivity

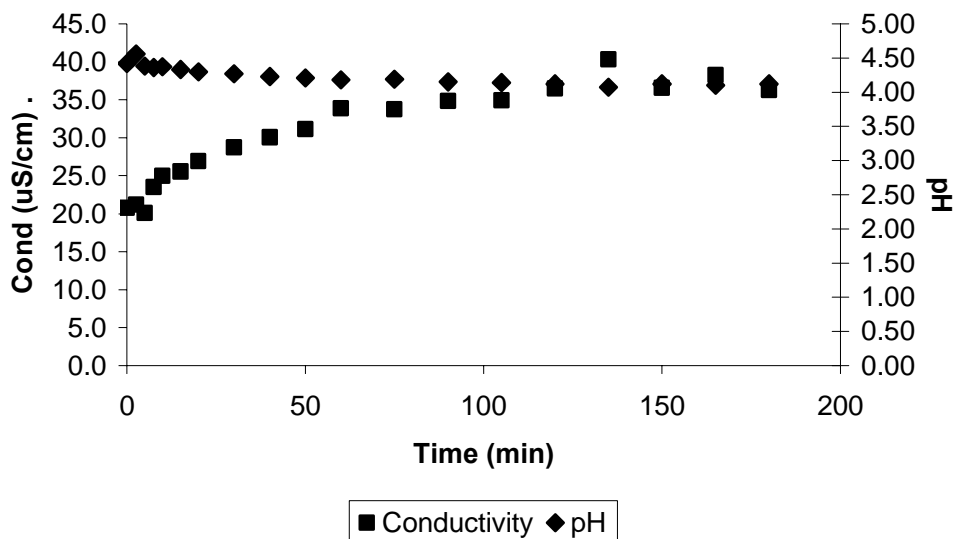


Figure 6.7 Experiment 5 pH and Conductivity Data;  
Influent pH = 3.27, Influent Conductivity = 232.7  $\mu$ S/cm

### E5 - Concentrations

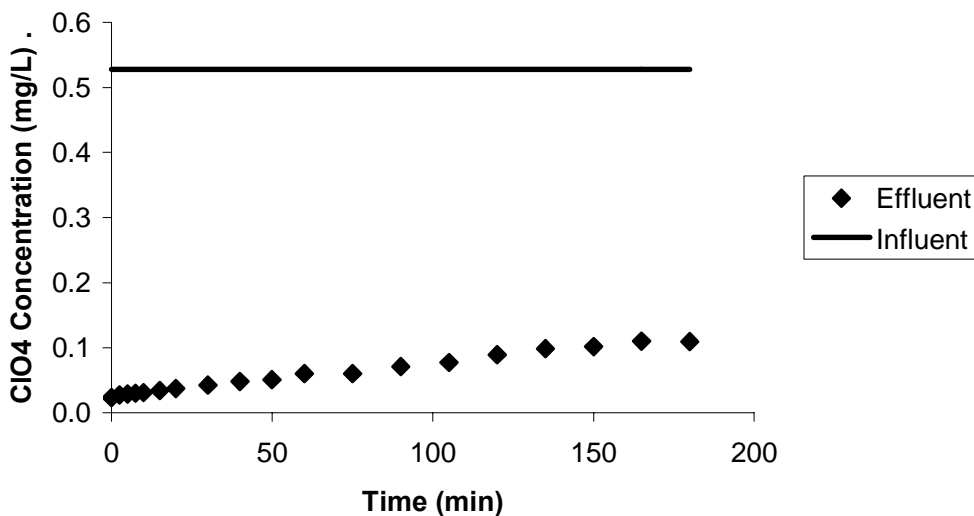


Figure 6.8 Experiment 5 Perchlorate Concentration Data;  
[HCOOH] = 2mM, pH = 3.27, HRT = 2.84 min

<b>Experiment 5 Byproduct Analysis Results</b>				
(Main Experiment Only)				
<b>Sample</b>	<b>Time (min)</b>	<b>Chlorate Conc (mg/L)</b>	<b>Chlorite Conc (mg/L)</b>	<b>Chloride Conc (mg/L)</b>
E5-003	0	0.000	0.000	0.004
E5-004	2.5	0.000	0.000	0.003
E5-006	7.5	0.000	0.000	0.003
E5-019	150	0.000	0.000	0.002
E5-020	165	0.000	0.000	0.006
E5-021	180	0.000	0.000	0.003

**Table 6.5 Experiment 5 Byproduct Analysis Results**

<b>Experiment 6:</b>				
[HCOOH] = 1mM				
Source pH = 3.47 (no NaOH added)				
Target Perchlorate Concentration = 0.5 mg/L				
Flow = 19.93 ml/min (average of 2 measurements - before/after)				
HRT = 2.90 min (based on flow and pore volume of 57.7 mL)				
<b>Influent Results (Main Experiment):</b>				
Sample	Time	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E6-001	Before Exp	0.5193	3.47	158.7
E6-002	Before Exp	0.5197	3.47	158.7
E6-022	After Exp	0.5266	3.5	149.1
E6-023	After Exp	0.5257	3.5	149.1
<b>Effluent Results (Main Experiment):</b>				
Sample	Time (min)	Perchlorate Concentration (mg/L)	pH	Conductivity (uS/cm)
E6-003	0	0.0667	4.46	19.12
E6-004	2.5	0.0780	4.55	16.3
E6-005	5	0.0911	4.49	18.79
E6-006	7.5	0.0852	4.46	19.76
E6-007	10	0.0849	4.45	19.47
E6-008	15	0.0866	4.46	19.48
E6-009	20	0.0906	4.45	19.79
E6-010	30	0.0912	4.45	19.85
E6-011	40	0.0935	4.45	19.75
E6-012	50	0.0997	4.45	19.81
E6-013	60	0.0996	4.46	19.36
E6-014	75	0.1001	4.49	18.58
E6-015	90	0.1026	4.44	19.57
E6-016	105	0.1100	4.47	19.14
E6-017	120	0.1159	4.47	18.66
E6-018	135	0.1222	4.49	18.42
E6-019	150	0.1202	4.48	18.45
E6-020	165	0.1276	4.47	18.76
E6-021	180	0.1295	4.48	18.45

**Table 6.6 Experiment 6 Results (Main Run)**

### E6 - Effluent pH and Conductivity (Main Run)

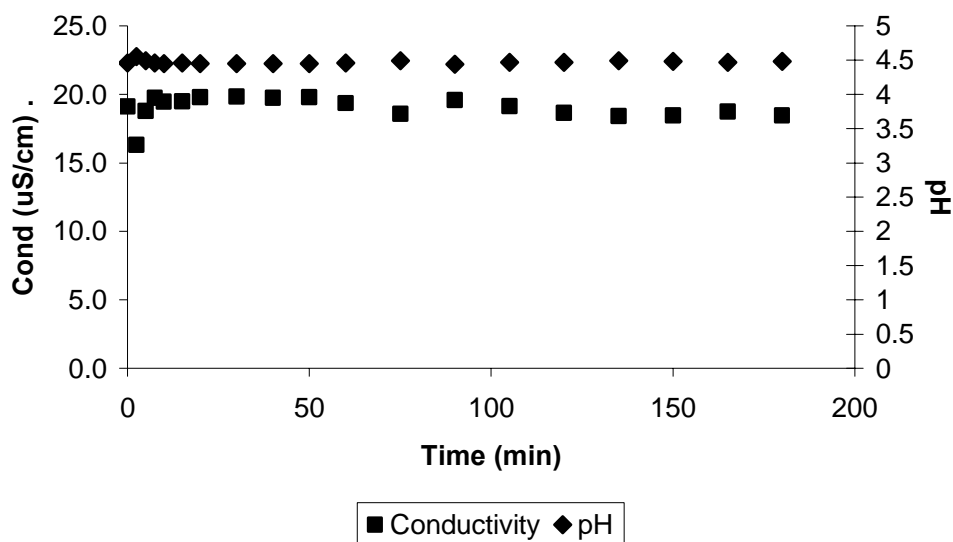


Figure 6.9 Experiment 6 pH and Conductivity Data;  
Influent pH = 3.47, Influent Conductivity = 158.7  $\mu\text{S}/\text{cm}$

### E6 - Concentrations - Main Run

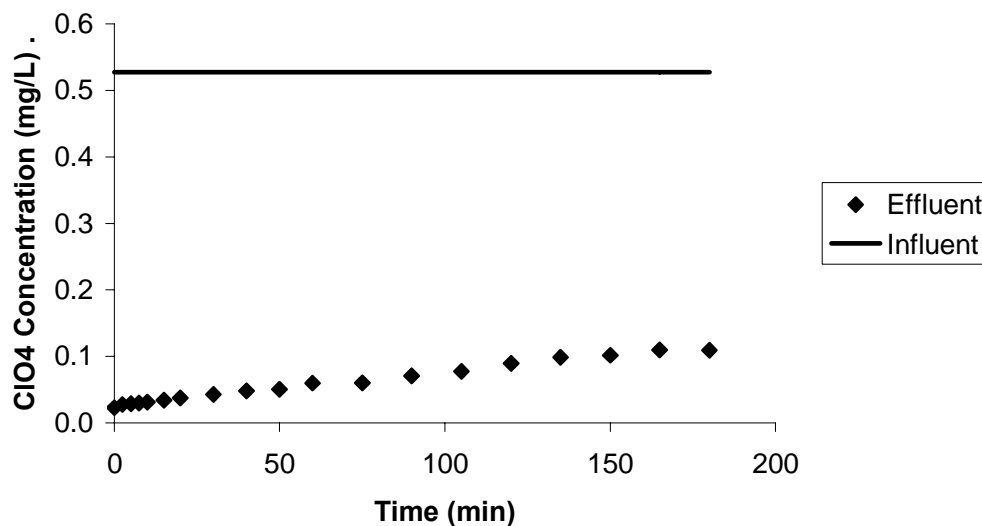


Figure 6.10 Experiment 6 Perchlorate Concentration Data (Main Run);  
[HCOOH] = 1mM, pH = 3.47, HRT = 2.90 min

<b>Experiment 6 Preflush Results:</b>				
<b>Sample</b>	<b>Time (min)</b>	<b>Perchlorate Concentration (mg/L)</b>	<b>pH</b>	<b>Conductivity (uS/cm)</b>
E6-PRE-1	0	0.5623	--	--
E6-PRE-2	30	0.0806	--	--
E6-PRE-3	45	0.0703	--	--
E6-PRE-4	60	0.0673	--	--
E6-PRE-5	75	0.0643	--	--
<b>Experiment 6 Postflush Results</b>				
<b>Sample</b>	<b>Time (min)</b>	<b>Perchlorate Concentration (mg/L)</b>	<b>pH</b>	<b>Conductivity (uS/cm)</b>
E6-PT-1	10	0.1102	--	--
E6-PT-2	20	0.1076	--	--
E6-PT-3	30	0.1094	--	--

**Table 6.7 Experiment 6 Results (Pre-Experiment Flush and Post-Experiment Flush)**

### E6 - Concentrations - Preflush

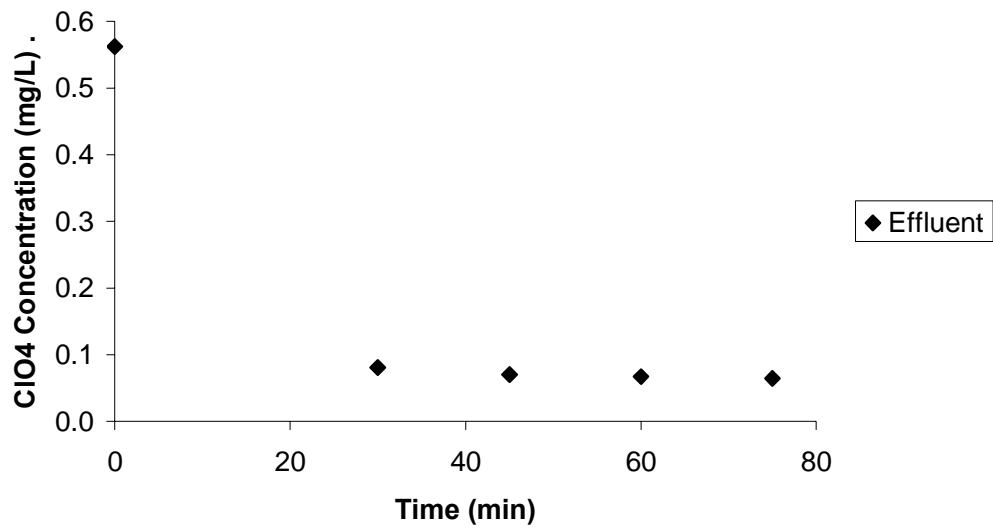


Figure 6.11 Experiment 6 Perchlorate Concentration Data (Pre-Experiment Flush);  
[HCOOH] = 1mM, HRT = 2.90 min

### E6 - Concentrations - Postflush

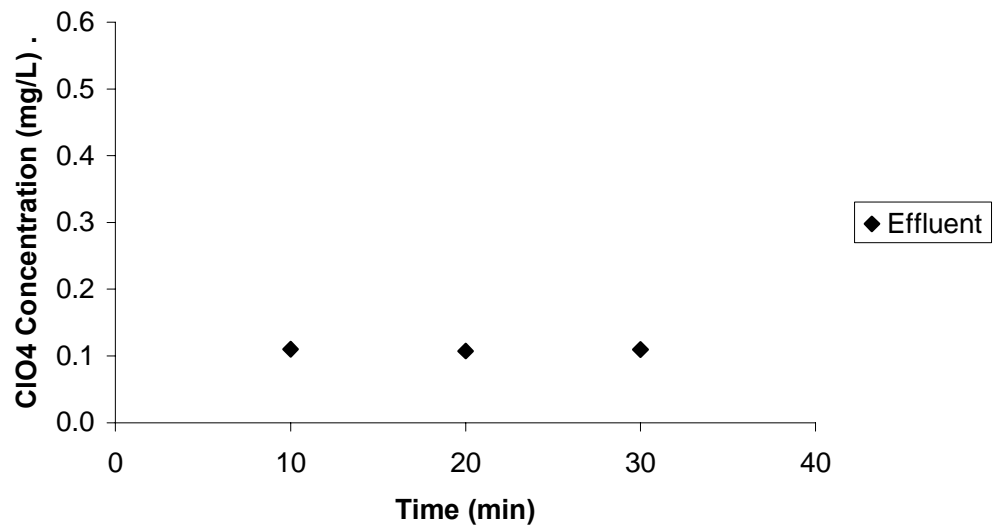


Figure 6.12 Experiment 6 Perchlorate Concentration Data (Post-Experiment Flush);  
[HCOOH] = 1mM, HRT = 2.90 min

<b>Experiment 7 (Flushing Only):</b>								
[HCOOH] = 1mM								
[ClO4] = 0								
Flow = 20.13 ml/min								
HRT = 2.87 min (based on flow and pore volume of 57.7 mL)								
<b>Effluent Results, Flush Session 1:</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E7-001	0	0.7150	--	--				
E7-002	2.5	0.3638	6.67	19.07	0.5394	2.5	0.02013	0.0271
E7-003	5	0.1920	--	--	0.2779	2.5	0.02013	0.0140
E7-004	7.5	0.1637	4.84	13.99	0.1779	2.5	0.02013	0.0090
E7-005	10	0.1523	4.66	14.22	0.1580	2.5	0.02013	0.0080
E7-006	15	0.1401	4.67	14.25	0.1462	5	0.02013	0.0147
E7-007	20	0.1357	4.62	14.42	0.1379	5	0.02013	0.0139
E7-008	30	0.1284	4.59	14.71	0.1321	10	0.02013	0.0266
E7-009	45	0.1236	4.57	15.05	0.1260	15	0.02013	0.0380
E7-010	61	0.1201	4.56	15.16	0.1219	16	0.02013	0.0392
E7-011	80	0.1179	4.57	14.97	0.1190	19	0.02013	0.0455
E7-012	100	0.1158	4.54	15.58	0.1169	20	0.02013	0.0470
E7-013	130	0.1153	4.53	15.78	0.1156	30	0.02013	0.0698
E7-014	160	0.1101	4.52	16.16	0.1127	30	0.02013	0.0681
E7-015	250	0.1081	4.52	16.60	0.1091	90	0.02013	0.1977
E7-016	300	0.1039	4.50	16.47	0.1060	50	0.02013	0.1067
E7-017	400	0.0989	4.48	17.41	0.1014	100	0.02013	0.2041
E7-018	450	0.0963	4.49	16.54	0.0976	50	0.02013	0.0982
Sum of Delta Mass-->								1.0276
<b>Effluent Results, Flush Session 2:</b>								
[HCOOH] = 2mM, pH = 4, [ClO4] = 0								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E7-020	0	0.4052	--	--				
E7-021	5	2.3242	--	--	1.3647	5	0.02013	0.1374
E7-022	7.5	2.2619	6.01	108.2	2.2931	2.5	0.02013	0.1154
E7-023	10	2.2619	6.05	116.6	2.2619	2.5	0.02013	0.1138
E7-024	20	1.5913	6.05	126.0	1.9266	10	0.02013	0.3878
E7-025	30	1.2154	6.03	127.7	1.4034	10	0.02013	0.2825
E7-026	330	0	5.89	125.6				
Sum of Delta Mass-->								1.0369

