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Comparison of Zero Valent Iron (ZVI) and ZVI+Sludge for the Removal of High Levels of Hexavalent Chromium and Chlorate from Waters

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COMPARISON OF ZERO VALENT IRON (ZVI) AND ZVI+SLUDGE FOR THE REMOVAL OF HIGH LEVELS OF HEXAVALENT CHROMIUM AND CHLORATE FROM WATERS

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Abstract

Remediation of contaminated groundwater is becoming increasingly more important as much of the U.S. population relies on groundwater for their drinking water. Contaminates such as Chromium, common pollutant at industrial waste sites, and Hexavalent chromium which is toxic to humans, animals, and plants are major concerns. Chlorate, another contaminate of concern, has been widely detected in ground and surface water in the United States and even locally in Henderson Nevada at the Nevada Environmental Response Trust (NERT) sites. To assist in mitigating this issue, this research focuses on the removal of high levels of hexavalent chromium (ppm range) (Cr(VI)) and chlorate (ClO_3^-) from water using zero valent iron (ZVI).

Zero valent iron is a proven technology for the biotic and abiotic reduction of a wide variety of environmental contaminants including Cr(VI), nitrate (NO_3^-), chlorinated organic compounds, arsenic, ClO_3^-, and ClO_4^-. There is a lack of research investigating the reduction of Cr(VI) using ZVI+Sludge, specifically examining how competing contaminants, such as chlorate, would affect Cr(VI) remediation. The overall goal of this research was to determine whether a combination of ZVI+Sludge can improve reduction kinetics of degradation of high levels of Cr(VI) and chlorate, when they occur together.

A series of batch tests were conducted in which a synthetic groundwater, containing the contaminants of interest, was added with various concentrations of ZVI, microbial seed, and an external carbon source (i.e. EOS emulsified oil). Depending on the method to be tested, varying concentrations of ZVI, Sludge, or a combination of ZVI+Sludge were added to the vials. Degradation experiments were performed first with single contaminants followed with the contaminants together. The analysis of the experiments related to ZVI+Sludge showed a statistically significant increase in the reduction of Cr(VI) alone over ZVI. The outcome of this research suggests an increase in contaminant reduction rates when combining chemical and biological treatment (ZVI+Sludge). Supporting the conclusion that a ZVI+Sludge treatment method could reduce the amount of ZVI material required and/or increase the longevity of the system.

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Chapter 1: Problem Statement

This research focuses on the removal of high levels of hexavalent chromium (Cr(VI)) (ppm range) and chlorate (ClO_3^-) from water using zero valent iron (ZVI). Reduction of both contaminants using ZVI alone (i.e. abiotic reduction) and ZVI augmented with biological reduction (ZVI+Sludge) are evaluated.

Chromium is one of the most abundant heavy metals in the earth's crust (0.014%) and is extensively used throughout society (Mitra, et al., 2011). Anthropogenic Cr(VI) is a result of petroleum refining, metallurgy, battery, textile, leather tanning, and electroplating industries (Yang, et al., 2015; Fu, et al., 2014). Additionally, chromium is extensively used as a corrosion inhibitor to prevent the corrosion of steel under wet conditions (ATSDR, 2018). Although Cr(VI) may occur naturally, a majority of the Cr(VI) found in soil and groundwater is due to anthropogenic activities (Di Palma, et al., 2015). Cr(VI) is very toxic, highly soluble at any pH, and mobile in soils. Because of this, chromium is highly regulated by the U.S. EPA with a drinking water standard of 0.100 mg/L (100 ppb) for total chromium (Li, et al., 2008). Current methods for the remediation of Cr(VI) include ion-exchange (IX) (Demiral, et al., 2008), adsorption, RO (Mitra, et al., 2011), and chemical reduction (Gheju, 2011).

Sodium Chlorate is one of the most widely used chemicals globally with some of the largest producers located in Canada and the United States (Mannsville Chemical Products, 2006; USDA, 2000; Alfredo, et al., 2015). It is widely used to produce chlorine dioxide to bleach paper products as well as for disinfection in drinking water treatment (WHO, 2005; U.S. EPA, 2016). The co-occurrence of chlorate and Cr(VI) as contaminants is common in the paper industry where Cr(VI) salts are used as anticorrosion agents. As with Cr(VI), ClO_3^- groundwater is primarily a result of anthropogenic activities. Chlorate is toxic both through ingestion and inhalation and is fatal at doses greater than 100 mg/kg (Alfredo, et al., 2015). Lower concentrations of ClO_3^- can result in renal failure, gastrointestinal irritation and hemoglobinuria (U.S. EPA, 2016; WHO, 2005). Chlorate has been added to the Third Chemical Contaminant List in 2010, but there is no current Federal regulation for the contaminant (U.S. EPA, 2016).

ZVI is a proven technology for the chemical reduction of toxic Cr(VI) to its less soluble form of Cr(III) (Fu, et al., 2014). The reaction between iron and water promotes the formation of dissolved hydrogen (H_2) (Equations 1-1 and 1-2) that is used to reduce Cr(VI) abiotically (Zhang, et al., 2017). Both Cr(VI) and chlorate can be degraded biologically because they are used as electron acceptors by bacteria, if a carbon source and an electron donor is provided. In the biotic reduction of contaminants using ZVI (ZVI+Sludge), microorganisms will utilize the hydrogen that is generated from the corrosion of the iron (ZVI) and water as an electron donor to degrade the contaminants (You, et al., 2017) .

Equation 1-1: Anaerobic iron corrosion, Fe^0 to Fe^{2+} (Gheju, 2011; Ponder, et al., 2000; Xu, et al., 2017)

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad (E^0 = -0.39V)$$

Equation 1-2: Anaerobic iron corrosion, Fe^{2+} to Fe^{3+} (Gheju, 2011)

$$2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Fe^{3+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad (E^0 = -1.60)$$

Current research has demonstrated that ZVI is capable of successfully reducing other contaminants including nitrate (NO_3^-), chlorinated organic compounds, arsenic, and chlorate (ClO_3^-) (Fu, et al., 2014), however, there has been little to no research into the reduction of Cr(VI) using ZVI or ZVI+Sludge in the presence of competing co-contaminants, such as chlorate. Scott, et al., (2011) pointed out that research on single contaminants could result in the overestimation for the removal of contaminants in actual applications. Multiple contaminants are more indicative of an actual contaminated groundwater.

It has been demonstrated that ClO_3^- and Cr(VI) can be degraded by bacteria (Guoxiang, et al., 2017; Brundrett, et al., 2015). For both in-situ and ex-situ remediation of contaminated groundwater, biological reduction is an appealing alternative to other technologies currently used for Cr(VI) and chlorate removal, such as ion exchange (IX), and membrane filtration (Zhu, et al., 2016). Biological reduction can also be utilized in concert with abiotic reductants such as that of ZVI (Son, et al., 2006). Although perchlorate (ClO_4^-) is thermodynamically reducible by ZVI, studies have shown that the reaction is slow (Son, et al., 2006) and the kinetics can be improved by ZVI+Sludge.

There have only been a few studies investigating the reduction of Cr(VI) using ZVI+Sludge. However, not one of the articles examined how competing contaminants, such as chlorate, would affect Cr(VI) remediation. This research will investigate the effectiveness of ZVI+Sludge as a treatment technology to remove Cr(VI) in the presence of chlorate. The primary question that this research will examine is whether ZVI alone or ZVI+Sludge can degrade high levels of hexavalent chromium in the presences of chlorate.

The overall goal of this research is to determine whether the combination of ZVI+Sludge can improve reduction kinetics of degradation of high levels of Cr(VI) and chlorate, when they occur together. The specific objectives of this research are: (1) To determine if ZVI alone degrade high levels of Cr(VI) and ClO_3^- at reasonable rates, (2) To investigate if when both Cr(VI) and ClO_3^- are present, if the reduction rates are impacted by the presence of the other contaminant, and (3) to evaluate whether ZVI+Sludge is more effective than ZVI alone for the reduction of Cr(VI) and ClO_3^-.

Chapter 2: Literature Review

Remediation of contaminated groundwater is becoming increasingly important because a majority of the U.S. population relies on groundwater for their drinking water (Karn, et al., 2009). Karn, et al. (2009) noted that there are hundreds of thousands of contaminated sites with varying degrees of contamination within the United States. In 1980 the U.S. Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The Environmental Protection Agency (EPA) utilized CERCLA to create a Superfund Program with a goal of protecting human health and the environment from the risks posed by hazardous waste sites. The EPA (2017) stated that within the United States more than 1,300 sites have been polluted to the extent that they have been designated as Superfund sites with the most serious sites being added to the National Priorities List (NPL). Karn et al., (2009) points out that of the sites that have been designated on the NPL list, more than 80% have contaminated groundwater. Hexavalent chromium (Cr(VI)) contamination in many areas of the world is becoming increasingly severe. Industrial and urban activities have resulted in elevated concentrations of Cr(VI) along with a wide range of other contaminants in soils and groundwater (Fu, et al., 2014). One such co-contaminant of concern is chlorate, ClO_3^-. Chlorate is often used to produce chlorine dioxide, which is utilized as a bleaching agent in the paper and pulp industry as well as the disinfection of drinking water (WHO, 2005; U.S. EPA, 2016). The industrial production of chlorate is typically performed by electrolysis (Zarei & Ghavi, 2016). Chromium is frequently used for its anti-corrosive properties and therefore often associated with electrolysis (Gheju, 2011). Other sources where chromium and chlorate are found as co-contaminants include manufacturers of perchlorate, such as at the Nevada Environmental Response Trust (NERT) site in Henderson, Nevada.

For decades, contaminated water was either pumped from the ground and treated off-site or permanently moved to another location for storage (Palmer & Wittbrodt, 1991). Contaminants often migrate with groundwater making it difficult to remediate (Hashim, et al., 2011). Newer methods of treating contaminated groundwater involve treating the contaminants on-site at the source of the pollution. These in-situ and ex-situ methods of remediation are further discussed in Section 2.3.

2.1 Hexavalent Chromium and Chlorate Contamination

2.1.1 Hexavalent Chromium [Cr(VI)]

Chromium is one of the most abundant heavy metals on earth at 122 ppm in the earth’s crust (Mitra, et al., 2011; Allwood, et al., 1998). Chromium often occurs in combination with a wide range of other elements, such as chromite ($FeCr_2O_3$) and magnesiochromite ($MgCr_2O_4$) (National Institutes of Health, 2018) (Mitra, et al., 2011). Nearly 95% of the world’s chromium resources are concentrated in Kazakhstan and southern Africa (USGS, 2017). USGS (2017) estimates that in the U.S. has a reserve of 6.2 million tons of shipping-grade ore.

Chromium for industrial use can be divided into three categories: 1) metallurgical (i.e., stainless steels and metal alloys), 2) refractory (i.e., heat resistant bricks and linings), and most commonly 3) chemical. The chemical applications of chromium include, but are not limited to, electroplating, leather tanning industries, textile dying, paint pigments, finishing of metals/plastics & leather (Agrawal, et al., 2006; ATSDR,

2018) Additionally, chromium is extensively used as a corrosion inhibitor to prevent the corrosion of steel under wet conditions (ATSDR, 2018).

Chromium is a common pollutant at industrial waste sites and exists in multiple oxidation states (Saha, et al., 2011). It is typically most stable in one of two oxidation states, hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] (Di Palma, et al., 2015; O'Carroll, et al., 2013; Li, et al., 1999). Cr(III) forms relatively insoluble oxide and hydroxide compounds and is insoluble at pH values greater than five, see Figure 2-1 (O'Carroll, et al., 2013; Chrysochoou, et al., 2012). Cr(VI) is very toxic, highly soluble at any pH, and extremely mobile in soils (Li, et al., 1999). Table 2-1 lists the properties of a few Cr(VI) compounds. Cr(VI) exists as chromate (CrO_4^{2-} or $HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) (Di Palma, et al., 2015; Gheju, 2011; Kotas & Stasicka, 2000; Saha, et al., 2011).

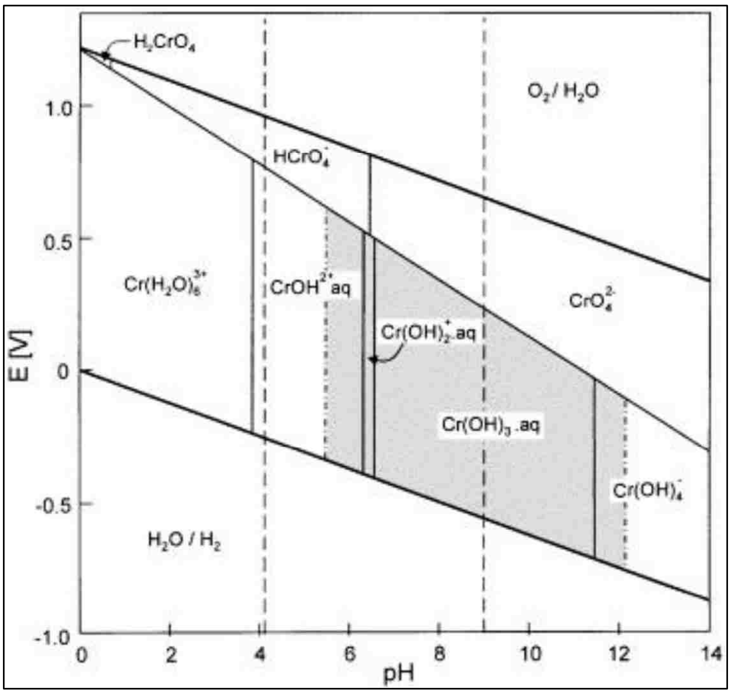


Figure 2-1: Pourbaix diagram of chromium species (Kotas & Stasicka, 2000)

Table 2-1: Physical and chemical properties of Cr(VI)

Property	Data	Reference
Chemical formula	Cr(VI)	
Synonyms	Chromium VI, Chromium Six, Chrome 6, Cr^{6+}	Pubchem (2018)
Molecular weight	51.9961 g/mol (calculated)	
Color/physical state *Sodium Chromate* (Na_2CrO_4) *Potassium Dichromate* ($K_2Cr_2O_7$)	Yellow crystalline solid Orange-red triclinic crystals	Pubchem (2018)
Melting point (°C) *Sodium Chromate* *Potassium Dichromate*	794°C 398°C	
Specific gravity (g/cm^3) *Sodium Chromate* *Potassium Dichromate*	2.7 2.7	
Solubility in water *Sodium Chromate* *Potassium Dichromate*	873 g/L @ 30°C 45 g/L @ 25°C	
Redox potential	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ ($E^0 = 1.33$ V) $CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$ ($E^0 = -0.12$ V)	Saha et al. (2011)

Naturally occurring Cr(VI) is the oxidation product of Cr(III) with atmospheric oxygen. Although hexavalent chromium may occur naturally, Table 2-2, a majority of the Cr(VI) found in soil and groundwater is due to anthropogenic activities (Di Palma, et al., 2015; Nemecek, et al., 2014). Anthropogenic Cr(VI) is a result of petroleum refining, metallurgy, battery, textile, leather tanning, and electroplating industries (Yang, et al., 2015; Fu, et al., 2014; Agrawal, et al., 2006). Hexavalent chromium has been released into the environment both accidentally and intentionally resulting in chromium becoming increasingly detected in both soil and groundwater, making it one of the top 20 contaminants on the Superfund priority list of hazardous substances (Chrysochoou, et al., 2012; Li, et al., 2008). Chromium is considered to be a high priority pollutant and is highly regulated by the U.S. EPA with a maximum contaminant level (MCL) for total chromium in drinking water at 0.100 mg/L (100 ppb) (Nemecek, et al., 2014; Li, et al., 2008).

Hexavalent chromium is toxic to humans, animals, and plants (Gheju, 2011). Due to its high solubility and mobility, Cr(VI) is easily absorbed into the body (Yang, et al., 2015). Exposure to Cr(VI) compounds causes skin ulcerations, asthma, cancer, liver damage, nasal ulcers, and even pulmonary congestion (Xu, et al., 2015; Nemecek, et al., 2014; Gheju, 2011; Demiral, et al., 2008). Although Cr(III) is an essential trace nutrient, it is toxic in large doses (Xu, et al., 2015; O'Carroll, et al., 2013). In 1989, the U.S. National Academy of Sciences estimated the recommended dietary intake of Cr(III) between 50-200 µg/day.

Table 2-2: Typical Cr(VI) concentrations in various types of water

Naturally Occurring Sources of Cr(VI)		
Water type	Concentration	Reference
Surface Water Sources	(µg/L)	
Rivers	0.2 - 114.4	Gheju (2011) Kotas & Stasicka (2000)
Lakes	0.07 - 36	
Seawater	0.005 - 0.8	
Groundwater Sources	(µg/L)	Reference
Groundwater	0.16 - 300	
Mojave Desert, CA	60	McNeill, et al. (2012)
Paradise Valley, AZ	up to 220	
San Francisco, CA	up to 98	
Yilgarn Craton, Australia	10 – 430	
La Spezia, Italy	5 – 73	
Anthropogenic Sources of Cr(VI)		
Water Sources	(mg/L)	Reference
Tannery effluent	40 – 25,000	Benazir, et al. (2010)
Mohawk Tannery, NH	67,800	U.S. EPA
Newark, NJ	10,900	Xiao-qin, et al. (2008)
Soil Sources	mg/kg	Reference
Jersey City, NJ	1,000-10,000	Xiao-qin, et al. (2008)

2.1.1.1 Common Treatment Methods for Cr(VI)

Common technologies for the remediation of Cr(VI) include extraction, ion-exchange (IX), activated carbon adsorption, biological reduction, chemical reduction with zero-valent iron (ZVI), coagulation using ferrous sulfate or calcium polysulfide, and membrane-based processes such as reverse osmosis (RO) (Mitra, et al., 2011; Demiral, et al., 2008; Natale, et al., 2015; Gheju, 2011).

Many of these processes, such as ion-exchange and membrane separation have significant disadvantages including incomplete metal removal, high energy requirements, and the generation of toxic waste that requires disposal (Demiral, et al., 2008). In contrast, chemical and biological reductions transform Cr(VI) to Cr(III), reducing both the toxicity and mobility of chromium in the environment (Chrysochoou, et al., 2012).

2.1.2 Chlorate [ClO_3^-]

An additional oxyanion contaminant of concern is chlorate (ClO_3^-). Chlorate has been widely detected in ground and surface water in the United States and even locally in Henderson, NV at the NERT sites (Shrestha, 2016; Duan & Batchelor, 2014; Cao, et al., 2005). Chlorate, or more precisely sodium chlorate, is one of the most widely used chemicals globally with some of the largest producers located in Canada and the United States (Mannsville Chemical Products, 2006; USDA, 2000). The global sodium chlorate market is growing and expected to exceed 4.7 million tons by 2022 (Expert Market Research, 2016).

Chlorate is also typically found in conjunction with perchlorate (ClO_4^-) (Batista, et al., 2002). Perchlorate refers to chlorine oxyanion in the +7 oxidation state. Perchlorate has been shown to have good solubility and strong mobility in groundwater (Xie, et al., 2016; Shrestha, 2016; Son, et al., 2006). As with Cr(VI), ClO_4^- is primarily the product of anthropogenic activities including propellant for missiles, fireworks, paint and enamel production, air bag inflators and in some fertilizer components. Perchlorate reduction in aqueous solutions typically follows the sequential reactions: perchlorate (ClO_4^-) → chlorate (ClO_3^-) → chlorite (ClO_2^-) → chloride + oxygen (Cl^- + O_2) (Xie, et al., 2016; Zhu, et al., 2016).

A majority of the sodium chlorate manufactured worldwide is utilized by the paper and pulp industry to generate chlorine dioxide for bleaching since chlorine gas was deemed too dangerous (U.S. EPA, 2016; Mannsville Chemical Products, 2006; Bruce, et al., 1999). It is also utilized as a bleaching agent flour and for the disinfections of drinking water (WHO, 2005; U.S. EPA, 2016; Expert Market Research, 2016). Major production of sodium chlorate is located in North America within the United States and Canada. Production in Canada is higher due to lower energy costs. Other global manufacturers include Brazil, China, and Finland.

Sodium chlorate is used to make chlorine dioxide, a common disinfectant used in drinking water treatment (Alfredo, et al., 2015). Chlorate is a disinfection by product from the production of hypochlorite or during the application of chlorine dioxide during the disinfection process of drinking water treatment (Breytus, et al., 2017; U.S. EPA, 2016). Figure 2-2 shows the distribution of the maximum reported chlorate concentrations in finished drinking water. Other uses for sodium chlorate include being used as a nonselective herbicide to kill weeds and grasses, hydraulic mining of uranium, and in the production of perchlorate (U.S. EPA, 2016; USDA, 2000; Mannsville

Chemical Products, 2006). Figure 2-3 shows the estimated sodium chlorate use on agriculture in the U.S. from 1992 to 2015 (USGS, 2017). Sodium chlorate is typically manufactured using an electrolysis process, see Equation 2-1.

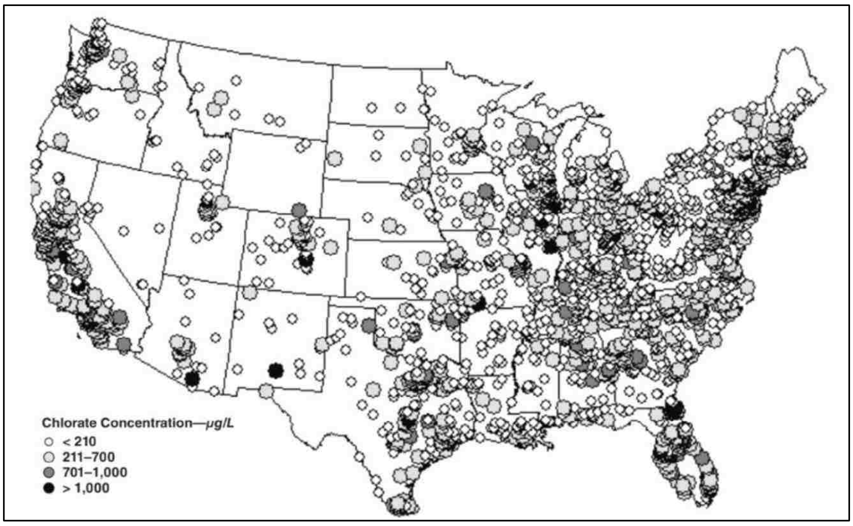


Figure 2-2: Distribution of maximum chlorate concentrations in finished water reported in UCMR 3 database as of April 2014 (Alfredo, et al., 2015).

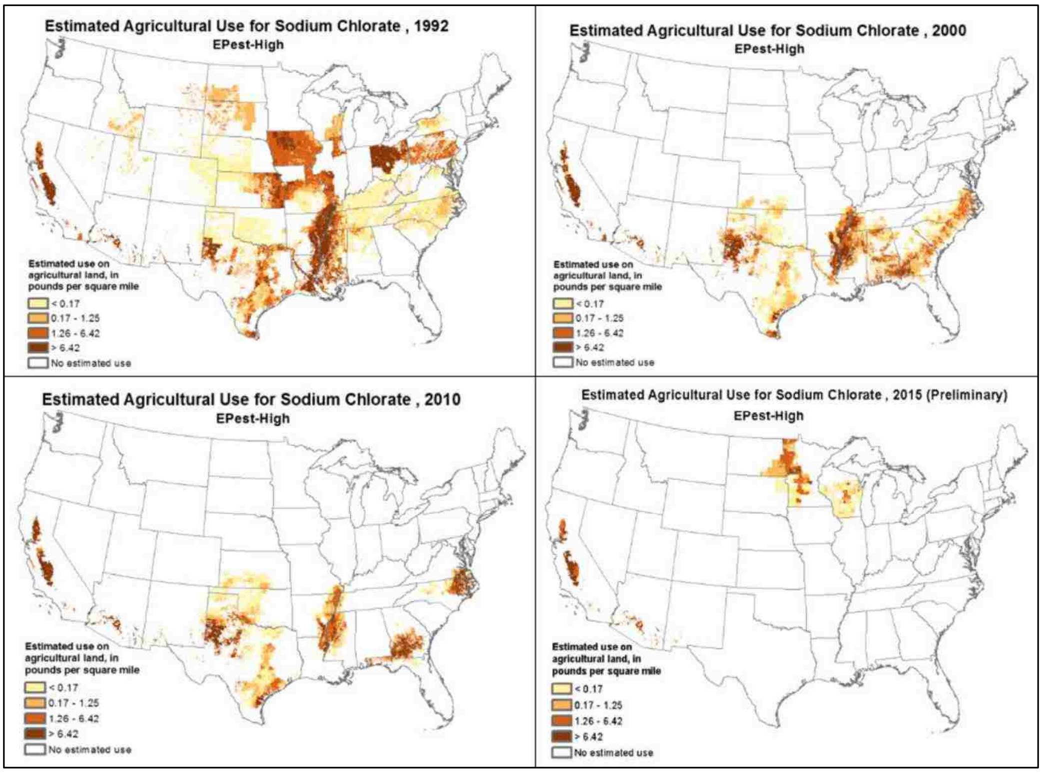


Figure 2-3: Estimated annual sodium chlorate for agricultural use in 1992, 2000, 2010, and 2015 (USGS, 2017)

Equation 2-1: Electrolysis of aqueous sodium chloride to produce sodium chlorate (Zarei & Ghavi, 2016; Chemtrade, 2018)

$$NaCl + 3H_2O \xrightarrow{\text{electrolysis}} NaClO_3 + 3H_2 \qquad \text{5,200 kW/MT}$$

As with Cr(VI), ClO_4^- is primarily the product of anthropogenic activities including propellant for missiles, fireworks, paint and enamel production, air bag inflators and in some fertilizer components (Xie, et al., 2016; Ricardo, et al., 2012; Son, et al., 2006; Hunter, 2002). Sodium perchlorate is produced in several stages, starting with the production of sodium chloride in Equation 2-1 and to the final product in Equation 2-2. As with sodium chlorate, each stage is uses electrolysis.

Equation 2-2: Electrochemical conversion of sodium chlorate to sodium perchlorate *(Zarei & Ghavi, 2016)*

$$NaClO_3 + H_2O \xrightarrow{\text{electrolysis}} NaClO_4 + H_2$$

Chlorate, in conjunction with other elements forms an assortment of salts, such as sodium chlorate and potassium chlorate. Chlorate refers to chlorine oxyanion in the +5 oxidation state (U.S. EPA, 2016). The physical and chemical properties for chlorate are listed in Table 2-3. Chlorate and its salts are powerful oxidizers (U.S. EPA, 2016). Chlorates can remain in the soil for up to five years (U.S. EPA, 2016; Gonce & Voudrias, 1994; Alfredo, et al., 2014). The oxidation and reduction of chlorate salts in water are dependent upon concentration, temperature, pH, and concentration of reductants. Chlorate is more stable in alkaline conditions (U.S. EPA, 2016).

Table 2-3: Physical and chemical properties of chlorate

Property	Data	Reference
Chemical formula	ClO_3^-	Pubchem (2018) Alfredo, et al., (2014)
Molecular weight	83.5 g/mol (calculated)	
Color/physical state	Colorless or white crystal	
Melting point *Potassium Chlorate ($KClO_3$)* *Sodium Chlorate ($NaClO_3$)*	368°C 248°C	
Density (g/cm^3) *Potassium Chlorate* *Sodium Chlorate*	2.34 2.5	
Solubility in water (g/L at 25°C) *Potassium Chlorate* *Sodium Chlorate*	70 790	
Redox potential	$ClO_3^- + 2H^+ + 3e^- \rightarrow ClO_2^- + H_2O$ $E^0 = +0.330V$	Crittendon, et al., (2012)

Both chlorate and perchlorate occur in arid environment naturally in relatively high concentrations, see Table 2-4. Bacteria prevents the natural accumulation in non-arid environments *(Brundrett, et al., 2015)*. Because of this, bacteria has been extensively investigated for their capacity to degrade both chlorate and perchlorate, discussed later.

Table 2-4: Typical chlorate and perchlorate concentrations in water

Natural Occurring Sources of ClO_3^-		
Water type Surface Water Sources	**Concentration** (µg/L)	**Reference**
Mineral water, Canada	0-260	Dabeka, et al. (2002)
Spring water, Canada	0-1,024	
Tap water, Canada	0-115	
DWTP, USA (using chlorine dioxide)	21-330	Alfredo, et al. (2015)
DWTP, USA (no chlorine dioxide)	10-660	
Anthropogenic Sources of ClO_3^-		
Water Sources	(µg/L)	**Reference**
Herbicides	2x10^7- 4x10^7	Ali, et al. (2017)
Pulp mills effluent	70,000-100,000	
Anthropogenic Sources of ClO_4^-		
Water Sources	(µg/L)	**Reference**
Northern California site (manufacturer of rocket engines for military)	250-900	Gu & Brown (2006)
Edwards AFB, U.S.	200-500	Gu & Brown (2006)
Lake Mead Inlet (LV Wash)	1,500-1,680	Motzer, W. (2001)
Henderson, NV	3,700,000	

Chlorate, similar to perchlorate, has an adverse impact on humans and the environment. Both oxyanions are linked to thyroid disorders, breakdown of red blood cells, and increased risk of birth defects (Breytus, et al., 2017; Alfredo, et al., 2014; Cao, et al., 2005; Duan & Batchelor, 2014). Chlorate is toxic both through ingestion and inhalation (Alfredo, et al., 2015). Sodium chlorate is fatal at doses greater than 100 mg/kg. Toxic doses can result in renal failure, cyanosis, gastrointestinal irritation, methemoglobinemia, and hemoglobinuria (U.S. EPA, 2016; WHO, 2005). Alfredo, et al.

(2015) estimated that a lethal dose of sodium chlorate could be as low as 20g. Bruce, et al. (1999) reported that the toxicity of chlorate to both pant and microorganisms is believed to be a consequence of the competitive uptake by the nitrate reductase system.

Currently, there is no federal drinking water level for chlorate, however the U.S. EPA has set a health reference level of 210µg/L and is currently evaluating it for further regulation (U.S. EPA, 2016; Breytus, et al., 2017). The World Health Organization (WHO) set guidelines at 700µg/L (Breytus, et al., 2017). Canada has set the maximum acceptable limit for chlorate at 1mg/L (Alfredo, et al., 2015). Perchlorate is regulated by the U.S. EPA and has a reference dose set at 15µg/L for drinking water in 2008 (Xie, et al., 2016; Ricardo, et al., 2012; U.S. EPA, 2017) and an oral reference dose (RfD) of 0.0007 mg/kg/day (U.S. EPA, 2017)

The U.S. EPA lists two standard method for determining chlorate concentrations in water. These are USEPA Method 300.0 and USEPA 300.1. Both methods use ion chromatography (Alfredo, et al., 2015; Hosseini, et al., 2009). Another method of detection is liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Alfredo, et al., 2015).

2.1.2.1 Technologies Used for Chlorate and Perchlorate Removal from Waters

Typical methods for the remediation for both chlorate and perchlorate from water include IX, RO, adsorption, nano-filtration (NF), biodegradation, adsorption using GAC, and chemical reduction (Hunter, 2002; Zhu, et al., 2016; Alfredo, et al., 2015). For drinking water, IX using anion exchange resins is most typically used to remove ClO_4^-. IX creates a concentrated brine that must then be treated or disposed, adding cost and additional steps (Ricardo, et al., 2012; Hunter, 2002; Alfredo, et al., 2015). Although RO can efficiently remove both ClO_3^- and ClO_4^-, it is energy-intensive and like IX, generates a concentrated brine that must then be further treated or disposed of (Alfredo, et al., 2014).

Perchlorate and chlorate are easily metabolized by perchlorate reducing bacteria (PCRB) making biological treatment an encouraging method of remediation (Ricardo, et al., 2012). Perchlorate reduction in aqueous solutions follows the sequential reactions: perchlorate (ClO_4^-) → chlorate (ClO_3^-) → chlorite (ClO_2^-) → chloride + oxygen ($Cl^- + O_2$) implying that chlorate is also easily metabolized by PCRB (Xie, et al., 2016; Zhu, et al., 2016). Biological reduction has an advantage over abiotic methods in that the PCRB will completely transform ClO_4^- into chloride (Cl^-). Additionally, co-contaminants can be remediated in the same system (Zhu, et al., 2016).