**Table 6.8 Experiment 7 Results with Mass Balance Calculations**

### E7 - Concentrations - Flush #1

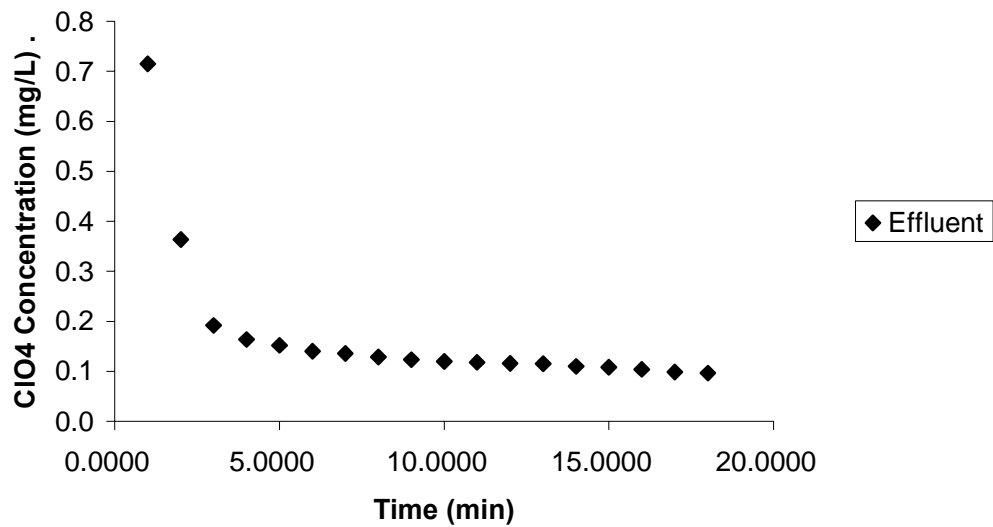


Figure 6.13 Experiment 7 Perchlorate Concentration Data (Post-Experiment Flush Session 1); [HCOOH] = 1mM, pH ~ 3.5, HRT = 2.87 min

### E7 - Concentrations - Flush #2

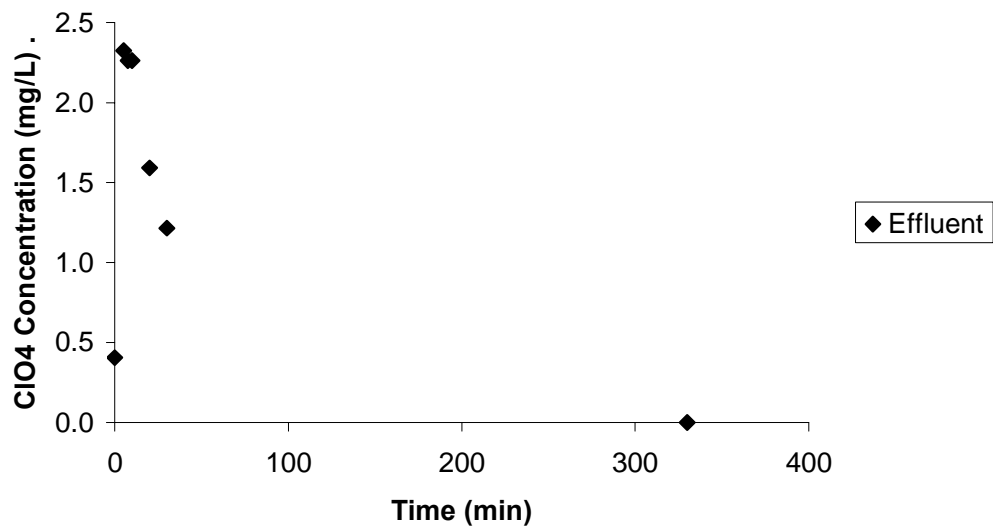


Figure 6.14 Experiment 7 Perchlorate Concentration Data (Post-Experiment Flush Session 2); [HCOOH] = 2mM, pH ~ 4, HRT = 2.87 min



<b>Experiment 8:</b>								
[HCOOH] = 2mM								
Source pH = 3.3 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 20.07 ml/min								
HRT = 2.87 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E8-001	Before Exp	0.5088	3.3	232.8				
E8-002	Before Exp	0.4975	3.3	232.8				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E8-003	0	0.0000	4.2	35.57				
E8-004	2.5	0.0000	4.4	26.8	0.0000	2.5	0.02007	0.0000
E8-005	5	0.0104	4.24	30.71	0.0052	2.5	0.02007	0.0003
E8-006	7.5	0.0140	4.21	34.36	0.0122	2.5	0.02007	0.0006
E8-007	10	0.0137	4.19	35.51	0.0139	2.5	0.02007	0.0007
E8-008	20	0.0193	4.15	38.67	0.0165	10	0.02007	0.0033
E8-009	30	0.0306	4.11	41.32	0.0250	10	0.02007	0.0050
E8-010	45	0.0364	4.07	45.82	0.0335	15	0.02007	0.0101
E8-011	60	0.0460	4.06	45.46	0.0412	15	0.02007	0.0124
E8-012	80	0.0509	4.04	47.7	0.0485	20	0.02007	0.0194
E8-013	100	0.0620	4.05	46.66	0.0565	20	0.02007	0.0227
E8-014	120	0.0742	4.04	47.42	0.0681	20	0.02007	0.0273
Sum of Delta Mass-->								0.1018

**Table 6.9 Experiment 8 Results with Mass Balance Calculations (Main Run)**

### E8 - Effluent pH and Conductivity (Main Run)

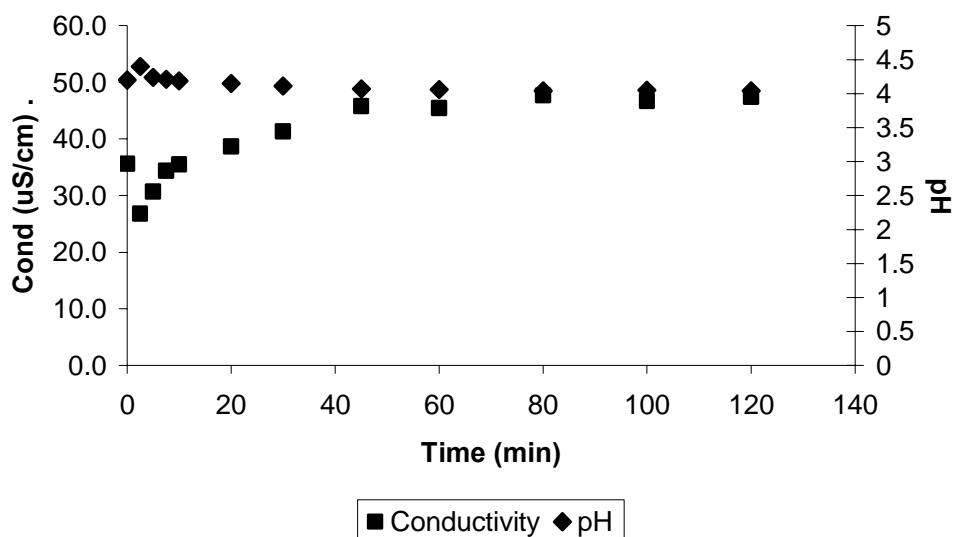


Figure 6.15 Experiment 8 pH and Conductivity Data;  
Influent pH = 3.30, Influent Conductivity = 232.8  $\mu\text{S}/\text{cm}$

### E8 - Concentrations - Main Run

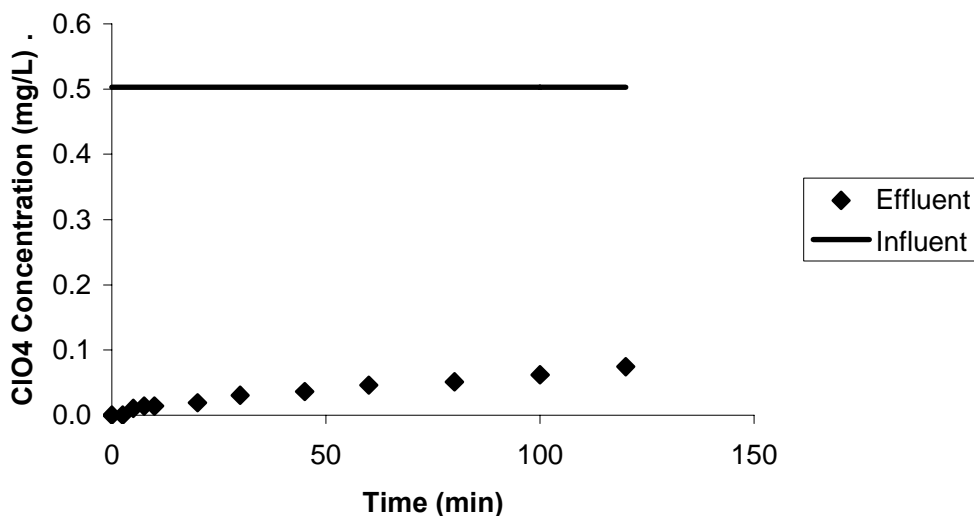


Figure 6.16 Experiment 8 Perchlorate Concentration Data (Main Run);  
[HCOOH] = 2mM, pH = 3.30, HRT = 2.87 min

<b>Experiment 8, Postflush Session 1 Results:</b>								
[HCOOH] = 2mM, pH = 4, [ClO4] = 0								
Flow = 20.07 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E8-015	0	0.0435	4.07	45.87				
E8-016	2.5	0.4736	4.54	45.22	0.2586	2.5	0.02007	0.0130
E8-017	5	0.7034	5.35	80.74	0.5885	2.5	0.02007	0.0295
E8-018	7.5	0.7441	5.51	114.7	0.7238	2.5	0.02007	0.0363
E8-019	10	0.7492	5.58	120.2	0.7467	2.5	0.02007	0.0375
E8-020	15	0.7231	5.62	127.4	0.7362	5	0.02007	0.0739
E8-021	20	0.6831	5.65	128.9	0.7031	5	0.02007	0.0706
E8-022	30	0.6088	5.71	130.4	0.6460	10	0.02007	0.1296
E8-023	45	0.4799	5.74	130.3	0.5444	15	0.02007	0.1639
E8-024	60	0.3782	5.78	131.1	0.4291	15	0.02007	0.1292
E8-025	75	0.304	5.82	131.1	0.3411	15	0.02007	0.1027
Sum of Delta Mass-->								0.7861
<b>Experiment 8, Postflush Session 2 Results:</b>								
[HCOOH] = 2mM, pH = 4, [ClO4] = 0								
Flow = 20.0 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E8-026	0.01	0.4443	--	--				
E8-027	2.5	0.394	6.76	408.3	0.4192	2.49	0.02	0.0209
E8-028	5	0.3576	6.35	138.1	0.3758	2.5	0.02	0.0188
E8-029	7.5	0.3306	6.17	141.7	0.3441	2.5	0.02	0.0172
E8-030	10	0.3005	6.09	145.4	0.3156	2.5	0.02	0.0158
E8-031	15	0.2619	6.06	147.3	0.2812	5	0.02	0.0281
E8-032	20	0.2289	6.06	147.3	0.2454	5	0.02	0.0245
E8-033	30	0.1757	6.05	148.2	0.2023	10	0.02	0.0405
E8-034	45	0.1200	6.06	148.5	0.1479	15	0.02	0.0444
E8-035	60.5	0.0844	6.08	148.6	0.1022	15.5	0.02	0.0317
E8-036	75	0.0574	6.09	148.8	0.0709	14.5	0.02	0.0206
E8-037	90	0.0422	6.08	148.8	0.0498	15	0.02	0.0149
Sum of Delta Mass-->								0.2774

**Table 6.10 Experiment 8 Results with Mass Balance Calculations (Post-Experiment Flush Sessions 1 and 2)**

### E8 - Concentrations - Postflush

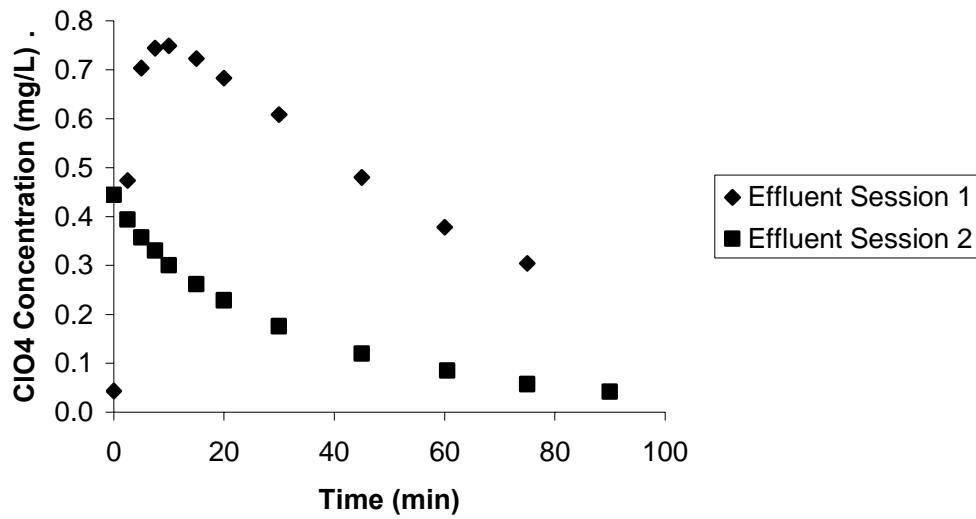


Figure 6.17 Experiment 8 Perchlorate Concentration Data (Post-Experiment Flush);  
 Session #1: [HCOOH] = 2mM, pH = 4.00, HRT = 2.87 min; Session #2: [HCOOH] =  
 2mM, pH = 4.11, HRT = 2.89 min

### E8 - Postflush Session 2 Exponential Trendline

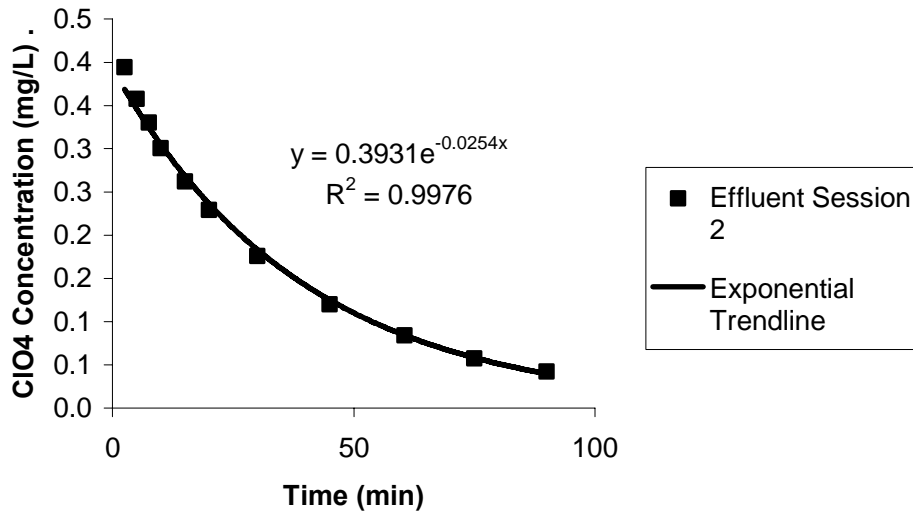


Figure 6.18 Experiment 8 Post-Experiment Flush Exponential Trendline

<b>Experiment 8: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.50315	(mg/L)	
Flowrate:	0.02007	(L/min)	
Duration:	120	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>1.2118</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.1018	(mg)	
Sum of Delta Mass from Post-Flush #1:	0.7861	(mg)	
Sum of Delta Mass from Postflush #2:	0.2774	(mg)	
Residual Mass in Tail*:	0.0313	(mg)	
<b>Total Mass Out (sum):</b>	<b>1.1966</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>98.75%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 90 to t = 300, then multiplying by postflush flowrate (0.020 L/min)			