2.2 ZVI as a Treatment Technology for Cr(VI) and ClO_3^-

Zero valent iron (ZVI) is a proven technology for the biotic and abiotic reduction of a wide variety of environmental contaminants including Cr(VI), nitrate (NO_3^-), chlorinated organic compounds, arsenic, ClO_3^-, and ClO_4^- (Fu, et al., 2014; Mueller, et al., 2012; Li, et al., 2008). Thiruvenkatachari, et al., (2008) states that ZVI is the most common reactive material used in the reduction of contaminants.

Oxidation/reduction reactions (redox reactions) are fundamental reactions in environmental systems (Wiesner & Bottero, 2016). Redox reactions involve the removal of electrons from a substance (oxidation) to another substance (reduction) (Crittenden, et al., 2012; Wiesner & Bottero, 2016; Watts, 1997). The tendency for a substance to donate or accept electrons is known as the redox potential of the substance. This is measured electrically in reference to a standard substance, H_2. The standard reduction potential is measured under specific conditions. These conditions are 25°C at 1atm. The redox potential is used to measure the tendency of a substance/species to donate or accept electrons (Madigan, et al., 1997). Redox potential is a method to determine the feasibility and directionality of a reaction.

Iron is a reactive metal that is a strong reducing agent with a standard redox potential (E^0 = -0.44V), see Equation 2-3 (Fu, et al., 2014; Gheju, 2011; Son, et al., 2006). To initiate the process, the iron undergoes a process of corrosion with water and dissolved oxygen (DO) thereby producing hydrogen gas (H_2) (Fu, et al., 2014). The H_2 that is produced, via iron corrosion, is utilized as an electron donor for the chemical reduction of contaminants. Also, bacteria or microorganisms that can utilize H_2 as a source of energy can be introduced to augment the treatment system, see ZVI+Sludge (Thiruvenkatachari, et al., 2008; You, et al., 2017). The aerobic and anaerobic processes are shown in Equation 2-4 through Equation 2-7 (Gheju & Iovi, 2006; Di Palma, et al., 2015). An oxide/hydroxide layer is formed on the metal surface as soon as the iron is exposed to water or air (Gheju, 2011). In the process of reducing contaminants, ZVI is oxidized to Fe^{+2} and Fe^{+3} oxidation states (Mukherjee, et al., 2016). As shown in Equation 2-6 and Equation 2-7, the oxidation of Fe^0 to Fe^{2+} and Fe^{3+} results in the formation of two moles of hydroxide for every mole of iron reduced. This results in an increase in pH of the solution which in some cases will cause minerals to precipitate (Thiruvenkatachari, et al., 2008). In an abiotic reduction, contaminants are transformed into non-toxic or less toxic species by means of directional transfer of electrons by the ZVI (electron donor) resulting in precipitation or degradation of the contaminants (electron acceptors), Figure 2-4A (Fu, et al., 2014; Thiruvenkatachari, et al., 2008). However, in the biotic reduction of contaminants using ZVI (ZVI+Sludge), microorganisms utilize the hydrogen that is generated as an energy source to degrade the contaminants using enzymes 2-4B (You, et al., 2017).

Equation 2-3: Standard potential of Fe^{2+}/Fe^0 couple (Gheju, 2011; Di Palma, et al., 2015; Xu, et al., 2017; Zarei & Ghavi, 2016)

$$Fe^{2+} + 2e^- \leftrightarrow Fe^0_{(s)} \qquad (E^0 = -0.447V)$$

Equation 2-4: Aerobic iron corrosion, Fe^0 to Fe^{2+} (Gheju, 2011)

$$2Fe^0_{(s)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \qquad (E^0 = +1.67V)$$

Equation 2-5: Aerobic iron corrosion, Fe^{2+} to Fe^{3+} (Gheju, 2011)

$$4Fe^{2+}_{(aq)} + 4H^+_{(aq)} + O_{2(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \qquad (E^0 = +0.46V)$$

Equation 2-6: Anaerobic iron corrosion, Fe^0 to Fe^{2+} (Gheju, 2011; Ponder, et al., 2000; Xu, et al., 2017)

$$Fe^0_{(s)} + 2H_2O_{(l)} \rightarrow Fe^{2+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad (E^0 = -0.39V)$$

Equation 2-7: Anaerobic iron corrosion, Fe^{2+} to Fe^{3+} (Gheju, 2011)

$$2Fe^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Fe^{3+}_{(aq)} + H_{2(g)} + 2OH^-_{(aq)} \qquad (E^0 = -1.60V)$$

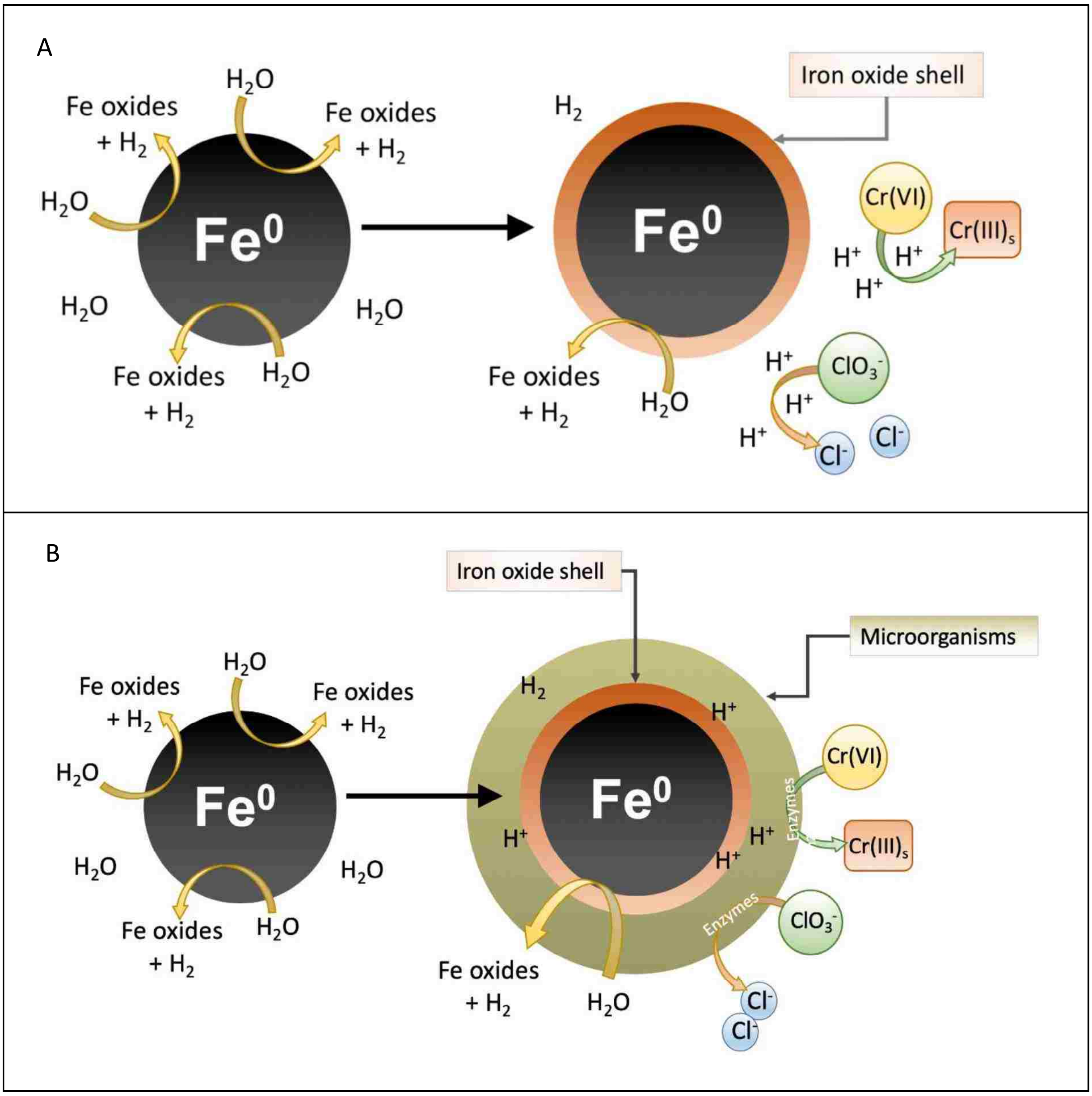


Figure 2-4: [A] Core-Shell structure of ZVI. [B] Biotic enhanced ZVI. Modified from (O'Carroll, et al., 2013; Mukherjee, et al., 2016).

2.2.1 Effects of Operating Parameters

The reduction of Cr(VI) by ZVI is highly dependent on external factors (You, et al., 2017). These include solution pH, initial contaminant concentration, ZVI dose, specific surface area (SSA), contact time, and competition from other contaminants (Selvarani & Prema, 2012; Gheju, 2011).

The reduction of Cr(VI) by ZVI is extremely sensitive to the pH of the water (Selvarani & Prema, 2012; You, et al., 2017; Gheju, 2011). As shown in the stoichiometry of Equation 2-9 through Equation 2-11, seven moles of hydrogen ion are required for each mole of Cr(VI). The reduction of Cr(VI) has been reported at a range of pH values (Gheju, 2011). Chen, et al., (2007) reported the optimum pH for Cr(VI) reduction at 1.5, whereas Gheju, (2011) suggested that the optimal pH actually be 2.5. The pH will increase in unbuffered systems due to the formation of OH^- ions from the anaerobic iron corrosion (Equation 2-7 and Equation 2-8) (Gheju, 2011). At neutral pH values, it is reported that Cr(VI) reduction will drastically decrease (Gheju & Iovi, 2006), even ceasing for a period under alkaline conditions (Alowitz & Sherer, 2002). Mitra, et al., (2011) investigated the reduction of Cr(VI) over a pH range of 3 to 5.5. It was noted that surface passivation of the ZVI occurred more at higher pH values. Higher reduction rates of Cr(VI) were shown at the lower pH values. Xiao-qin, et al., (2008) reported that Cr(VI) removal efficiency was a function of pH, which was confirmed by Selvarian & Prema, (2012), (Xu, et al., 2014)

Equation 2-8: Reduction of chromate by ZVI (Xu, et al., 2014)

$$2CrO_4^{2-} + 3Fe^0_{(s)} + 16H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Fe^{2+}_{(aq)} + 8H_2O_{(l)}$$

Equation 2-9: Reduction of hydrogen chromate by ZVI (Gheju, 2011)

$$HCrO^-_{4(aq)} + Fe^0_{(s)} + 7H^+_{(aq)} \rightarrow Cr^{3+}_{(aq)} + Fe^{3+}_{(aq)} + 4H_2O_{(l)}$$

Equation 2-10: Reduction of dichromate by ZVI (Mitra, et al., 2011; Gheju & Iovi, 2006; Fu, et al., 2014)

$$Cr_2O^{2-}_{7(aq)} + 2Fe^0_{(s)} + 14H^+_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 2Fe^{3+}_{(aq)} + 7H_2O_{(l)}$$

Equation 2-11: Reduction of perchlorate by ZVI (Cao, et al., 2005; Zarei & Ghavi, 2016)

$$ClO^-_{4(aq)} + 4Fe^0_{(s)} + 8H^+_{(aq)} \leftrightarrow 4Fe^{2+}_{(aq)} + Cl^-_{(aq)} + 4H_2O_{(l)} \qquad (E^0 = +1.727\ )$$

Equation 2-12: Reduction of nitrate by ZVI (Alowitz & Sherer, 2002; Westerhoff, 2003)

$$NO^-_{3(aq)} + 4Fe^0_{(s)} + 10H^+_{(aq)} \leftrightarrow 4Fe^{2+}_{(aq)} + NH^+_4 + 3H_2O_{(l)} \qquad (E^0 = +1.32\ V)$$

Equation 2-13: Reduction of chlorate by ZVI (Westerhoff, 2003; Zarei & Ghavi, 2016)

$$ClO^-_{3(aq)} + 3Fe^0_{(s)} + 6H^+_{(aq)} \leftrightarrow 3Fe^{2+}_{(aq)} + Cl^-_{(aq)} + 3H_2O_{(l)} \qquad (E^0 = +1.89\ V)$$

Significant research has gone into the effect of specific surface area (SSA) with regards to the reduction of degradation of contaminants (You, et al., 2017). Often, size or SSA is the parameter used to distinguish between the types of iron (Thiruvenkatachari, et al., 2008). ZVI is categorized in three different sizes (milli, micro, and nano-scale) (Karn, et al., 2009). Research has shown that ZVI particles with a greater surface area will have faster reduction rates (Gheju, 2011). Milli-scale ZVI (mZVI) have been utilized in permeable reactive barriers (PRBs) to effectively reduce contaminants such as Cr(VI) and is often referred to as granular iron, iron filings, or iron chips (U.S. EPA, 2000). Micro-scale (µZVI) and Nano-scale ZVI (nZVI) are significantly more reactive than conventional ZVI due to the increased active surface area (Mueller, et al., 2012). Nano-scale ZVI particle sizes range from 10 to 100 nm in diameter (Karn, et al., 2009). Because of their size, nZVI can be directly injected easily into shallow and deep aquifers to remediate contaminated plumes, alleviating the need for excavation in conventional PRBs (Lefevre, et al., 2016; Mueller, et al., 2012). Physical movement through soil and water is controlled by Brownian motion, thus allowing the particles to remain in suspension longer (Karn, et al., 2009). As a result, an in-situ treatment zone can be established (Zhang, 2003). Agglomeration of bare nZVI will typically occur due to magnetic interaction of the particles and van der Waals attractive forces, resulting in a reduced surface area and mobility (Xie, et al., 2016). To avoid this, coatings can be applied to alter the surface properties and stabilize the particles (O'Carroll, et al., 2013; Karn, et al., 2009).

The size of ZVI will have an impact on overall reduction rates of the contaminant. Table 2-5 shows data collected from literature on the capacity of various sizes of ZVI to reduce Cr(VI). Di Palma, et al., (2005) compared chemical reduction of Cr(VI) by nZVI with that of ferrous sulfate. Experiments demonstrated that both technologies are effective at reducing Cr(VI) however nZVI proved to be faster and more effective. However, nZVI has a tendency to rapidly agglomerate and/or react with other constituents resulting in a reduction soil mobility and reactivity (Selvarani & Prema, 2012). Shi, et al., (2011) demonstrated that nZVI became more effective with the support of bentonite by reducing aggregation. Gheju et al. (2008), investigated the effect of initial Cr(VI) concentration on the removal efficiency. It was reported that as the initial Cr(VI) increased, the observed pseudo first-order rate constants decreased considerably, nearly three times. (Shi, et al., 2011).

Table 2-5: Experimentally determined capacity for the reduction of Cr(VI) using ZVI.

Iron Type	Capacity mg Cr(VI)/g Fe^0	Type of Water	Reference
nZVI	50 – 180	DI water	Xiao-qin, et al. (2008)
	50	GW	
ZVI shavings	0.3 – 14.4	DI water	Gheju, et al. (2008)
µZVI	263 - 961	Electroplating wastewater	Chen, et al. (2007)
ZVI filings (acid washed)	0.65	Synthetic GW	Lai, et al. (2008)
µZVI	25	DI water	Astrup, et al. (2000)
ZVI filings	4	Synthetic GW	Lo, et al. (2006)
Chitosan-ZVI	32	DI water	Tielong, et al. (2009)

Passivation of the iron surface will result in a decrease of reactivity. As shown in Equation 2-7 and Equation 2-8, oxygen is effective at oxidizing ZVI to create a layer of hydroxides on the surface of the iron. Also, during the initial reactions, dissolved H_2 may temporarily passivate the iron surface (Thiruvenkatachari, et al., 2008). This diminishes the effectiveness of the ZVI. Thiruvenkatachari, et al., (2008) reported that an effective method to counter this problem is to create a pre-treatment barrier of sand and pae gravel with approximately 10-15% ZVI by weight. This barrier will remove the dissolved oxygen from the solution while preventing passivation of the treatment system. In a different study, Song, et al,. (2005) was able to conclude that a ZVI mixed with sand enhanced Cr(VI) reduction with the adsorptive nature of the sand.

It has been demonstrated that an increase in Cr(VI) concentration will adversely affect the overall reduction rate in a ZVI system (Gheju, 2011). For instance, Li, et al., (2008) demonstrated that over a similar duration, significantly higher Cr(VI) solutions (1,000 mg/L) were noticeably reduced. Also, it was shown in an experiment by Geng, et al., (2009) and corroborated by Shi, et al., (2011), that rate constants for Cr(VI) removal declined significantly with an increase in initial concentration. Ponder, et al., (2000) theorized that the cause of the reduced rate was a result of oxidation kinetics of ZVI and not a product of the Cr(VI) being reduced. Gheju, (2011) noted that at the higher Cr(VI) concentrations, there was an increase in ZVI surface passivation.

Increasing the mass of iron has been generally accepted as a method to increase reduction efficiency of Cr(VI) removal (Gheju, 2011). This has been corroborated in numerous studies. For instance, Franco et al., (2009), demonstrated a direct correlation between the molar ratio and the kinetic rate constant. Gheju, (2011) points out from previous studies that the maximum possible rate of Cr(VI) reduction occurs with a ZVI concentration of 3.75%. However, higher doses of iron could have a detrimental effect on a ZVI+Sludge system by increasing the pH beyond that for optimal bacterial growth. Due to this, Gheju, (2011) suggests that a ZVI+Sludge system should primarily depend on contact time and the buffering capacity of the aquifer.

It was believed that the process of ClO_4^- losing an oxygen atom to form ClO_3^- is a rate-limiting step, see Equation 2-14 and Equation 2-15, with the remainder of the reduction, ClO_3^- on, will be rapid (Srinivasan, et al., 2009; Gu, et al., 2002). In a series of batch experiments, Srinivasan, et al. (2009) demonstrated that the reaction kinetics for chlorate were significantly faster than perchlorate (Srinivasan, et al., 2009). Zarei and Ghavi (2016) looked at taking advantage of the reaction kinetics of ClO_4^- and ClO_3^- with ZVI to remove ClO_3^- impurities from ammonium perchlorate. In a series of experiments, Zarei and Ghavi, (2016) demonstrated that: (1) chlorate reduction was at its peak at pH values of 7 to 8, (2) both ClO_4^- and ClO_3^- removal efficiency improved as temperature increased (25°C to 65°C), but over 80% reduction of ClO_3^- was achieved at 25°C, and (3) within 90 min nearly ClO_3^- was reduced by nearly 90% whereas ClO_4^-

achieved only 10% removal. From the preliminary experimentation, Zarei and Ghavi, (2016) were able to achieve nearly complete removal of ClO_3^- impurities from the ammonium chlorate.

Equation 2-14: Reduction of chlorate to chloride (Zarei & Ghavi, 2016)

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O \qquad (E^0 = 1.45V)$$

Equation 2-15: Reduction of perchlorate to chloride (Zarei & Ghavi, 2016; Srinivasan, et al., 2009)

$$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O \qquad (E^0 = 1.287V)$$

Gheju, (2011) concluded that the efficiency of an abiotic ZVI system increases with dose, temperature, HRT, and increasingly acidic pH, larger SSA, and a lower initial Cr(VI) concentration. Studies have shown that ZVI can reduce perchlorate, however, under ambient conditions the reaction is very slow whereas the reduction of chlorate is much faster (Son, et al., 2006; Zarei & Ghavi, 2016).

An alternative to the ZVI alone (abiotic) is to utilize microorganisms that can utilize the hydrogen gas that the ZVI generates as an energy source (i.e., as an electron donor) to promote biological reduction (Thiruvenkatachari, et al., 2008; Brundrett, et al., 2015). It has been shown that microorganisms can inhabit ZVI PRBs and that this could assist in the stimulation of Cr(VI) biodegradation (Gheju, 2011). In a ZVI+Sludge system, bacteria will utilize the hydrogen that is generated as an electron donor to degrade the contaminants and reduce the contaminants (You, et al., 2017; Gu, et al., 2002; Xu, et al., 2015). In this scenario, abiotic reduction many still be occurring alongside the biological reduction.

Some microorganisms have developed the ability to survive, and thrive in high concentrations of Cr(VI). Unfortunately, water contaminated with high levels of Cr(VI) can be too toxic for a majority of microorganisms (Němeček, et al., 2015). Megharaj, et al., (2003) notes that most Cr(VI) reducing bacteria are able to endure Cr(VI) concentrations up to 50 mg/L Cr(VI).

The impact of microorganisms on ZVI permeable reactive barriers (PRBs) is dependent on the groundwater geochemistry (Gu, et al., 2002). Passivation of fouling of the barrier surface might result from a reduction of reactive sites as a consequence of biofilm formation, the formation of gas bubbles, and contaminant precipitation (Gheju, 2011). However, Son, et al., (2006) suggests that a ZVI+Sludge system might be more economical and environmentally friendly than other methods for contaminant removal. Thiruvenkatachari, et al., (2008) noted that PRBs augmented with bacteria seem to be more successful when multiple contaminants are present.

The optimal pH for the growth of functional bacteria is at a neutral pH, which is within the pH range for the reduction of a majority of contaminants (You, et al., 2017). You, et al., (2017) indicates that in a ZVI+Sludge system, the higher pH levels will not only have an effect on the reduction rate of Cr(VI) but will also impact microbial activities. However, as Xu, et al., (2017) points out, the neutralization of the pH is assisted by the consumption of H^+ and formation of alkaline byproducts.

2.3 Engineered Reduction of Cr(VI) and ClO_3^- Reduction in Contaminated Groundwater

Remediation of contaminated groundwater in the field is separated into two broad categories, ex-situ and in-situ. Ex-situ remediation is the treatment of water and/or soil after it has been removed from the ground. In-situ remediation is the treatment of water and/or soil in the location without removal (U.S. EPA, 2006). The various techniques for in-situ and ex-situ remediation are broken down in Figure 2-5.

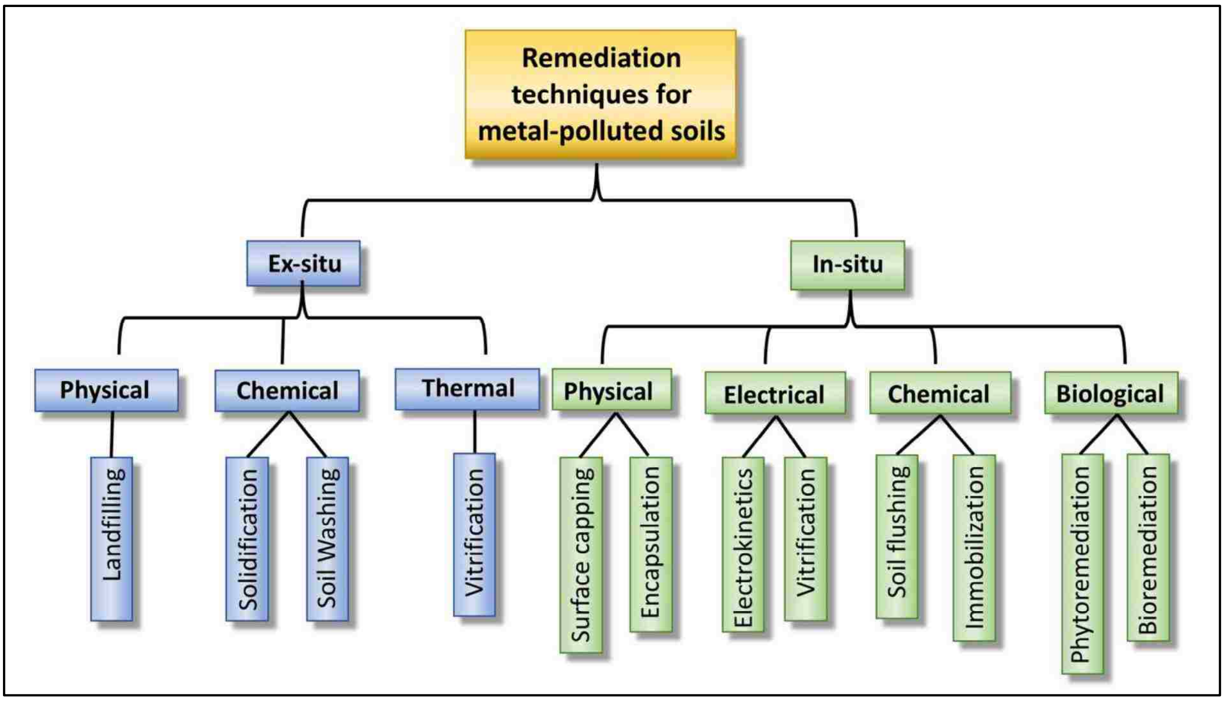


Figure 2-5: Typical remediation techniques for metal-polluted soils. Modified from *(Liu, et al., 2018)*

2.3.1 Ex-situ

Early treatment remedies for Cr(VI) groundwater, amongst other contaminants, included pump and treat (P&T) operations. This method involves extracting contaminated groundwater via wells or trenches and treated the groundwater above ground or off site (ex-situ) using methods such as air stripping, carbon adsorption, biological reactors, or chemical precipitation (Palmer & Wittbrodt, 1991). Many of these processes produce highly contaminated waste products that then have to be disposed

(Karn, et al., 2009). Other purposes of P&T were to prevent contaminants from migrating further by maintaining gradient control through pumping (Palmer & Wittbrodt, 1991).

Studies by the U.S. Environmental Protection Agency (EPA) found that the commonly used P&T technologies (pump the water and treat it at the surface) rarely restored sites that had contaminated groundwater to background conditions. Palmer & Wittbrodt, (1991) noted that the removal of contaminants from the subsurface left residual concentrations of contaminants well above MCLs. This was confirmed in a much more extensive 1994 National Research Council (NRC) study that explicitly reviewed 77 sites across the United States where full- scale pump-and-treat was being used (Thiruvenkatachari, et al., 2008).

Typical P&T operations can last for decades of operation (Palmer & Wittbrodt, 1991). Karn, et al., (2009) estimates the average annual cost (2001) to be approximately $767,000/site. Average pump and treat system can be operated for 5 years treating an average of 118 million gallons of water per site for an average cost of $9.4 million to clean up a single site. Pump and treat projects represent the largest number of treatments at Superfund sites, 38% (Karn, et al., 2009).

Other ex-situ techniques include excavation which is the process of the removal of contaminated soil and moving it to a waste site. This method is not practiced often since the fundamental problem (i.e., contaminant) is not being addressed. The contaminant is transferred to another location, generally safer, but it is not treated. There is also the potential for exposure during the excavation and shipping (Palmer & Wittbrodt, 1991).

2.3.2 In-situ

Contaminated groundwater is often located deep below the ground surface and spread over significant areas. This makes established methods of treatment difficult and/or impossible to employ (Hashim, et al., 2011). In these situations, an in-situ chemical treatment technologies might be ideal.

One method for in-situ remediation of Cr(VI) is by using ZVI in permeable reactive barriers (PRB) (Chrysochoou, et al., 2012; Wilkin, et al., 2002; Karn, et al., 2009). The U.S. EPA, (2015) defines PRBs as “an engineered zone of reactive material that extends below the water table to intercept and treat contaminated groundwater. In general, a permeable reactive material is placed in the subsurface through which a contaminated groundwater plume will naturally flow through. The contaminants in the groundwater plume will interact with the reactive material in the barrier and either degrade or be retained in them, see Figure 2-6 (Thiruvenkatachari, et al., 2008; Cundy, et al., 2008). So as to maintain adequate groundwater hydrogeology, the barrier is designed to be more permeable than the materials of the surrounding aquifer (Guoxiang, et al., 2017). PRBs can be installed as permanent, semi-permanent, or replaceable (Karn, et al., 2009). To prevent changes to the surrounding groundwater hydrology, PRBs are therefore designed to be more permeable (Thiruvenkatachari, et al., 2008). The reactive material(s) selected for the PRB is based on the contaminant of concern (COC) (Karn, et al., 2009). ZVI is often used in PRBs because it is readily available, inexpensive, and nontoxic (Li, et al., 2008). PRBs operate under anaerobic conditions and the kinetics of ZVI in PRB will typically be low due to pH range of natural waters (Gheju, 2011; Ritter, et al., 2003).

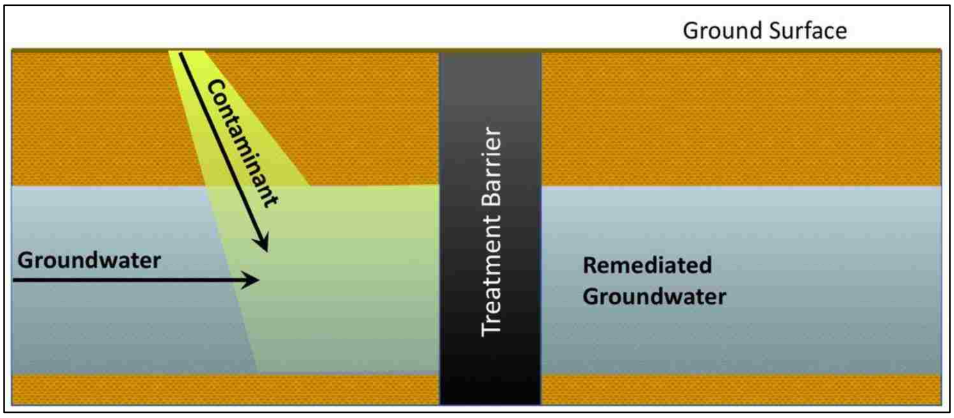


Figure 2-6: Conceptual illustration of permeable reactive barrier (PRB). Adapted from Mulligan, et al., (2001)

Wilken, et al., (2003) reported a field-scale example of a PRB utilizing ZVI. A chrome-plating shop operated at the U.S. Coast Guard Support Center near the Pasquotank River for 30 years and closed in 1984. Cr(VI) concentrations in the soil beneath the shop reached up to 14,500 mg/kg. A Cr(VI) plume extending from the shop to the Pasquotank River had concentrations >10mg/L. A PRB (46 m long, 7.3 m deep, and 0.6 m wide) was constructed approximately 30 m from the river. Approximately 2.1 m^3 of iron was used for the barrier. The pH of the groundwater was 5.94 ± 0.44 and DO was 0.5 ± 0.4. Over 130 subsurface sampling points were installed to monitor changes in porewater geochemistry. Cr(VI) concentrations have been reduced to <0.01 mg/L. Flow characteristics were determined to be unaffected since available pore space within the barrier was not filled (Wilkin, et al., 2003; Wilkin, et al., 2002). Chromium removal was reported to have continued even after eight years of operation (Cundy, et al., 2008).

Other methods of in-situ treatment utilizing iron include nano-scale ZVI (nZVI) dispersion via injection, pneumatic fracturing, and liquid atomization injection (Cook, 2009). These methods have several advantages over the trench-style PRB. The utilization of nZVI allows for higher reaction rates thus reducing the contaminants in a shorter time frame (Mueller, et al., 2012). Injection allows for the direct treatment of contaminated plumes in places where it would be difficult or impossible to build a trench (e.g., under a building). Finally, injection allows for the treatment of deep aquifers (Thiruvenkatachari, et al., 2008). Technical challenges for the use of nZVI include agglomeration, passivation from co-contaminants (Mueller, et al., 2012).

Chapter 3: Methodology

This research focuses on the removal of high levels (ppm range) of Cr(VI) and ClO_3^- using abiotic reduction with ZVI and biological reduction. The reduction rates of both contaminants were measured for both treatment technologies using batch tests.

For this thesis, biological reduction will be referred to as the Sludge test. The combination of biological reduction and ZVI will be referred to as ZVI+Sludge. Micro-scale ZVI will be referred to as ZVI powder.

3.1 Experimental Approach

A series of batch tests were conducted in which a synthetic groundwater, containing the contaminants of interest, was added with various concentrations of ZVI, microbial seed, and an external carbon source (i.e. EOS emulsified oil). In the batch test, the groundwater and desired components were added to 40mL borosilicate glass bottles. The bottles were then placed in a rotary shaker for mixing and samples were taken at predetermined time intervals for analysis of the contaminants of interest. The seed microbial culture was taken from existing fluidized bed reactors that are currently being used to treat groundwater contaminated with Cr(VI), ClO_3^-, and other inorganic contaminants. Because ZVI application typically results in an increase of pH, the final pH was also monitored in the batch tests. The reduction rates of the contaminants were computed using the decrease in concentration with time.