**Table 6.11 Experiment 8 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 9:</b>								
[HCOOH] = 10mM								
Source pH = 3.08 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 20.0 ml/min								
HRT = 2.89 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E9-001	Before Exp	0.5439	3.08	554.3				
E9-002	Before Exp	0.5154	3.08	554.3				
E9-015	After Exp	0.5336	3.02	539.9				
E9-016	After Exp	0.5132	3.02	539.9				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E9-003	0	0.0000	3.4	221				
E9-004	2.5	0.0197	3.6	188	0.0099	2.5	0.02	0.0005
E9-005	5	0.0170	3.47	195.8	0.0184	2.5	0.02	0.0009
E9-006	7.5	0.0228	3.43	198.8	0.0199	2.5	0.02	0.0010
E9-007	10	0.0251	3.41	228.8	0.0240	2.5	0.02	0.0012
E9-008	15	0.0401	3.4	228.1	0.0326	5	0.02	0.0033
E9-009	20	0.0460	3.39	237.2	0.0431	5	0.02	0.0043
E9-010	30	0.0700	3.38	244.3	0.0580	10	0.02	0.0116
E9-011	45	0.0899	3.38	251.1	0.0800	15	0.02	0.0240
E9-012	60	0.1289	3.36	250.4	0.1094	15	0.02	0.0328
E9-013	75	0.1517	3.36	254.4	0.1403	15	0.02	0.0421
E9-014	90	0.1658	3.34	257	0.1588	15	0.02	0.0476
Sum of Delta Mass-->								0.1693

**Table 6.12 Experiment 9 Results with Mass Balance Calculations (Main Run)**

### E9 - Effluent pH and Conductivity (Main Run)

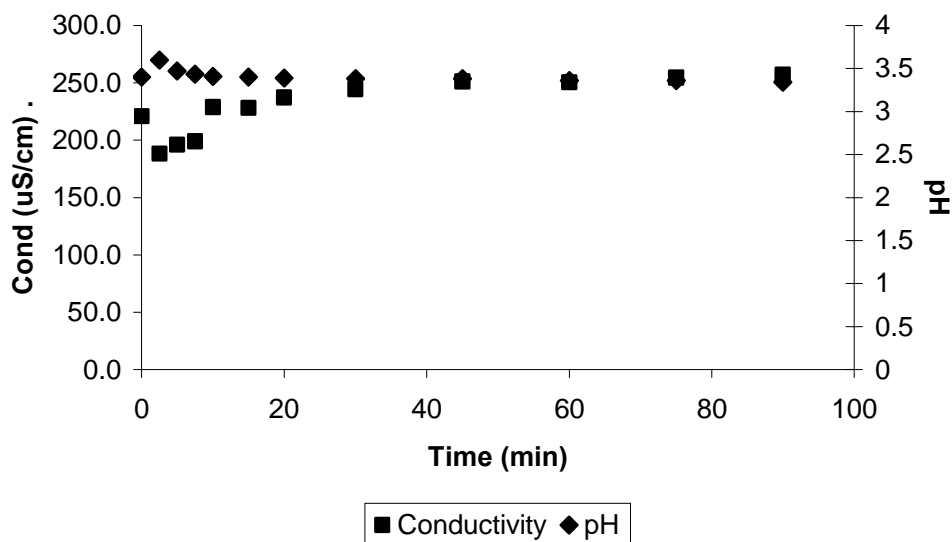


Figure 6.19 Experiment 9 pH and Conductivity Data; Influent pH = 3.08, Influent Conductivity = 554.3  $\mu$ S/cm

### E9 - Concentrations - Main Run

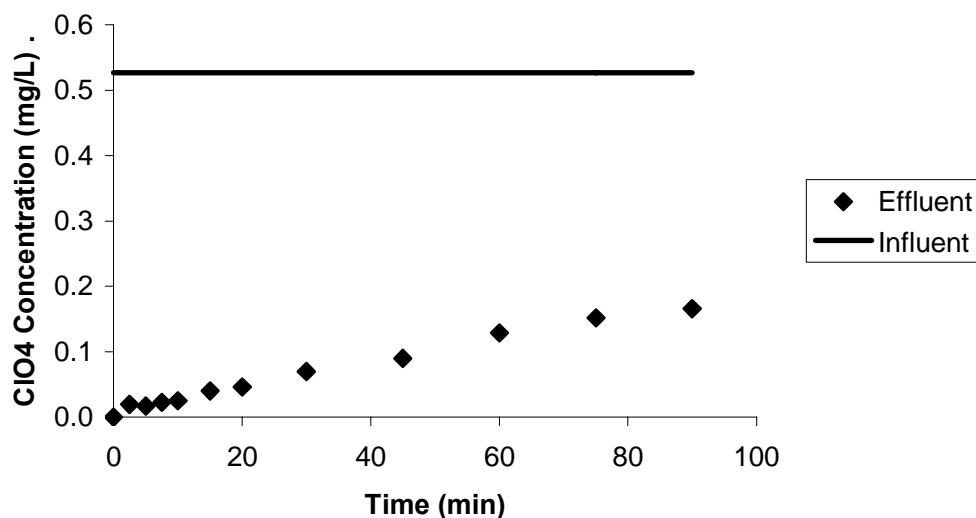


Figure 6.20 Experiment 9 Perchlorate Concentration Data (Main Run); [HCOOH] = 10mM, pH = 3.08, HRT = 2.89 min

<b>Experiment 9 Postflush Results:</b>								
[HCOOH] = 10mM, pH = 4.01, [ClO4] = 0								
Flow = 19.42 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E9-017	0	0.0775	3.36	234.6				
E9-018	2.5	0.9922	4.38	232.3	0.5349	2.5	0.01942	0.0260
E9-019	5	1.1640	5.27	484.1	1.0781	2.5	0.01942	0.0523
E9-020	7.5	1.1250	5.43	554.1	1.1445	2.5	0.01942	0.0556
E9-021	10	0.9926	5.42	584.8	1.0588	2.5	0.01942	0.0514
E9-022	15	0.8341	5.36	622.3	0.9134	5	0.01942	0.0887
E9-023	20	0.6842	5.35	629.5	0.7592	5	0.01942	0.0737
E9-024	30	0.4676	5.26	638.8	0.5759	10	0.01942	0.1118
E9-025	45	0.2618	5.15	641.1	0.3647	15	0.01942	0.1062
E9-026	60	0.1582	5.14	645.7	0.2100	15	0.01942	0.0612
E9-027	75	0.0800	5.11	649.2	0.1191	15	0.01942	0.0347
E9-028	90	0.0510	5.12	650.7	0.0655	15	0.01942	0.0191
Sum of Delta Mass-->								0.6807

**Table 6.13 Experiment 9 Results with Mass Balance Calculations (Post-Experiment Flush)**



### E9 - Concentrations - Postflush

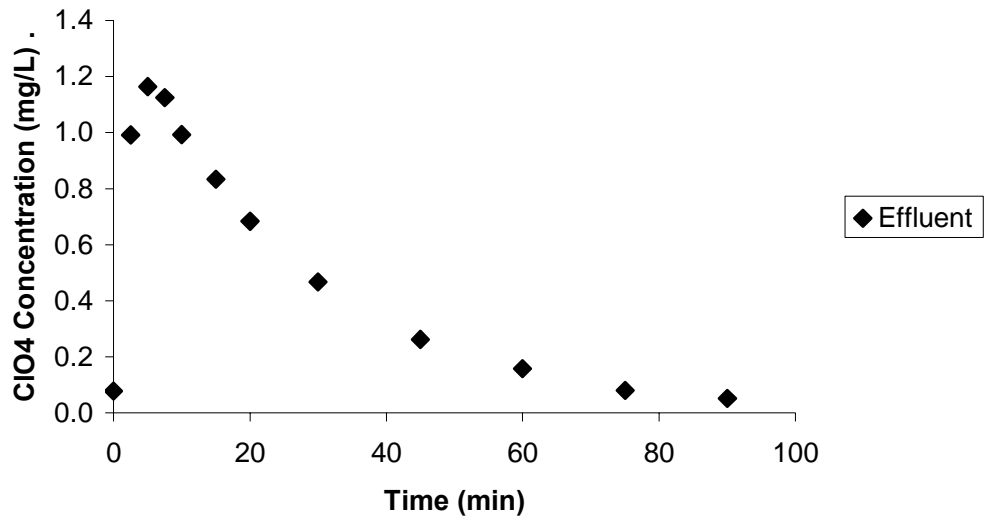


Figure 6.21 Experiment 9 Perchlorate Concentration Data (Post-Experiment Flush); [HCOOH] = 10mM, pH = 4.01, HRT = 2.97 min

### E9 - Postflush Exponential Trendline

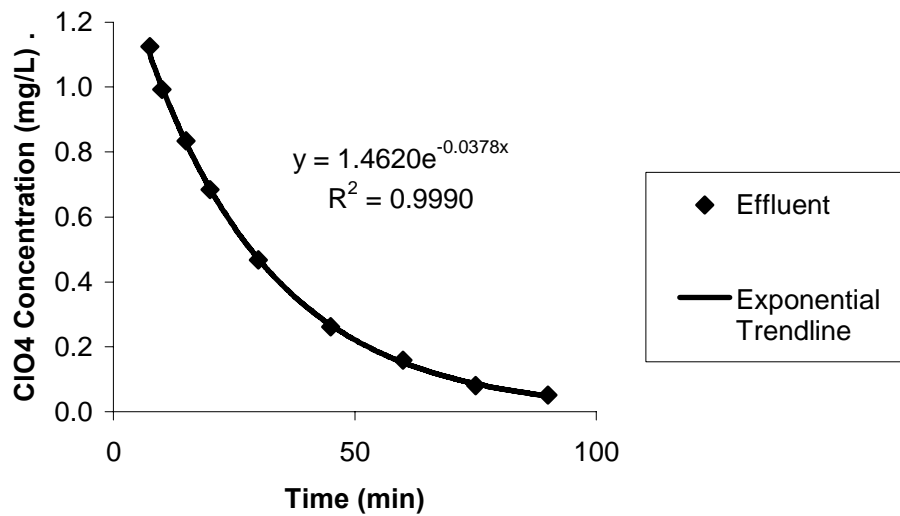


Figure 6.22 Experiment 9 Post-Experiment flush Exponential Trendline

<b>Experiment 9: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5265	(mg/L)	
Flowrate:	0.02	(L/min)	
Duration:	90	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>0.9477</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.1693	(mg)	
Sum of Delta Mass from Postflush:	0.6807	(mg)	
Residual Mass in Tail*:	0.0250	(mg)	
<b>Total Mass Out (sum):</b>	<b>0.8750</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>92.32%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 90 to t = 300, then multiplying by postflush flowrate (0.01942 L/min)			

**Table 6.14 Experiment 9 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 10:</b>								
[HCOOH] = 10mM								
Source pH = 3.00 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 4.67 ml/min								
HRT = 12.36 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E10-001	Before Exp	0.5163	3.00	559.6				
E10-002	Before Exp	0.5186	3.00	559.6				
E10-017	After Exp	0.5404	3.08	556.3				
E10-018	After Exp	0.5384	3.08	556.3				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E10-003	0	0.0000	4.56	39.23				
E10-004	5	0.0000	4.52	37.5	0.0000	5.0000	0.00467	0.0000
E10-005	10	0.0000			0.0000	5.0000	0.00467	0.0000
E10-006	15	0.0000	4.61	36.07	0.0000	5.0000	0.00467	0.0000
E10-007	20	0.0000	4.61	37.96	0.0000	5.0000	0.00467	0.0000
E10-008	30	0.0000	4.6	39.21	0.0000	10.0000	0.00467	0.0000
E10-009	45	0.0000	4.61	41.51	0.0000	15.0000	0.00467	0.0000
E10-010	60	0.0000	4.61	42.84	0.0000	15.0000	0.00467	0.0000
E10-011	83	0.0000	4.6	44.14	0.0000	23.0000	0.00467	0.0000
E10-012	100	0.0067	4.58	45.71	0.0034	17.0000	0.00467	0.0003
E10-013	120	0.0081	4.58	47.54	0.0074	20.0000	0.00467	0.0007
E10-014	140	0.0127	4.52	53.13	0.0104	20.0000	0.00467	0.0010
E10-015	160	0.0128	4.56	51.49	0.0128	20.0000	0.00467	0.0012
E10-016	180	0.0164	4.54	52.54	0.0146	20.0000	0.00467	0.0014
Sum of Delta Mass-->								0.0045

**Table 6.15 Experiment 10 Results with Mass Balance Calculations (Main Run)**

### E10 - Effluent pH and Conductivity (Main Run)

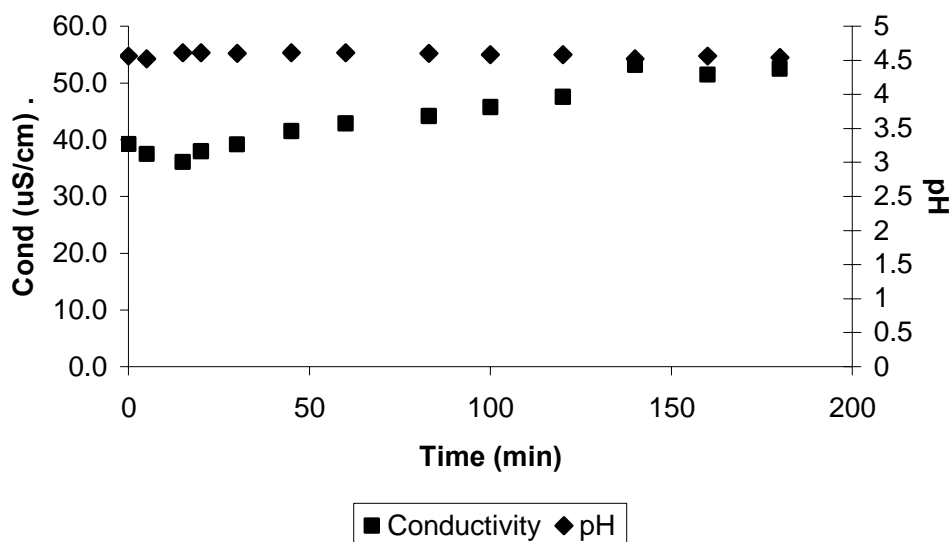


Figure 6.23 Experiment 10 pH and Conductivity Data; Influent pH = 3.00, Influent Conductivity = 559.6  $\mu\text{S}/\text{cm}$

### E10 - Concentrations - Main Run

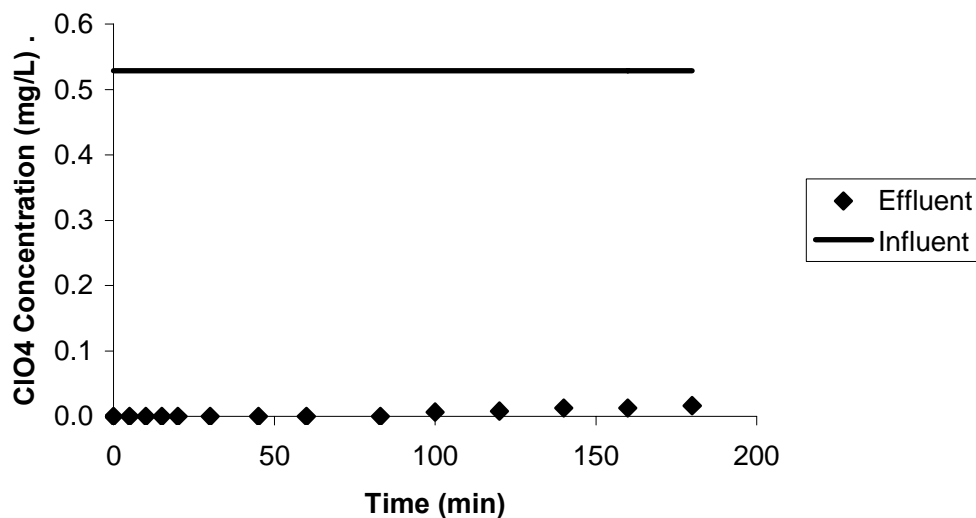


Figure 6.24 Experiment 10 Perchlorate Concentration Data (Main Run);  $[\text{HCOOH}] = 10\text{mM}$ ,  $\text{pH} = 3.00$ ,  $\text{HRT} = 12.36\text{ min}$

<b>Experiment 10 Postflush Results:</b>								
Pure DI Water Used for Flush								
[HCOOH] = 0, pH = 5.70, [ClO4] = 0								
Flow = 19.60 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E10-019	0	0.0142	--	--				
E10-020	2.5	0.0204	4.38	49.45	0.0173	2.5	0.0196	0.0008
E10-021	5	0.0149	4.37	48.44	0.0177	2.5	0.0196	0.0009
E10-022	7.5	0.0111	4.37	35.6	0.0130	2.5	0.0196	0.0006
E10-023	10	0.0114	4.39	33.44	0.0113	2.5	0.0196	0.0006
E10-024	15	0.0115	4.42	31.27	0.0115	5	0.0196	0.0011
E10-025	20	0.0064	4.44	27.4	0.0090	5	0.0196	0.0009
E10-026	30	0.0081	4.48	23.07	0.0073	10	0.0196	0.0014
E10-027	45	0.0071	4.54	19.32	0.0076	15	0.0196	0.0022
E10-028	60	0.0066	4.57	16.82	0.0069	15	0.0196	0.0020
E10-029	75	0	4.62	15.22	0.0033	15	0.0196	0.0010
Sum of Delta Mass-->								0.0115

**Table 6.16 Experiment 10 Results with Mass Balance Calculations (Post-Experiment flush)**

### E10 - Concentrations - Postflush

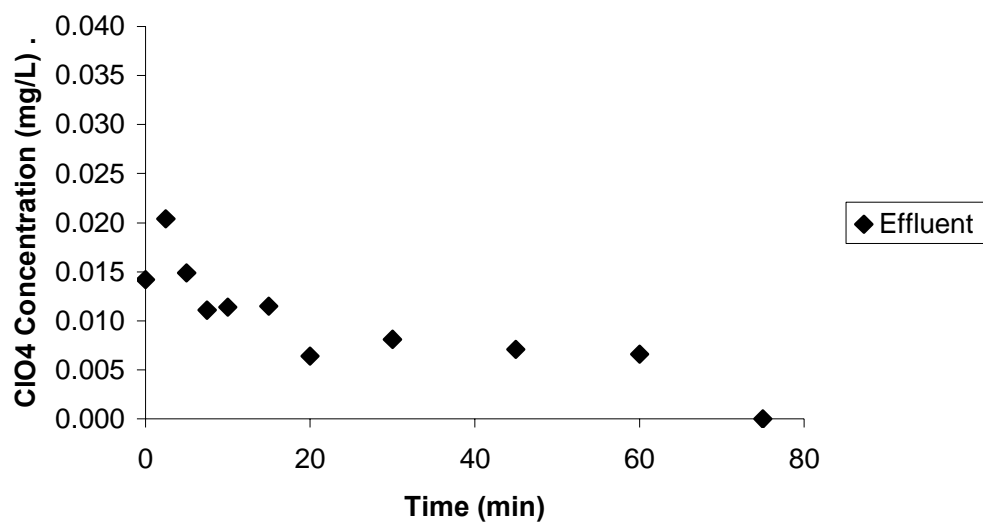


Figure 6.25 Experiment 10 Perchlorate Concentration Data (Post-Experiment Flush);  
Pure DI Water ([HCOOH] = 0), pH = 5.70, HRT = 2.94 min

<b>Experiment 10: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5284	(mg/L)	
Flowrate:	0.00467	(L/min)	
Duration:	180	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>0.4442</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.0045	(mg)	
Sum of Delta Mass from Postflush:	0.0115	(mg)	
Residual Mass in Tail*:	0.0000	(mg)	
<b>Total Mass Out (sum):</b>	<b>0.0160</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>3.61%</b>		
* Concentration in the t = 75min postflush sample was 0; no residual mass in reactor.			

**Table 6.17 Experiment 10 Mass Recovery Percentage (MRP) Calculation**

Sample #	Experiment Phase	Time (min)	Chlorate Concentration (mg/L)	Chlorite Concentration (mg/L)	Chloride Concentration (mg/L)
E10-008	Main Run	30	0.000	0.000	0.003
E10-010	Main Run	60	0.000	0.000	0.004
E10-012	Main Run	100	0.000	0.000	0.003
E10-014	Main Run	140	0.000	0.000	0.002
E10-016	Main Run	180	0.000	0.000	0.002
E10-021	Postflush	5	0.000	0.000	0.008
E10-023	Postflush	10	0.000	0.000	0.003
E10-025	Postflush	20	0.000	0.000	0.002
E10-027	Postflush	45	0.000	0.000	0.007

**Table 6.18 Experiment 10 Byproduct Analysis Results (Main Run and Post-Experiment Flush)**

<b>Experiment 11:</b>								
[HCOOH] = 10mM								
Source pH = 2.98 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 7.58 ml/min								
HRT = 7.61 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E11-001	Before Exp	0.5048	2.98	543.9				
E11-002	Before Exp	0.5377	2.98	543.9				
E11-015	After Exp	0.5425	2.99	541.7				
E11-016	After Exp	0.5166	2.99	541.7				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E11-003	0	0.0558	3.91	89.69				
E11-004	5	0.0631	4.04	90.55	0.0595	5	0.00758	0.0023
E11-005	10	0.0623	3.97	87.41	0.0627	5	0.00758	0.0024
E11-006	15	0.0624	3.93	94.25	0.0623	5	0.00758	0.0024
E11-007	20	0.0647	3.91	93.58	0.0635	5	0.00758	0.0024
E11-008	30	0.0726	3.88	100.8	0.0686	10	0.00758	0.0052
E11-009	45	0.0787	3.82	107.4	0.0756	15	0.00758	0.0086
E11-010	60	0.0852	3.84	108.1	0.0819	15	0.00758	0.0093
E11-011	80	0.0889	3.81	110.9	0.0871	20	0.00758	0.0132
E11-012	124	0.1083	3.78	115.6	0.0986	44	0.00758	0.0329
E11-013	150	0.1254	3.74	122.5	0.1169	26	0.00758	0.0230
E11-014	180	0.1448	3.72	128.8	0.1351	30	0.00758	0.0307
Sum of Delta Mass-->								0.1324

**Table 6.19 Experiment 11 Results with Mass Balance Calculations (Main Run)**



### E11 - Effluent pH and Conductivity (Main Run)

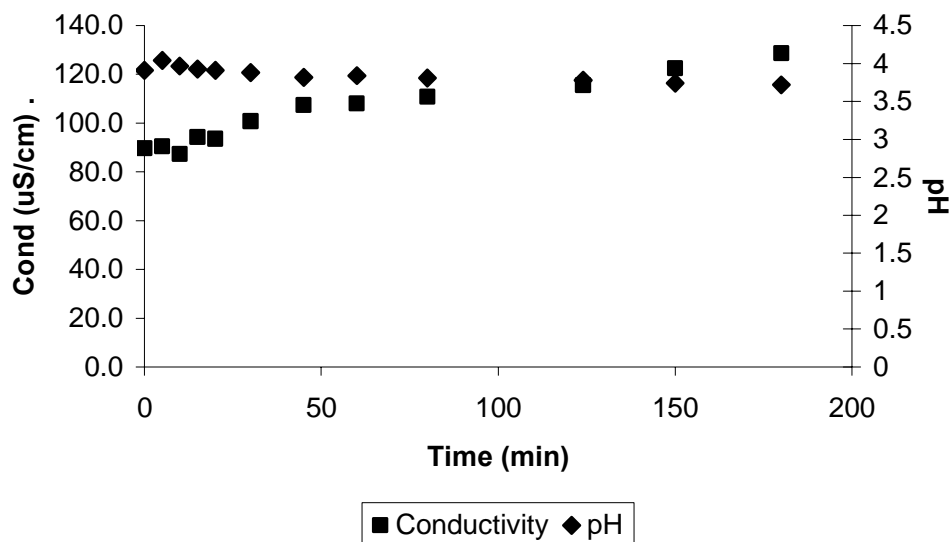


Figure 6.26 Experiment 11 pH and Conductivity Data; Influent pH = 2.98, Influent Conductivity = 543.9  $\mu$ S/cm

### E11 - Concentrations - Main Run

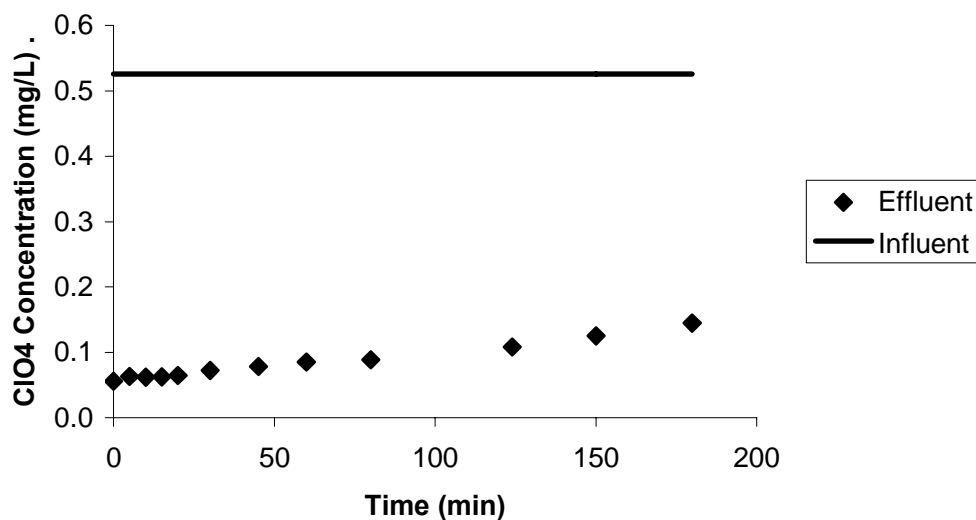


Figure 6.27 Experiment 11 Perchlorate Concentration Data (Main Run); [HCOOH] = 10mM, pH = 2.98, HRT = 7.61 min

<b>Experiment 11 Postflush Results:</b>								
[HCOOH] = 10mM, pH = 3.95, [ClO4] = 0								
Flow = 20.41 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E11-017	0	0.1499						
E11-018	2.5	1.0972	4.08	203.4	0.6235	2.5	0.02041	0.0318
E11-019	5	1.3229	4.59	505.9	1.2101	2.5	0.02041	0.0617
E11-020	7.5	1.2757	4.7	571.7	1.2993	2.5	0.02041	0.0663
E11-021	10	1.1877	4.72	583.1	1.2317	2.5	0.02041	0.0628
E11-022	15	1.0089	4.68	605	1.0983	5	0.02041	0.1121
E11-023	20	0.8720	4.67	616.1	0.9405	5	0.02041	0.0960
E11-024	30	0.6357	4.67	620.6	0.7538	10	0.02041	0.1539
E11-025	45	0.3766	4.68	630.1	0.5061	15	0.02041	0.1550
E11-026	60	0.2215	4.66	626.9	0.2990	15	0.02041	0.0915
E11-027	75	0.1352	4.64	623.8	0.1783	15	0.02041	0.0546
E11-028	90	0.0815	4.66	625	0.1084	15	0.02041	0.0332
E11-029	101	0.0544	4.65	631.4	0.0680	11	0.02041	0.0153
Sum of Delta Mass-->								0.9342

**Table 6.20 Experiment 11 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E11 - Concentrations - Postflush

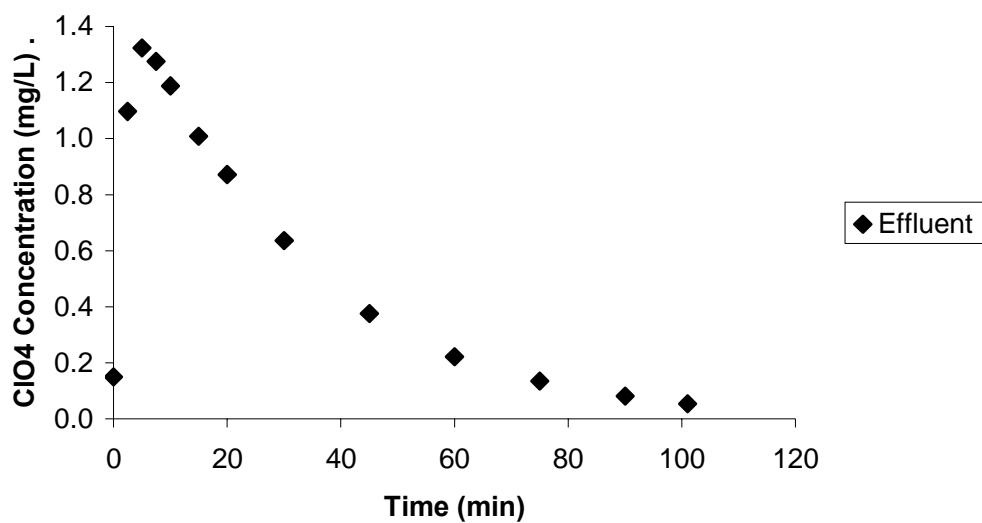


Figure 6.28 Experiment 11 Perchlorate Concentration Data (Post-Experiment Flush); [HCOOH] = 10mM, pH = 3.98, HRT = 2.83 min

### E11 - Postflush Exponential Trendline

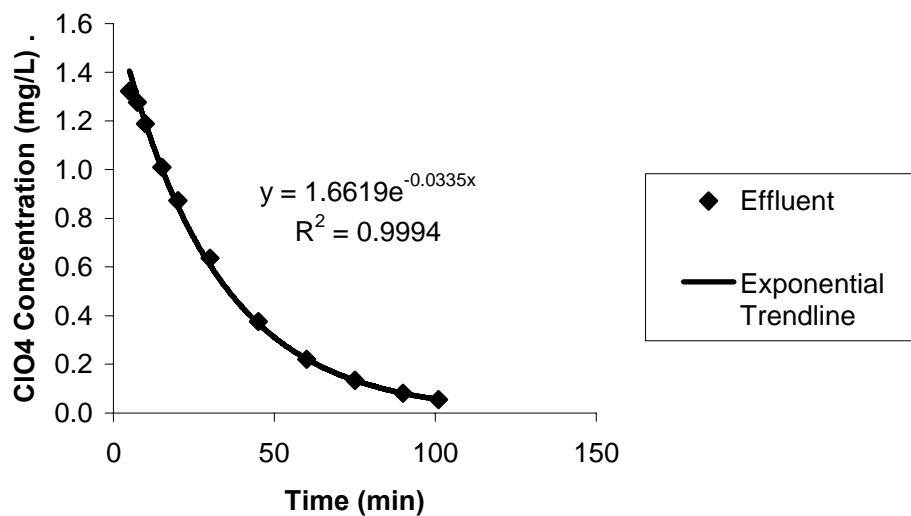


Figure 6.29 Experiment 11 Post-Experiment Flush Exponential Trendline

<b>Experiment 11: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5254	(mg/L)	
Flowrate:	0.00758	(L/min)	
Duration:	180	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>0.7169</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.1324	(mg)	
Sum of Delta Mass from Postflush:	0.9342	(mg)	
Residual Mass in Tail*:	0.0344	(mg)	
<b>Total Mass Out (sum):</b>	<b>1.1010</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>153.59%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 101 to t = 500, then multiplying by postflush flowrate (0.02041 L/min)			