3.1.1 Stoichiometric Ratios

Stoichiometric ratios were used to establish a relationship between the amount of ZVI added and the concentration of contaminant present. The ratios were obtained from Equation 2-8 for Cr(VI) and Equation 2-13 for ClO_3^- and are listed in Table 3-1.

Table 3-1: Stoichiometric ratios for ZVI to contaminants [Cr(VI) and ClO_3^-].

Ratio	Stoichiometric Molar Ratio	Stoichiometric Mass Ratio
	(mol ZVI: mol Contaminant)	(wt. ZVI: wt. Contaminant)
ZVI : Cr(VI)	1.50	1.61
ZVI : ClO_3^-	3.00	2.00

3.1.2 Statistical Analysis

Tests of statistical significance beyond the expected error were performed to evaluate whether or not the differences between the averages of two groups of tests reflect a real difference in the population from the groups that were sampled (Neda, 2018). This was accomplished using the one-way analysis of variance (ANOVA). A comparison of the percent contaminant removed was performed using ANOVA single factor. The independent variable was the method used to reduce the contaminants (e.g., ZVI, Sludge, etc.) and the dependent variable was the percent contaminant (Cr(VI) or ClO_3^-) removed. If a statistically significant result was returned, post hoc tests using a two-tail Student's t-test assuming unequal variance would be used to evaluate the significance between individual methods. The null hypothesis was; that there was no statistically significant difference in the percent contaminant (Cr(VI) or ClO_3^-) removed between the methods being compared. The confidence interval (CI) was set at 95%. Data analysis was done using Microsoft Excel. Results for all statistical tests are presented in the Results and Discussion and also Appendix B.

3.2 Materials

3.2.1 Contaminant Solutions

A stock solution of 10,000 mg/L Cr(VI) was prepared using $K_2Cr_2O_7$ (EM Science, 99.9% purity) and 10,000 mg/L ClO_3^- using $NaClO_3$ (Aldrich Chemical Company Inc., 99+% purity), respectively were prepared. Synthetic groundwater was prepared using tap water from the Las Vegas Valley Water District (LVVWD), amended with the contaminants of interest. Table 3-2 lists several substances in the source water. A full water quality summary is shown in Appendix E.

Table 3-2: Las Vegas Valley Water District 2018 Water Quality (Las Vegas Valley Water District, 2019)

Substance	Average Value	MCL	Units
Alkalinity	134	N/A	ppm
Bromate	5	10	ppb
Chromium, Total	<3	100	ppb
Nitrate (as Nitrogen)	0.4	10	ppm
Perchlorate	0.7	N/A	ppm
Total Dissolved Solids	594	1000	ppm

3.2.2 ZVI Sources

Two types of ZVI were tested in the Preliminary Phase Experiments, (please see Section 3.5.1). Degreased iron filings (50-70 mesh) from Fisher Chemical (Fair Lawn, NJ), and micro-scale ZVI (ZVI powder) from Connelly-GPM, (Chicago) #CC-1200, 50% passing U.S. screen number 100. Specifications and lot information are listed in Appendix E. Connelly GPM micro-scale ZVI was utilized through the rest of the experimentation period.

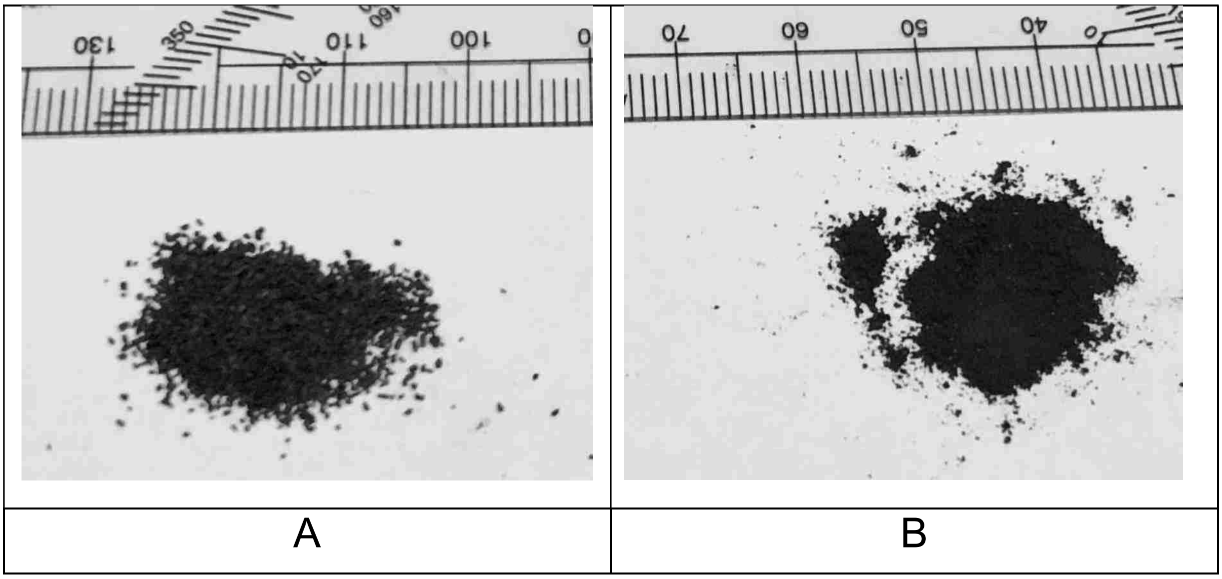


Figure 3-1: Image of ZVI utilized in batch tests. [A] Fisher Chemical ZVI filings and [B] Connelly-GPM ZVI powder.

3.2.3 Seed Bacteria Source

As mentioned previously, biomass from fluidized bed reactors (FBRs, currently treating groundwater contaminated with Cr(VI), nitrate, chlorate, and perchlorate was used as the inoculum in this research.

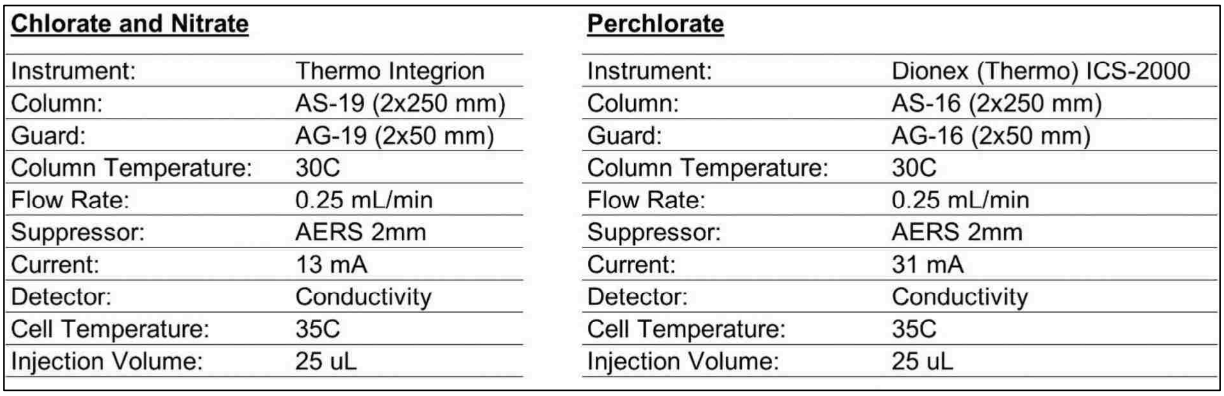
Emulsified vegetable oil (EOS-PRO) was used as an additional carbon source to support anaerobic degradation of the contaminants of concern. EOS-PRO is comprised of 59.8% soybean oil, 10% surfactant, and 4% rapidly biodegradable soluble substrate (Appendix D).

3.3 Analytical Methods

3.3.1 Cr(VI) and ClO_3^- Analysis

Cr(VI) was measured using Hach DR 900 colorimeter using the U.S. EPA 1,5-Diphenylcarbohydrazide method (EPA method 314.0 for ion chromatography). The range of the test is 0.010mg/L Cr(VI) to 0.700mg/L Cr(VI). DI water was used for dilution of samples. Two ion chromatographs (IC) were used for testing, IC#1 was the Dionex ICS-2000 and IC#2 was the Dionex Integrion HPIC, Table 3-3. A QC check of the standard to verify the performance of the IC was analyzed every 5 samples.

Table 3-3: Methods and instrumentation used for detection limits for chlorate, nitrate, and perchlorate are valid for analyses using the conditions below.



Chlorate and Nitrate		**Perchlorate**	
Instrument:	Thermo Integrion	Instrument:	Dionex (Thermo) ICS-2000
Column:	AS-19 (2x250 mm)	Column:	AS-16 (2x250 mm)
Guard:	AG-19 (2x50 mm)	Guard:	AG-16 (2x50 mm)
Column Temperature:	30C	Column Temperature:	30C
Flow Rate:	0.25 mL/min	Flow Rate:	0.25 mL/min
Suppressor:	AERS 2mm	Suppressor:	AERS 2mm
Current:	13 mA	Current:	31 mA
Detector:	Conductivity	Detector:	Conductivity
Cell Temperature:	35C	Cell Temperature:	35C
Injection Volume:	25 uL	Injection Volume:	25 uL

3.3.2 pH Analysis

pH was measured on all samples using a Fisher Scientific AR25 Dual Channel pH/Ion meter. The pH meter was calibrated using a two-point calibration with pH 7 and 10 buffers. To ensure precision, the pH was measured a minimum of three times for each sample. The average of the pH measurements was reported.

3.3.3 Chemical Oxygen Demand (COD) Analysis

COD was used as a surrogate measure of carbon source present in the batch tests (i.e. measurement of EOS-PRO present). Analysis was carried out using the U.S.

EPA Reactor Digestion Method. This was done using HACH Method 8000 utilizing the Hach DR5000 spectrophotometer.

3.4 Quality Assurance / Quality Control (QA/QC)

Parameters measured in this research include Cr(VI) concentration, ClO_3^- concentration, pH, COD. All glassware was soaked in Micro-80 cleaning solution for a minimum of 24 hours. After soaking, the glassware was washed with tap water and soap and rinsed a minimum of three times with DI water. New 40mL glass vials were used in each batch experiment to ensure no iron contamination in sample bottles. Blanks containing only contaminant solution were used in both beta-testing and final experiments to ensure consistency. All samples were filtered using single-use 0.45µm syringe filters and were refrigerated at 4°C for the remainder of the experiment. Cr(VI) samples were measured within 48 hours of sampling.

The pH meter was recalibrated every 10 samples using two-point calibration with pH 7 and pH 10 buffers standards. The ion-chromatograph was calibrated with chlorate standards and acceptable calibration curves had correlation coefficient > 99.97%.

3.5 Batch Tests

Batch tests were performed for each experiment. Synthetic groundwater, containing the contaminant of interest, was added to vials. Depending on the method to be tested, varying concentrations of ZVI, Sludge, or a combination of ZVI+Sludge were added to the vials. Blank samples containing only contaminant solution and no ZVI or Sludge were used to ensure QA/QC. Additionally, 50% replicates were used in the degradation experiment and a minimum of 30% replicates were used in a majority of the preliminary experiments. Replicate data was used to calculate the standard deviations reported in the error bars to show variability in the data. EOS-PRO oil was added to a selection of Sludge and ZVI+Sludge samples to compare whether an additional carbon source would impact the reduction of the contaminants. The vials were placed on a rotary shaker at approximately 30rpm, Figure 3-2, for a specified period of time. At indicated times, samples were sacrificed and filtered using 0.45µm syringe filters. Each experiment was tested for contaminant/s of concern as well as pH. Results and discussion for preliminary experiments are shown in Appendix A. Experimental data is listed in Appendix D.

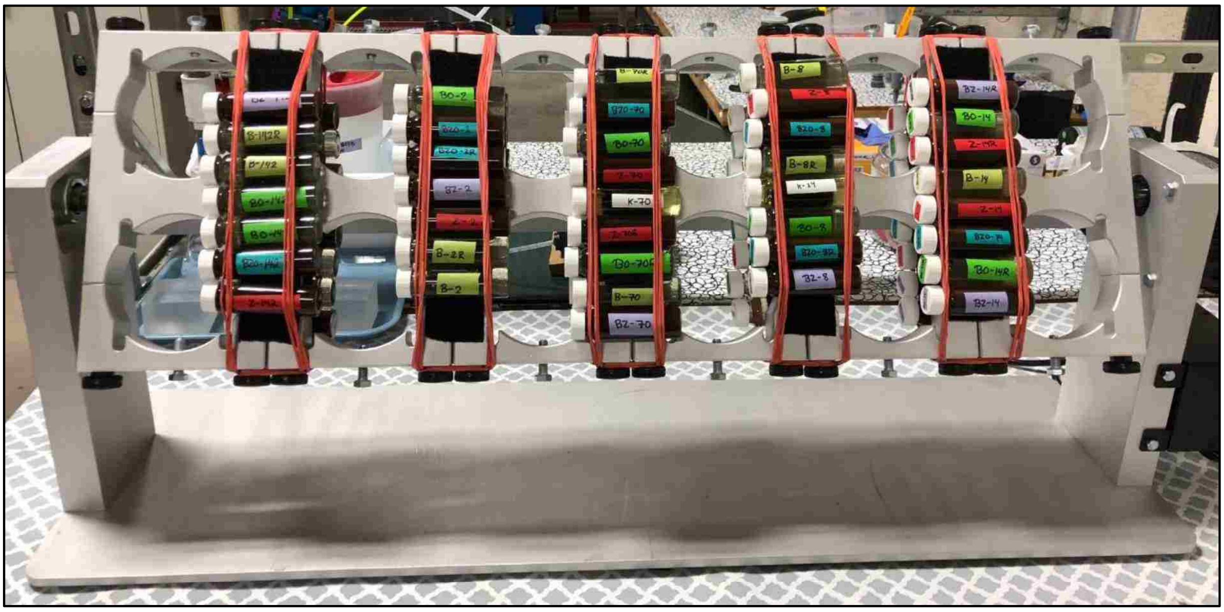


Figure 3-2: Image of a typical experimental batch test set-up on a rotary shaker.

3.6 Testing of Major Parameters that Influence the Sludge / Abiotic Reduction

A series of preliminary batch tests, Table 3-4, were performed to assist in the determination of parameters that most impact contaminant reduction. Batch test for preliminary experiments were performed as described in Section 3-5.

Table 3-4: Summary of Preliminary and Final Experiments Performed in This Research.

No.	Test Title	Objective
Preliminary Experiments		
1	Variables Influencing Reduction: Impact of ZVI Size Particle	Investigate the significance of surface area on contaminant reduction.
2	Variables Influencing Reduction: Impact of ZVI Dosages	Investigate the impact lower ZVI dosages on the reduction of Cr(VI).
3	Variables Influencing Reduction: Impact of Decreased ZVI Dosage and Increased Contaminant Concentration	Investigate the impact of lower dosages of ZVI on the removal efficiency of higher concentrations of Cr(VI).
4	Variables Influencing Reduction: Impact of Chlorate Reduction using ZVI	Investigate the removal efficiency of ClO_3^- with varying doses of ZVI for low and high concentrations of ClO_3^-.
5	Variables Influencing Reduction: Impact of Varying Concentrations of ClO_3^-	Investigate the removal efficiency of ClO_3^- varying doses of ZVI with low (10mg/L) to very high (1,000mg/L) concentrations of ClO_3^-.
6	Testing Major Parameters: ZVI+Sludge vs ZVI alone	Investigate viability of ZVI in combination with biological for contaminant removal.
7	Testing Major Parameters: Impact of Bioaugmentation with Sludge	Investigate Cr(VI) reduction for increasing concentrations of Cr(VI) using varying doses of Sludge.
8	Abiotic ZVI Molar Ratio Test	Investigate the impact of ZVI/Cr ratios on Cr(VI) reduction. Objective was to identify ideal ratios for future experiments.
9	ZVI+Sludge Molar Ratio Test	Investigate the impact of ZVI/Cr ratios on low to high concentrations of Cr(VI) with varying doses of sludge. Objective was to identify ideal range (molar ratio) for future experiments and determine sludge dosage.
Final Experiments		
10	Degradation Experiment: Hexavalent Chromium [Cr(VI)]	Investigate the reduction of Cr(VI) using Sludge alone, abiotic ZVI alone, and Sludge+ZVI.
11	Degradation Experiment: Chlorate (ClO_3^-)	Investigate the reduction of ClO_3^- using Sludge alone, abiotic ZVI alone, and Sludge+ZVI.
12	Degradation Experiment: Multiple Contaminant	Investigate the reduction of both Cr(VI) and ClO_3^- using Sludge alone, abiotic ZVI alone, and Sludge+ZVI.
13	Degradation Experiment: ZVI+Sludge Using Increasing and Decreasing Stoichiometric Ratios	Investigate the reduction of both Cr(VI) and ClO_3^- ZVI+Sludge with varying stoichiometric ratios. Objective was to determine whether varying ratios from the multiple contaminants experiment would reduce efficiency.

3.6.1 Variables Influencing Reduction: Impact of ZVI Size

ZVI can be broken down into three size categories (milli, micro, and nano-scale). There has been extensive research into the effect of surface area on the degradation of contaminants (Karn, et al., 2009). Milli-scale ZVI filings Fisher Chemical (Fair Lawn, NJ) and ZVI powder from Connelly-GPM (Chicago). Nano-ZVI was not tested. Initial Cr(VI) concentration was 10mg/L as Cr(VI) and ZVI dose was 20g/L and 40g/L. No replicates were used.

3.6.2 Variables Influencing Reduction: Impact of Varying ZVI Dosages

Decreasing dosages of ZVI powder from Connelly-GPM were tested. Initial Cr(VI) concentrations were 10mg/L Cr(VI) and 20mg/L Cr(VI). ZVI dosages were 10g/L and 2g/L.

Increasing concentrations of ClO_3^- were tested at two concentrations of ZVI to investigate the chemical reductive capabilities of abiotic ZVI. Initial ClO_3^- concentrations were 10mg/L and 100mg/L ClO_3^- ZVI dosages ranged from 4 to 10g/L. Contact time for experiment ranged from 14-hours to 86-hours. No replicates were used.

The removal of high levels of ClO_3^- (10mg/L, 100mg/L, and 1,000mg/L ClO_3^-) was investigated using a 70X and 130X stoichiometric ratio. Contact time ranged from 8-hours to 48-hours. Thirty percent replicates were used.

3.6.3 Testing Major Parameters: ZVI+Sludge vs. ZVI Alone

The feasibility of ZVI+Sludge was tested using sludge with increasing concentrations of Cr(VI). This was compared to a similar batch experiment utilizing abiotic ZVI. Initial Cr(VI) concentrations were 5mg/L, 10mg/L, 20mg/L, and 50mg/L

Cr(VI). ZVI dose was 10g/L. Sludge dose for ZVI+Sludge was 360mg SS/L. EOS-PRO dosage varied according to initial Cr(VI) concentration. Hundred percent replicates used.

3.6.4 Sludge Dosage

Cr(VI) reduction for increasing reduction of increasing concentrations of Cr(VI) was investigated. Cr(VI) concentrations ranged from 10mg/L to 100mg/L. Sludge doses were 36mg SS/L, 72mg SS/L, 180mg SS/L, and 360mg SS/L. EOS-PRO doses varied according to initial Cr(VI) concentration. Thirty percent replicates used.

3.6.5 Molar Ratio

A series of batch experiments were performed to investigate the effectiveness of abiotic ZVI to reduce increasing concentrations of Cr(VI) with increasing molar ratios (mol ZVI:mol Cr(VI)) were performed. Initial concentrations of Cr(VI) were 10mg/L, 20mg/L, 50mg/L, 75mg/L and 100mg/L Cr(VI). Molar ratios (mol ZVI:mol Cr(VI)) ranged from 100 times molar ratio to 1,800 times molar ratio (67X to 1,200X stoichiometric ratio). Thirty percent replicates used.

An additional series of batch experiment was performed to investigate the effectiveness of ZVI+Sludge to reduce increasing concentrations of Cr(VI) using increasing molar ratios (mol ZVI:mol Cr(VI)). Concentrations of 10mg/L and 100mg/L Cr(VI) were tested at molar ratios ranging from 100 to 1,800 times with 360mg SS/L and 180mg SS/L sludge doses. Concentrations of 20mg/L and 50mg/L Cr(VI) were tested with only 180mg SS/L sludge doses. EOS-PRO doses varied according to initial Cr(VI) concentration. Thirty percent replicates used.

3.7 Degradation Experiments

Degradation experiments of contaminants of concern were performed, Table 3-3, utilizing criteria obtained from preliminary batch experiments in Section 3.6. Batch tests for degradation experiments were performed as described in Section 3-5.

3.7.1 Hexavalent Chromium [Cr(VI)]

The reductive capabilities of Sludge (with and without EOS-PRO oil), ZVI, and ZVI+Sludge (with and without EOS-PRO oil) to reduce 30mg/L Cr(VI) were investigated. ZVI doses for ZVI and ZVI+Sludge were 6.25g/L. Sludge doses were 180mg SS/L. Contact time ranged from 0.5-hour to 6-hours. Fifty percent replicates used.

3.7.2 Chlorate [ClO3-]

A comparison of Sludge, ZVI, and ZVI+Sludge to remediate 100mg/L ClO3- was investigated. ZVI dose was 14g/L. Sludge, see Section 3.2.3, dose for was 12.5mL/L. No additional carbon source was used. Samples were tested from 4-hours to 60-hours. Fifty percent replicates used.

3.7.3 Multiple Contaminants

The reductive capabilities of Sludge (with and without EOS-PRO oil), ZVI, and ZVI+Sludge (with and without EOS-PRO oil) to reduce both 30mg/L Cr(VI) and 100mg/L ClO_3^- were investigated. ZVI doses were 20g/L. Sludge doses were 180mg SS/L. Samples were tested from 0.5 hours to 168 hours (7 days). Fifty percent replicates used.

3.7.4 ZVI+Sludge using Increasing and Decreasing Stoichiometric Ratios

The effect of increasing and decreasing stoichiometric ratios on ZVI+Sludge (no additional carbon source) to reduce both 30mg/L Cr(VI) and 100mg/L ClO_3^- was investigated. Samples were tested for a period of time ranging from 0.5-hours to 168-hours (7 days). Fifty percent replicates used.

Chapter 4: Results and Discussion

4.1 Cr(VI) Reduction with ZVI, Biological Reduction (Sludge), and ZVI+Sludge

The results of the batch testing using Sludge, ZVI, and ZVI in conjunction with sludge (ZVI+Sludge) are depicted in Figure 4-1. Reaction kinetics and statistical analysis (ANOVA and Student’s t-test), are shown in Table 4-1, Table 4-2 and Table 4-3.

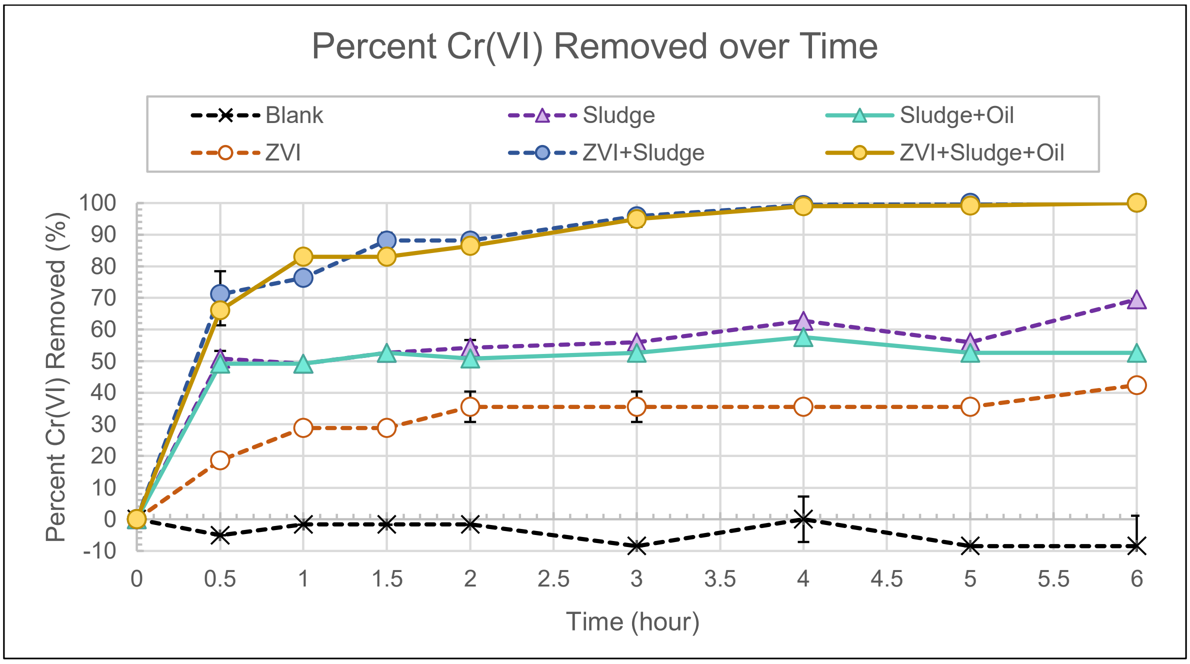


Figure 4-1: Percent Cr(VI) removed over time for Sludge (with and without EOS-PRO oil), ZVI, ZVI+Sludge (with and without EOS-PRO oil), and Blank. Forty mL vials were used for the batch experiment. Initial Cr(VI) concentration was 30 mg/L Cr(VI). ZVI dose was 6.32 g/L. Sludge dose was 180mg SS/L. Laboratory temperature was 24°C. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

Table 4-1: Results for ANOVA single factor for co-contaminants for the percent removal of Cr(VI) using Sludge, Sludge+Oil, ZVI, ZVI+Sludge, ZVI+Sludge+Oil, and Blank.

	Contaminant	F	p value	F_{crit}
Determine whether there was a significant difference between the reduction methods.	Cr(VI)	18.9	2.43E-10	2.41

Table 4-2: Cr(VI) Removal rates using ZVI and ZVI combined with biological reduction. Initial Cr(VI) concentration was 30mg/L.

Method	Stoichiometric Ratio + Solids	Maximum Rate	Overall Rate
		mg Cr(VI)$\cdot$L$^{-1}\cdot$hr^{-1}	
Sludge	180mg SS/L	30	3.42
Sludge+Oil	180mg SS/L	29	2.33
ZVI	133X	11	2.08
ZVI+Sludge	133X + 180mg SS/L	42	4.92
ZVI+Sludge+Oil	133X + 180mg SS/L	39	4.92

Table 4-3: Summary of paired Student's t-test Results for percent Cr(VI) removed for ZVI+Sludge, ZVI, and Sludge methods.

Description/Category	Student's t-test Analysis Between	P-value
Determine whether there was a significant difference between the Cr(VI) reduction methods.	ZVI+Sludge and ZVI	3.89E-8
	ZVI+Sludge and Sludge	1.56E-5
	Sludge and ZVI	7.93E-6
Determine whether there was a significant difference in the reduction methods and the Blank.	ZVI+Sludge and Blank	4.88E-5
	Sludge and Blank	2.11E-5
	ZVI and Blank	3.92E-5
Determine whether an additional carbon source (oil) would increase the reduction of Cr(VI).	ZVI+Sludge+Oil and ZVI+Sludge	0.958
	Sludge+Oil and Sludge	0.675

Statistical analysis was performed to for means of removal efficiencies among the methods used for Cr(VI) removal. ANOVA analysis revealed, at the 95% confidence interval (CI), that there was a statistically significant difference between each of the three methods (Sludge, ZVI, and ZVI+Sludge) in the percent removal of Cr(VI), Table 4-1. Additional post hoc analysis using the Student's t-test statistics revealed, at the

95% CI, that all the methods were statistically significantly different in the percent removal of Cr(VI). Additionally, the very small p values (<< 0.05), indicate that the methods used were statistically significantly different from the blank samples demonstrating the three methods evaluated had a significant impact on the percent Cr(VI) reduced. Furthermore, the Student's t-tests indicated that the addition of oil as an external carbon source did not have any significant impact on Cr(VI) reduction. Therefore, the carbon present in the sludge itself was sufficient to promote Cr(VI) reduction. This finding can also be observed in Figure 4-1 that shows that the removal of Cr(VI) was basically the same in batch tests where oil was added to sludge and ZVI and where oil was added to sludge.

Figure 4-1 also shows that the highest percentage chromium removal was obtained with the combination of ZVI and Sludge. The Cr(VI) reduction rate for Sludge alone was the second highest and that for ZVI alone was the smallest. These results agree with published data stating that ZVI combined with biotic reduction reduced Cr(VI) at higher rates than ZVI alone (Weizhao, et al., 2017; Zhong, et al., 2017; Zhang, et al., 2017; Němeček, et al., 2015). Weizhao et al, (2017) showed that within 5 days, a biotic augmented ZVI system (ZVI+Sludge) could reduce over 70% more Cr(VI) than abiotic ZVI alone. The reduction of Cr(VI) occurred more rapidly in this study. This is possibly due to the difference in biotic inoculum utilized or the type of ZVI used. Both methods started with identical concentrations of Cr(VI) and nearly identical doses of ZVI.

Within a half hour, 71% of the Cr(VI) was removed using ZVI+Sludge, whereas 49% (14.5 mg/L) and 19% (5.5 mg/L) were removed for Sludge and ZVI alone, respectively (Figure 4-1). Complete (100%) reduction by ZVI+Sludge was achieved within 4-hours whereas neither Sludge nor ZVI achieved complete reduction within 6-hours. As expected, no reduction of Cr(VI) occurred in the Blank samples.

The degradation rates shown in Table 4-2 include both the maximum and overall rate of chromium reduction in mg Cr(VI)•L^{-1}•hr^{-1}. The maximum removal rates were calculated by determining the time period with the highest contaminant reduction. The overall removal rates were calculated from either the duration of the entire experiment or the time to reach complete reduction. The highest rate of reduction for all the methods tested occurred within the first hour, and after that period the rate of degradation slowed down considerably. The reduction for both Sludge and ZVI plateaued showing minimal reduction after 1-hour and 2-hours, respectively. Minimal reduction occurred afterwards. The degradation rate of ZVI combined with sludge (average 40.5mg Cr(VI)•L^{-1}•hr^{-1}) was about 27% greater than that of sludge alone (average 29.5 mg Cr(VI)•L^{-1}•hr^{-1}). Therefore, the contribution of ZVI was approximately 11 mg Cr(VI)•L^{-1}•hr^{-1}, and that matches the values computed in Table 4-2. Therefore, more Cr(VI) was biologically reduced than abiotically reduced by in this case.

Narayani & Shetty, (2013), reported that the initial reduction rate of Cr(VI) by *Bacillus sp.* was 2.69 mg Cr(VI)•L^{-1}•hr^{-1} over a 10-hr period with an initial Cr(VI) concentration of 100mg/L and 1.73 mg Cr(VI)•L^{-1}•hr^{-1} for an initial concentration of 50 mg/L Cr(VI). Benazir et al. (2010) reported reduction rates by various individual organisms averaging 1.875 mg Cr(VI)•L^{-1}•hr^{-1} and reduction rates by consortia at 2.017 mg Cr(VI)•L^{-1}•hr^{-1}. In the current research, the overall rate of reduction for Sludge over the 6-hr duration of the experiment was 3.42mg Cr(VI)•L^{-1}•hr^{-1}, 1.97 times higher than reported by Narayani & Shetty, (2013) for an Cr(VI) concentration of 50mg/L.

As mentioned earlier, incorporating an additional carbon source (EOS-PRO oil) did not promote a significant difference between ZVI+Sludge and ZVI+Sludge+Oil ($p = 0.8787$); and Sludge alone and Sludge+Oil ($p = 0.1307$) (Table 4-3). The average COD for the sludge samples used was 28,000 mg/L COD. The COD of the EOS-PRO added was an additional 10.4mg/L COD, a 2.97% increase. Therefore, the amount of carbon contained in the sludge was sufficient to provide for the demand of carbon during the tests. Initially, the researcher did not expect the COD in the sludge to be that high.