**Table 6.21 Experiment 11 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 12:</b>								
[HCOOH] = 10mM								
Source pH = 10.58 (adjusted w/ NaOH)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 7.68 ml/min								
HRT = 7.51 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E12-001	Before Exp	0.5200	10.58	1054				
E12-002	Before Exp	0.5186	10.58	1054				
E12-016	After Exp	0.5264	10.13	1009				
E12-017	After Exp	0.5261	10.13	1009				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E12-003	0	0.0136	6.58	979.2				
E12-004	5	0.0672	6.56	978.5	0.0404	5	0.00768	0.0016
E12-005	10	0.1783	6.58	964.5	0.1228	5	0.00768	0.0047
E12-006	15	0.2289			0.2036	5	0.00768	0.0078
E12-007	20	0.2868	6.57	959.6	0.2579	5	0.00768	0.0099
E12-008	30	0.3481	6.56	952.2	0.3175	10	0.00768	0.0244
E12-009	45	0.4094	6.6	947.7	0.3788	15	0.00768	0.0436
E12-010	60	0.4524	6.61	947.9	0.4309	15	0.00768	0.0496
E12-011	80	0.4810	6.6	947.2	0.4667	20	0.00768	0.0717
E12-012	100	0.5155	6.65	946.5	0.4983	20	0.00768	0.0765
E12-013	120	0.5079	6.65	945.8	0.5117	20	0.00768	0.0786
E12-014	168	0.5446	6.7	947.7	0.5263	48	0.00768	0.1940
E12-015	180	0.5298	6.75	951.3	0.5372	12	0.00768	0.0495
Sum of Delta Mass-->								0.6120

**Table 6.22 Experiment 12 Results with Mass Balance Calculations (Main Run)**

### E12 - Effluent pH and Conductivity (Main Run)

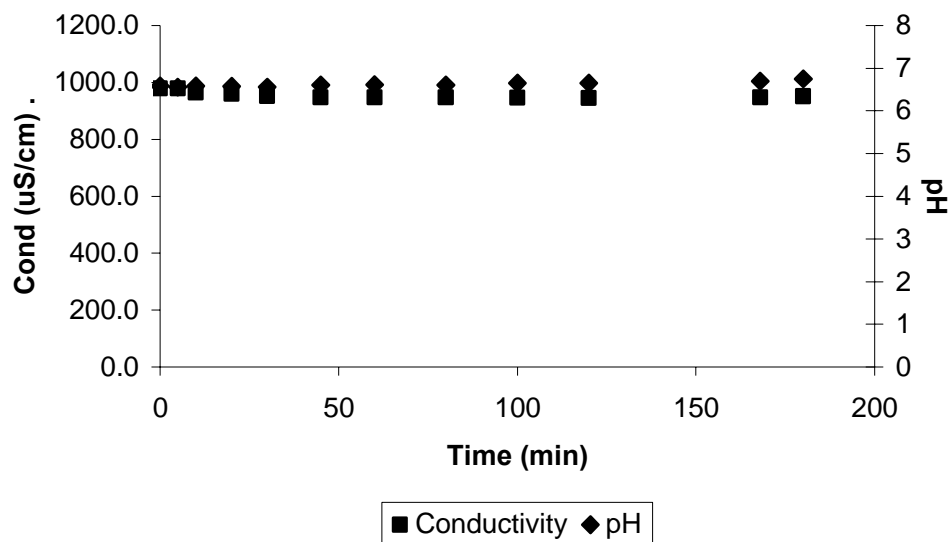


Figure 6.30 Experiment 12 pH and Conductivity Data; Influent pH = 10.58, Influent Conductivity = 1054  $\mu$ S/cm

### E12 - Concentrations - Main Run

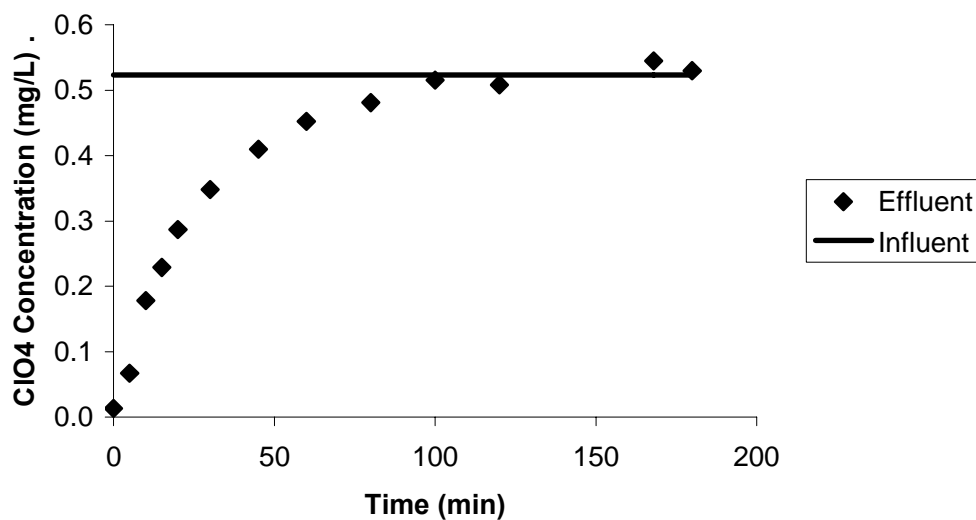


Figure 6.31 Experiment 12 Perchlorate Concentration Data (Main Run); [HCOOH] = 10mM, pH = 10.58, HRT = 7.51 min

<b>Experiment 12 Postflush Results:</b>								
[HCOOH] = 10mM, pH = 10.20, [ClO4] = 0								
Flow = 19.61 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E12-018	0	0.5160						
E12-019	2.5	0.3538	7.42	959.2	0.4349	2.5	0.01961	0.0213
E12-020	5	0.2236	7.05	966.6	0.2887	2.5	0.01961	0.0142
E12-021	7.5	0.1634	6.88	966.4	0.1935	2.5	0.01961	0.0095
E12-022	10	0.1348	6.81	968.1	0.1491	2.5	0.01961	0.0073
E12-023	15	0.1048	6.8	966.7	0.1198	5	0.01961	0.0117
E12-024	20	0.0708	0	964.7	0.0878	5	0.01961	0.0086
E12-025	30	0.0414	6.94	965.4	0.0561	10	0.01961	0.0110
E12-026	45	0.0216	6.85	964.9	0.0315	15	0.01961	0.0093
E12-027	60	0.0091	6.86	963.6	0.0154	15	0.01961	0.0045
E12-028	75	0.0000	6.88	963.8	0.0046	15	0.01961	0.0013
Sum of Delta Mass-->								0.0987

**Table 6.23 Experiment 12 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E12 - Concentrations - Postflush

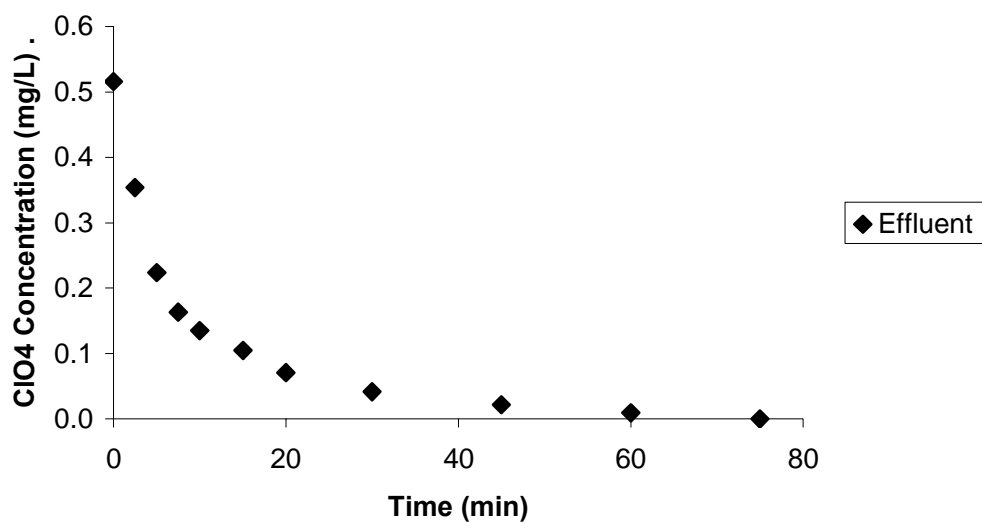


Figure 6.32 Experiment 12 Perchlorate Concentration Data (Post-Experiment Flush); [HCOOH] = 10mM, pH = 10.20, HRT = 2.94 min

### E12 - Postflush Exponential Trendline

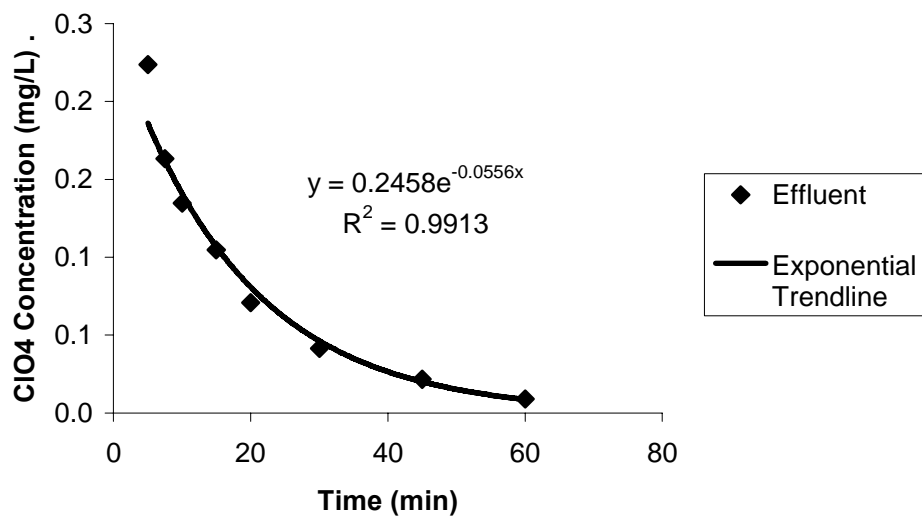


Figure 6.33 Experiment 12 Post-Experiment Flush Exponential Trendline



<b>Experiment 12: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5228	(mg/L)	
Flowrate:	0.00768	(L/min)	
Duration:	180	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>0.7227</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.6120	(mg)	
Sum of Delta Mass from Postflush:	0.0987	(mg)	
Residual Mass in Tail*:	0.0000	(mg)	
<b>Total Mass Out (sum):</b>	<b>0.7107</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>98.34%</b>		
* Concentration in the t = 75min postflush sample was 0; no residual mass in reactor.			

**Table 6.24 Experiment 12 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 13:</b>								
[HCOOH] = 0 (Hydrogen Used as Reductant in this Experiment)								
Source pH = 4.21 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 18.0 ml/min								
HRT = 3.21 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E13-001	Before Exp	0.4855	4.21	24.83				
E13-002	Before Exp	0.4988	4.21	24.83				
E13-015	After Exp	0.5162	4.23	24.73				
E13-016	After Exp	0.5186	4.23	24.73				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E13-003	0	0.0000	4.36	20.86				
E13-004	2.5	0.0092	4.48	19.86	0.0046	2.5	0.018	0.0002
E13-005	5	0.0090	4.39	20.22	0.0091	2.5	0.018	0.0004
E13-006	7.5	0.0110	4.37	20.93	0.0100	2.5	0.018	0.0005
E13-007	10	0.0112	4.36	21.31	0.0111	2.5	0.018	0.0005
E13-008	15	0.0121	4.35	21.52	0.0117	5	0.018	0.0010
E13-009	20	0.0109	4.34	21.75	0.0115	5	0.018	0.0010
E13-010	30	0.0164	4.33	21.83	0.0137	10	0.018	0.0025
E13-011	45	0.0166	4.33	21.76	0.0165	15	0.018	0.0045
E13-012	60	0.0190	4.33	21.78	0.0178	15	0.018	0.0048
E13-013	80	0.0220	4.33	21.74	0.0205	20	0.018	0.0074
E13-014	100	0.0197	4.33	21.68	0.0197	20	0.018	0.0071
Sum of Delta Mass-->								0.0298

**Table 6.25 Experiment 13 Results with Mass Balance Calculations (Main Run)**

### E13 - Effluent pH and Conductivity (Main Run)

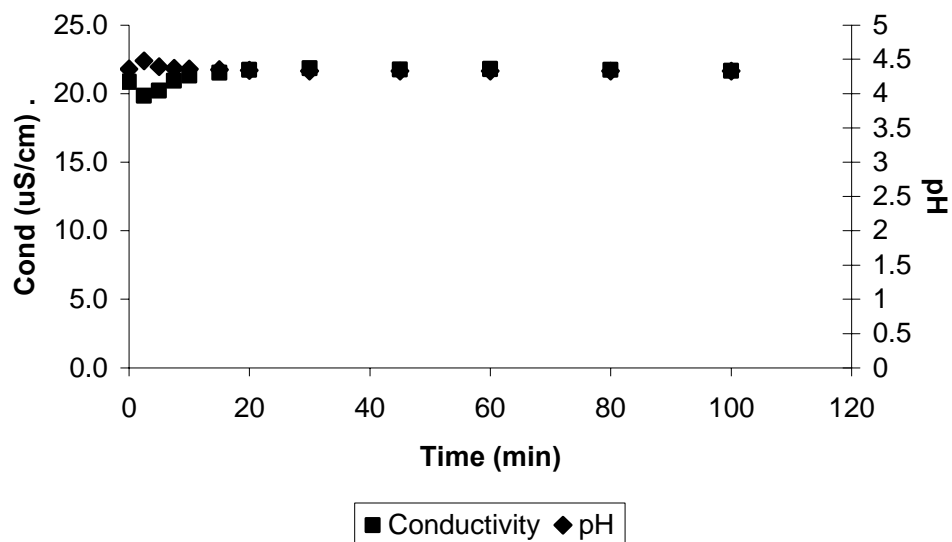


Figure 6.34 Experiment 13 pH and Conductivity Data; Influent pH = 4.21, Influent Conductivity = 24.83  $\mu\text{S}/\text{cm}$

### E13 - Concentrations - Main Run

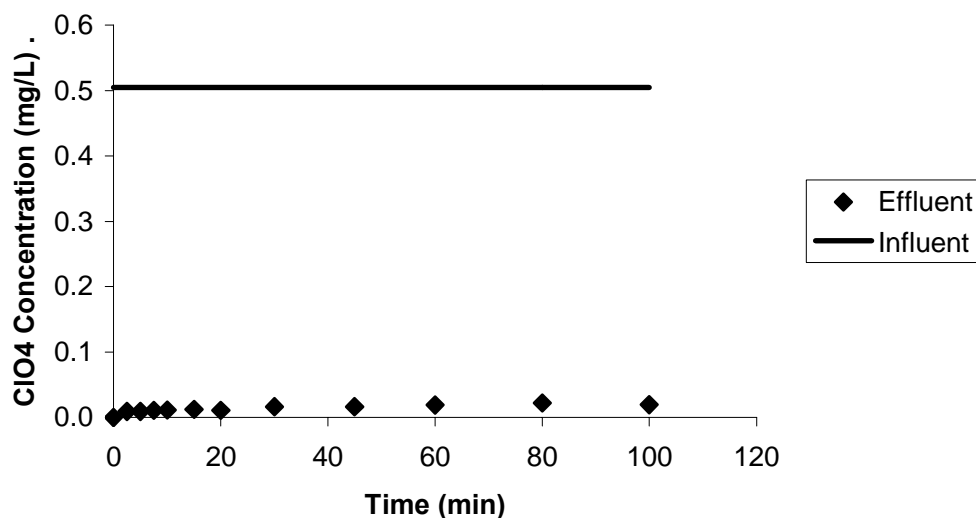


Figure 6.35 Experiment 13 Perchlorate Concentration Data (Main Run); Hydrogen Reductant ( $[\text{HCOOH}] = 0$ ), pH = 4.21, HRT = 3.21 min

<b>Experiment 13 Postflush Results:</b>								
[HCOOH] = 2mM, pH = 9.80, [ClO4] = 0								
Flow = 19.55 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E13-017	0	0.0122						
E13-018	2.5	0.3361	4.65	24.2	0.1742	2.5	0.01955	0.0085
E13-019	5	0.6732	5.68	87.23	0.5047	2.5	0.01955	0.0247
E13-020	7.5	0.784	5.96	127.1	0.7286	2.5	0.01955	0.0356
E13-021	10	0.8315	6.07	146.1	0.8078	2.5	0.01955	0.0395
E13-022	15	0.8318	6.17	164.9	0.8317	5	0.01955	0.0813
E13-023	20	0.7862	6.28	172.4	0.8090	5	0.01955	0.0791
E13-024	30	0.6815	6.38	190.2	0.7339	10	0.01955	0.1435
E13-025	45	0.5084	6.49	196.1	0.5950	15	0.01955	0.1745
E13-026	60	0.3694	6.55	200.5	0.4389	15	0.01955	0.1287
E13-027	75	0.2543	6.61	203.6	0.3119	15	0.01955	0.0915
Sum of Delta Mass-->								0.8067

**Table 6.26 Experiment 13 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E13 - Concentrations - Postflush

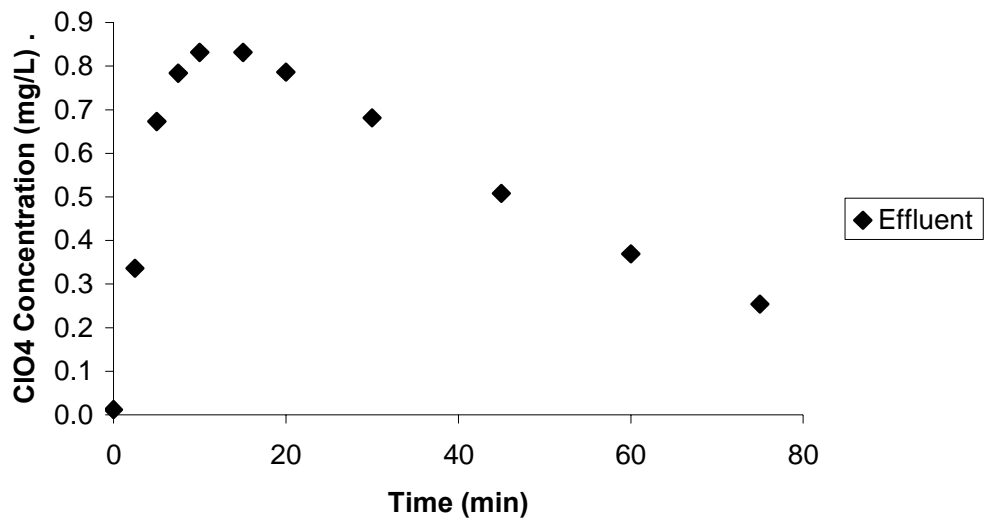


Figure 6.36 Experiment 13 Perchlorate Concentration Data (Post-Experiment Flush);  
[HCOOH] = 2mM, pH = 9.90, HRT = 2.95 min

### E13 - Postflush Exponential Trendline

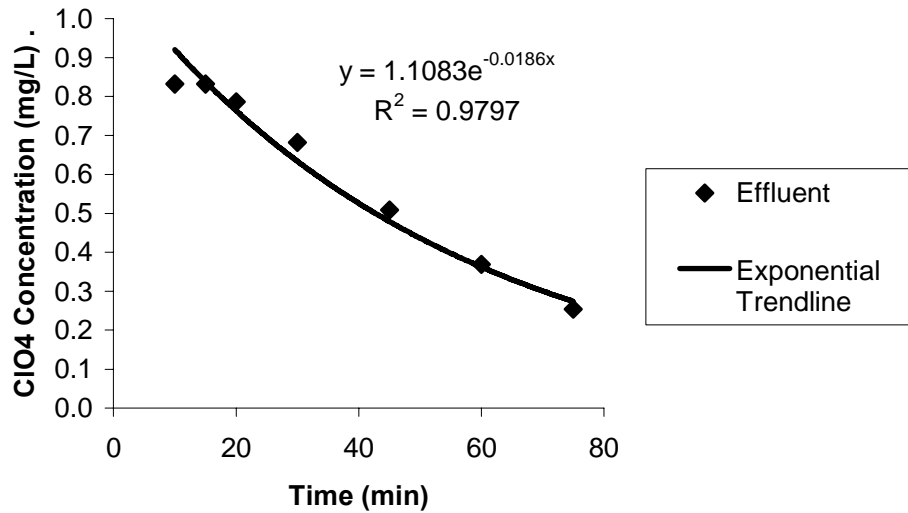


Figure 6.37 Experiment 13 Post-Experiment Flush Exponential Trendline

<b>Experiment 13: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5048	(mg/L)	
Flowrate:	0.018	(L/min)	
Duration:	100	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>0.9086</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.0298	(mg)	
Sum of Delta Mass from Postflush:	0.8067	(mg)	
Residual Mass in Tail*:	--	(mg)	
<b>Total Mass Out (sum):</b>	<b>0.8366</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>92.07%</b>		
* Residual mass was not calculated because trendline fit was poor ( $R^2 < 0.99$ )			

**Table 6.27 Experiment 13 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 14: (Chlorate Used as Substrate Instead of Perchlorate)</b>								
[HCOOH] = 10mM								
Source pH = 2.96 (no NaOH added)								
Target Chlorate Concentration: 1.0 mg/L								
Flowrate = 7.23 ml/min								
HRT = 7.98 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	Chlorate Conc (mg/L)	pH	Cond (uS/cm)				
E14-001	Before Exp	1.0324	2.96	563.4				
E14-002	Before Exp	1.0611	2.96	563.4				
E14-015	After Exp	1.0864	--	--				
E14-016	After Exp	1.1233	--	--				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	Chlorate Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E14-003	0	0.0018	4.33	58.19				
E14-004	5.67	0.0000			0.0009	5.67	0.00723	0.0000
E14-005	10	0.0079	4.33	59.52	0.0040	4.33	0.00723	0.0001
E14-006	15	0.0000	4.27	60.36	0.0040	5	0.00723	0.0001
E14-007	20	0.0051	4.2	67.75	0.0026	5	0.00723	0.0001
E14-008	30	0.0059	4.12	71.23	0.0055	10	0.00723	0.0004
E14-009	45	0.0147	4.07	83	0.0103	15	0.00723	0.0011
E14-010	60	0.0216	4.01	93.27	0.0182	15	0.00723	0.0020
E14-011	80	0.0263	3.95	102.6	0.0240	20	0.00723	0.0035
E14-012	100	0.0393	3.92	106.6	0.0328	20	0.00723	0.0047
E14-013	120	0.0499	3.85	116.2	0.0446	20	0.00723	0.0064
E14-014	180	0.1002	3.75	131.7	0.1002	60	0.00723	0.0435
Sum of Delta Mass-->								0.0620

**Table 6.28 Experiment 14 Results with Mass Balance Calculations (Main Run)**

### E14 - Effluent pH and Conductivity (Main Run)

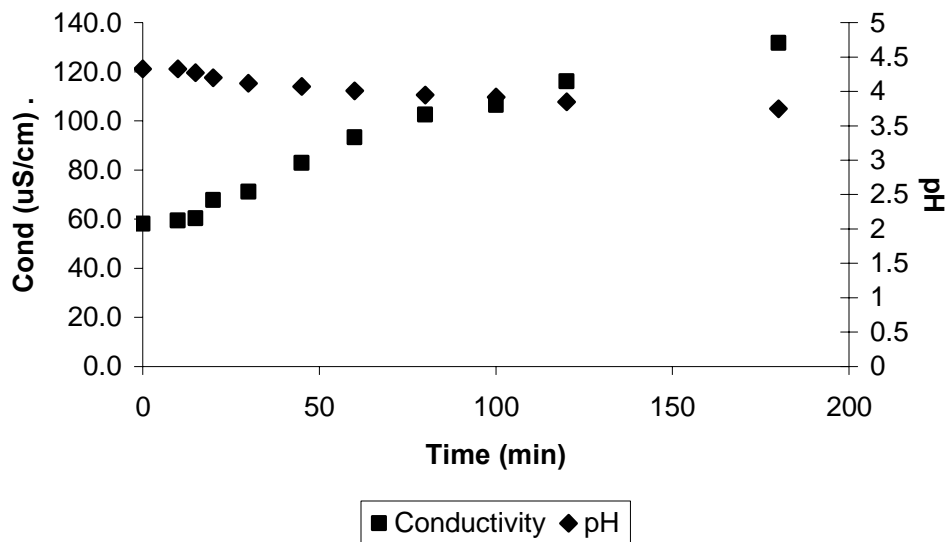


Figure 6.38 Experiment 14 pH and Conductivity Data;  
Influent pH = 2.96, Influent Conductivity = 563.4

### E14 - Chlorate Concentrations - Main Run

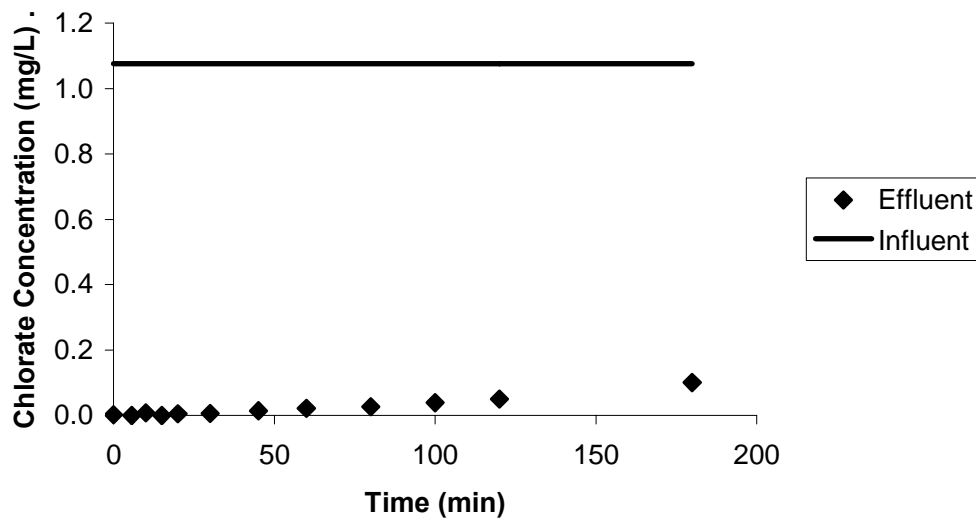


Figure 6.39 Experiment 14 Chlorate Concentration Data (Main Run);  
[HCOOH] = 10mM, pH = 2.96, HRT = 7.98 min



<b>Experiment 14 Postflush Results:</b>								
[HCOOH] = 10mM, pH = 10.55, [ClO4] = 0								
Flow = 19.36 ml/min								
Sample	Time (min)	Chlorate Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E14-017	0	0.1169						
E14-018	2.5	1.459	4.49	355.9	0.7880	2.499	0.01936	0.0381
E14-019	5	1.7308	5.19	799.8	1.5949	2.5	0.01936	0.0772
E14-020	7.5	1.6654	5.42	872.4	1.6981	2.5	0.01936	0.0822
E14-021	10	1.6149	5.51	894.9	1.6402	2.5	0.01936	0.0794
E14-022	15	1.3666	5.65	936.2	1.4908	5	0.01936	0.1443
E14-023	20	1.1705	5.73	963.3	1.2686	5	0.01936	0.1228
E14-024	30	0.7558	5.89	965.1	0.9632	10	0.01936	0.1865
E14-025	45	0.4648	6.06	973.4	0.6103	15	0.01936	0.1772
E14-026	60	0.2345	6.19	984.8	0.3497	15	0.01936	0.1015
Sum of Delta Mass-->								1.0092

**Table 6.29 Experiment 14 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E14 - Chlorate Concentrations - Postflush

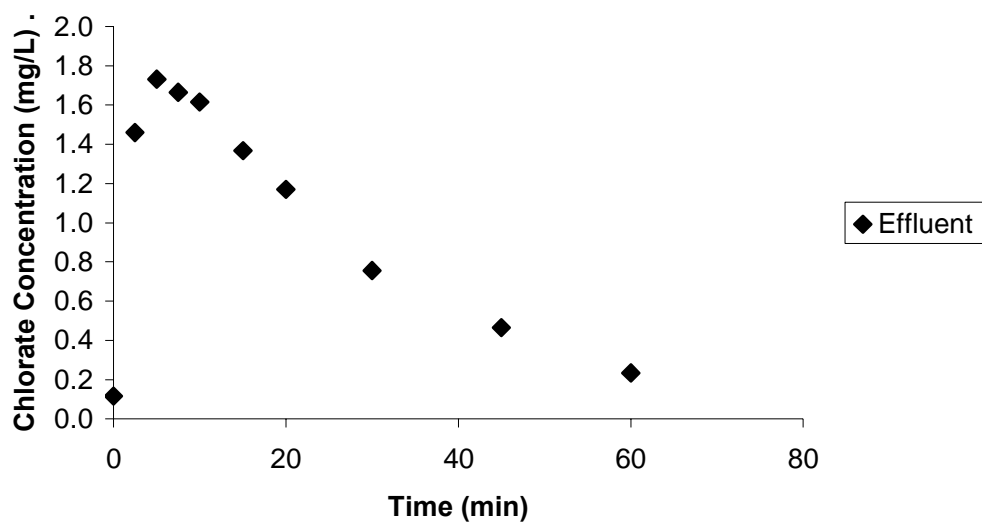


Figure 6.40 Experiment 14 Chlorate Concentration Data (Post-Experiment Flush);  
[HCOOH] = 10mM, pH = 10.55, HRT = 2.98 min

### E14 - Postflush Exponential Trendline

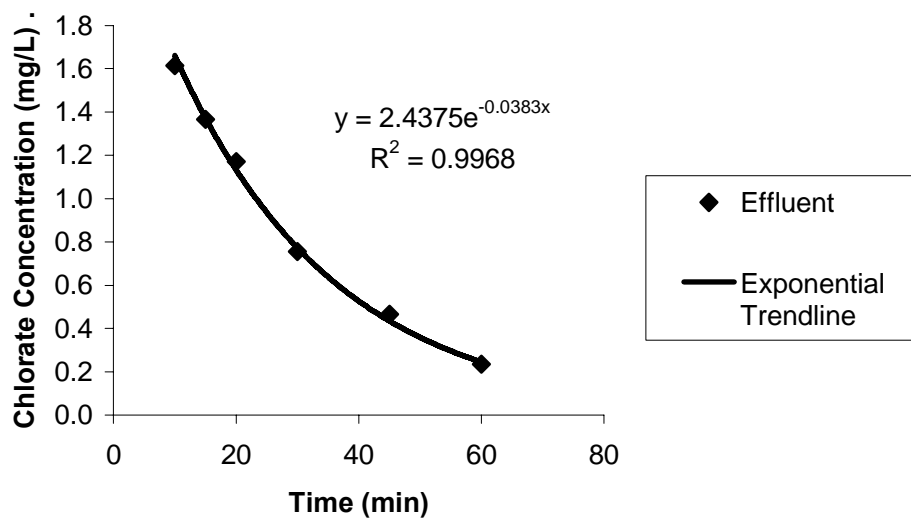


Figure 6.41 Experiment 14 Post-Experiment Flush Exponential Trendline

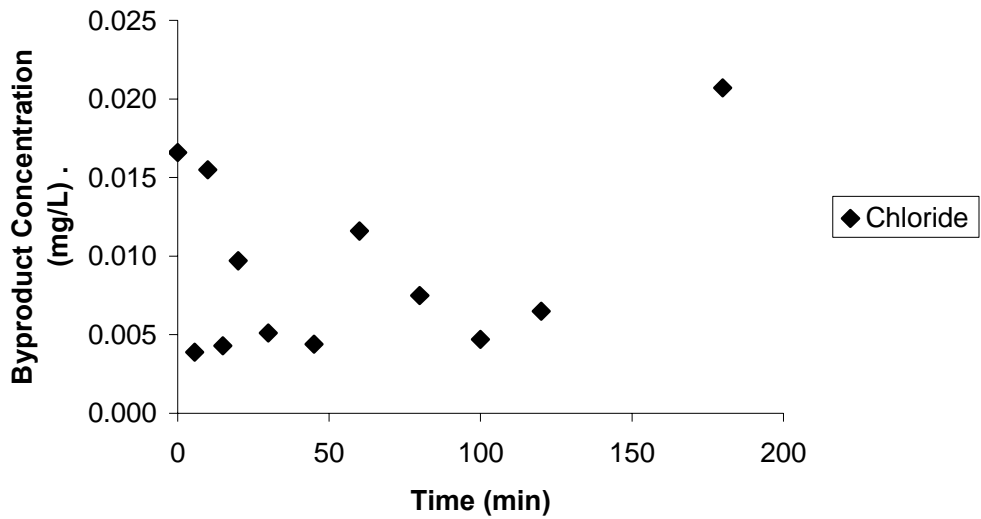
<b>Experiment 14: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	1.0758	(mg/L)	
Flowrate:	0.00723	(L/min)	
Duration:	180	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>1.4000</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.0620	(mg)	
Sum of Delta Mass from Postflush:	1.0092	(mg)	
Residual Mass in Tail*:	0.1238	(mg)	
<b>Total Mass Out (sum):</b>	<b>1.1950</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>85.35%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 60 to t = 400, then multiplying by postflush flowrate (0.01936 L/min)			