A comparison of Cr(VI) reduction rates computed from the published literature is shown in Table 4-4. The maximum and overall reaction rates are shown along with the calculated stoichiometric ratio for comparison with the experimental results from this study. The experimental criteria including ZVI dose, type of ZVI, initial Cr(VI) concentration, pH, and temperature are also listed to facilitate discussion. Table 4-4 is arranged in descending order according to maximum reaction rate. Results from this study are placed accordingly.

The maximum reaction rate for Cr(VI) with ZVI only (abiotic) found in this research is similar (42mg $Cr(VI) \cdot L^{-1} \cdot hr^{-1}$) is similar to those reported in literature for maximum reaction rates of starch nano-ZVI (nZVI) experiments with a much lower stoichiometric ratios (41.6 times lower). Dutta et al. (2009) performed a batch test with a similar stoichiometric ratio also using ZVI powder and achieved a reaction rate of 60mg $Cr(VI) \cdot L^{-1} \cdot hr^{-1}$. The increased reaction rate found by Dutta et al. (2010), is likely due to the acidity of the solution ($pH = 3.5$) and increased temperature (30°C compared to 24°C in this study). Higher reduction rates have been shown at lower pH values (Xiao-qin, et al., 2008). ZVI+Sludge produced similar Cr(VI) reduction rates to those reported to an abiotic ZVI with 2.22 times the stoichiometric ratio and an augmented nZVI experiment with 21.1 times lower stoichiometric ratio. As previously stated, additional variables assisted in the increased reduction of Cr(VI) for the starch nZVI experiment including ZVI type, initial pH, and temperature. Given nZVI is much more expensive than powder ZVI, the addition of sludge to ZVI to combine biological and abiotic reduction seems to be an attractive treatment option for Cr(VI).

Synthetic water for the experiments was prepared using tap water from the LVVWD. Table 3-2 in the Methodology shows a short list of co-contaminants present in the water. The full list is in Appendix E. Nitrate and perchlorate are listed at 0.4ppm and 0.7ppm, respectively. The contaminant concentrations are relatively low. Additionally, these contaminants all reduce after Cr(VI) and should have little impact.

Table 4-4: Comparison or Reaction Rate with Literature. Abiotic ZVI alone, ZVI with biological agent, and biological reduction.

Reaction Rate (mg Cr(VI)•L^{-1}•hr $^{-1}$)		k_{obs}	Stoichiometric Ratio[1]	Experimental Criteria	Reference
Max	Overall	min^{-1}			
11	2.1	3.68E-3	133X	6.32g/L ZVI powder. 30mg/L Cr(VI). pH$_0$ = 7.15. 24°C.	This Study, ZVI single contaminant Cr(VI)
12	6	9.70E-3	3.2X	0.1g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 7. T = 28°C.	Selvarani & Prema (2012)
20	5.4	1.60E-2	6.3X	0.2g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 10. T = 28°C.	Selvarani & Prema (2012)
26	8.0	1.60E-2	6.3X	0.2g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 10. T = 28°C.	Selvarani & Prema (2012)
27	9.0	3.80E-2	8.4X	0.2g/L starch nZVI. 15mg/L Cr(VI). pH$_0$ = 7. T = 28°C.	Selvarani & Prema (2012)
30	3.4	1.12E-2	n/a	29.5mg/L Cr(VI). 180 mg SS/L Sludge. pH$_0$ = 7.15. 24°C.	This Study, Sludge single contaminant Cr(VI)
36	13	3.90E-2	6.3X	0.2g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 5. T = 28°C.	Selvarani & Prema (2012)
39	10	1.11E-1	13X	0.2g/L starch nZVI. 10mg/L Cr(VI). pH$_0$ = 7. 28°C.	Selvarani & Prema (2012)
40	8.3	1.55E-2	190X	15g/L ZVI powder. 50mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
42	19	2.82E-2	295X	20g/L ZVI powder. 43mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
42	4.9	1.83E-2	133X	6.25g/L ZVI powder. 29.5mg/L Cr(VI). 180mg SS/L Sludge. pH$_0$ = 7.15. 24°C.	This Study, ZVI+Sludge single contaminant Cr(VI)
42	11	4.60E-2	6.3X	0.2g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 7. T = 28°C.	Selvarani & Prema (2012)
50	25	1.57E-2	105X	20g/L ZVI powder. 121mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
52	29	2.25E-2	195X	20g/L ZVI powder. 65mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
54	17	5.70E-2	9.5X	0.3g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 7. 28°C.	Selvarani & Prema (2012)
54	22	2.82E-2	253X	20g/L ZVI powder. 50mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
57	15	4.60E-2	5.1X	0.2g/L starch nZVI. 25mg/L Cr(VI). pH$_0$ = 7. 28°C.	Selvarani & Prema (2012)
60	20	6.20E-2	6.3X	0.2g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 3. T = 28°C.	Selvarani & Prema (2012)
60	42	2.00E-2	127X	20g/L ZVI powder. 100mg/L Cr(VI). pH$_0$ = 3.5. 30°C.	Dutta et al. (2010)
66	19	7.40E-2	13X	0.4g/L starch nZVI. 20mg/L Cr(VI). pH$_0$ = 7. 28°C.	Selvarani & Prema (2012)
80	24	3.55E-2	253X	20g/L ZVI powder. 50mg/L Cr(VI). pH$_0$ = 1.5. 30°C.	Dutta et al. (2010)
108	6.0	9.30E-3	6.3X	0.4g/L chitosan ZVI. 40mg/L Cr(VI). pH$_0$ = 6. 20°C.	Geng et al. (2009)
120	6.4	6.50E-4	1.3X	0.08g/L chitosan ZVI. 40mg/L Cr(VI). pH$_0$ = 6. 20°C.	Geng et al. (2009)

Note:

[1] Ratio of 1.5 ZVI to 1 Cr(VI) used to calculate stoichiometric ratio.

4.1.1 Determination of Order and Reaction Rate Coefficients for Cr(VI) Reduction Experiment

Analysis was performed to determine reaction order and rate coefficients for the experimental data obtained in this research (Table 4-5). Detailed computation of reaction rates and rate coefficients are shown in Appendix C. Between the pH values of 5 to 9, Weizhou et al. (2017) determined their ZVI+Sludge system to follow a pseudo first-order reaction. For this research, only the final contaminant concentrations were measured. The final ZVI, Sludge, and/or EOS-PRO oil concentrations were not. The rate of the degradation with time is proportional to the concentration of the Cr(VI) and ZVI and/or Sludge. In these experiments, the concentrations of both Sludge and/or ZVI were used in excess and are large enough to not impact the reaction rate. Therefore, pseudo first order was assumed, and reaction rate coefficients were determined for each method.

Both ZVI+Sludge and ZVI+Sludge+Oil were determined to have high R^2 values (R^2 = 0.954 and 0.956, respectively). Because the reaction rate was the result of abiotic and biotic reduction and one of the components dominated (biological reduction), then it can also be said that this reaction is pseudo-first order. The reaction rates calculated in Table 4-2 demonstrate that biological reduction is faster than abiotic reduction. This is confirmed with the k_{obs} values of 1.12E-2 min^{-1} and 3.68E-3 min^{-1} for Sludge and ZVI, respectively. Both Sludge and ZVI+Sludge are a factor of 10 greater than abiotic ZVI. In Table 4-4, the k_{obs} are compared with k_{obs} from literature and show that the calculated k_{obs} are similar to those reported in literature. A low R^2 would indicate possible impact from material.

Table 4-5: Summary of reaction order rate constants and coefficients of determination for Cr(VI) degradation experiment.

Kinetic Parameters	Sludge	Sludge+Oil	ZVI	ZVI+Sludge	ZVI+Sludge+Oil
Pseudo First-Order Reaction					
K_{obs} (min^{-1})	1.12E-2	7.50E-3	3.68E-3	1.83E-2	1.54E-2
R^2	0.713	0.680	0.860	0.954	0.956

4.1.2 pH Changes for Cr(VI) Reduction Experiment

As explained in the literature review (Section 2.2.1) ZVI use results in a pH increase because of the hydroxide formation. The optimal pH range for Cr(VI) removal with ZVI has been reported to range from 1.5 to 2.5 (Gheju, 2011). This pH range posed several issues: Values for pH in the range of 1.5 to 2.5 would be extremely acidic to many microorganisms (Gheju, 2011; Vendruscolo, et al., 2017; Narayani & Shetty, 2013). The optimal pH range for microorganisms has been reported to be within 7.0 to 8.0 (You, et al., 2017). Therefore, the use of optimum pH for ZVI reduction of Cr(VI) would prevent the testing of ZVI+Sludge and Sludge alone. Therefore, initial pH of the water was adjusted to be between 6.0 and 7.15 in this study. The pH values for all samples containing the bacteria inoculum (Sludge) increased rapidly from an initial pH value of 7.15 to above 8.0 (Figure 4-2). The pH for the blank samples remained near the initial pH of 7.15 with a standard deviation of 0.048. The test results with ZVI+Sludge had the largest pH increase (+1.32 units) reflecting the high pH of the sludge plus the hydroxide generated by ZVI. Gheju M. (2011), pointed out that reactions due to ZVI will increase the pH in the water in an unbuffered system. This fact was also confirmed in this research as the pH of the ZVI+Sludge sample increased gradually, with a lag time of four hours to reach a similar value.

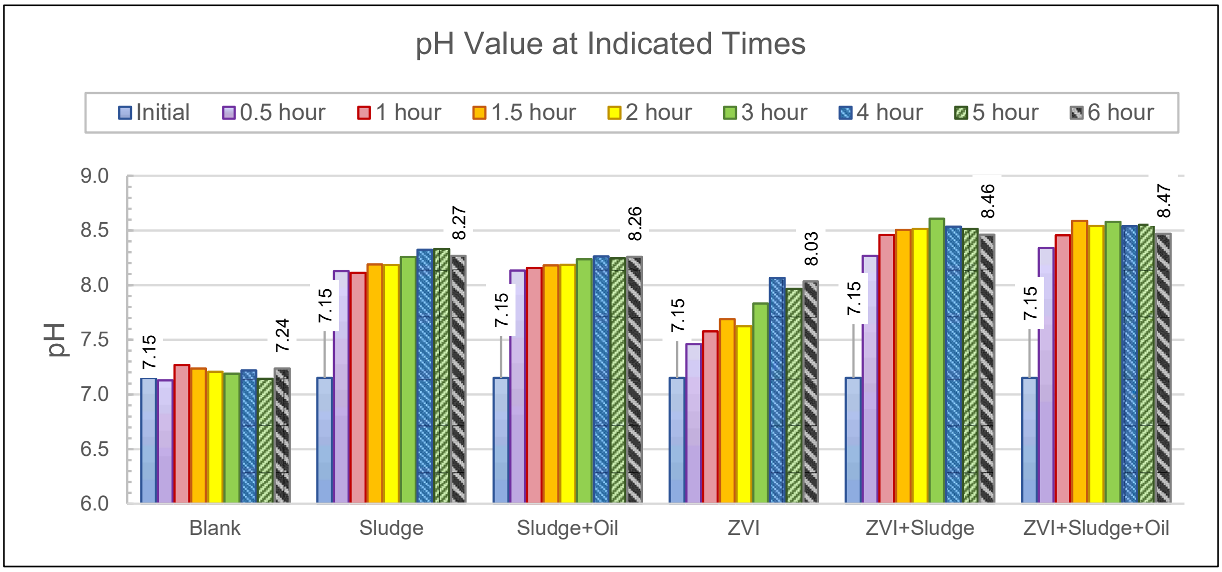


Figure 4-2: pH values at indicated times. Initial pH was 7.15.

4.2 Chlorate (ClO_3^-) Reduction Experiment Using Abiotic Reduction with ZVI, Sludge, and ZVI+Sludge

The results of the batch testing using Sludge, ZVI, and ZVI+Sludge are depicted in Figure 4-3. Reaction order and kinetics are listed in Table 4-6. Statistical analyses consisting of ANOVA and Student's t-tests are shown in Table 4-7 and Table 4-8, respectively.

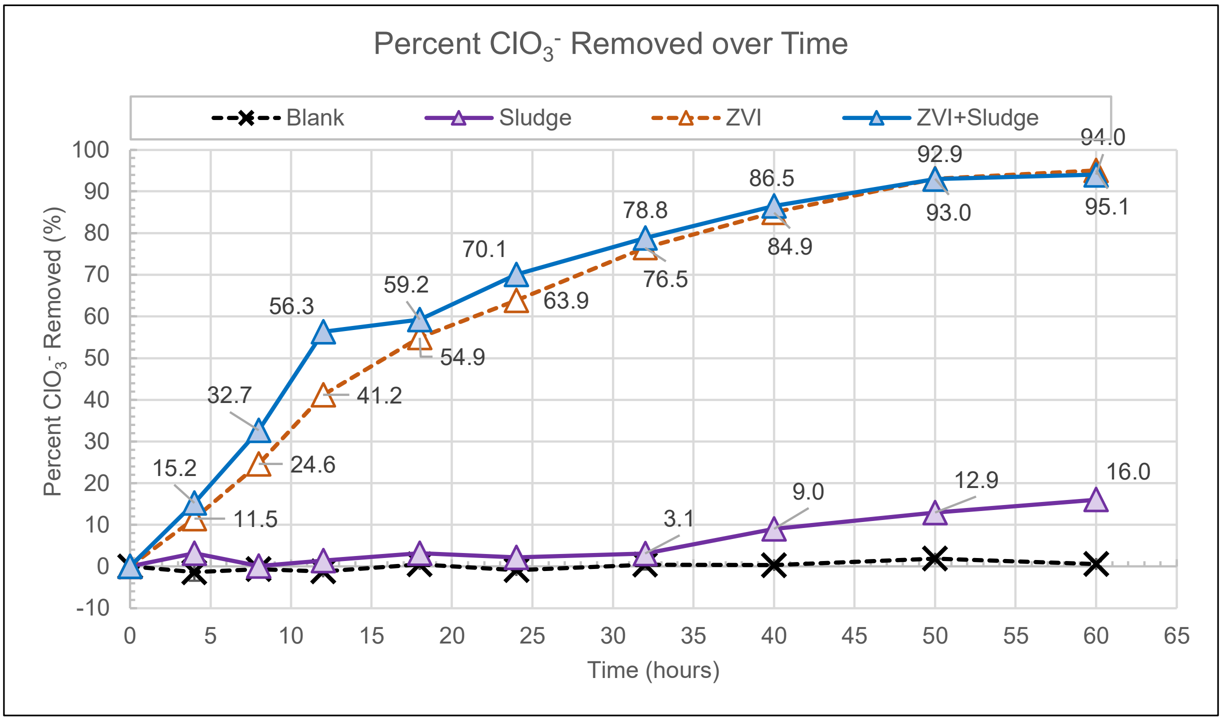


Figure 4-3: Percent ClO_3^- removed over time for Sludge, abiotic ZVI (ZVI), ZVI+Sludge, and Blank. 40 mL vials were used for the batch experiment. Initial ClO_3^- concentration was 98.3 mg/L. ZVI dose was 13.5 g/L. Sludge dose was 180mg SS/L. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

Table 4-6: Reaction kinetics for ClO_3^- removal at indicated times periods per liter • hour. Initial ClO_3^- concentration was 100 mg/L.

Method	Stoichiometric Ratio + Solids	Maximum Rate	Overall Rate
		mg Cr(VI)•L-1•hr $^{-1}$	
Sludge	180mg SS/L	0.7875	0.2625
ZVI	70X = 13.5g/L ZVI	4.0750	1.5655
ZVI+Sludge	70X = 13.5g/L ZVI + 180mg SS/L	5.8125	1.5398

Table 4-7: Results for ANOVA single factor for co-contaminants for the percent removal of ClO_3^- using Sludge, ZVI, ZVI+Sludge, and Blank.

Description/Category	Contaminant	F	p value	F_{crit}
Determine whether there was a significant difference between the reduction methods.	ClO_3^-	17.15	4.41E-7	2.87

Table 4-8: Results for paired Student's t-test for percent ClO_3^- removed for ZVI-Sludge, ZVI, Sludge, and blank samples. Student's t-test is two-tailed with assumed unequal variance.

Description/Category	Student's t-test Analysis Between	P-value
Determine whether there was a significant difference between the ClO_3^- reduction methods.	ZVI+Sludge and ZVI	0.792
	ZVI+Sludge and Sludge	4.87E-4
	Sludge and ZVI	1.46E-3
Determine whether there was a significant difference between each reduction methods and the Blank.	ZVI+Sludge and Blank	3.25E-4
	Sludge and Blank	1.81E-2
	ZVI and Blank	6.99E-4

Both ZVI+Sludge and ZVI effectively reduced ClO_3^- at a rapid rate compared to Sludge alone, Figure 4-3. ZVI+Sludge degraded 15.2% ClO_3^- (14.9mg/L) within 4 hours. ZVI, similarly degraded 11.5% ClO_3^- (11.3mg/L). Sludge had negligible removal up to 32-hours, at which point ClO_3^- reduction started to occur, reducing 16% ClO_3^- (16mg/L) by the end of the experiment. Both ZVI and ZVI+Sludge degraded 94% and 95%, respectively, ClO_3^- within the 60-hour time frame of the experiment. This suggests that chlorate needs longer to degrade biologically. None of the methods tested were able to completely reduce ClO_3^- within the allotted time of the experiment, although ZVI and ZVI+Sludge were within 5% of that target. The results indicate that Sludge alone had little impact on the reduction of ClO_3^- and due to this, ZVI+Sludge performs similar to ZVI. Therefore, the chlorate degradation was mostly abiotic and due to ZVI. EOS-PRO was not used in the single contaminant ClO_3^- experiments because after the single contaminant Cr(VI) experiments it was determined that the amount of carbon source present in the sludge was sufficient.

Initial statistical analysis using ANOVA revealed there to a statistically significant difference in the methods tested, Table 4-7. Additional post hoc analysis using the Student's t-test revealed there to a statistically significant difference between Sludge and the other two methods (ZVI and ZVI+Sludge). Additionally, statistical analysis confirmed the observations mentioned above, that there was no significant difference in the percent ClO_3^- removed between ZVI and ZVI+Sludge within a 95% CI, Table 4-8. Sludge was statistically significantly different ($p < 0.05$) from both ZVI and ZVI+Sludge. This fact confirms that the ZVI is the primary method of reduction in ZVI+Sludge for ClO_3^-. There was a statistically significant difference between the Blank samples and the other methods tested (Sludge, ZVI, and ZVI+Sludge).

Previous research has demonstrated that ZVI is capable of reducing ClO_3^- (Srinivasan, et al., 2009; Zarei & Ghavi, 2016; Westerhoff, 2003). Srinivasan et al. (2009) achieved 70% removal of ClO_3^- within 8-hrs using 40g/L ZVI and 40% removal using a lower dosage. Comparatively, in this research 24.6% removal of ClO_3^- in an 8-hour period was achieved using 13.5g/L ZVI. This finding reflects that the reduction of chlorate is impacted by the ZVI dosage. Table 4-6 shows how both ZVI and ZVI+Sludge reduced ClO_3^- at a faster rate than the biological reduction where there was negligible removal of ClO_3^- by Sludge until the 24-hour to 40-hour period. This contradicts Srinivasan et al., (2009) who found that the abiotic reduction rates of ZVI were slower than biological reduction rates shown in literature.

4.2.1 Determination of Reaction Order Rate Constants for Chlorate Degradation Experiment

Kinetic analyses were performed on the experimental data to determine reaction coefficients. The results of pseudo first order reactions are shown in Table 4-9. The R^2 results for each method were high (> 0.97). The k_{obs} for the Sludge method was a factor of 10 lower than both ZVI and ZVI+Sludge. The k_{obs} for ZVI and ZVI+Sludge were nearly identical. Because ZVI dominated the rate, this order and reaction rate reflect abiotic chlorate reduction by ZVI. This indicates that the ZVI component is dominating the reaction. This is confirmed in Table 4-6 which shows that the reaction rates for both ZVI and ZVI+Sludge are much greater than Sludge alone for the reduction of ClO_3^-. Running this test longer in the future will allow the rates and reaction order to be determined with more certainty.

Table 4-9: Summary of Reaction order and reaction rate coefficients for ClO_3^- degradation experiment.

Kinetic Parameters	Sludge	ZVI	ZVI+Sludge
Pseudo First-Order Reaction			
K_{obs} (min^{-1})	7.67E-5	8.65E-4	8.10E-4
R^2	0.971	0.992	0.988

4.2.2 pH Obtained for ClO_3^- Reduction Experiment

The pH values for the abiotic ZVI and ZVI+Sludge were reduced slightly within the first four hours (7.36 and 7.32 respectively) but finished with a similar value. Whereas the Sludge samples ended nearly 1.40 pH units lower than the initial value, Figure 4-4. The initial pH for the contaminated water was 7.97. The Blank samples remained near a pH of 7.97 throughout the experiment (mean of 7.92 and standard deviation of 0.114).

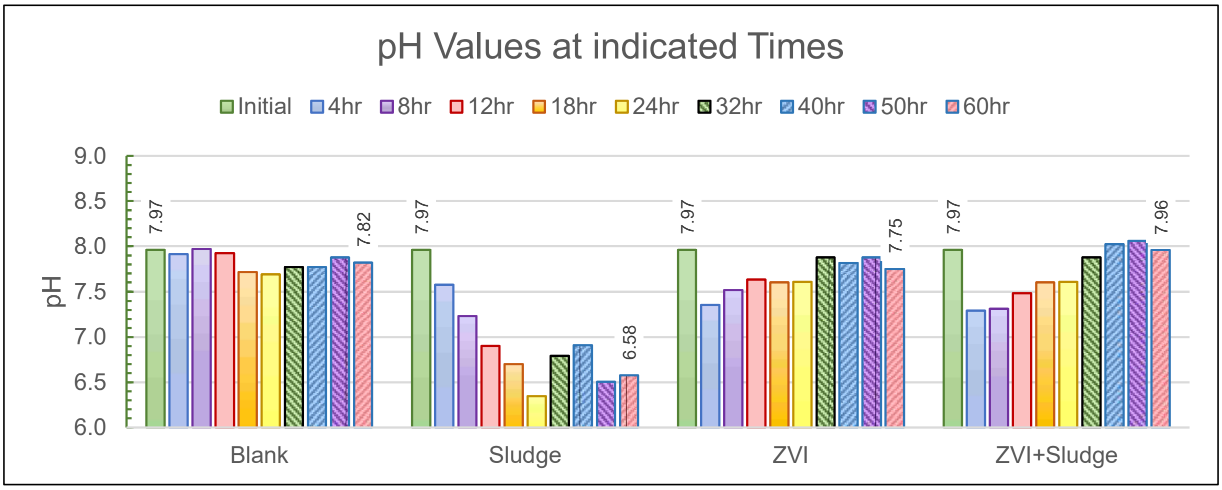


Figure 4-4: pH values for ClO_3^- degradation experiment at indicated times for Sludge, ZVI, ZVI+Sludge, and blank samples. Initial pH for all samples was 7.97.

4.3 Results for Reduction of Co-contaminant [Cr(VI) and ClO_3^-] Experiments

The results of the batch testing using Sludge, ZVI, and ZVI in conjunction with sludge (ZVI+Sludge) are depicted in Figure 4-5 and Figure 4-6. Reaction kinetics is listed in Table 4-10. The statistical analysis, ANOVA and Student's t-test results are shown in Table 4-11 and Table 4-12, respectively.

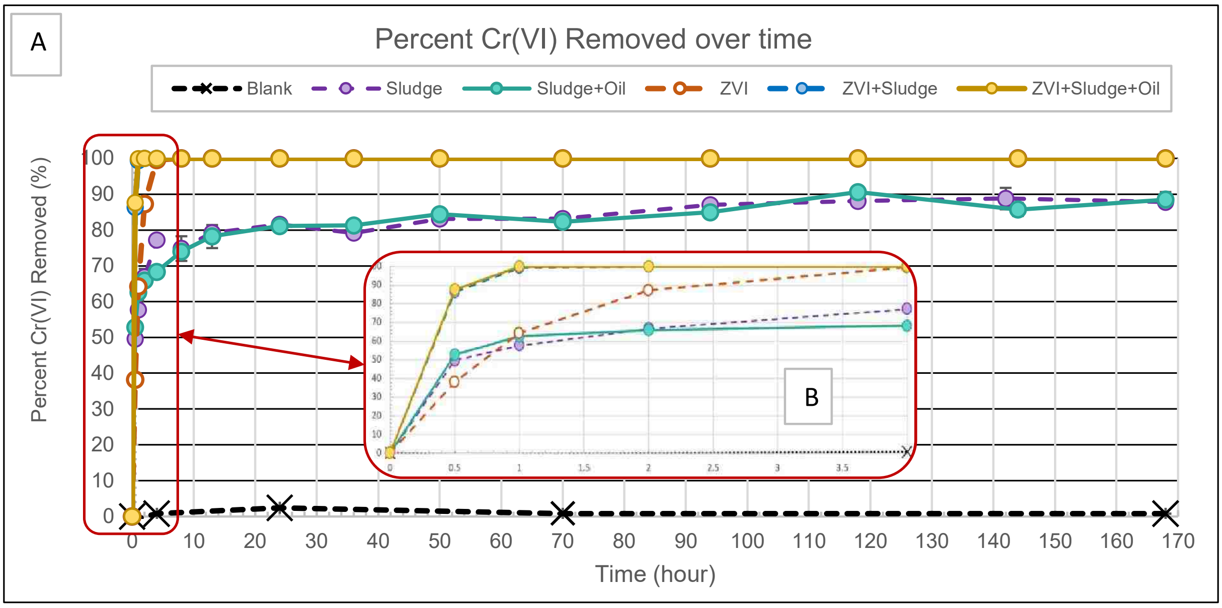


Figure 4-5: Percent Cr(VI) removed over time for multiple contaminants experiment. [A] shows degradation for the entire duration of the experiment (168 hours). Insert [B] shows a close-up from 0 hours to 4 hours. Volume of vial was 40mL. Initial contaminant concentrations were 30 mg/L Cr(VI) and 100 mg/L ClO_3^- (degradation shown in Figure 4-6). ZVI dosage for both ZVI+Sludge and abiotic ZVI was 19.8 g/L. Stoichiometric ratio was 80X. Sludge dosage for both Sludge and ZVI+Sludge was 180mg SS/L. EOS-PRO oil was added for comparison. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

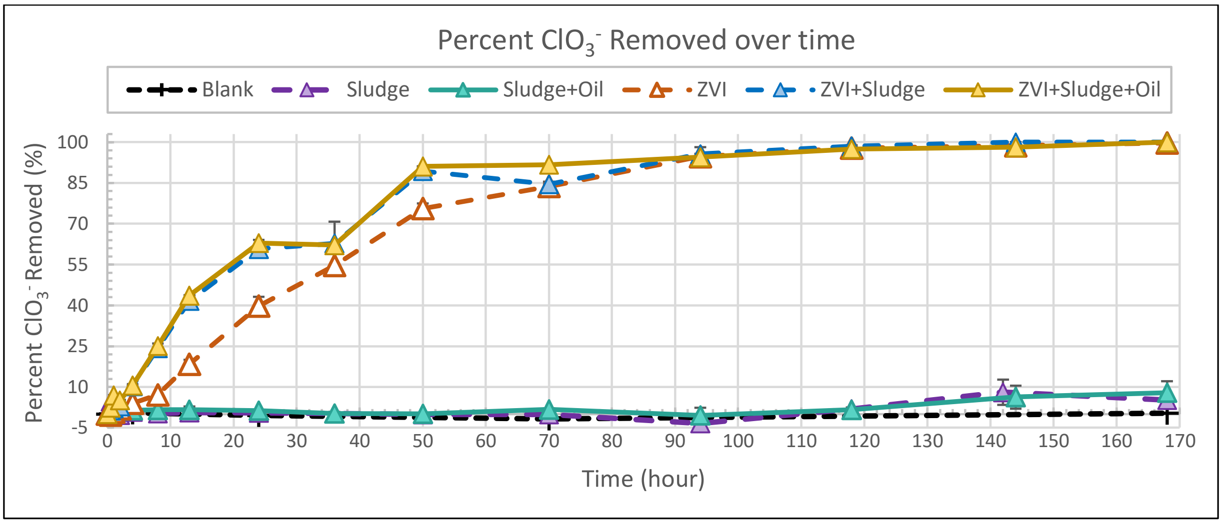


Figure 4-6: Percent chlorate removed over time for multiple contaminants experiment by Sludge (with and without EOS-PRO oil), ZVI, and ZVI+Sludge (with and without EOS-PRO oil). Volume of vial was 40mL. Initial contaminant concentrations were 30 mg/L Cr(VI) (degradation shown in Figure 4-5) and 100 mg/L ClO_3^- ZVI dosage for both ZVI+Sludge and abiotic ZVI was 19.8 g/L. Stoichiometric ratio was 80X. Sludge dosage for both Sludge and ZVI+Sludge was 180mg SS/L. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

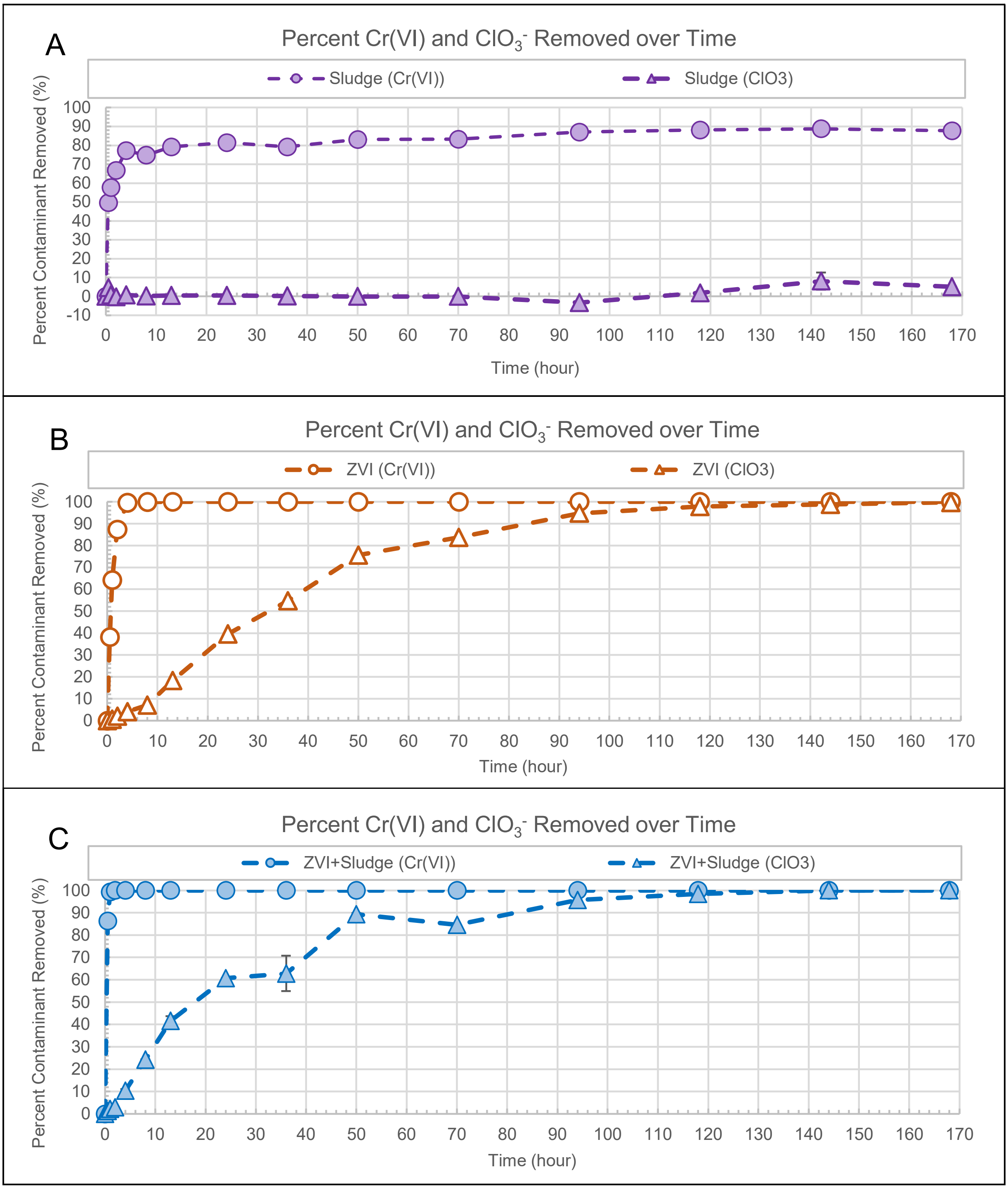


Figure 4-7: Comparison of percent Cr(VI) and ClO_3^- removed using [A] Sludge, [B] ZVI, and [C] ZVI+Sludge. Initial contaminant concentrations were 30mg/L Cr(VI) (degradation shown in Figure 4-5) and 100 mg/L ClO_3^- ZVI dosage for both ZVI+Sludge and abiotic ZVI was 19.8g/L. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

Table 4-10: Reaction kinetics for multiple contaminants (Cr(VI) and ClO_3^-) for indicated time intervals. Initial contaminant concentrations were 30 mg/L Cr(VI) and 100 mg/L ClO_3^-.

Method	Stoichiometric Ratio + Solids	Contaminant	Maximum Rate	Overall Rate
			mg Contaminant$\cdot L^{-1}\cdot hr^{-1}$	
Sludge	180mg SS/L	Cr(VI)	30.5	1.50
		ClO_3^-	1.00	2.78E-2
Sludge+Oil	180mg SS/L	Cr(VI)	32.5	1.51
		ClO_3^-	0.50	9.23E-3
ZVI	80X	Cr(VI)	23.5	2.36
		ClO_3^-	2.18	0.573
ZVI+Sludge	80X + 180mg SS/L	Cr(VI)	53.1	15.4
		ClO_3^-	3.60	0.671
ZVI+Sludge+Oil	80X + 180mg SS/L	Cr(VI)	53.9	18.7
		ClO_3^-	8.60	0.575

Table 4-11: Results for ANOVA single factor for co-contaminants removed for ZVI+Sludge at 50X, 80X, 100X and 200X stoichiometric ratios.

	Contaminant	F	p value	F_{crit}
Determine whether there was a significant difference between the reduction methods.	Cr(VI)	0.039	0.989	2.769
	ClO_3^-	1.486	0.228	2.769

Table 4-12: Results for paired Student's t-test for co-contaminants removed for ZVI+Sludge, ZVI, Sludge, and blank samples. Student's t-test is two-tailed with assumed unequal variance.

	Analysis between	Contaminant	P-value
Determine whether there was a significant difference between the reduction methods.	ZVI+Sludge and ZVI	Cr(VI)	0.532
		ClO_3^-	0.677
	ZVI+Sludge and Sludge	Cr(VI)	3.20E-2
		ClO_3^-	3.50E-4
	Sludge and ZVI	Cr(VI)	0.170
		ClO_3^-	1.38E-3
Determine whether an additional carbon source would increase the reduction of contaminants.	Sludge+Oil and Sludge	Cr(VI)	0.978
		ClO_3^-	0.616
	ZVI+Sludge+Oil and ZVI+Sludge	Cr(VI)	0.989
		ClO_3^-	0.938
Determine whether there was a significant difference in the reduction methods and the Blank.	ZVI+Sludge and Blank	Cr(VI)	1.62E-9
		ClO_3^-	2.66E-4
	ZVI and Blank	Cr(VI)	2.46E-8
		ClO_3^-	1.05E-3
	Sludge and Blank	Cr(VI)	9.17E-9
		ClO_3^-	7.57E-2

ANOVA analysis showed statistically significant difference ($p < 0.05$) between the methods evaluated for the percent removal of Cr(VI) and also the percent removal of ClO_3^-. Further post hoc analyses, consistent of Student's t-test (paired two-sample) at the 95% CI, indicated no significant difference (p values > 0.05) in the removal of either Cr(VI) or ClO_3^- between ZVI and ZVI+Sludge (Table 4-12). Therefore, ZVI lead the reduction. There was a significant difference, p values < 0.05, in the removal of Cr(VI) and ClO3- between Sludge and ZVI and also between Sludge and ZVI+Sludge. Additionally, small p values < 0.05 indicate that the methods were significantly different from the blank samples demonstrating the three methods that were evaluated had a significant impact on the percent Cr(VI). However, p values > 0.05, suggest that the methods are not statistically significantly different from the blank samples for the percent reduction of ClO_3^-, because not much degradation of chlorate occurred in this instance.

Similar to the experiment in Section 4.1, an additional carbon source (EOS-PRO oil) was added to both Sludge and ZVI+Sludge and compared to samples without the additional carbon source.

Statistical analysis showed no significant difference between ZVI+Sludge and ZVI+Sludge+Oil ($p = 0.919$ and $p = 0.953$) for Cr(VI) and ClO_3^- respectively; also, no significant difference was found when comparing Sludge and Sludge+Oil ($p = 0.966$ and 0.515) for Cr(VI) and ClO_3^- respectively (Table 4-12). As in the single contaminant Cr(VI) experiment in Section 4.1, the amount of carbon contained in the sludge was sufficient to provide for the demand of carbon during the tests. The addition of EOS-PRO made no significant difference.

Cr(VI) reduction occurred rapidly for ZVI+Sludge and ZVI, Figure 4-5, with ZVI+Sludge promoting 100% reduced within 1-hour and ZVI alone within 4-hours. Sludge alone reduced 77% of the Cr(VI) within 4 hours and only achieved 88% reduction within the total 168 hours of the experiment. In comparison, in the single contaminant Cr(VI) experiment in Section 4.1, ZVI+Sludge (133X) completely reduced the same concentration of Cr(VI) within 4-hours, an additional 3-hours longer than the multiple contaminant experiment with a lower stoichiometric ratio (80X). Abiotic ZVI was only able to reduce 42.4% of the Cr(VI) within the 6-hour duration of the experiment. Sludge was similar in that in both experiments, approximately 50% of the Cr(VI) was reduced within the first 0.5-hour and approximately 70% of the Cr(VI) was reduced within 6-hours.

Chlorate reduction took place after chromium concentrations became very low. Figure 4-7 shows a comparison of the reduction of Cr(VI) and ClO_3^- together for Sludge, ZVI, and ZVI+Sludge. The ClO_3^- reduction for both ZVI and ZVI+Sludge occurred after the reduction of Cr(VI). For Sludge however, minimal ClO_3^- reduction only seemed to start after 120-hours.

The reaction kinetic summary shows the maximum and overall rate of the Cr(VI) and ClO_3^- reduction (Table 4-9). The maximum rate of Cr(VI) removal for Sludge was equivalent to the individual contaminant experiments in Section 4.1 and 4.2. The maximum rate for Cr(VI) reduction was 23.5mg Cr(VI)$\cdot L^{-1} \cdot hr^{-1}$ compared to 11mg Cr(VI)$\cdot L^{-1} \cdot hr^{-1}$ in the individual contaminant experiment in Section 4.1. The maximum rate for ClO_3^- was 2.18mg $ClO_3^- \cdot L^{-1} \cdot hr^{-1}$ compared to 4.08mg $ClO_3^- \cdot L^{-1} \cdot hr^{-1}$ in the individual contaminant ClO_3^- experiment in Section 4.2. Similarly, the maximum rate for Cr(VI) reduction, for ZVI+Sludge was increased to 53.1 Cr(VI)$\cdot L^{-1} \cdot hr^{-1}$ and decreased to 3.60mg $ClO_3^- \cdot L^{-1} \cdot hr^{-1}$ for chlorate. The stoichiometric ratio for both the individual ClO_3^- experiment in Section 4.2 and the multiple contaminant experiment was 70X and 80X respectively. The increased ratio does account for some of the increase in reaction rate, but the results indicate that the competing co-contaminant ClO_3^- did not inhibit the reduction of Cr(VI) and that the contaminants are reduced in following order; Cr(VI) > ClO_3^-.

4.3.1 Determination of Reaction Rate Constants for Multiple Contaminant Reduction Experiment

Kinetic analyses were performed on the experimental data to determine the contaminant degradation rates and the orders of the reduction reactions. Results of this analysis are shown in Table 4-13 and the graphical determination of the pseudo first order rate constants is shown in Appendix C. For the reduction of Cr(VI) the k_{obs} for Sludge decreased by a factor of 10 compared to the single contaminant Cr(VI) experiment, Section 4.1. ZVI+Sludge increased by a factor of 4.5 and abiotic ZVI increased by over a factor of 10. The increase in k_{obs} is likely due to the increase in ZVI dosage for multiple contaminants, although the single contaminant Cr(VI) experiment had a higher stoichiometric ratio (133X). As shown in this experiment, ClO_3^- is reduced after Cr(VI), therefore the higher dosage of ZVI would be used to increase the rate of degradation of Cr(VI).

For the reduction of ClO_3^-, both ZVI and ZVI+Sludge had nearly identical k_{obs} values (5.60E-4 min^{-1} and 5.65E-4 min^{-1}, respectively). Also, both ZVI and ZVI+Sludge were a factor of 10 greater than the k_{obs} for Sludge. Unlike with the Cr(VI), the k_{obs} are less than the k_{obs} for the single contaminant ClO_3^- experiment. This is likely due to the reduction of Cr(VI) occurring before the ClO_3^-.

Table 4-13: Summary of Reaction order and coefficients for multiple contaminant experiment

Kinetic Parameters	**Sludge**	**Sludge+Oil**	**ZVI**	**ZVI+Sludge**	**ZVI+Sludge+Oil**
Pseudo First-Order Reaction [Cr(VI)]					
k (min^{-1})	5.20E-3	8.00E-3	1.74E-2	8.39E-2	0.122
R^2	0.817	0.706	0.973	0.986	0.942
Pseudo First-Order Reaction [ClO_3^-]					
k (min^{-1})	3.00E-5	2.17E-5	5.60E-4	5.65E-4	4.93E-4
R^2	0.909	0.969	0.988	0.970	0.962

4.3.2 pH Results for Co-contaminant Experiment

In this study, the pH values for all samples containing the bacteria inoculum (Sludge) increased rapidly from an initial pH value of 6.74 to above 8.4. The pH for the Sludge only samples slowly decreased to near initial pH values. The final pH for all the samples containing ZVI was greater than 8.2. The pH values for the Blank sample exhibited higher variabilities than in the previous experiments. The higher pH in this experiment also reflects the greater use of iron to reduce the contaminants present.

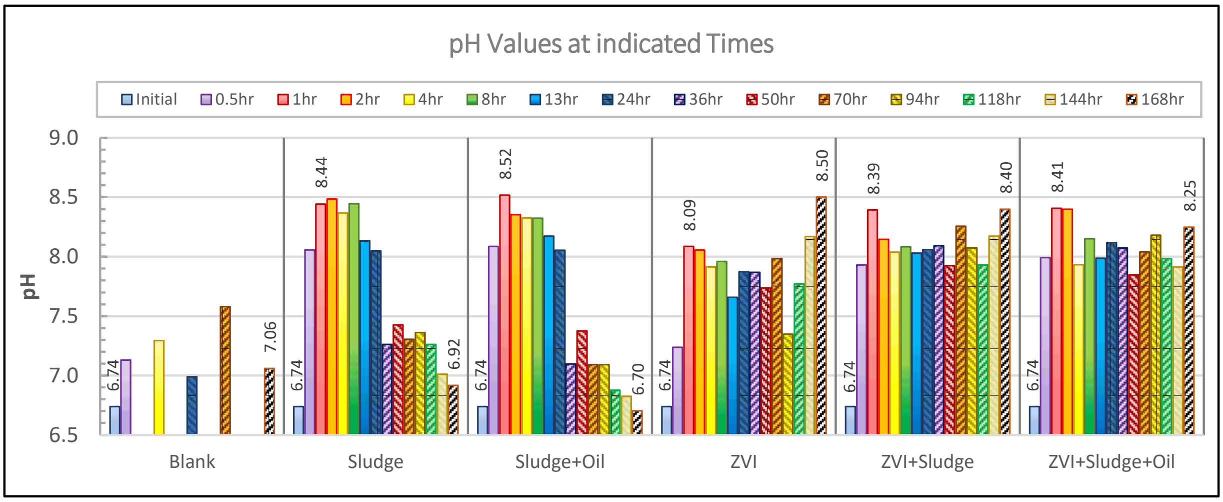


Figure 4-8: Final pH values at indicated times for multiple contaminants experiment. Initial pH for contaminated water was 6.74. Initial, 1-hr, and final pH are listed.

4.4 Results for ZVI+Sludge Reduction of Co-contaminants using Varying Stoichiometric Ratios

The results of the batch testing using ZVI+Sludge at varying stoichiometric ratios are depicted Figure 4-9 and Figure 4-10. Reaction kinetics are listed in Table 4-14. The statistical analysis, ANOVA and Student’s t-tests are shown in Table 4-15.

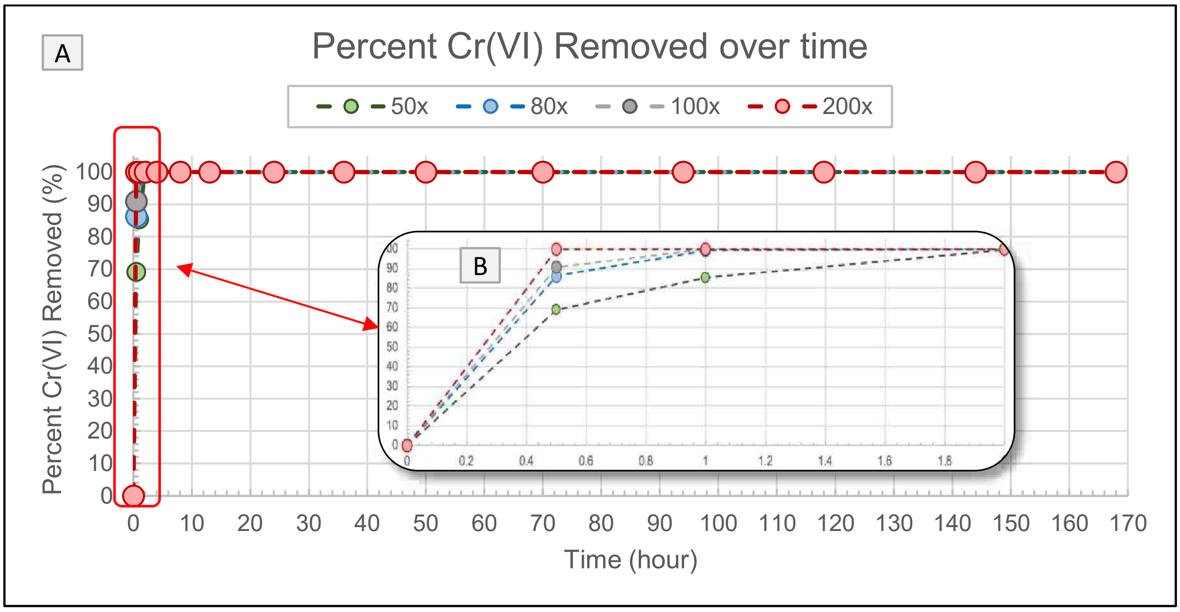


Figure 4-9: Percent Cr(VI) removed over time forZVI+Sludge at 50X, 100X, and 200X stoichiometric ratios. 80X stoichiometric ratio, from multiple contamination degradation experiment included for comparison. [A] shows Cr(VI) degradation over entire period of the experiment (168 hours). [B] shows Cr(VI) degradation from 0 hour to 2 hours. Initial contaminant concentrations were 30 mg/L Cr(VI) and 100 mg/L ClO_3^- (shown in Figure 4-10). ZVI dosage was 12.4 g/L, 25.0 g/L, and 50 g/L for 50X, 100X, and 200X respectively. Sludge dosage was 180mg SS/L. EOS-PRO was not used. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

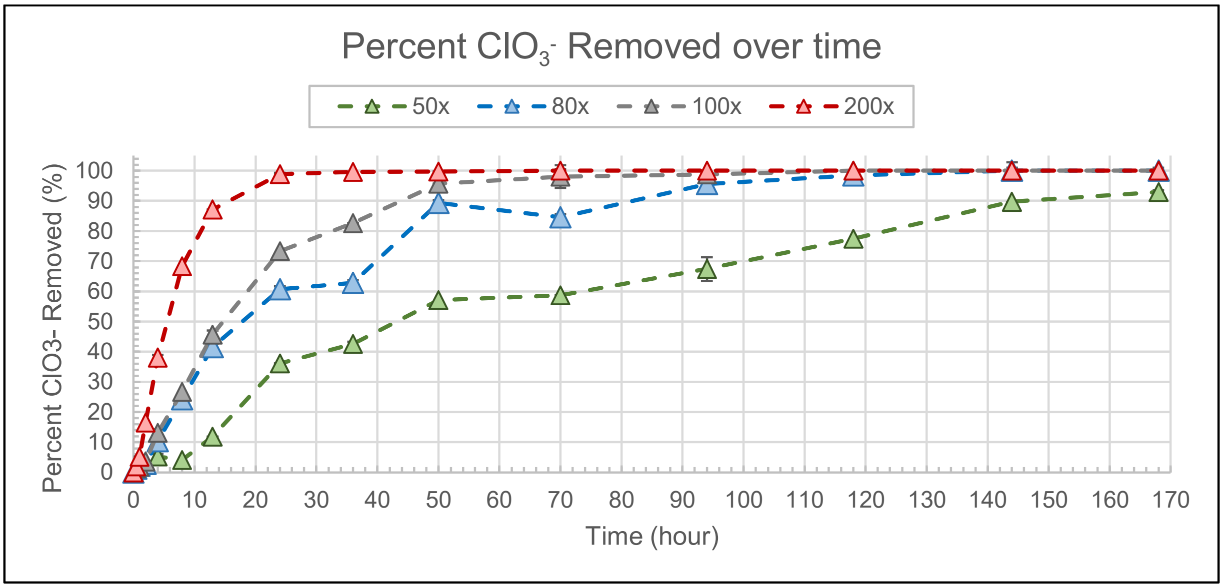


Figure 4-10: Percent chlorate removed over time for ZVI+Sludge at 50X, 100X, and 200X stoichiometric ratios. 80X stoichiometric ratio, from multiple contamination reduction experiment (Section 4.3) included for comparison. Initial contaminant concentrations were 30mg/L Cr(VI) (shown in Figure 4-9) and 100 mg/L ClO$_3^-$. ZVI dosage was 12.4g/L, 25.0g/L, and 50g/L for 50X, 100X, and 200X respectively. Sludge dosage was 180mg SS/L. No EOS-PRO was used. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

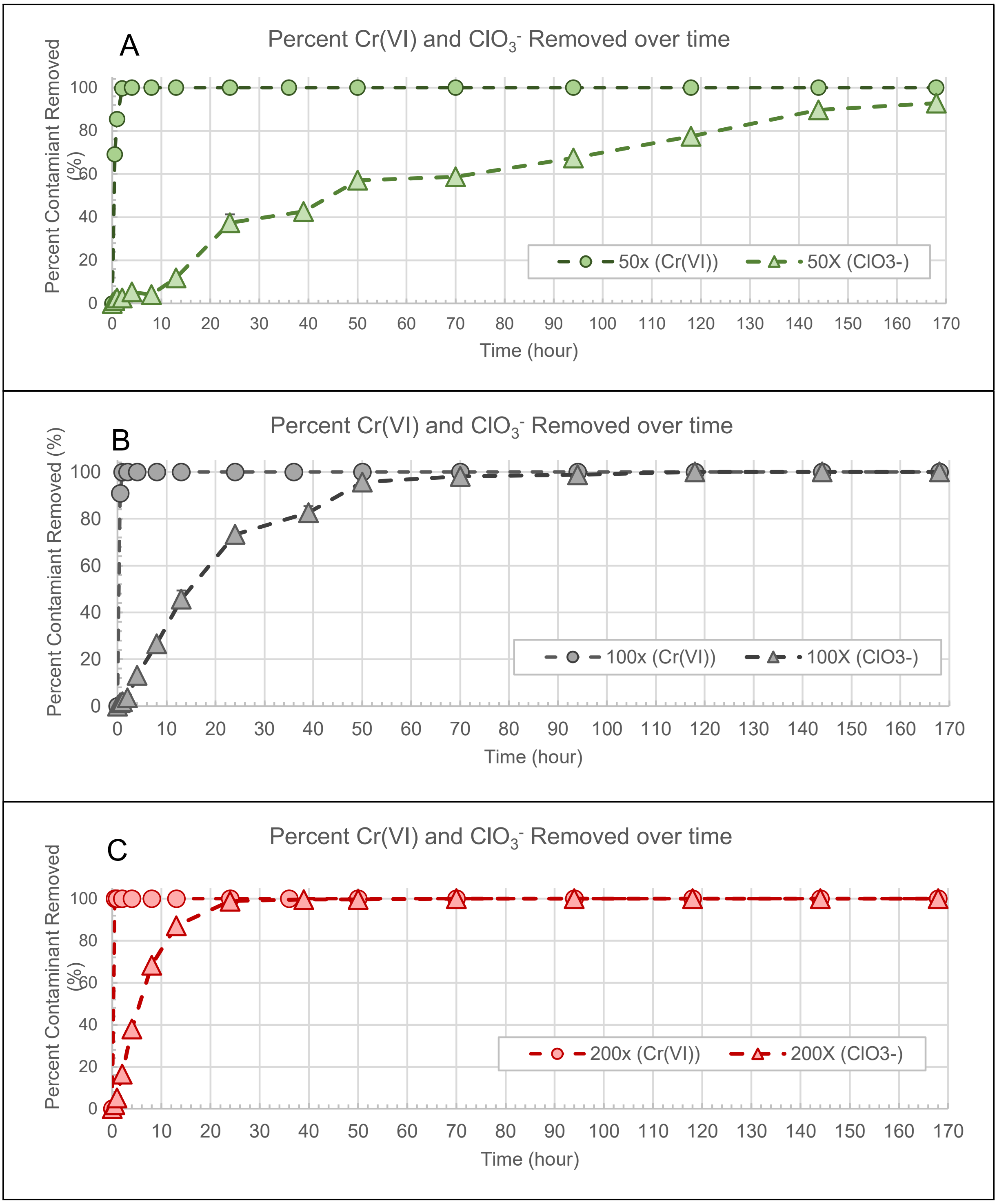


Figure 4-11: Comparison of percent Cr(VI) and ClO_3^- removed using ZVI+Sludge [A] 50X stoichiometric ration, [B] 100X, and [C] 200X. Initial contaminant concentrations were 30 mg/L Cr(VI) and 100 mg/L ClO_3^- ZVI dosage for both ZVI+Sludge and abiotic ZVI was 19.8g/L. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

Table 4-14: Reaction kinetics for varying stoichiometric ratios of ZVI+Sludge to degrade multiple contaminants (Cr(VI) and ClO_3^-) for indicated time intervals. Initial contaminant concentrations were 30mg/L Cr(VI) and 100 ClO_3^-.

Method	Stoichiometric Ratio + Solids	Contaminant	Maximum Rate	Overall Rate
			mg Cr(VI)•L^{-1}•hr^{-1}	
50X	50X +180mg SS/L	Cr(VI)	42.6	7.70
		ClO_3^-	2.80	0.534
80X[1]	80X +180mg SS/L	Cr(VI)	53.1	15.4
		ClO_3^-	3.60	0.671
100X	100X + 180mg SS/L	Cr(VI)	56.0	15.4
		ClO_3^-	4.60	0.818
200X	200X + 180mg SS/L	Cr(VI)	61.5	61.5
		ClO_3^-	6.40	1.93

[1] Results for 80X from Section 4.3.

Table 4-15: Results for ANOVA single factor for co-contaminants removed for ZVI+Sludge at 50X, 80X, 100X and 200X stoichiometric ratios.

	Contaminant	F	p value	F_{crit}
Determine whether there was a significant difference between the reduction methods.	Cr(VI)	0.039	0.989	2.77
	ClO_3^-	1.486	0.228	2.77

ANOVA analysis for both the percent Cr(VI) and ClO_3^-, Table 4-15, removed showed no statistically significant difference ($p > 0.05$ and $F < F_{crit}$) in the percent Cr(VI) removed and also the percent ClO_3^- removed between the increasing and decreasing stoichiometric ratios. Further post hoc testing is unwarranted.

Reduction of Cr(VI) occurred rapidly at all three stoichiometric ratios or ZVI+Sludge tested. Cr(VI) was completely reduced within the first half hour by the 200X ZVI+Sludge. 100X and 50X ZVI+Sludge completely reduced the Cr(VI) within 1-hour and 2-hours, respectively. Comparatively, the 80X ZVI+Sludge from Section 4.3 achieved 99.3% reduction of Cr(VI) within the first hour. Chlorate reduction occurred after the reduction of Cr(VI) just as in the multiple contaminant experiment in Section 4.3. Complete reduction of ClO_3^- occurred between 50-hours and 70-hours for 200X ZVI+Sludge and after 94-hours for 100X. Only 89.7% reduction of ClO_3^- was achieved for 50X ZVI+Sludge.

Table 4-14, lists reaction kinetics results for both the maximum and overall rate of Cr(VI) and ClO_3^- reduction. The maximum rate for both Cr(VI) and ClO_3^- increased with the increase in stoichiometric ratio. For Cr(VI) the percent increase for 50X to 80X, 80X to 100X, and 100X to 200X was 24.6%, 5.46%, and 9.80%, respectively. For ClO_3^- the percent increase for 50X to 80X, 80X to 100X, and 100X to 200X was 28.6%, 27.8%, and 39.1%, respectively. Additionally, the overall reaction also increased with the increase in stoichiometric ratio.

4.4.1 Determination of Reaction Order and Reaction Rate for Increasing and Decreasing Stoichiometric Ratio Experiment

Kinetic analysis was performed on the experiment data to determine reaction rates coefficients and reaction order. All reactions were assumed to be pseudo first order. Relatively high R^2 values were obtained for each ratio tested. The reaction order for the 200X ZVI+Sludge Cr(VI) could not be determined because the reaction was too fast. The k_{obs} increased, for both Cr(VI) and ClO_3^-, as the stoichiometric ratios increased. ZVI+Sludge (80X) from the multiple contaminant experiment, Section 4.3, fits within this pattern with a k_{obs} = 8.39E-2 min^{-1} and k_{obs} = 5.64 min^{-1} for Cr(VI) and ClO_3^-, respectively.

Table 4-16: Summary of Reaction order and coefficients for multiple contaminant degradation using ZVI+Sludge at varying stoichiometric ratios.

Kinetic Parameters	50X	100X	200X
Pseudo First-Order Reaction [Cr(VI)]			
k (min^{-1})	4.59E-2	0.111	---[1]
R^2	0.964	0.971	---[1]
Pseudo First-Order Reaction [ClO_3^-]			
k (min^{-1})	2.47E-4	8.67E-4	2.21E-3
R^2	0.977	0.976	0.957

[1] Reaction occurred too fast to determine reaction order.

4.4.2 pH Results for ZVI+Sludge at Varying Stoichiometric Ratios

The pH values for the increasing and decreasing stoichiometric ratio ZVI+Sludge experiment are shown in Figure 4-12. The initial pH for the synthetic contaminated water was 6.74. All three stoichiometric ratios tested had an initial pH increase. The final measurements where the pH for 50X experiments decreased, for 100X remained around 8.00, and for the 200X gradually increased to approximately 8.50. The pH values for all the samples seemed to fluctuate somewhat over the course of the experiment. This may be related to sensitivity of the pH meter used.

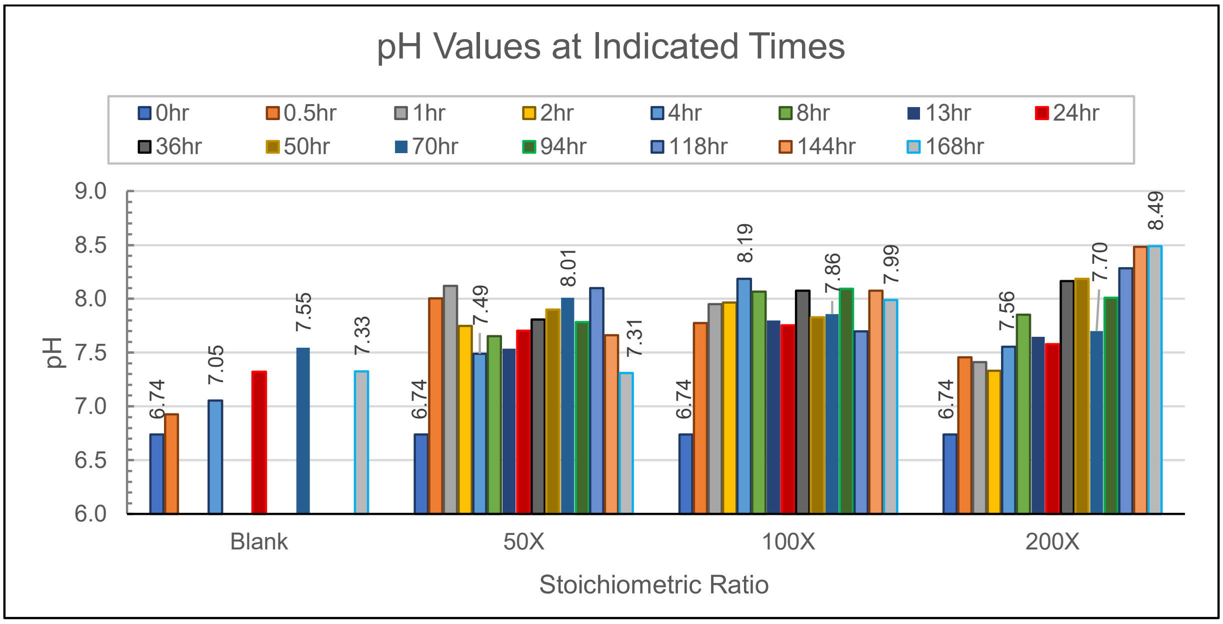


Figure 4-12: pH values at indicated times for ZVI+Sludge at 50X, 100X, and 200X stoichiometric ratios. Initial pH was 6.74. 80X stoichiometric ratio shown in Figure 4-8 (ZVI+Sludge).

Chapter 5: Conclusion and Implications

5.1 Conclusion

This research focuses on the removal of high levels (ppm range) of Cr(VI) and ClO_3^- using abiotic reduction with ZVI and biological reduction (ZVI+Sludge). The objectives of this research were to evaluate the effectiveness of ZVI alone and ZVI+Sludge to reduce Cr(VI) and ClO_3^- individually and then together. Batch experiments were performed to investigate contaminant reduction. The results were evaluated statistically to determine if ZVI+Sludge was more effective than ZVI alone for the reduction of Cr(VI) and ClO_3^-. Reaction rates were measured to evaluate if the presence of additional contaminants would impact reduction rates.

The following conclusions can be drawn from the results of this research:

1. ZVI+Sludge showed a statistically significant increase in the reduction of Cr(VI) alone over ZVI. There was a 281% increase in the maximum removal rate and a 136% increase in the overall removal rate of Cr(VI). The inoculum used showed a significant ability to reduce Cr(VI).
2. The addition of an additional carbon source had no statistically significant impact on the reduction of Cr(VI). The carbon present in the sludge itself was sufficient to promote Cr(VI) reduction.
3. ZVI+Sludge showed no statistically significant difference to ZVI alone when reducing ClO_3^- alone. The sludge had low impact on the reduction of ClO_3^-. It is likely that ClO_3^- will require a longer time period to degrade biologically.
4. There was no statistically significant difference between ZVI alone and ZVI+Sludge in the reduction of Cr(VI) in the presence of ClO_3^-. Removal rates for

Cr(VI) increased for each method tested but decreased for ClO_3^-. This is due to the order of reduction for the contaminants (Cr(VI) > ClO_3^-), signifying that an increased amount of ZVI was reducing Cr(VI) prior to reducing ClO_3^-.

5. Reducing the stoichiometric ratio of ZVI+Sludge from 80X to 50X or increasing the ratio from 80X to 100X or even 200X had no statistically significant impact on the reduction of Cr(VI) in the presence of ClO_3^-. Decreasing the stoichiometric ratio would be a cost savings in materials used.