**Table 6.30 Experiment 14 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 14 Byproduct Analysis Results</b>				
(Main Experiment Only)				
Sample	Time (min)	Chlorate Conc (mg/L)	Chlorite Conc (mg/L)	Chloride Conc (mg/L)
E14-003	0	0.0018	0	0.0166
E14-004	5.67	0.0000	0	0.0039
E14-005	10	0.0079	0	0.0155
E14-006	15	0.0000	0	0.0043
E14-007	20	0.0051	0	0.0097
E14-008	30	0.0059	0	0.0051
E14-009	45	0.0147	0	0.0044
E14-010	60	0.0216	0	0.0116
E14-011	80	0.0263	0	0.0075
E14-012	100	0.0393	0	0.0047
E14-013	120	0.0499	0	0.0065
E14-014	180	0.1002	0	0.0207

**Table 6.31 Experiment 14 Byproduct Results (Main Run)**

**E14 - Byproduct Concentrations - Main Run**



**Figure 6.42 Experiment 14 Reduction Byproduct Concentration Data (Main Run)**

<b>Experiment 15: (Chlorate Used as Substrate Instead of Perchlorate)</b>								
[HCOOH] = 1mM								
Source pH = 3.47 (no NaOH added)								
Target Chlorate Concentration: 1.0 mg/L								
Flowrate = 7.51 ml/min								
HRT = 7.68 min (based on flow and pore volume of 57.7 mL)								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	Chlorate Conc (mg/L)	Chlorite Conc (mg/L)	Chloride Conc (mg/L)	pH	Cond (uS/cm)		
E15-001	Before Exp	0.9193	0	0.005	3.47	140.8		
E15-002	Before Exp	0.9224	0	0.004	3.47	140.8		
E15-015	After Exp	0.9582	0	0.005	--	--		
E15-016	After Exp	0.9601	0	~ 0.004	--	--		
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	Chlorate Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E15-003	0	0.0000	4.96	12.38				
E15-004	6	0.0000	4.94	12.34	0.0000	6	0.00751	0.0000
E15-005	10	0.0000	4.95	11.75	0.0000	4	0.00751	0.0000
E15-006	15	0.0000	4.93	11.56	0.0000	5	0.00751	0.0000
E15-007	20	0.0000	4.9	11.24	0.0000	5	0.00751	0.0000
E15-008	30	0.0000	4.9	11.02	0.0000	10	0.00751	0.0000
E15-009	45	0.0056	4.86	10.72	0.0028	15	0.00751	0.0003
E15-010	60	0.0000	4.9	10.6	0.0028	15	0.00751	0.0003
E15-011	80	0.0048	4.89	10.45	0.0024	20	0.00751	0.0004
E15-012	100	0.0059	4.9	10.44	0.0054	20	0.00751	0.0008
E15-013	120	0.0060	4.88	10.31	0.0060	20	0.00751	0.0009
E15-014	180	0.0106	4.88	10.17	0.0106	60	0.00751	0.0048
Sum of Delta Mass-->								0.0075

**Table 6.32 Experiment 15 Results with Mass Balance Calculations (Main Run)**

### E15 - Effluent pH and Conductivity (Main Run)

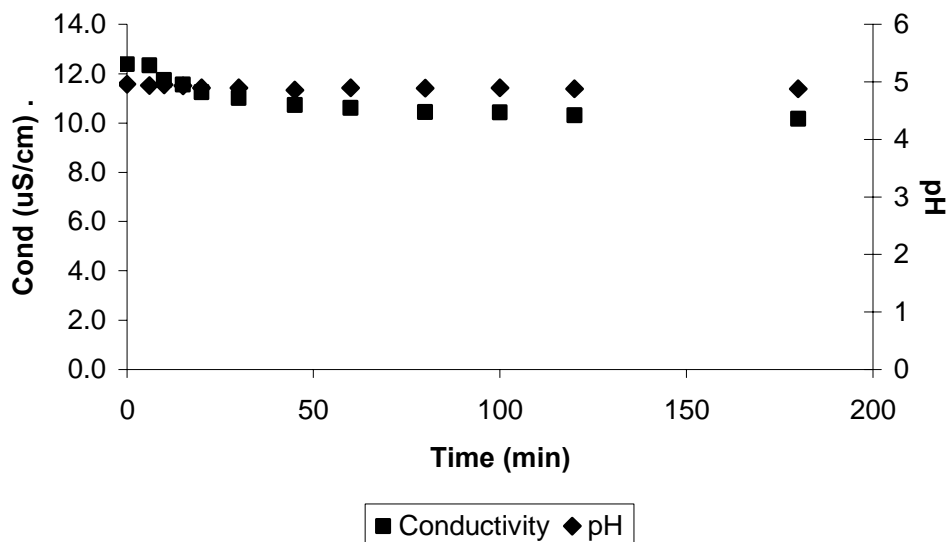


Figure 6.43 Experiment 15 pH and Conductivity Data; Influent pH = 3.47, Influent Conductivity = 140.8  $\mu$ S/cm

### E15 - Chlorate Concentrations - Main Run

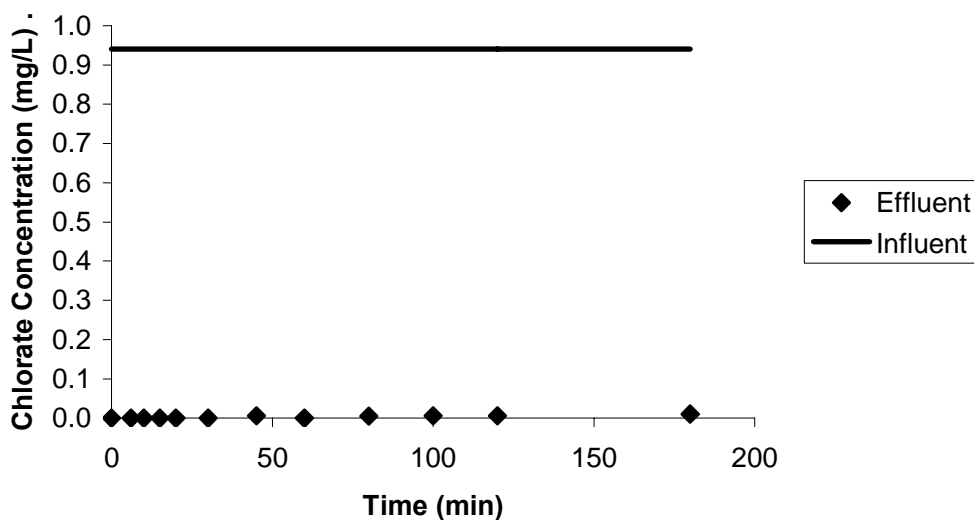


Figure 6.44 Experiment 15 Chlorate Concentration Data (Main Run); [HCOOH] = 10mM, pH = 2.96, HRT = 7.68 min

<b>Experiment 15 Postflush Results:</b>								
[HCOOH] = 2mM, pH = 10.38, [ClO3] = 0								
Flow = 19.48 ml/min								
Sample	Time (min)	Chlorate Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E15-017	0	0.007						
E15-018	2.5	0.7675	5.34	13.71	0.3873	2.5	0.01948	0.0189
E15-019	5	1.2179	6.15	127.2	0.9927	2.5	0.01948	0.0483
E15-020	7.5	1.2852	6.34	179.7	1.2516	2.5	0.01948	0.0610
E15-021	10	1.2546	6.41	197.2	1.2699	2.5	0.01948	0.0618
E15-022	15	1.1349	6.48	206.6	1.1948	5	0.01948	0.1164
E15-023	20	1.0091	6.55	216.3	1.0720	5	0.01948	0.1044
E15-024	30	0.8013	6.64	221.3	0.9052	10	0.01948	0.1763
E15-025	45	0.5755	6.74	222.3	0.6884	15	0.01948	0.2012
E15-026	60	0.4122	6.83	224.1	0.4939	15	0.01948	0.1443
E15-027	75	0.2963	6.86	224.5	0.3543	15	0.01948	0.1035
E15-028	90	0.2127	6.96	225.1	0.2545	15	0.01948	0.0744
Sum of Delta Mass-->								1.1104

**Table 6.33 Experiment 15 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E15 - Chlorate Concentrations - Postflush

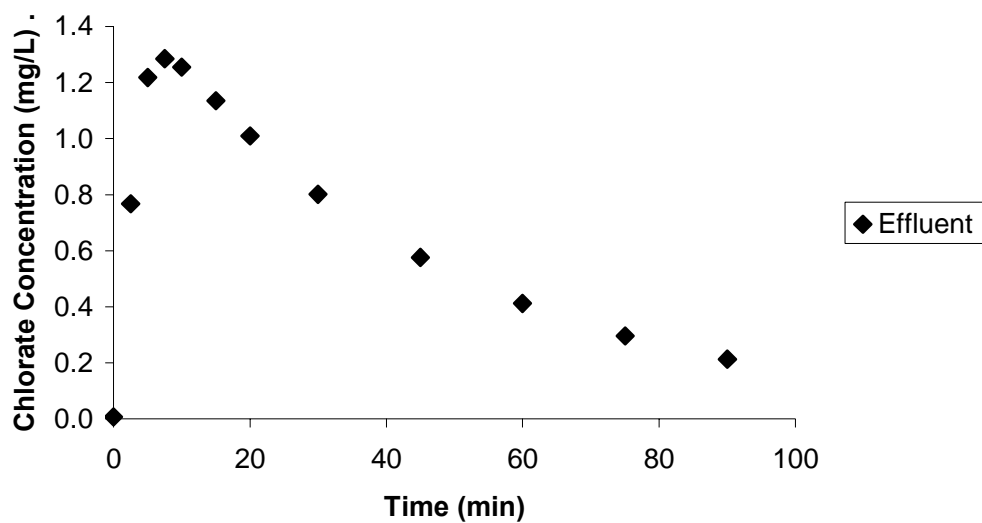


Figure 6.45 Experiment 15 Chlorate Concentration Data (Post-Experiment Flush);  
[HCOOH]= 2mM, pH = 10.38, HRT = 2.96 min

### E15 - Postflush Exponential Trendline

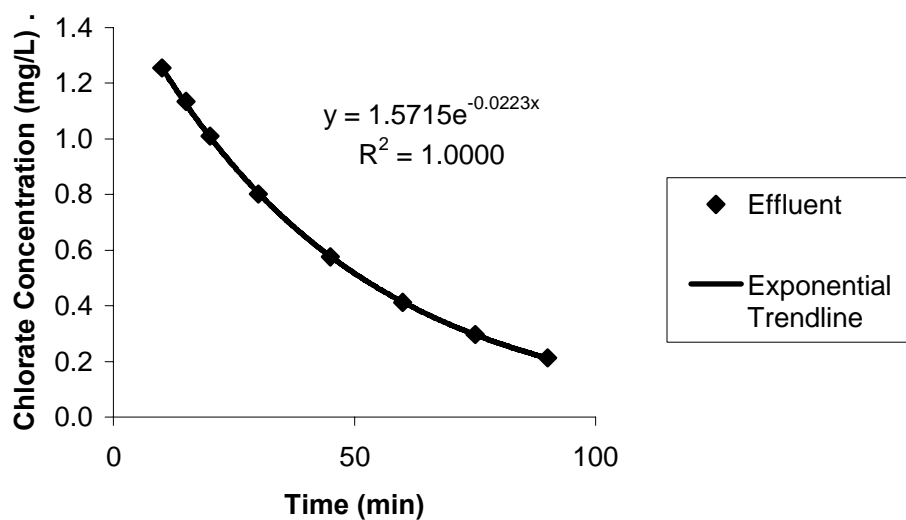


Figure 6.46 Experiment 15 Post-Experiment Flush Exponential Trendline



<b>Experiment 15: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.9400	(mg/L)	
Flowrate:	0.00751	(L/min)	
Duration:	180	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>1.2707</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.0075	(mg)	
Sum of Delta Mass from Postflush:	1.1104	(mg)	
Residual Mass in Tail*:	0.1843	(mg)	
<b>Total Mass Out (sum):</b>	<b>1.3022</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>102.48%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 90 to t = 400, then multiplying by postflush flowrate (0.01948 L/min)			

**Table 6.34 Experiment 15 Mass Recovery Percentage (MRP) Calculation**

<b>Experiment 15 Byproduct Analysis Results</b>				
(Main Experiment Only)				
<b>Sample</b>	<b>Time (min)</b>	<b>Chlorate Conc (mg/L)</b>	<b>Chlorite Conc (mg/L)</b>	<b>Chloride Conc (mg/L)</b>
E15-003	0	0.0000	0.0000	0.0000
E15-004	6	0.0000	0.0000	0.0000
E15-005	10	0.0000	0.0000	0.0000
E15-006	15	0.0000	0.0000	0.0000
E15-007	20	0.0000	0.0000	0.0000
E15-008	30	0.0000	0.0000	0.0000
E15-009	45	0.0056	0.0000	0.0000
E15-010	60	0.0000	0.0000	0.0000
E15-011	80	0.0048	0.0000	0.0000
E15-012	100	0.0059	0.0000	0.0000
E15-013	120	0.0060	0.0000	0.0000
E15-014	180	0.0106	0.0000	0.0000

**Table 6.35 Experiment 15 Byproduct Results (Main Run)**

<b>Experiment 16:</b>								
[HCOOH] = 10								
Source pH = 2.96 (no NaOH added)								
Target Perchlorate Concentration: 0.5 mg/L								
Flowrate = 19.11 ml/min								
HRT = 3.02 min (based on flow and pore volume of 57.7 mL)								
24 Hours between main run and postflush								
<b>Influent Results (Main Experiment):</b>								
Sample	Time	ClO4 Conc (mg/L)	pH	Cond (uS/cm)				
E16-001	Before Exp	0.5387	2.96	563.3				
E16-002	Before Exp	0.5229	2.96	563.3				
E16-016	After Exp	0.5345	--	--				
E16-017	After Exp	0.4975	--	--				
<b>Effluent Results (Main Experiment):</b>								
Sample	Time (min)	ClO4 Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E16-003	0	0.0000	3.62	131.6				
E16-004	2.5	0.0181	3.84	92.7	0.0091	2.5	0.01911	0.0004
E16-005	5	0.0128	3.68	105.7	0.0155	2.5	0.01911	0.0007
E16-006	7.5	0.0187	3.63	123.9	0.0158	2.5	0.01911	0.0008
E16-007	10	0.0206	3.63	124.3	0.0197	2.5	0.01911	0.0009
E16-008	15	0.0232	3.61	126.3	0.0219	5	0.01911	0.0021
E16-009	20	0.0310	3.59	140.0	0.0271	5	0.01911	0.0026
E16-010	30	0.0465	3.56	151.2	0.0388	10	0.01911	0.0074
E16-011	45	0.0712	3.53	161.9	0.0589	15	0.01911	0.0169
E16-012	60	0.0798	3.53	160.6	0.0755	15	0.01911	0.0216
E16-013	80	0.1136	3.50	174.2	0.0967	20	0.01911	0.0370
E16-014	100	0.1421	3.48	184.8	0.1279	20	0.01911	0.0489
E16-015	120	0.1844	3.45	192.4	0.1633	20	0.01911	0.0624
Sum of Delta Mass-->								0.2017