5.2 Implications of Research

Both ZVI and biological reduction are proven technologies for the removal of Cr(VI) alone and ClO_3^- alone (Fu, et al., 2014; Mueller, et al., 2012; Megharaj, et al., 2003). The addition of a biological component to ZVI has been studied and has been shown to effectively remove Cr(VI) alone and perchlorate (ClO_4^-) alone amongst other contaminants (Nemecek, et al., 2015; Zhong, et al., 2017). The results of this study suggest an increase in contaminant reduction rates when combining chemical and biological treatment (ZVI+Sludge). Water contaminated with multiple contaminants, such as Cr(VI) and ClO_3^-, are challenging to treat and often involve unique methods. A ZVI+Sludge treatment method could reduce the amount of ZVI material required and/or increase the longevity of the system. Notwithstanding, there is a possibility of cost saving if such a treatment is implemented for remediation.

5.3 Future Work

There is much potential for a ZVI+Sludge treatment method, but additional research must be conducted, including:

1. Evaluate the role of Sludge on the enhancement of ClO_3^- removal. The sludge utilized in this experiment reduced Cr(VI) effectively but was ineffective at reducing ClO_3^- in the timeframe of the experiment. Possibly changing one or more parameters such at time, temperature, dose, or pH could enhance ClO_3^- removal. This data could be used to improve the effectiveness of the ZVI+Sludge method.
2. Evaluate ZVI+Sludge for the removal of additional contaminants such as nitrate (NO_3^-), chloroform, and perchlorate (ClO_4^-). As with this study, this would need to be tested with each contaminant individually followed by a combination of the contaminants of interest.
3. Evaluate the longevity of a ZVI+Sludge System. It would be interesting to see if a ZVI+Sludge system improved the longevity over an abiotic ZVI only system. This could be accomplished in bench scale column testing.

Appendix A: Preliminary Evaluation of Major Influencing Variables

A.1 Variables influencing reduction: Impact of ZVI Size

Two types of ZVI were selected for testing. Milli-scale iron filings (50-70 Mesh from Fisher Chemical, Fair Lawn, NJ), and micro-scale ZVI from Connelly-GPM (Chicago) were compared in a batch test. Nano-ZVI was not tested. The percent Cr(VI) removed over time is shown in Figure A-1.

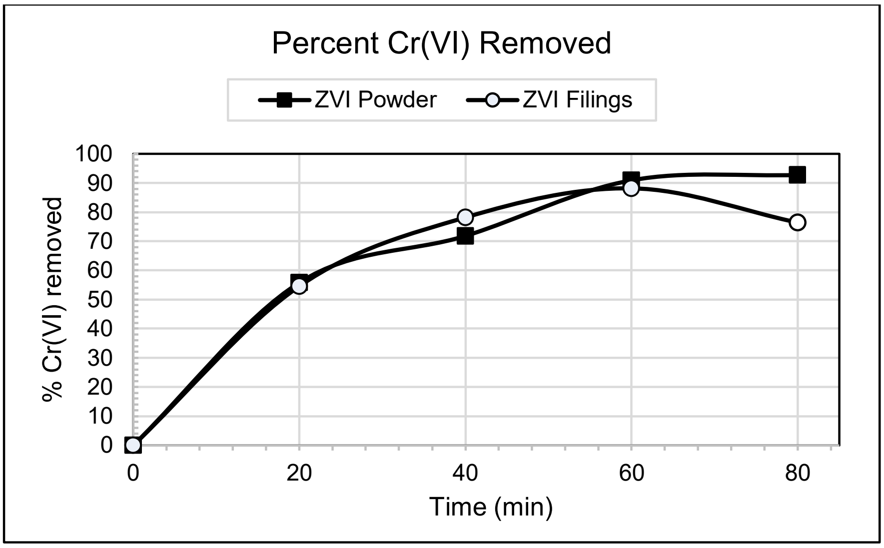


Figure A-1: Percent Cr(VI) removed over time. Batch tests performed using with 25mL of contaminant solution in 30mL vials. Initial Cr(VI) concentration was 10mg/L. ZVI dosage was 15g/L. Iron filings and powder were tested. No replicates used.

Table A-1: Statistical analysis for percent Cr(VI) removed for selection of ZVI.

Student's t-test: Two-tail, Assuming Unequal Variances – (Iron Filings and Iron Powder)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between iron filings and iron powder.		
	Iron Filings	Iron Powder
Mean	59.454	62.254
Variance	1255.206	1439.547
Observations	5	5
df	8	
P(T<=) two-tail	0.090697 (p-value > 0.05, cannot reject H_0)	

Table A-2: Cr(VI) Removal rates using abiotic ZVI filings and abiotic ZVI powder.

Method	Stoichiometric Ratio	Maximum Rate	Overall Rate
		(mg Cr(VI) • L^{-1} • hr^{-1})	
ZVI Filings	931X	18.0	6.3
ZVI Powder	931X	18.4	7.6

There was no significant difference, at the 95% CI, in the percent Cr(VI) removed between the two sizes of iron, Table A-1. This suggests that neither ZVI size is greater at reducing Cr(VI) for the parameters of the experiment. The reaction rates in Table A-2 also show similar removal rates for each ZVI size. Therefore, all following experiment were performed using ZVI powder. pH was not measured during this test.

A.2 Variables Influencing Reduction: Impact of Varying ZVI Dosages

Varying ZVI dosages were tested over multiple batch tests for Cr(VI) and ClO_3^- reduction. Cr(VI) is shown in both Section A.2.1 and Section A.2.2. ZVI dosage tests utilizing ClO_3^- are shown in Section A.2.3.

A.2.1 Impact of Decreased ZVI Dosage

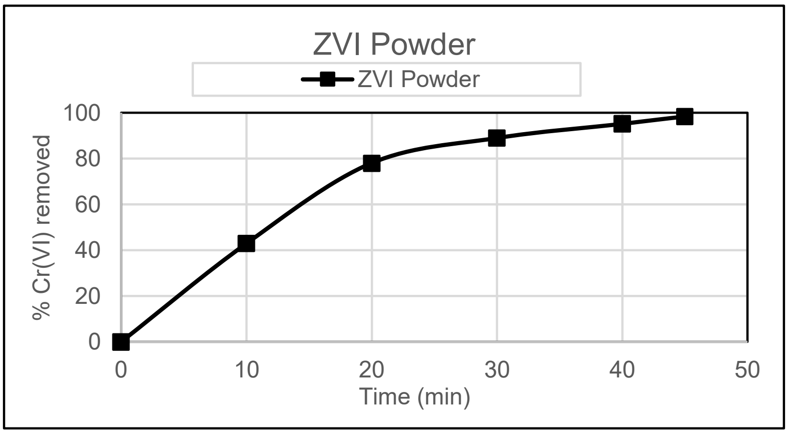


Figure A-2: Percent Cr(VI) removed over time. Initial Cr(VI) concentration was 10mg/L. ZVI dose was 10g/L. Batch test was performed using 30mL glass vials. No replicates were used.

Table A-3: Reaction kinetics for ZVI dosage test #1.

Method	Stoichiometric Ratio	Maximum Rate	Overall Rate
		(mg Cr(VI) • L^{-1} • hr^{-1})	
ZVI Powder	931X	25.8	7.4

The reaction kinetics, shown in Table A-3 show the rate maximum and overall rate of Cr(VI) removal for the reduced dosage of ZVI. Although a lower ZVI dosage was used, when compared to the Impact of the ZVI Size batch tests (Section A.1), the removal rates increased 40.2%. Nearly 100% Cr(VI) removal within 45 minutes, see Figure A-2.

A.2.2 Impact of Decreased ZVI Dosage and Increased Contaminant Concentration

Further testing using a lower ZVI dosage and higher Cr(VI) concentration was also performed. It was theorized that it would take Cr(VI) longer to degrade due to a lower stoichiometric ratio (ZVI : Cr(VI)). This approach proved to be correct (Figure A-3). Nearly 43% reduction occurred over a 62-hour period. The reduced dosage of ZVI (2g/L) coupled with the increased contaminant concentration (30mg/L Cr(VI)) as expected, caused the chromium reduction to be much slower. This fact is shown in the reaction kinetics in Table A-4. For the first half hour, the ZVI powder reduced Cr(VI) at a rate of 6.0mg Cr(VI)•L^{-1}•hr^{-1} for 63X stoichiometric ratio compared to 18.4mg Cr(VI)•L^{-1}•hr^{-1} for a 931X stoichiometric ratio in the ZVI selection tests (see Section A.1.). The pH, (Figure A-4), shows an increase in the pH of 0.84 units (from 6.87 to 7.71) over the 62-hour duration. This is likely due to the hydroxide formation when the ZVI reacts with water.

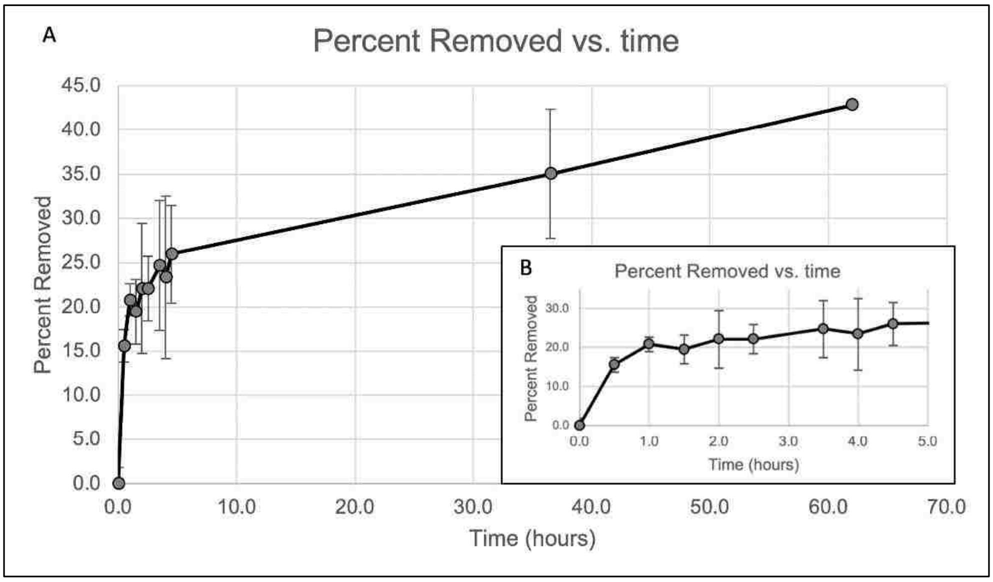


Figure A-3: Percent Cr(VI) removed over time. [A] From 0 to 62 hours and [B] from 0 to 5 hours. Batch tests performed using 30mL vials. Initial Cr(VI) concentration was 20mg/L. ZVI dosage was 2g/L. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

Table A-4: Reaction kinetics for ZVI dosage test #2.

Method	Stoichiometric Ratio	Maximum Rate	Overall Rate
		(mg Cr(VI) • L^{-1} • hr^{-1})	
ZVI Powder	63X	6.0	0.177

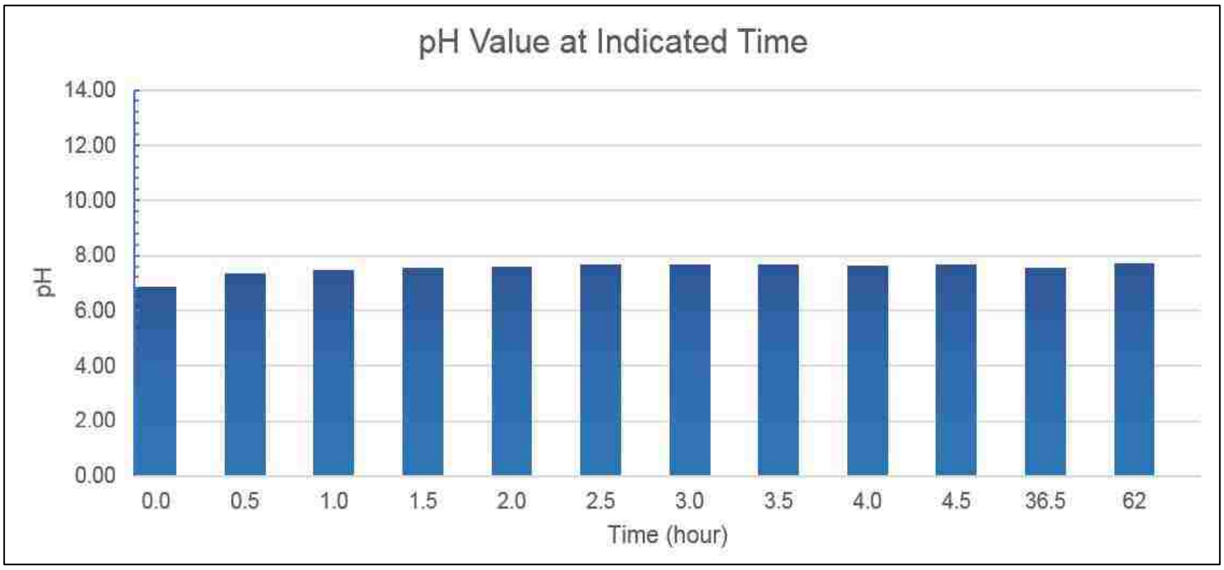


Figure A-4: pH values at indicated times for the impact of decreased ZVI dosage and increased contaminant concentration experiment. Error bars indicate one standard deviation computed from duplicates.

A.2.3 Variables Influencing Reduction: Impact of Chlorate Reduction Using ZVI

Two concentrations of ClO_3^- (10mg/L and 100mg/L) were tested with two dosages of ZVI (4g/L and 10g/L), total of four tests. The percent ClO_3^- removed over time is shown in Figure A-5. ZVI can effectively reduce ClO_3^-. The time that it takes to reduce ClO_3^- was greater than that to reduce Cr(VI). The reaction kinetic, Table A-5, show both the maximum and overall removal rates for each test. The highest maximum removal rate was for the 50X stoichiometric ratio (10g/L ZVI:100mg/L ClO_3^-) a 32.3% increase from the 20X ratio. The two higher ratios, 200X and 499X, both had the lowest removal rates, over a 150% difference from the 50X ratio. It is also noted that the highest removal rates are for the batches that contained the 100mg/L ClO_3^- vs the 10mg/L ClO_3^-. There was a slight increase in pH (between 0.3 to 0.5 pH units), Figure A-6, for all ratios tested.

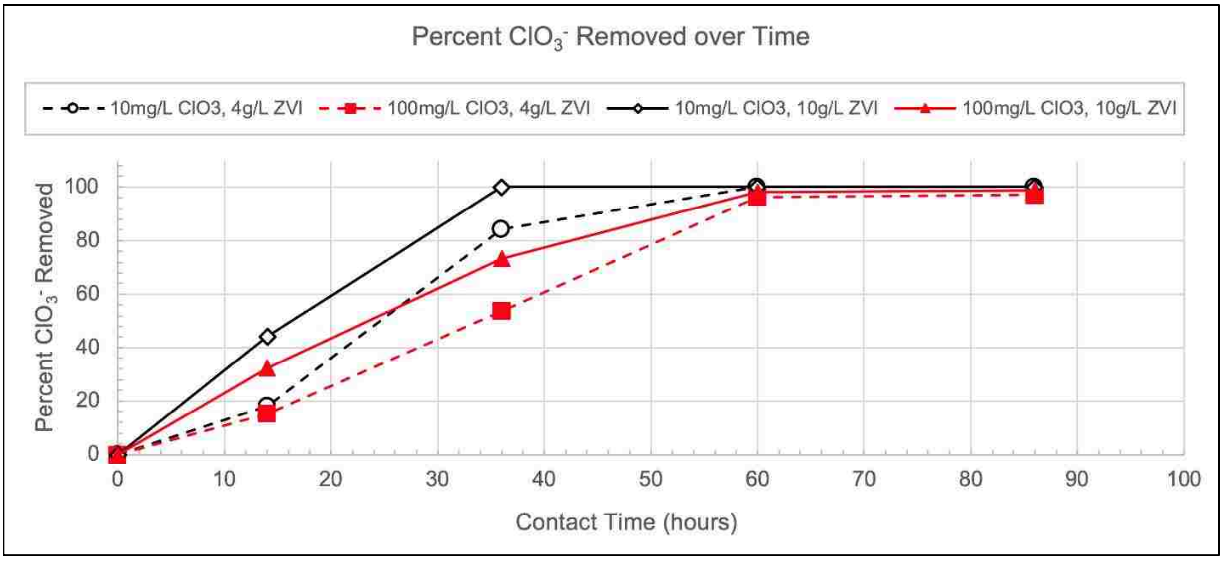


Figure A-5: Percent ClO_3^- removed over time. Initial ClO_3^- concentrations were 10mg/L and 100mg/L. ZVI doses were 4g/L and 10g/L. Batch tests were performed using 40mL glass vials. No replicates were used.

Table A-5: Reaction kinetics for chlorate ZVI dosage experiment.

Ratio	Stoichiometric	Maximum Rate	Overall Rate
g/L ZVI : mg/L ClO_3^-	Ratio	mg ClO_3^- • L^{-1} • hr^{-1}	
4:10	200X	0.3159	0.1750
10:10	499X	0.2971	0.2917
4:100	20X	1.7818	1.1524
10:100	50X	2.3571	1.1729

*Indicates complete reduction of ClO_3^-

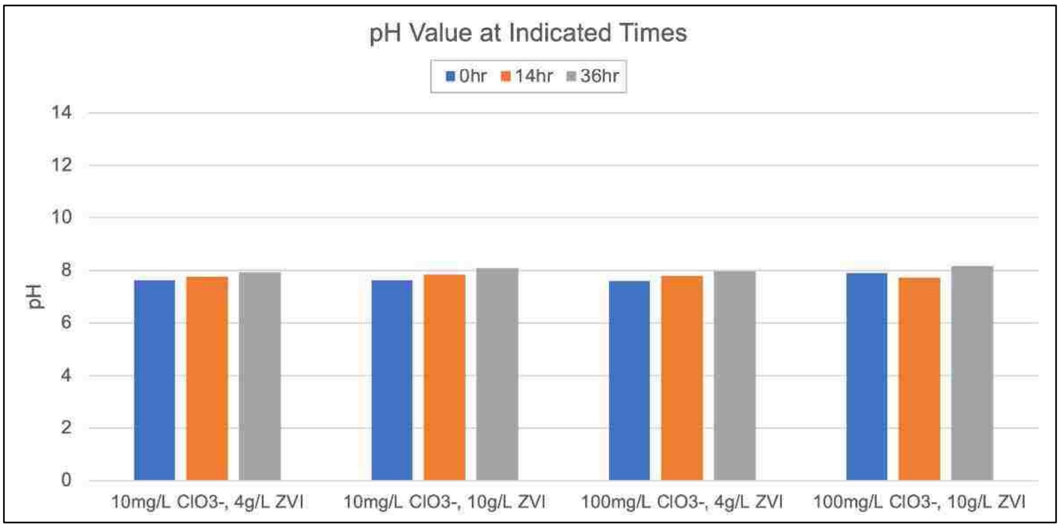


Figure A-6: pH values at indicated times for preliminary chlorate reduction batch test.

A.2.4 Variables Influencing Reduction: Impact of Varying Concentrations of ClO_3^-

Two stoichiometric ratios (70X and 130X) were investigated for the removal efficiency of low (10mg/L) to very high (1,000mg/L) concentrations of ClO_3^-. The percent ClO_3^- removed over time is shown in Figure A-7. The 1,000mg/L ClO_3^- was reduced faster than the 100mg/L and 10mg/L ClO_3^-. This is confirmed with the reaction kinetics in Table A-5. Both the maximum and overall rates for the removal of 1,000mg/L ClO_3^- are remarkably higher than the other concentrations tested. This might be due to the increase in ZVI dosage for that concentration, creating a larger amount of surface area contact with the contaminant.

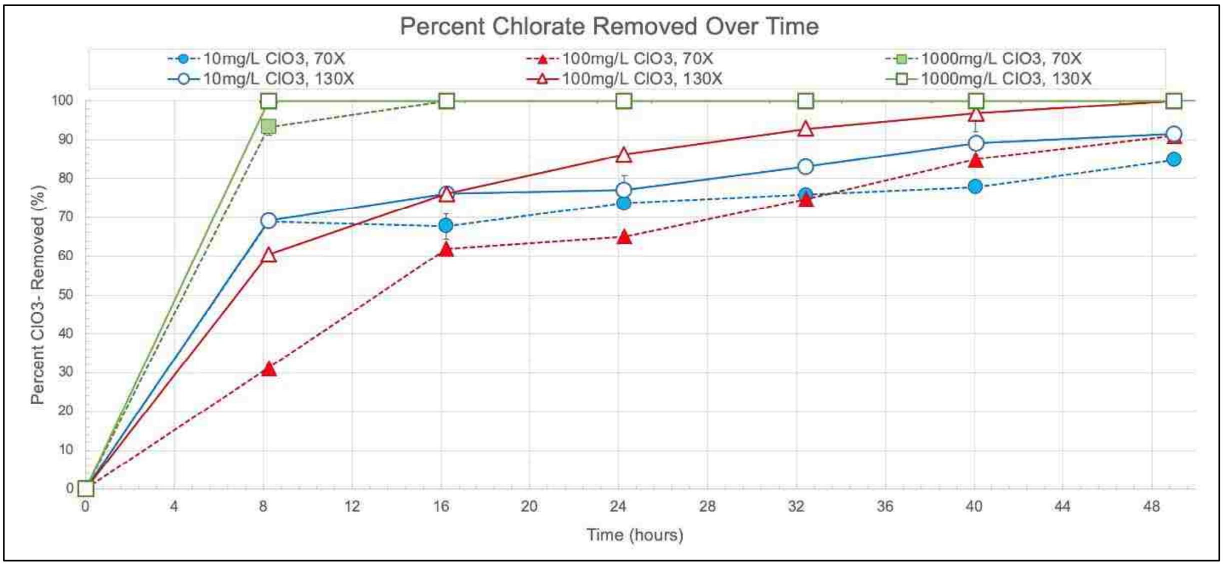


Figure A-7: Percent ClO_3^- removed over time. Batch test performed using 40ml glass vials. ClO_3^- concentrations were 10mg/L (blue), 100mg/L (red), and 1,000mg/L (green) ClO_3^-. ZVI doses ranged from 1.3g/L to 268g/L. No bacteria were used. Error bars indicate one standard deviation computed from duplicates. 30% replicates were used.

Table A-6: Reaction kinetics for impact of varying concentrations of chlorate.

Ratio	Stoichiometric	Maximum Rate	Overall Rate
ClO_3^- Concentration	Ratio	mg ClO_3^- • L^{-1} • hr^{-1}	
10mg/L	70X	0.9661	0.2002
	130X	0.9697	0.2157
100mg/L	70X	3.9636	1.9733
	130X	7.6848	2.1428
1,000mg/L	70X	113.76	61.907
	130X	121.94	121.94

*Indicates complete reduction of ClO_3^-

Table A-7: Statistical analysis comparing 70X and 130X stoichiometric ratios on the reduction of increasing levels of ClO_3^- using ZVI at 70X and 130X stoichiometric ratios. Initial ClO_3^- concentrations were 10mg/L, 100mg/L and 1,000mg/L ClO_3^-.

Student's t-test: Two-tail, Assuming Unequal Variances – (70X and 130X)		
H_0 #1: There is no significant difference in the percent ClO_3^- removed 70X and 130X for an initial concentration of **10**mg/L ClO_3^-.		
	70X	130X
Mean	64.0784	69.4188
Variance	831.375	996.976
Observations	7	7
df	12	
P(T<=) two-tail	0.74708 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent ClO_3^- removed 70X and 130X for an initial concentration of **100**mg/L ClO_3^-.		
	70X	130X
Mean	58.3878	73.1629
Variance	1040.4	1226.15
Observations	7	7
df	12	
P(T<=) two-tail	0.4276 (p-value > 0.05, cannot reject H_0)	
H_0 #3: There is no significant difference in the percent ClO_3^- removed 70X and 130X for an initial concentration of **1,000**mg/L ClO_3^-.		
	70X	130X
Mean	84.75	85.71
Variance	1402.94	1428.57
Observations	7	7
df	12	
P(T<=) two-tail	0.9625 (p-value > 0.05, cannot reject H_0)	

A t-test was performed for means or removal efficiencies among the methods tested, Table A-6. There was no statistically significant difference ($p > 0.05$) between the ratios tested (70X and 130X) in the percent ClO_3^- removed for each concentration tested. This implies that the 70X stoichiometric ratio is sufficient for the removal of the ClO_3^- present.

The pH for the batches for the removal of 1,000mg/L ClO_3^- had a higher overall increase compared to the lower ClO_3^- concentrations, Figure A-8. Average increase (average of 70X and 130X) for 10mg/L, 100mg/L and 1,000mg/L ClO_3^- was 7.77, 8.38, and 8.77, respectively. The higher increase for 1,000mg/L ClO_3^- could be due to: 1) the increase in ZVI dosage and 2) the increase in reaction rate.

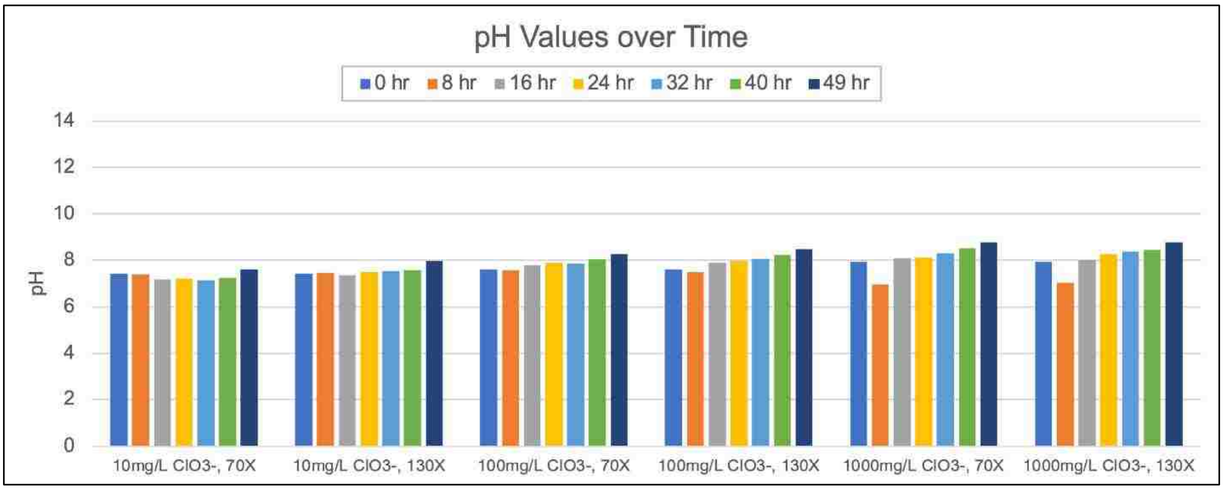


Figure A-8: pH increase over time for impact of varying concentrations of ClO_3^- experiment.

A.3 Testing Major Parameters: ZVI+Sludge vs. ZVI Alone

Abiotic ZVI and ZVI+Sludge were used to investigate the viability of ZVI in combination with biological for the removal of increasing concentrations of Cr(VI). The percent Cr(VI) removed is shown in Figure A-9. The percent Cr(VI) removed for ZVI+Sludge shows improvement over ZVI. Figures A-10 through A-13 compare the percent removal for each contaminant concentration with ZVI and ZVI+Sludge.

A t-test (paired two-sample) was performed for means or removal efficiencies among the methods used to removed increasing concentrations of Cr(VI), Table A-8. There was no statistically significant difference ($p > 0.05$) between abiotic ZVI and ZVI+Sludge for the percent Cr(VI) removed at each of the concentrations tested.

Reaction kinetics, Table A-9, showed increases in removal rates as the Cr(VI) concentrations increase. Additionally, ZVI+Sludge showed an increase in removal rates (with the exception of 5mg/L Cr(VI)) over ZVI. Percent increases ranged from 19% to over 450% for the 50mg/L Cr(VI).

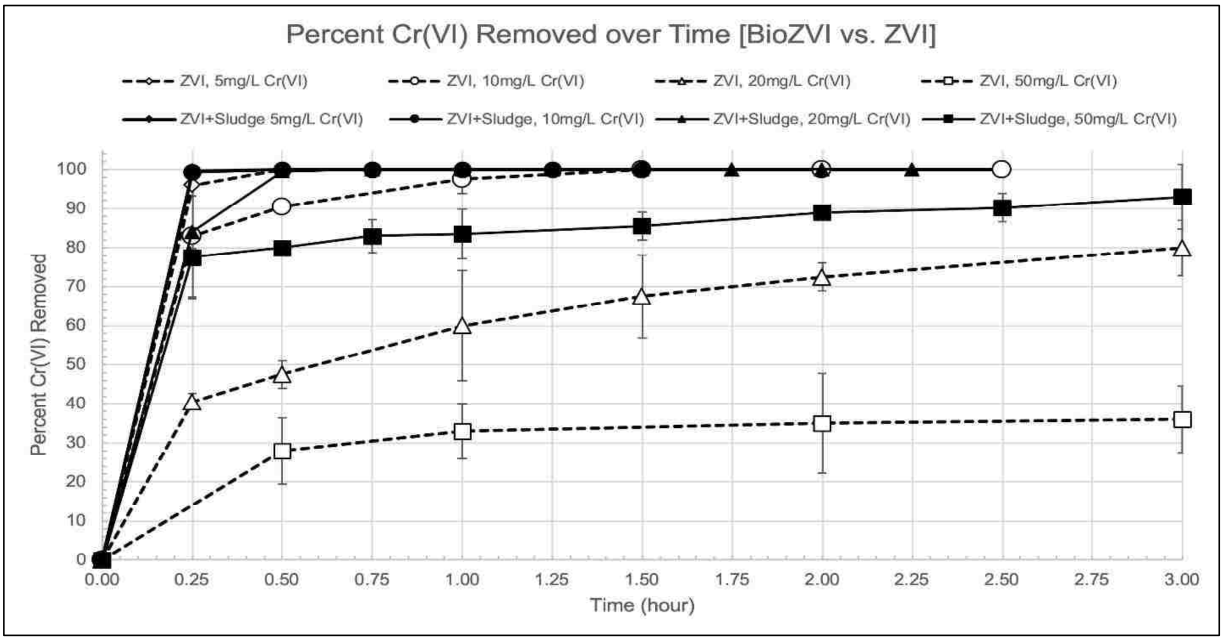


Figure A-9: Cr(VI) removed over time for ZVI+Sludge and ZVI. Batch test was performed using 40mL glass vials. Initial Cr(VI) concentration was 5mg/L, 10mg/L, 20mg/L and 50mg/L. ZVI dosage was 10g/L. Sludge dosage was 360mg SS/L. EOS-PRO was used as an additional carbon source. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

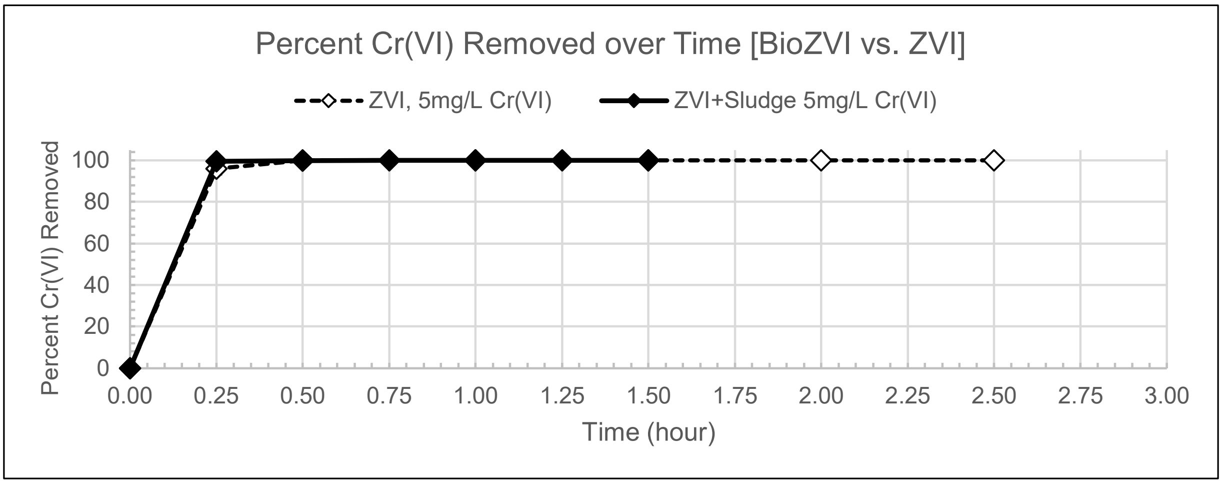


Figure A-10: 5.0 mg/L Cr(VI) removed over time for ZVI+Sludge and ZVI. Batch test was performed using 40mL glass vials. Initial Cr(VI) concentration was 5mg/L, 10mg/L, 20mg/L and 50mg/L. ZVI dosage was 10g/L. Sludge dosage was 360mg SS/L. EOS-PRO was used as an additional carbon source. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

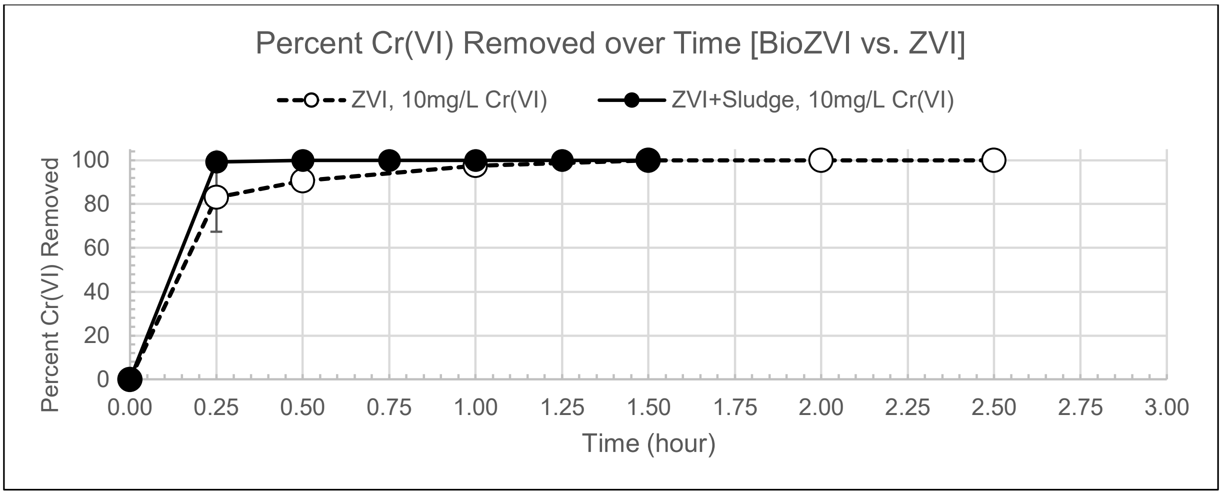


Figure A-11: 10mg/L Cr(VI) removed over time for ZVI+Sludge and ZVI. Batch test was performed using 40mL glass vials. Initial Cr(VI) concentration was 5mg/L, 10mg/L, 20mg/L and 50mg/L. ZVI dosage was 10g/L. Sludge dosage was 360mg SS/L. EOS-PRO was used as an additional carbon source. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

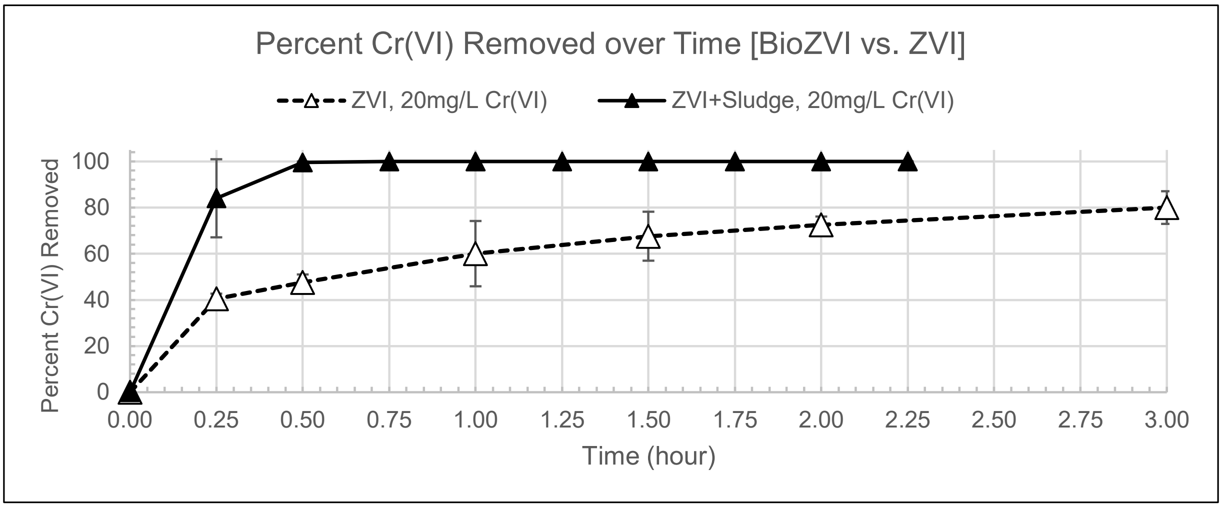


Figure A-12: 20mg/L Cr(VI) removed over time for ZVI+Sludge and ZVI. Batch test was performed using 40mL glass vials. Initial Cr(VI) concentration was 5mg/L, 10mg/L, 20mg/L and 50mg/L. ZVI dosage was 10g/L. Sludge dosage was 360mg SS/L. EOS-PRO was used as an additional carbon source. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

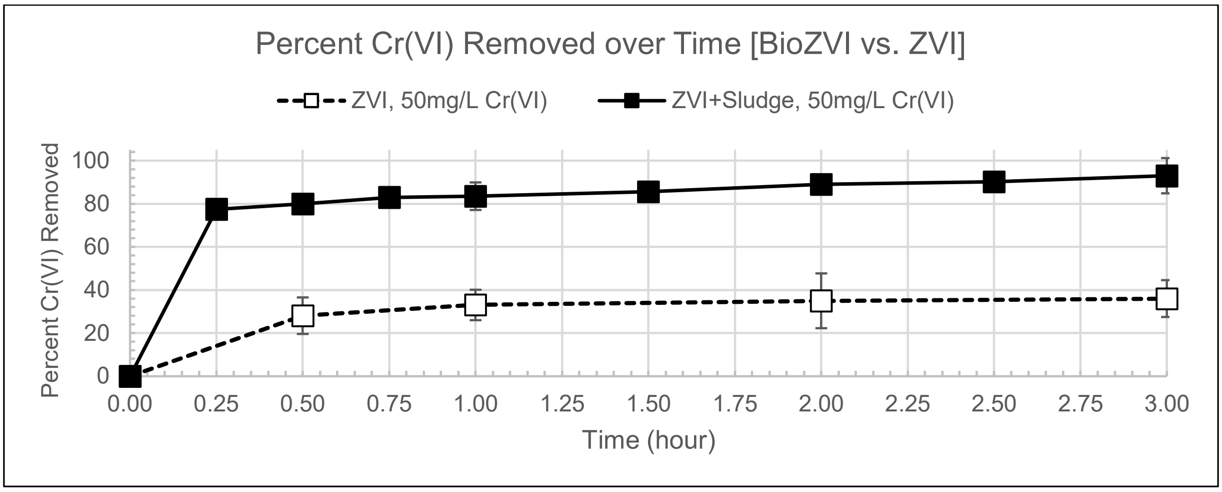


Figure A-13: 50mg/L Cr(VI) removed over time for ZVI+Sludge and ZVI. Batch test was performed using 40mL glass vials. Initial Cr(VI) concentration was 5mg/L, 10mg/L, 20mg/L and 50mg/L. ZVI dosage was 10g/L. Sludge dosage was 360mg SS/L. EOS-PRO was used as an additional carbon source. Error bars indicate one standard deviation computed from duplicates. 100% replicates were used.

Table A-8: Statistical analysis comparing ZVI and ZVI+Sludge for the percent Cr(VI) removed. Initial Cr(VI) concentrations were 15mg/L, 10mg/L 20mg/L and 50mg/L Cr(VI).

Student's t-test: Two-tail, Assuming Unequal Variances **–** (70X and 130X)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between ZVI and ZVI+Sludge for an initial concentration of **5**mg/L Cr(VI)		
	ZVI	ZVI+Sludge
Mean	85.1428	85.6428
Variance	1411.809	1426.213
Observations	7	7
df	12	
P(T<=) two-tail	0.9805 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent Cr(VI) removed between ZVI and ZVI+Sludge for an initial concentration of **10**mg/L Cr(VI)		
	ZVI	ZVI+Sludge
Mean	81.5714	85.5929
Variance	1334.702	1424.602
Observations	7	7
df	12	
P(T<=) two-tail	0.8428 (p-value > 0.05, cannot reject H_0)	
H_0 #3: There is no significant difference in the percent Cr(VI) removed between ZVI and ZVI+Sludge for an initial concentration of **20**mg/L Cr(VI)		
	ZVI	ZVI+Sludge
Mean	66.2	88.35
Variance	968.956	988.781
Observations	10	10
df	18	
P(T<=) two-tail	0.1308 (p-value > 0.05, cannot reject H_0)	
H_0 #3: There is no significant difference in the percent Cr(VI) removed between ZVI and ZVI+Sludge for an initial concentration of **50**mg/L Cr(VI)		
	ZVI	ZVI+Sludge
Mean	26.4	69.1
Variance	227.3	1517.1
Observations	5	5
df	5	
P(T<=) two-tail	0.07099 (p-value > 0.05, cannot reject H_0)	

Table A-9: Reaction kinetics for ZVI+Sludge vs. ZVI batch tests.

$\mathrm{Cr(VI)}_0$	Stoichiometric	Method	Maximum Rate	Overall Rate
	Molar Ratio		(mg Cr(VI) • L^{-1} • hr^{-1})	
5mg/L	2,146X	ZVI	19.2	9.60
		ZVI+Sludge	19.2	6.67
10mg/L	1,073X	ZVI	33.2	6.67
		ZVI+Sludge	39.7	13.3
20mg/L	536X	ZVI	32.4	4.00
		ZVI+Sludge	67.2	26.7
50mg/L	214X	ZVI	28.0	1.06
		ZVI+Sludge	155	13.3

A.3.1 Testing Major Parameters: Impact of Bioaugmentation with Sludge

Varying concentration of sludge were tested against increasing concentrations of Cr(VI) to find an optimal dosage for the degradation experiments. The concept was to find a dosage of sludge that would work in concert with the ZVI to improve degradation. Figure A-14 shows the percent Cr(VI) removed for each dosage of Sludge at increasing concentrations of Cr(VI). This experiment indicated that biotic reduction of Cr(VI) is both a function of sludge dosage as well as initial contaminant concentrations, i.e. larger doses of Sludge will increase the reduction of Cr(VI) as well in lower initial concentrations of Cr(VI).

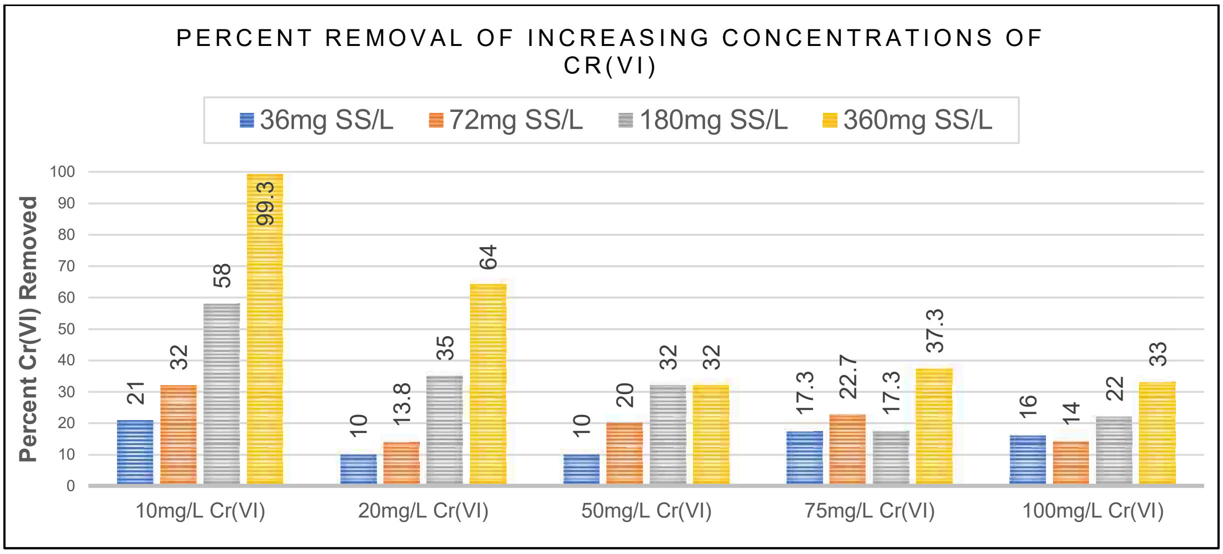


Figure A-14: Percent Cr(VI) removal as a function of contaminant concentration. Contact time was 30 minutes. Batch tests performed using 40mL glass vials. Cr(VI) concentrations were 10mg/L, 20mg/L, 50mg/L, 75mg/L, and 100mg/L. Sludge doses ranged from 36mg SS/L to 360mg SS/L. EOS-PRO was used as an additional carbon source.

A.4 Variables Influencing Reduction: Molar Ratio

Molar ratio experiments were performed to investigate the impact of a range of ZVI to Cr(VI) ratios on the reduction of Cr(VI).

A.4.1 Abiotic ZVI Molar Ratio Test

Increasing ratios of ZVI to Cr(VI) were investigated for the removal of increasing concentrations of Cr(VI). Each sample was mixed in a rotary shaker for a 30-minute duration before testing. Figure A-15 shows the percent Cr(VI) removal for each contaminant concentration as a function of molar ratios (mol ZVI : mol Cr(VI)). Each concentration appears to be following a similar path.

There was no statistically significant difference ($p > 0.05$) between each of the batch tests for the percent Cr(VI) at increasing molar ratios, Table A-10. This indicates increasing molar ratios will increase the removal of Cr(VI). Additionally, the removal of Cr(VI) is not impacted by increasing Cr(VI) concentrations as long as the ratio of ZVI to Cr(VI) is kept consistent.

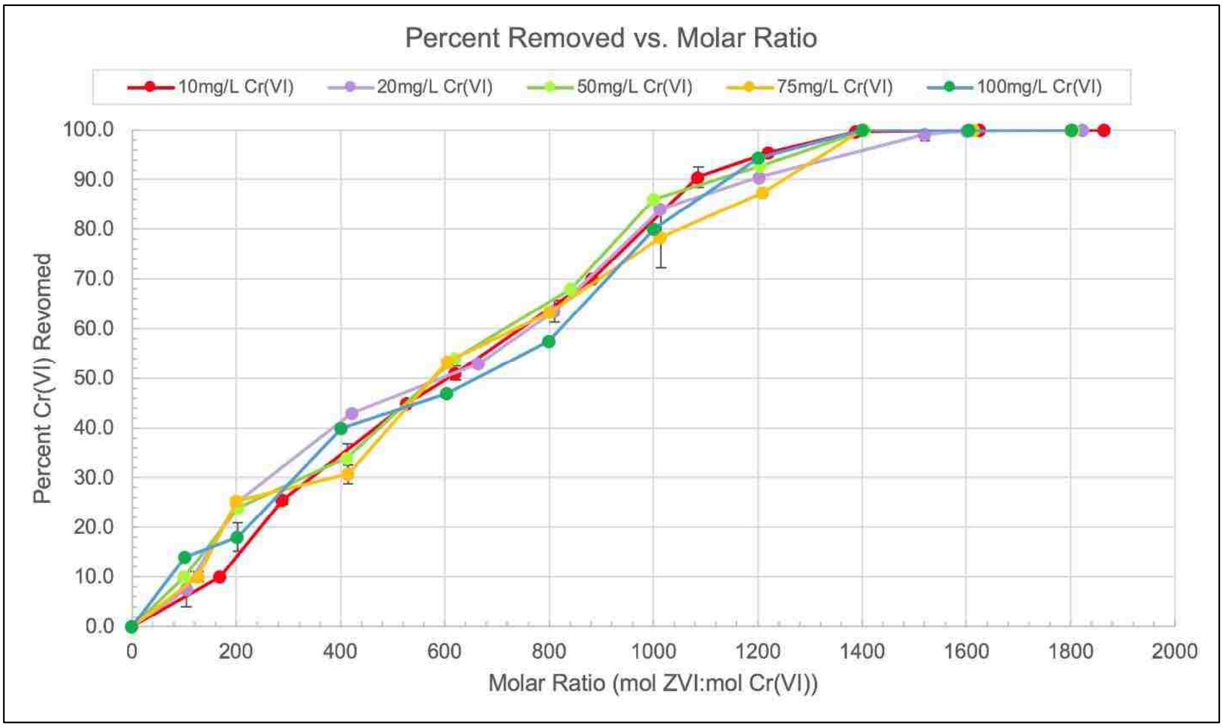


Figure A-15: Percent Cr(VI) removed as a function of molar ratio. Initial Cr(VI) concentrations were 10mg/L, 20mg/L, 50mg/L, 75mg/L, and 100mg/L. ZVI dose ranged from 1.8g/L to 194g/L. Batch test was performed using 40mL glass jars. Tests were abiotic. Error bars indicate one standard deviation computed from duplicates. 30% replicates used.

Table A-10: Statistical analysis comparing percent Cr(VI) removed for each Cr(VI) concentration.

SUMMARY

Groups	Count	Sum	Average	Variance
10mg/L Cr(VI)	11	687.1	62.4	1458.8
20mg/L Cr(VI)	11	665.5	60.5	1415.6
50mg/L Cr(VI)	11	668.8	60.8	1471.7
75mg/L Cr(VI)	11	648.3	58.9	1408.9
100mg/L Cr(VI)	11	651.9	59.3	1440.6

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	86.5	4	21.6	0.01503	0.9995	2.5572
Within Groups	71955.8	50	1439.1			
Total	72042.4	54				

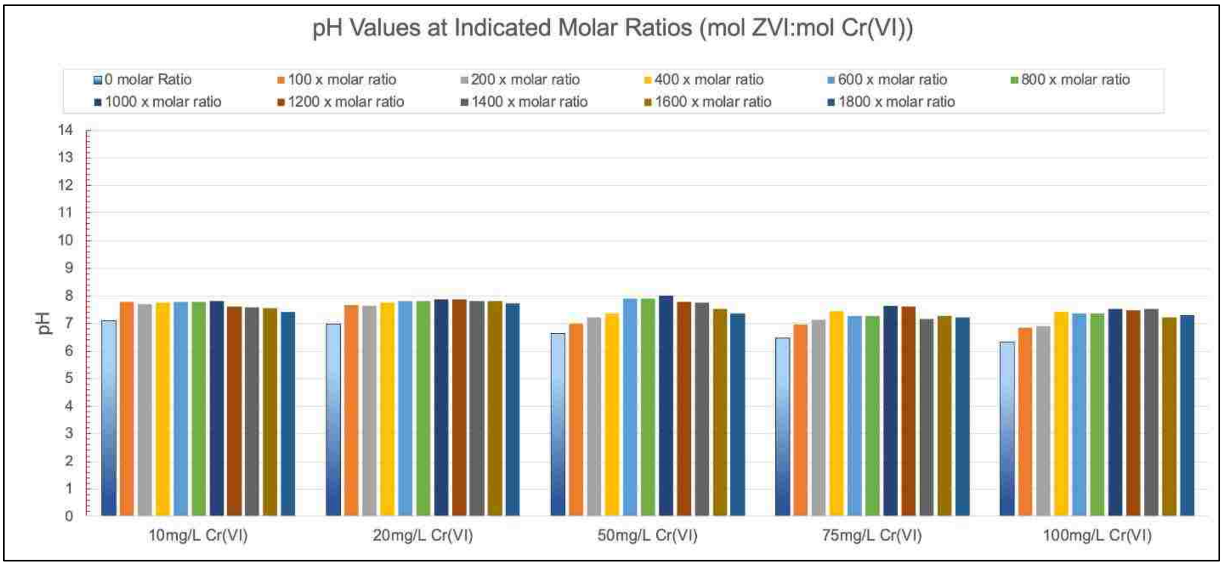


Figure A-16: pH values at indicated molar ratios for ZVI molar ratio batch tests.

The pH increased from the initial pH value, Figure A-16. This is likely due to the hydroxide formed from the reaction with ZVI and water. Initial pH was 6.65 and the largest increase was for 50mg/L Cr(VI) at the 1,000 times molar ratio.

A.4.2 ZVI+Sludge Molar Ratio Tests

An additional molar ratio test was performed to investigate the addition of biological removal of Cr(VI). The percent Cr(VI) removal is shown in Figure A-17. The ZVI+Sludge batch tests (solid and double lines) indicate some improvement over the abiotic reduction of Cr(VI) (circles with dashed lines). Figure A-18 compares the abiotic ZVI molar ratio results with ZVI+Sludge results. There is a significant increase in the removal of Cr(VI) at the lower contaminant concentrations (Figure A-18A). The addition of Sludge seems to have little impact on the higher concentrations of Cr(VI) (Figure A-18D)

The pH increase was somewhat higher (up to pH = 8.3) in this experiment compared to the abiotic ZVI molar ratio, an increase of approximately 0.3. It is unknown how much impact the sludge had on the increase in pH.

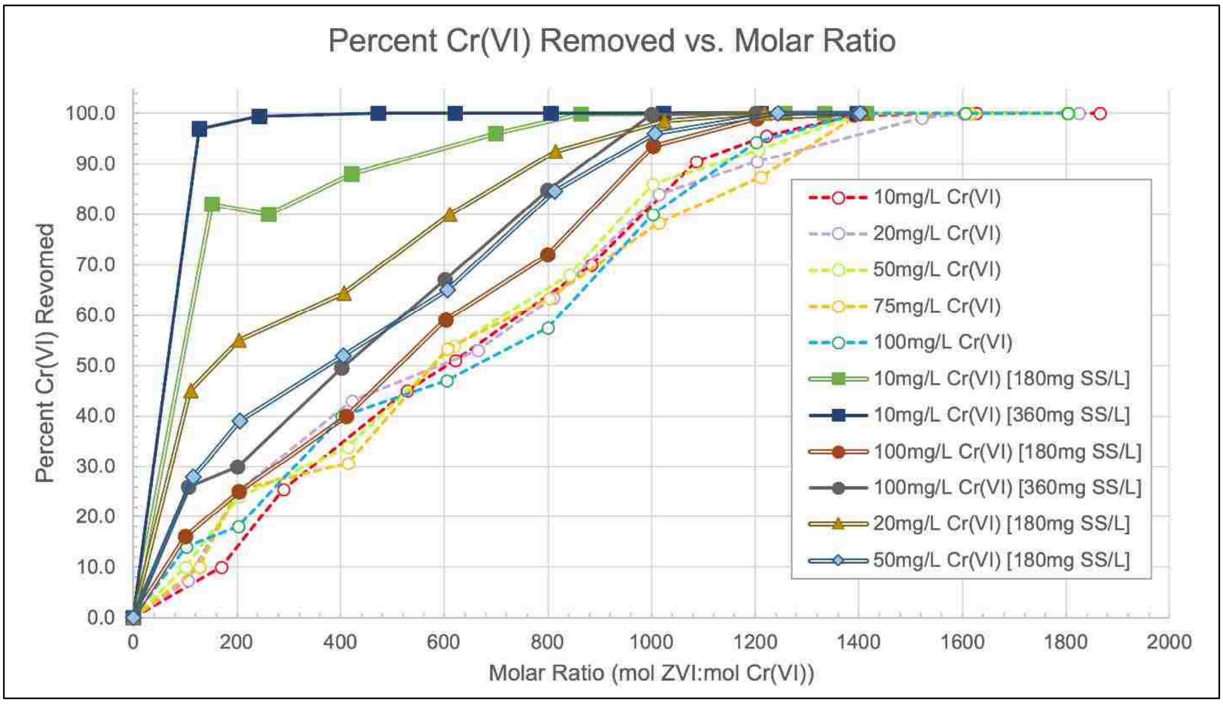


Figure A-17: Percent Cr(VI) removed as a function of molar ratio for Sludge+ZVI. Abiotic ZVI is shown for comparison as dotted lines. Initial Cr(VI) concentrations were 10mg/L, 20mg/L, 50mg/L and 200mg/L. ZVI doses ranged from 1.4g/L to 150g/L. Sludge doses were 180mg SS/L and 360mg SS/L. EOS-PRO was used as an additional carbon source. 40mL glass vials were used. 30% replicates used.

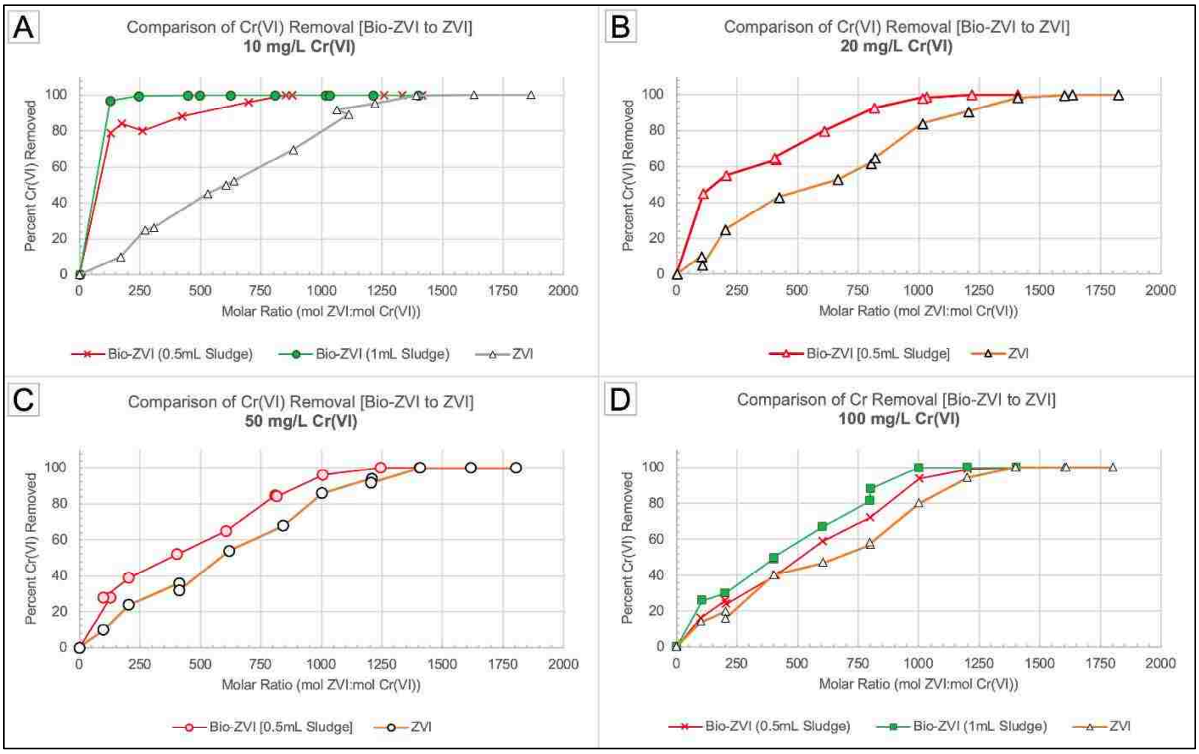


Figure A-18: Comparison of ZVI and ZVI+Sludge molar ratio batch tests at increasing Cr(VI) concentrations. [A] and [D] compares ZVI with ZVI+Sludge with two sludge doses at 10mg/L Cr(VI) and 100 mg/L Cr(VI), respectively. [B] and [C] compare ZVI with ZVI+Sludge with a sludge dose of 12.5mL/L at 20mg/L Cr(VI) and 50 mg/L Cr(VI), respectively.

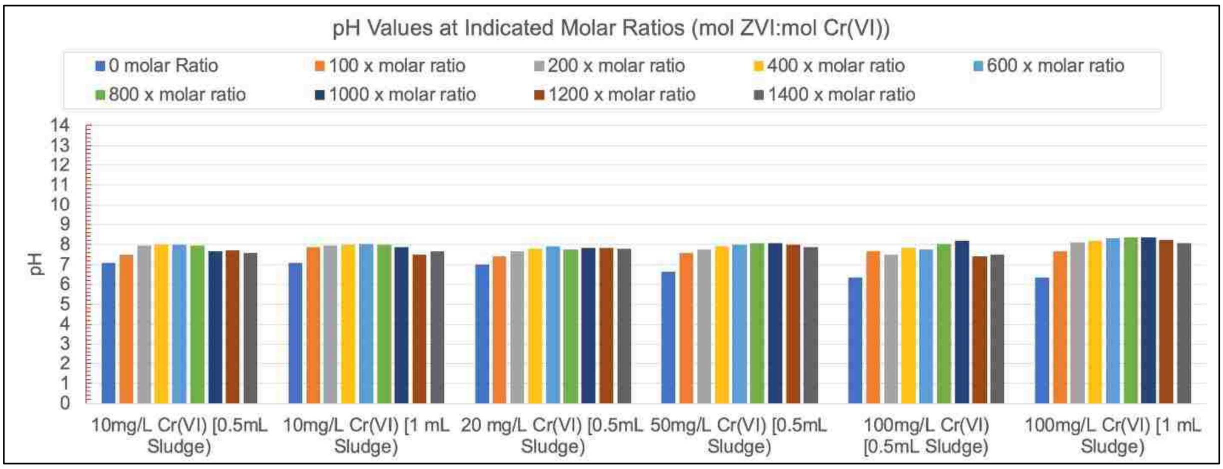


Figure A-19: pH values at indicated molar ratios for Sludge+ZVI molar ratio batch test.

Appendix B: Statistical Analysis for Contaminant Degradation Experiments

B.1 Statistical Analysis for Single Contaminant Cr(VI) Degradation Experiment

Single factor ANOVA was utilized to test for statistical significance of the percent Cr(VI) removed between the methods tested, Table B-1. Results revealed, at a 95% CI, that there was a statistically significant difference among the methods tested. Additional post hoc analysis using the Student’s two-tail t-test, assuming unequal variances to determine whether there was a statistical difference in the percent Cr(VI) removed between the individual methods of remediation. Table B-2 shows that there was a statistically significant difference between the Blank samples and each method tested. There was a statistically significant difference ($p < 0.05$) between the primary methods tested (ZVI, Sludge, and ZVI+Sludge). Table B-3 shows that there was no statistically significant difference between the Sludge and ZVI+Sludge samples with and without an additional carbon source.

Table B-1: ANOVA analysis for percent Cr(VI) removed for methods tested (Blank, Sludge, Sludge+Oil, ZVI, ZVI+Sludge, and ZVI+Sludge+Oil).

H_0 = No statistically significant difference in the percent Cr(VI) removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	45362.7	5	9072.5	18.9	2.43E-10	2.41
Within Groups	23049.2	48	480.2			
Total	68412.0	53				

Table B-2: Analysis for statistical difference in the percent Cr(VI) removed between Blank samples and primary methods (Sludge, ZVI, and ZVI+Sludge) in Cr(VI) degradation experiment.

Student's t-test: Two-tail, Assuming Unequal Variances – (% Cr(VI) Removed)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between ZVI+Sludge and blank samples.		
	ZVI+Sludge	Blank
Mean	79.97	-3.97
Variance	1005.54	13.73
Observations	9	9
df	9	
P(T<=) two-tail	4.88E-05 (p-value < 0.05, Reject H_0)	
H_0 #2: There is no significant difference in the percent Cr(VI) removed between ZVI +Sludge and blank samples.		
	Sludge	Blank
Mean	50.08	-3.97
Variance	392.03	13.73
Observations	9	9
df	9	
P(T<=) two-tail	2.11E-05 (p-value < 0.05, Reject H_0)	
H_0 #6: There is no significant difference in the percent Cr(VI) removed between ZVI and blank samples.		
	ZVI	Blank
Mean	29.00	-3.97
Variance	162.88	13.73
Observations	9	9
df	9	
P(T<=) two-tail	3.92E-05 (p-value < 0.05, Reject H_0)	

Table B-3: Statistical analysis of significant difference of percent Cr(VI) removed for experimental methods.