**Table 6.36 Experiment 16 Results with Mass Balance Calculations (Main Run)**

### E16 - Effluent pH and Conductivity (Main Run)

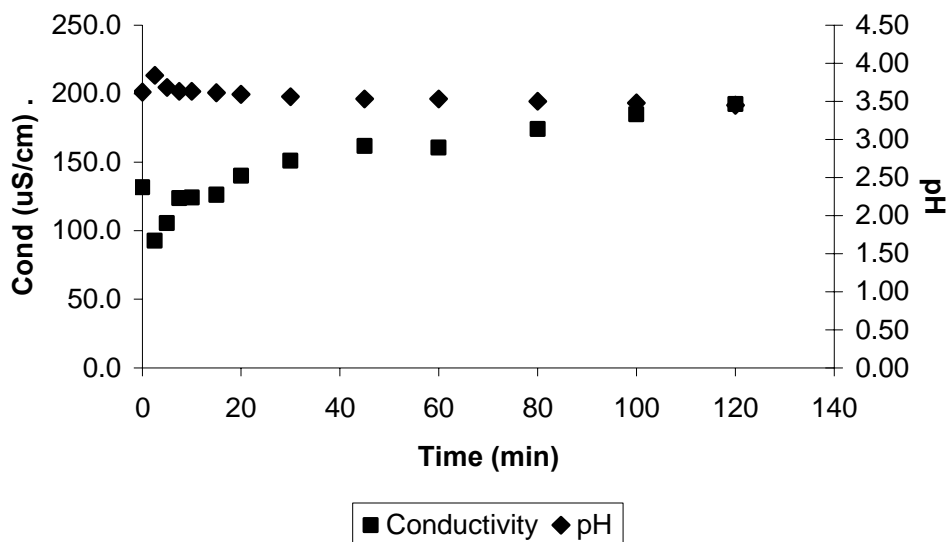


Figure 6.47 Experiment 16 pH and Conductivity Data; Influent pH = 2.96, Influent Conductivity = 563.3  $\mu$ S/cm

### E16 - Concentrations - Main Run

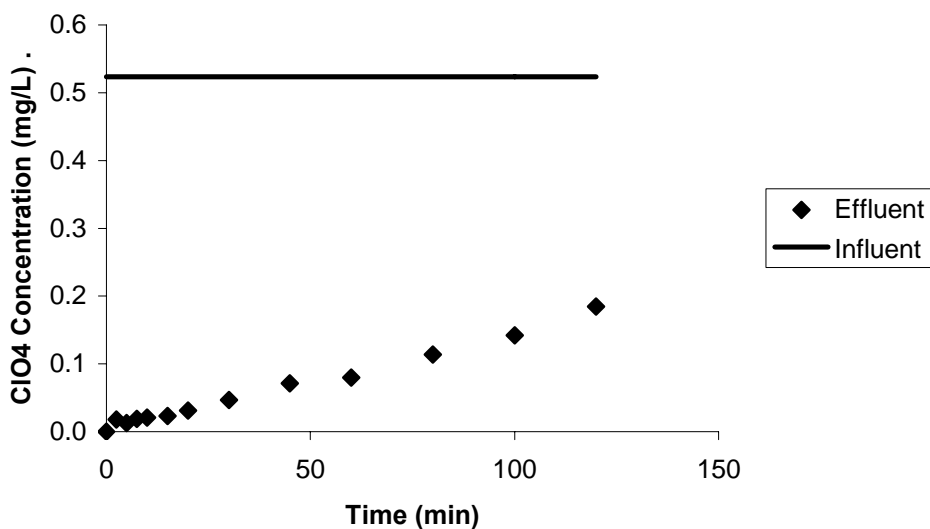


Figure 6.48 Experiment 16 Perchlorate Concentration Data (Main Run); [HCOOH] = 10mM, pH = 2.96, HRT = 3.02 min

<b>Experiment 16 Postflush Results:</b>								
[HCOOH] = 2mM, pH = 9.24, [ClO <sub>4</sub> ] = 0, 24 hours after main run								
Flow = 18.81 ml/min								
Sample	Time (min)	Perc Conc (mg/L)	pH	Cond (uS/cm)	Avg Conc (mg/L)	Delta T (min)	Flow (L/min)	Delta Mass (mg)
E16-020	0	0.1208						
E16-021	2.5	0.6645	5.37	78.0	0.3927	2.5	0.01881	0.0185
E16-022	5	0.7900	5.43	145.2	0.7273	2.5	0.01881	0.0342
E16-023	7.5	0.8030	5.55	173.1	0.7965	2.5	0.01881	0.0375
E16-024	10	0.7858	5.62	180.9	0.7944	2.5	0.01881	0.0374
E16-025	15	0.7228	5.71	186.4	0.7543	5	0.01881	0.0709
E16-026	20	0.6676	5.81	189.1	0.6952	5	0.01881	0.0654
E16-027	30	0.5562	5.88	192.9	0.6119	10	0.01881	0.1151
E16-028	45	0.4185	5.99	194.1	0.4874	15	0.01881	0.1375
E16-029	60	0.3139	6.13	194.9	0.3662	15	0.01881	0.1033
E16-030	75	0.2295	6.14	195.1	0.2717	15	0.01881	0.0767
E16-031	90	0.1709	6.23	195.5	0.2002	15	0.01881	0.0565
Sum of Delta Mass-->								0.7529

**Table 6.37 Experiment 16 Results with Mass Balance Calculations (Post-Experiment Flush)**

### E16 - Concentrations - Postflush

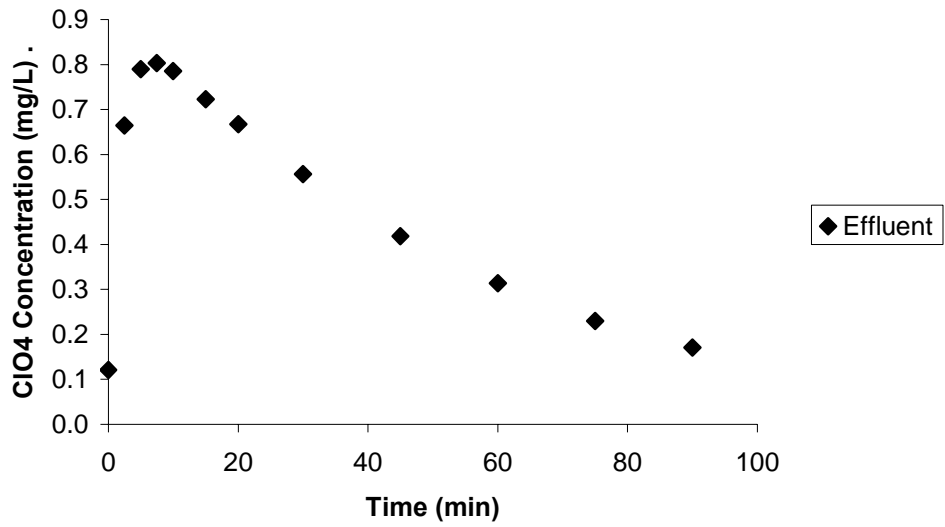


Figure 6.49 Experiment 16 Perchlorate Concentration Data (Post-Experiment Flush);  
[HCOOH] = 2mM, pH = 9.24, HRT = 3.07 min

### E16 - Postflush Exponential Trendline

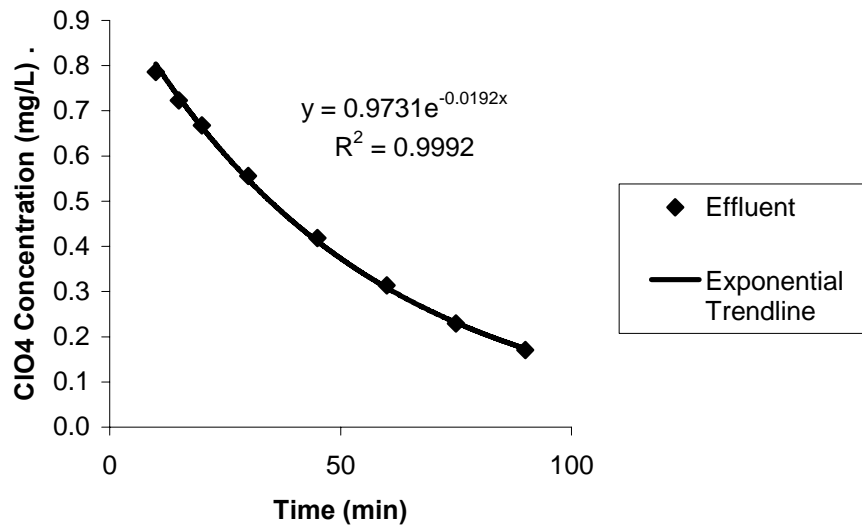


Figure 6.50 Experiment 16 Post-Experiment Flush Exponential Trendline

<b>Experiment 16: MRP Calculation</b>			
<b>Mass In:</b>			
Avg Influent Conc:	0.5234	(mg/L)	
Flowrate:	0.01911	(L/min)	
Duration:	120	(min)	
Total Mass In = (A.I.C)(Flow)(Duration)			
<b>Total Mass In =</b>	<b>1.2003</b>	<b>(mg)</b>	
<b>Mass Out:</b>			
Sum of Delta Mass from Main Exp:	0.2017	(mg)	
Sum of Delta Mass from Postflush:	0.7529	(mg)	
Residual Mass in Tail*:	0.1689	(mg)	
<b>Total Mass Out (sum):</b>	<b>1.1235</b>	<b>(mg)</b>	
<b>MRP</b>	$MRP = (\text{Mass Out})/(\text{Mass In}) \times 100$		
<b>MRP =</b>	<b>93.60%</b>		
* Residual mass calculated by integrating postflush trendline equation from t = 90 to t = 400, then multiplying by postflush flowrate (0.01881 L/min)			

**Table 6.38 Experiment 16 Mass Recovery Percentage (MRP) Calculation**

## 6.2 Appendix B: Feedstock Preparation Calculations (Example)

---

In this section, the desired feedstock properties are entered:

---

Solution Volume (L):  $V := 4$

Desired Formic Acid conc (mol/L):  $C := 0.010$

Desired perchlorate conc (mg/L):  $C_{\text{perc}} := 0.5$

Perc Stock Conc (mg/L)  
(for liquid cal std)  $C_{\text{perc\_stock}} := 994$

Desired pH:  $\text{pH} := 4$

Concentration of NaOH solution:  $C_{\text{NaOH}} := 2 \frac{\text{mol}}{\text{L}}$

---

This section will calculate the volume of 88% formic acid required to achieve target FA conc:

---

Total HCOOH (mol):  $\text{TOT}_{\text{form}} := V \cdot C$

$$\text{TOT}_{\text{form}} = 0.04 \quad (\text{mol})$$

$$\text{MW}_{\text{HCOOH}} := 46.03 \quad (\text{g/mol})$$

$$\text{Mass}_{\text{HCOOH}} := \text{TOT}_{\text{form}} \cdot \text{MW}_{\text{HCOOH}}$$

$$\text{Mass}_{\text{HCOOH}} = 1.841 \quad (\text{grams})$$

$$\text{Mass}_{\text{FA\_soln}} := \frac{\text{Mass}_{\text{HCOOH}}}{.88}$$

$$\text{Mass}_{\text{FA\_soln}} = 2.092 \quad (\text{grams})$$

$$\text{Density}_{\text{FA\_soln}} := 1.2 \quad (\text{g/mL})$$

$$\text{Volume}_{\text{FA\_soln}} := \frac{\text{Mass}_{\text{FA\_soln}}}{\text{Density}_{\text{FA\_soln}}}$$

$$\text{Volume}_{\text{FA\_soln}} = 1.744$$



---

This section calculates the sodium hydroxide volume required to achieve desired pH  
(takes formate concentration into account by incorporating charge balance)

---

Convert desired pH to [H], [OH]:

$$H := 10^{-\text{pH}}$$

$$H = 1 \times 10^{-4}$$

$$\text{OH} := \frac{10^{-14}}{H}$$

$$\text{OH} = 1 \times 10^{-10}$$

Formate speciation calculations:

$$k_a := 1.7 \cdot 10^{-4} \quad (\text{formic acid})$$

$$\alpha_0 := \frac{H}{k_a + H} \quad \alpha_0 = 0.37$$

$$\alpha_1 := \frac{k_a}{k_a + H} \quad \alpha_1 = 0.63$$

$$\text{HCOOH} := \alpha_0 \cdot \text{TOT}_{\text{form}} \quad \text{HCOOH} = 0.015$$

$$\text{COOH} := \alpha_1 \cdot \text{TOT}_{\text{form}} \quad \text{COOH} = 0.025$$

Determine Na concentration that will satisfy charge balance for given Formate, pH

Overall charge balance:  $H + \text{Na} = \text{OH} + \text{COOH}$

Guess Na concentration:  $\text{Na} := 1$

Use Mathcad "Find" function to solve for required Na Concentration:

Given

$$\text{Na} = \text{OH} + \text{COOH} - H$$

$$\text{Na}_{\text{solution}} := \text{Find}(\text{Na})$$

$$\text{Na}_{\text{solution}} = 0.02509$$

Feedstock Preparation Calculations (cont.)
--

Calculate volume of stock sodium hydroxide solution required

Moles of NaOH required:  $\text{Mol}_{\text{NaOH}} := \text{Na}_{\text{solution}} \cdot \text{mol}$

$$\text{Mol}_{\text{NaOH}} = 0.02509 \text{ mol}$$

Concentration of NaOH solution  $C_{\text{NaOH}} = 2 \frac{\text{mol}}{\text{L}}$

Volume of NaOH solution required  $V_{\text{NaOH}} := \frac{\text{Mol}_{\text{NaOH}}}{C_{\text{NaOH}}}$

$$V_{\text{NaOH}} = 0.013 \text{ L}$$

$$V_{\text{NaOH}} = 12.543 \text{ mL}$$

---

This section will calculate the amount of (solid) sodium perchlorate salt required to achieve the desired perchlorate concentration

---

Desired ClO4 conc (mg/L)  $C_{\text{perc}} = 0.5$

Required ClO4 Mass (mg):  $\text{Mass}_{\text{perc}} := C_{\text{perc}} \cdot V$

$$\text{Mass}_{\text{perc}} = 2$$

Convert to sodium perc mass:  $\text{Mass}_{\text{sod\_perc}} := \text{Mass}_{\text{perc}} \cdot \left(\frac{1}{99.5}\right) \left(\frac{140.46}{1}\right)$  <--(molar conversion)

$$\text{Mass}_{\text{sod\_perc}} = 2.8233 \text{ (milligrams)}$$

---

This section will calculate the amount of (liquid) perchlorate calibration standard Required to achieve desired perchlorate concentration

---

Desired perchlorate feed concentration (mg/L):  $C_{\text{perc}} = 0.5$

Stock standard concentration (mg/L):  $C_{\text{perc\_stock}} = 994$

Calculate volume of stock required:

$$V_{\text{stock}} := \frac{C_{\text{perc}} \cdot V}{C_{\text{perc\_stock}}} \cdot L$$

$$V_{\text{stock}} = 2.012 \text{ mL}$$

---

**Data Summary:**

**INPUT**

Solution Volume (L):  $V = 4$

Formate conc (mol/L):  $C = 0.01$

Desired perchlorate conc (mg/L):  $C_{\text{perc}} = 0.5$

Desired pH:  $\text{pH} = 4$

Concentration of NaOH:  $C_{\text{NaOH}} = 2 \frac{\text{mol}}{\text{L}}$

**OUTPUT**

Required Formic Acid (mL):  $\text{Volume}_{\text{FA\_soln}} = 1.744$

Required NaOH:  $V_{\text{NaOH}} = 12.543 \text{ mL}$

Required sodium perchlorate (mg):  $\text{Mass}_{\text{sod\_perc}} = 2.823$

(or)

Required liquid perc stock:  $V_{\text{stock}} = 2.012 \text{ mL}$

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## Vita

Captain Eric G. Barney graduated from Kearney High School in Kearney, Nebraska. He entered undergraduate studies at the University of Nebraska in Lincoln, Nebraska where he graduated with a Bachelor of Science degree in Chemical Engineering in May 1997. In 1998, he received a Direct Commission to the Air Force Medical Service.

His first assignment was at Keesler AFB, MS where he was assigned to the 81<sup>st</sup> Aerospace Medicine Squadron, supervising environmental protection programs for the Bioenvironmental Engineering Flight. In 2001, he was assigned to the 52<sup>nd</sup> Aerospace Medicine Squadron at Spangdahlem AB, Germany. At Spangdahlem, he led the Environmental Protection Element of the Bioenvironmental Engineering Flight and also led the 52<sup>nd</sup> Medical Group's Nuclear/Biological/Chemical mobility team. In August 2003, he entered the Graduate Environmental Engineering and Science program of the Graduate School of Engineering and Management, Air Force Institute of Technology. Upon graduation, he will be assigned to Detachment 3, Air Force Institute for Operational Health, Kadena AB, Japan.