Student’s t-test: Two-tail, Assuming Unequal Variances – (% Cr(VI) Removed)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between ZVI+Sludge and ZVI.		
	ZVI+Sludge	ZVI
Mean	89.844	32.625
Variance	123.958	50.988
Observations	8	8
df	12	
P(T<=) two-tail	3.892E-08 (p-value < 0.05, Reject H_0)	
H_0 #1: There is no significant difference in the percent Cr(VI) removed between ZVI+Sludge and Sludge methods of reduction.		
	ZVI+Sludge	Sludge
Mean	89.844	56.344
Variance	123.958	44.924
Observations	8	8
df	11	
P(T<=) two-tail	1.560E-05 (p-value < 0.05, Reject H_0)	
H_0 #2: There is no significant difference in the percent Cr(VI) removed between Sludge and ZVI methods.		
	Sludge	ZVI
Mean	56.344	32.625
Variance	44.924	50.988
Observations	8	8
df	14	
P(T<=) two-tail	7.932E-06 (p-value < 0.05, Reject H_0)	

Table B-4: Statistical analysis for Sludge methods in Cr(VI) degradation experiment.

Student’s t-test: Two-tail, Assuming Unequal Variances – (Sludge Methods)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between the Sludge and Sludge+Oil samples.		
	Sludge	Sludge+Oil
Mean	50.08	46.31
Variance	392.03	307.78
Observations	9	9
df	16	
P(T<=) two-tail	0.675 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent Cr(VI) removed between ZVI+Sludge with and without additional carbon source.		
	ZVI+Sludge	ZVI+Sludge+Oil
Mean	79.87	79.08
Variance	1005.54	999.19
Observations	9	9
df	16	
P(T<=) two-tail	0.958 (p-value > 0.05, cannot reject H_0)	

B.2 Statistical Analysis for Single Contaminant ClO_3^- Degradation Experiment

Single factor ANOVA was utilized to test for statistical significance of the percent ClO_3^- removed between the methods tested, Table B-5. Results revealed, at a 95% CI, that there was a statistically significant difference among the methods tested. Additional post hoc analysis was performed using the Student's two-tail t-test. There was no statistically significant difference in the percent ClO_3^- removed ($p < 0.05$) between the blank samples and the primary methods tested, Table B-6. Table B-7 shows that there was a significant difference in the percent ClO_3^- removed between bacteria and ZVI and also Sludge and ZVI+Sludge. There was no significant difference in the percent ClO_3^- removed between ZVI+Sludge and ZVI.

Table B-5: ANOVA analysis for percent ClO_3^- removed for methods tested (Blank, Sludge, ZVI, and ZVI+Sludge).

H_0 = No statistically significant difference in the percent Cr(VI) removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	29361.2	3	9787.1	17.15	4.41E-7	2.87
Within Groups	20548.4	36	570.8			
Total	49909.7	39				

Table B-6: Statistical analysis of significant difference of percent chlorate removed for Blank samples and experimental methods

Student's t-test: Two-tail, Assuming Unequal Variances (Blanks and Individual Methods)		
H_0 #4: There is no significant difference in the percent ClO_3^- removed between ZVI+Sludge and blank samples.		
	ZVI+Sludge	Blank
Mean	58.87	0.043
Variance	1082.48	0.993
Observations	10	10
df	9	
P(T<=) two-tail	3.25E-04 (p-value < 0.05, Reject H_0)	
H_0 #5: There is no significant difference in the percent ClO_3^- removed between Sludge and blank samples.		
	Sludge	Blank
Mean	5.100	0.043
Variance	31.097	0.993
Observations	10	10
df	20	
P(T<=) two-tail	1.81E-02 (p-value < 0.05, Reject H_0)	
H_0 #6: There is no significant difference in the percent ClO_3^- removed between ZVI and blank samples.		
	ZVI	Blank
Mean	54.56	0.043
Variance	1168.60	0.993
Observations	10	10
df	10	
P(T<=) two-tail	6.99E-04 (p-value < 0.05, Reject H_0)	

Table B-7: Statistical analysis of significant difference of percent chlorate removed for experimental methods

Student's t-test: Two-tail, Assuming Unequal Variances – (% ClO$_3^-$ Removed)		
H_0 #1: There is no significant difference in the percent ClO$_3^-$ removed between ZVI +Sludge and abiotic ZVI.		
	ZVI+Sludge	ZVI
Mean	58.57	54.56
Variance	1082.48	1168.60
Observations	10	10
df	16	
P(T<=) two-tail	0.792 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent ClO$_3^-$ removed between ZVI +Sludge and Sludge.		
	ZVI+Sludge	Sludge
Mean	58.57	5.100
Variance	1082.48	31.087
Observations	10	10
df	9	
P(T<=) two-tail	4.87E-04 (p-value < 0.05, Reject H_0)	
H_0 #3: There is no significant difference in the percent ClO$_3^-$ removed between Sludge and abiotic ZVI.		
	Sludge	ZVI
Mean	5.100	54.56
Variance	31.087	1168.60
Observations	10	10
df	9	
P(T<=) two-tail	1.46E-03 (p-value < 0.05, Reject H_0)	

B.3 Statistical Analysis for Multiple Contaminants (Cr(VI) and ClO$_3^-$) Experiment

ANOVA analysis showed statistically significant difference ($p < 0.05$) between the methods evaluated for the percent removal of Cr(VI) and also the percent removal of ClO$_3^-$, Table B-8 and Table B-9. Additional post hoc analysis using the Student's t-test was performed to compare individual methods. Statistical significance for Sludge and ZVI+Sludge methods, with and without additional carbon source, are shown in Table B-10 and Table B-11 respectively. For both, there was no statistically significant difference between the Sludge and ZVI+Sludge with and without additional carbon source with concern of percent Cr(VI) removed and percent ClO_3^- removed.

The significant difference in the percent Cr(VI) removed between Sludge, ZVI, and ZVI+Sludge is shown in Table B-12. There was a significant difference between ZVI+Sludge and Sludge ($p < 0.05$). There was no significant difference between ZVI+Sludge and ZVI ($p > 0.05$) and also no difference between ZVI and Sludge in the percent Cr(VI) removed. The significant difference in the percent ClO_3^- removed between bacteria, ZVI, and ZVI+Sludge is shown in Table B-13. As with Table B-12, there was no significant difference between ZVI+Sludge and ZVI and also no significant difference between ZVI and Sludge in the percent ClO_3^- removed. There was a significant difference between ZVI+Sludge and Sludge.

Table B-8: ANOVA analysis for percent Cr(VI) removed for methods tested (Blank, Sludge, Sludge+Oil, ZVI, ZVI+Sludge, and ZVI+Sludge+Oil).

H_0 = No statistically significant difference in the percent Cr(VI) removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	44008.3	7	8801.7	14.5	6.17E-10	2.34
Within Groups	45477.7	75	606.4			
Total	89485.9	80				

Table B-9: ANOVA analysis for percent chlorate removed for methods tested (Blank, Sludge, Sludge+Oil, ZVI, ZVI+Sludge, and ZVI+Sludge+Oil).

H_0 = No statistically significant difference in the percent chlorate removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	47774.4	5	9554.9	9.78	3.18E-07	2.34
Within Groups	73263.1	75	976.8			
Total	121037.5	80				

Table B-10: Statistical analysis of significant difference for Sludge with and without and additional carbon source.

Student's t-test: Two-tail, Assuming Unequal Variances – (Sludge)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between Sludge without EOS-PRO oil and Sludge with EOS-PRO oil.		
	Sludge	Sludge+Oil
Mean	72.267	72.04
Variance	529.27	509.698
Observations	15	15
Df	28	
P(T<=) two-tail	0.9784 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent ClO_3^- removed between Sludge without EOS-PRO oil and Sludge with EOS-PRO oil.		
	Sludge	Sludge+Oil
Mean	1.2787	1.7507
Variance	7.565	5.4075
Observations	15	15
df	27	
P(T<=) two-tail	0.6159 (p-value > 0.05, cannot reject H_0)	

Table B-11: Statistical analysis of significant difference for ZVI+Sludge with and without an additional carbon source.

Student's t-test: Two-tail, Assuming Unequal Variances – (ZVI+Sludge)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between ZVI+Sludge method with and without additional carbon source.		
	ZVI+Sludge	ZVI+Sludge+Oil
Mean	92.375	92.505
Variance	665.434	665.016
Observations	15	15
Df	28	
P(T<=) two-tail	0.9891 (p-value > 0.05, cannot reject H_0)	
H_0 #2: There is no significant difference in the percent ClO_3^- removed between ZVI+Sludge method with and without additional carbon source.		
	ZVI+Sludge	ZVI+Sludge+Oil
Mean	51.6	52.776
Variance	1721.764	1682.258
Observations	15	15
df	28	
P(T<=) two-tail	0.9383 (p-value > 0.05, cannot reject H_0)	

Table B-12: Statistical analysis of significant difference of percent Cr(VI) removed for experimental methods

Student’s t-test: Two-tail, Assuming Unequal Variances – (% Cr(VI) Removed)		
H_0 #1: There is no significant difference in the percent Cr(VI) removed between the ZVI+Sludge and Sludge reduction.		
	ZVI+Sludge	Sludge
Mean	92.375	72.267
Variance	665.435	529.269
Observations	15	15
Df	28	
P(T<=) two-tail	0.03227 (p-value < 0.05, Reject H_0)	
H_0 #2: There is no significant difference in the percent Cr(VI) removed between the ZVI+Sludge and ZVI.		
	ZVI+Sludge	ZVI
Mean	92.375	85.947
Variance	665.435	878.569
Observations	15	15
df	27	
P(T<=) two-tail	0.53165 (p-value > 0.05, cannot reject H_0)	
H_0 #3: There is no significant difference in the percent Cr(VI) removed between the Sludge and ZVI.		
	Sludge	ZVI
Mean	72.267	85.947
Variance	529.269	878.569
Observations	15	15
df	26	
P(T<=) two-tail	0.16978 (p-value < 0.05, Reject H_0)	

Table B-13: Statistical analysis of significant difference of percent chlorate removed for experimental methods.

Student's t-test: Two-tail, Assuming Unequal Variances – Percent ClO_3^- Removed		
H_0 #1: There is no significant difference in the percent ClO_3^- removed between the ZVI+Sludge and Sludge methods.		
	ZVI+Sludge	Sludge
Mean	51.6	1.2787
Variance	1721.76	7.565
Observations	15	15
Df	14	
P(T<=) two-tail	3.50E-04 (p-value < 0.05, Reject H_0)	
H_0 #2: There is no significant difference in the percent ClO_3^- removed between the ZVI+Sludge and ZVI.		
	ZVI+Sludge	ZVI
Mean	51.6	45.127
Variance	1721.76	1815.849
Observations	15	15
df	28	
P(T<=) two-tail	0.6766 (p-value > 0.05, cannot reject H_0)	
H_0 #3: There is no significant difference in the percent ClO_3^- removed between the Sludge and ZVI methods.		
	Sludge	ZVI
Mean	1.2787	45.127
Variance	7.565	1815.849
Observations	15	15
df	14	
P(T<=) two-tail	1.38E-03 (p-value < 0.05, Reject H_0)	

B.4 Statistical Analysis of Increasing and Decreasing Stoichiometric Ratios Experiment

ANOVA analysis for both the percent Cr(VI) and percent ClO_3^- removed showed no statistically significant difference ($p > 0.05$ and $F < F_{crit}$) in the percent Cr(VI) removed and also in the percent ClO_3^- removed between the increasing and decreasing stoichiometric ratios. No further statistical analysis is warranted.

Table B-14: ANOVA analysis for percent Cr(VI) removed for ZVI+Sludge at varying stoichiometric ratios.

H_0 = No statistically significant difference in the percent Cr(VI) removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	79.4	3	26.5	0.039	0.989	2.769
Within Groups	37686.3	56	672.9			
Total	37765.7	59				

Table B-15: ANOVA analysis for percent chlorate removed for methods tested for ZVI+Sludge at varying stoichiometric ratios.

H_0 = No statistically significant difference in the percent chlorate removed between methods.						
Source of Variation	**SS**	**dF**	**MS**	**F**	**P-value**	**F crit**
Between Groups	7383.5	3	2461.16	1.486	0.228	2.769
Within Groups	92704.4	56	1655.44			
Total	100087.9	59				

Appendix C: Graphical Determination of Pseudo First Order Reaction Rate Coefficients

The reaction rate order and coefficients (k) were determined graphically by plotting the -ln(C/C_0) verses time. A linear trend line was added along with equation. R^2 was used to measure how well the data fit to the trend lines.

C.1 Determination of Reaction Rate Constants for Cr(VI) Degradation Experiment.

Graphical determination of pseudo first-order reaction rate coefficients was determined for each method in the single contaminant Cr(VI) experiment. Figure C-1 shows the concentration of Cr(VI) versus time for the five method and the Blanks. Several methods ceased degrading after a period of time and/or the degradation was minimal. This was the case for both Sludge (Figure C-2) and Sludge+Oil (Figure C-3). As shown in both Figures, the data points were reduced to limit distortion of the rates. Additionally, both ZVI+Sludge and ZVI+Sludge+Oil completely degraded the Cr(VI). Only the first 100% degradation point was included.

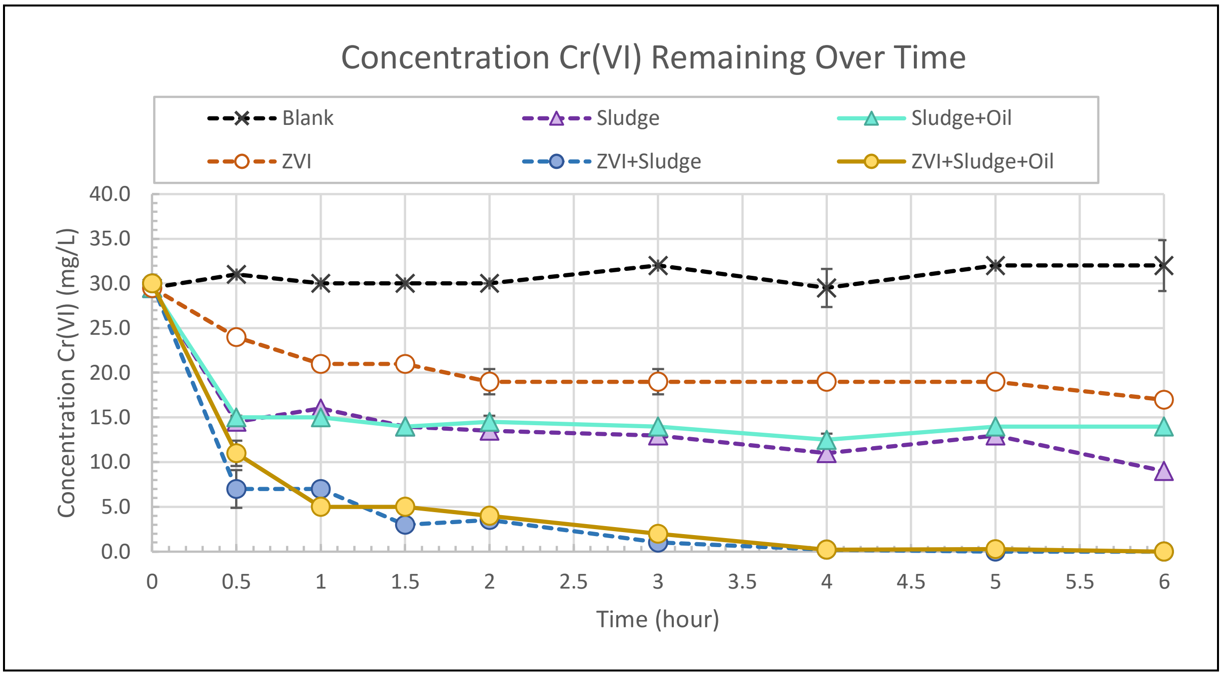


Figure C-1: Concentration of Cr(VI) remaining over time for Sludge, Sludge+Oil, ZVI, ZVI+Sludge, ZVI+Sludge+Oil, and Blanks. Forty mL vials were used for the batch experiment. Initial Cr(VI) concentration was 30 mg/L Cr(VI). ZVI dose was 6.32 g/L. Sludge dose was 180mg SS/L. Laboratory temperature was 24°C. Error bars indicate one standard deviation computed from duplicates. 50% replicates used.

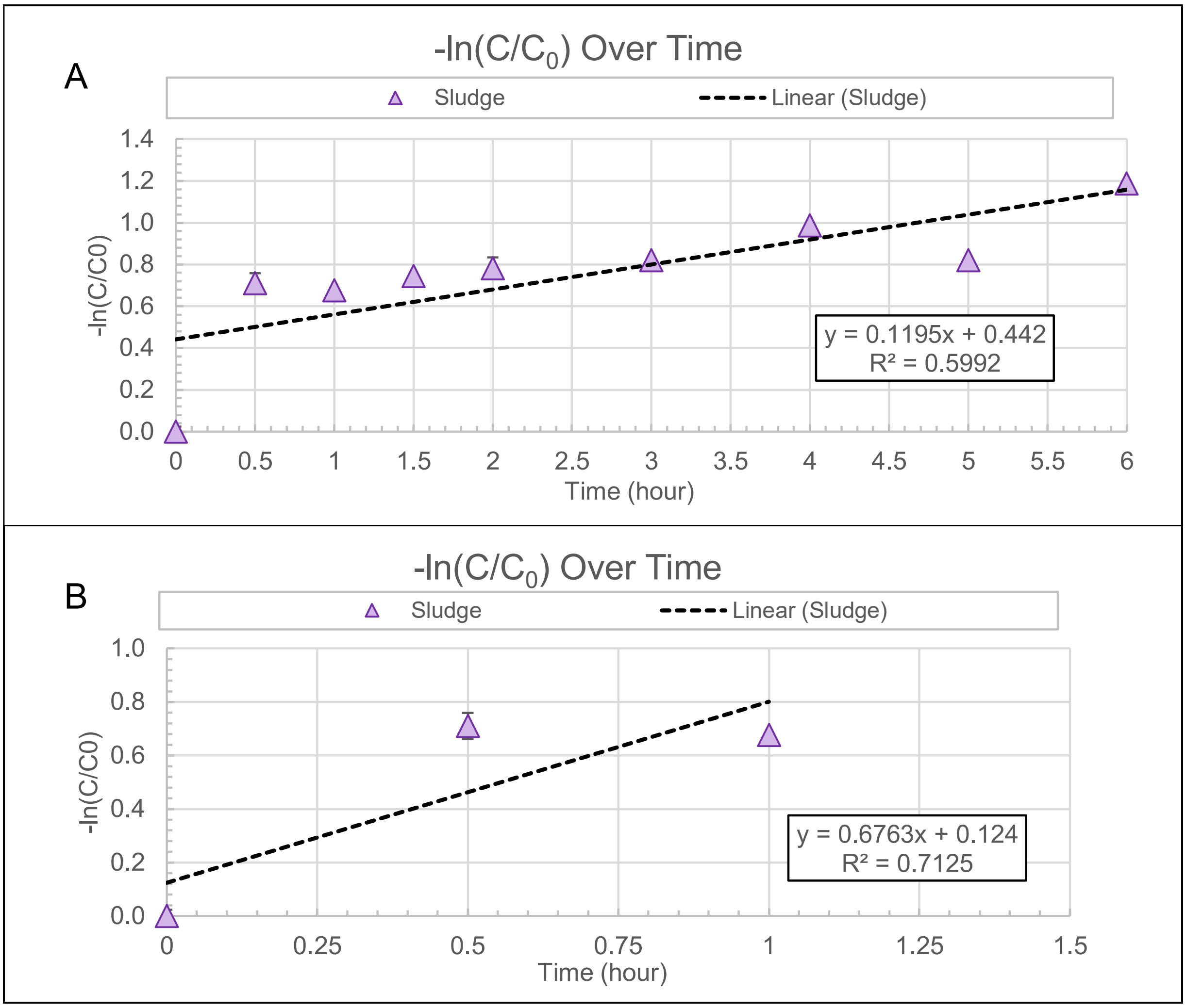


Figure C-2: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using Sludge alone in the single contaminant Cr(VI) experiment. [A] is -ln(C/C_0) from time 0 to 6 hours and [B] is from time 0 to 1 hour. Linear trend lines have been added with corresponding R^2 value and equation.

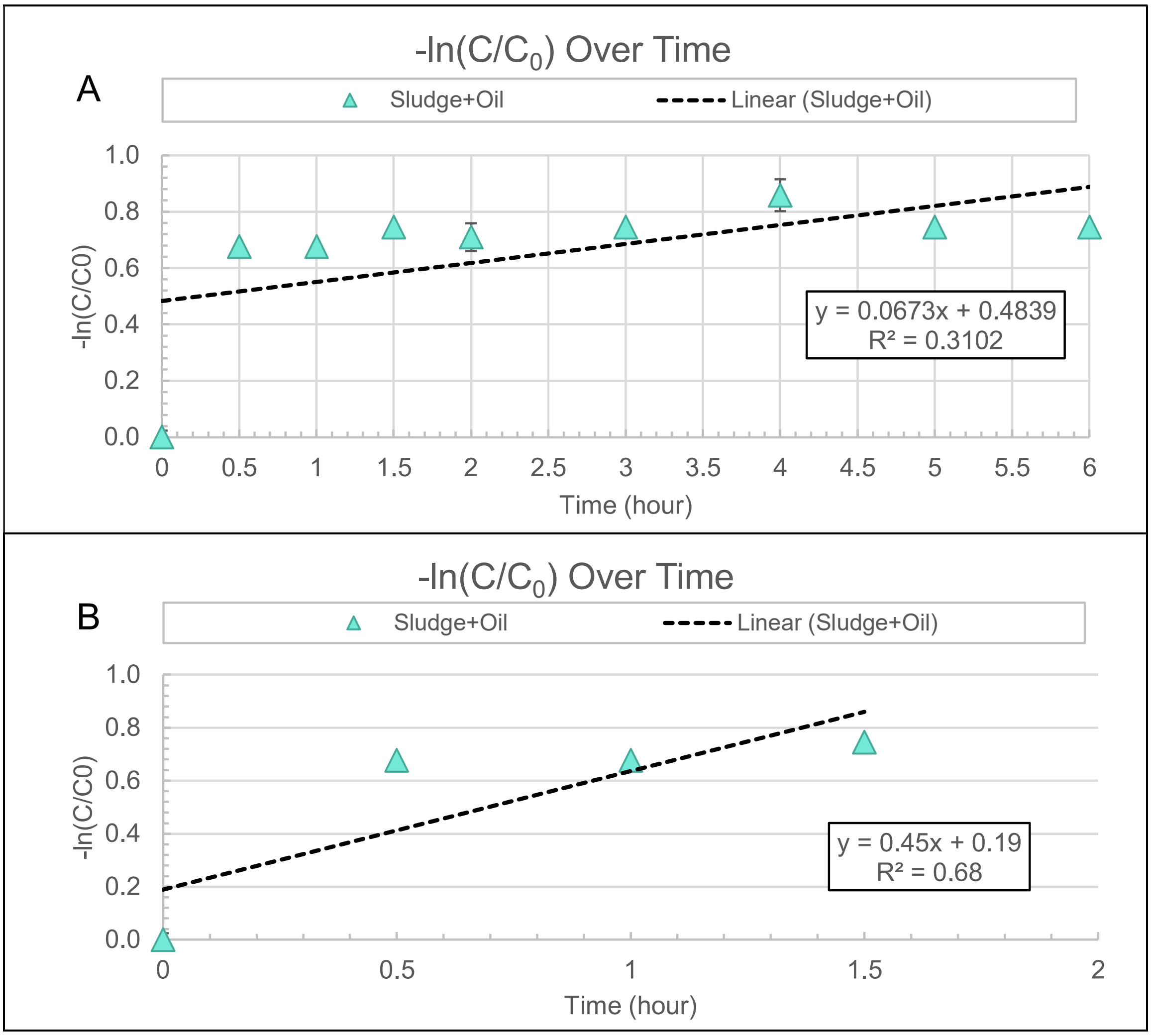


Figure C-3: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using Sludge+Oil alone in the single contaminant Cr(VI) experiment. [A] is $-\ln(C/C_0)$ from time 0 to 6 hours and [B] is from time 0 to 1 hour. Linear trend lines have been added with corresponding R^2 value and equation.

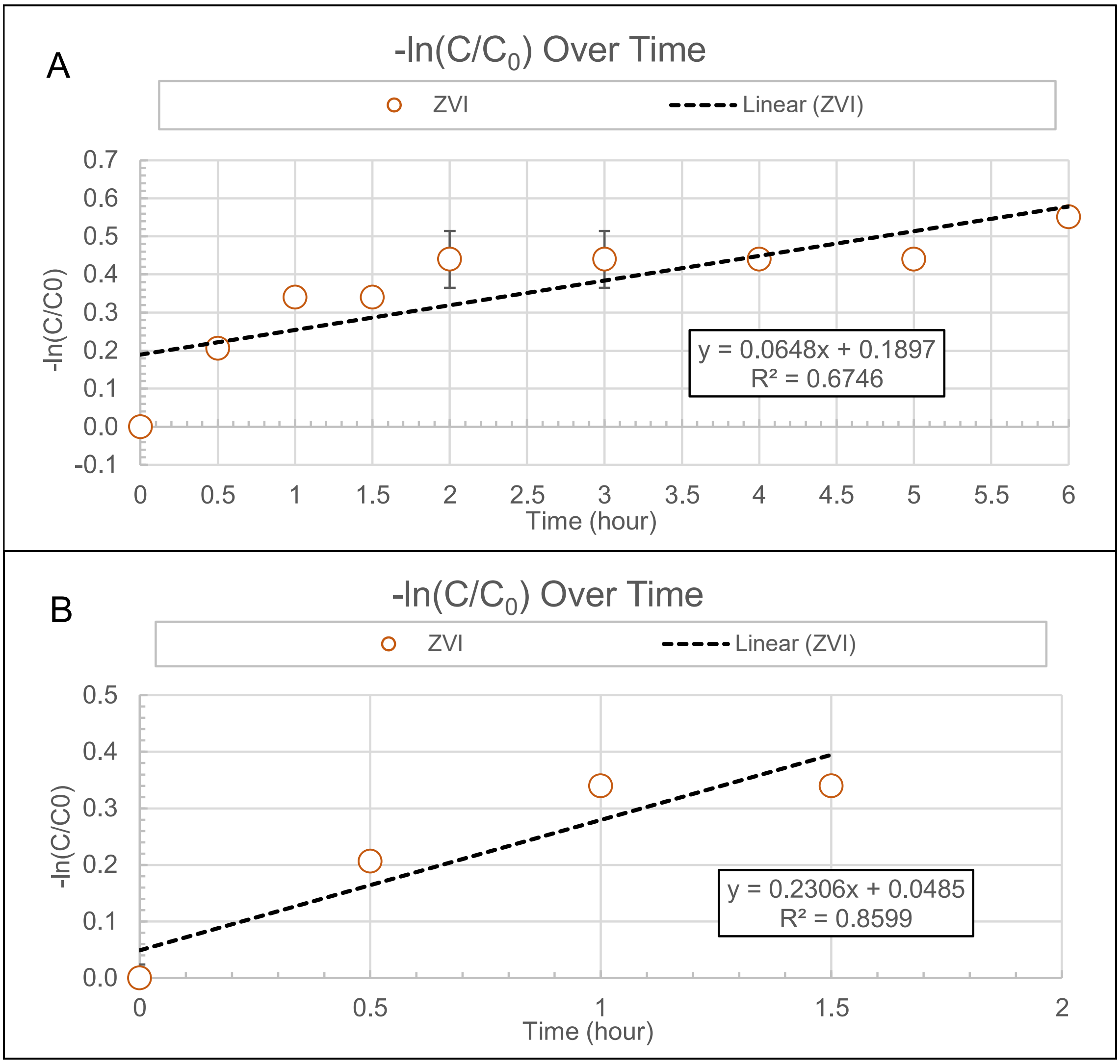


Figure C-4: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using abiotic ZVI alone in the single contaminant Cr(VI) experiment. [A] is -ln(C/C$_0$) from time 0 to 6 hours and [B] is from time 0 to 1 hour. Linear trend lines have been added with corresponding R^2 value and equation.

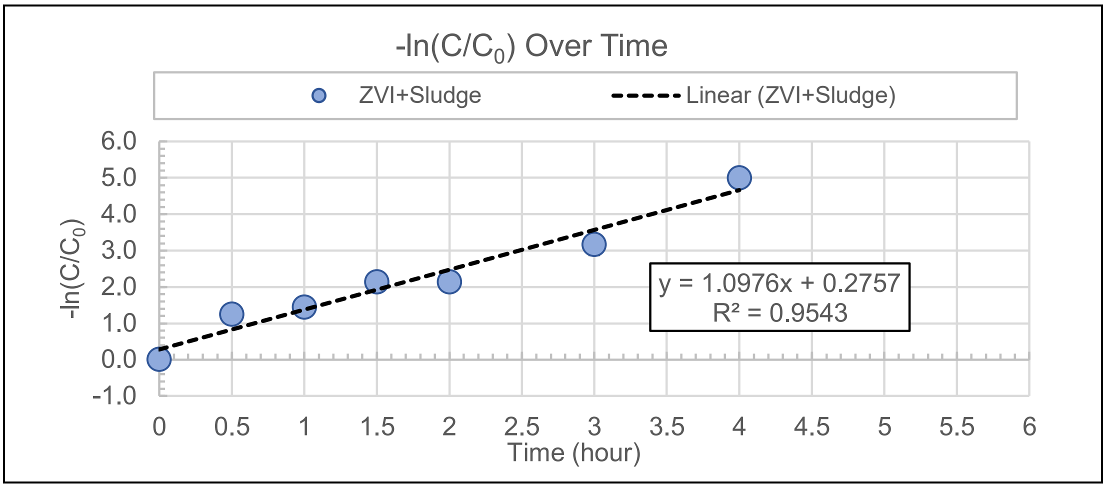


Figure C-5: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using ZVI+Sludge in the single contaminant Cr(VI) experiment. Linear trend lines have been added with corresponding R^2 value and equation.

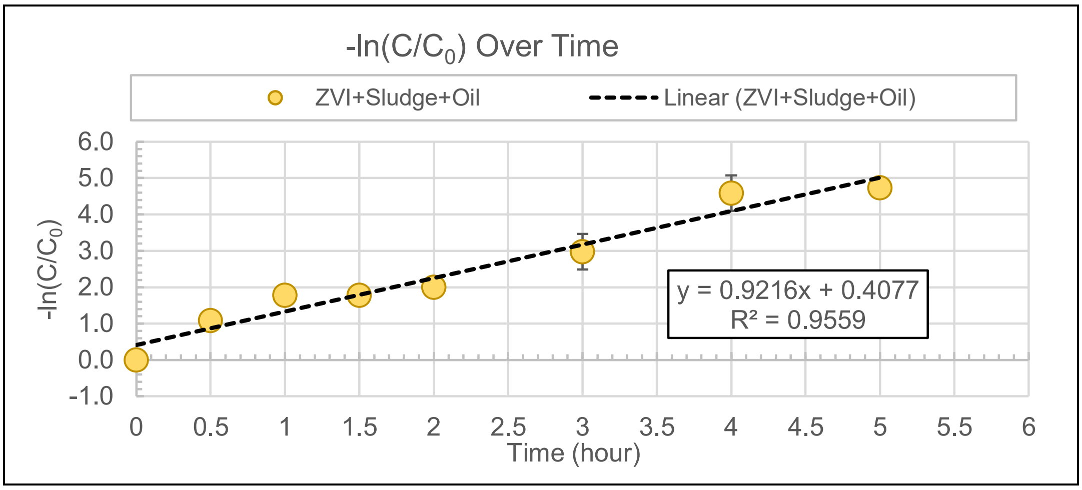


Figure C-6: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using ZVI+Sludge+Oil in the single contaminant Cr(VI) experiment. Linear trend lines have been added with corresponding R^2 value and equation.

C.2 Determination of Reaction Order Rate Constant for ClO_3^- Degradation Experiment

Graphical determination of pseudo first-order reaction rate coefficients was determined for each method in the single contaminant ClO_3^- experiment. As with the single contaminant Cr(VI) experiment in Section C.1, data points were reduced for several methods to limit distortion of the rates.

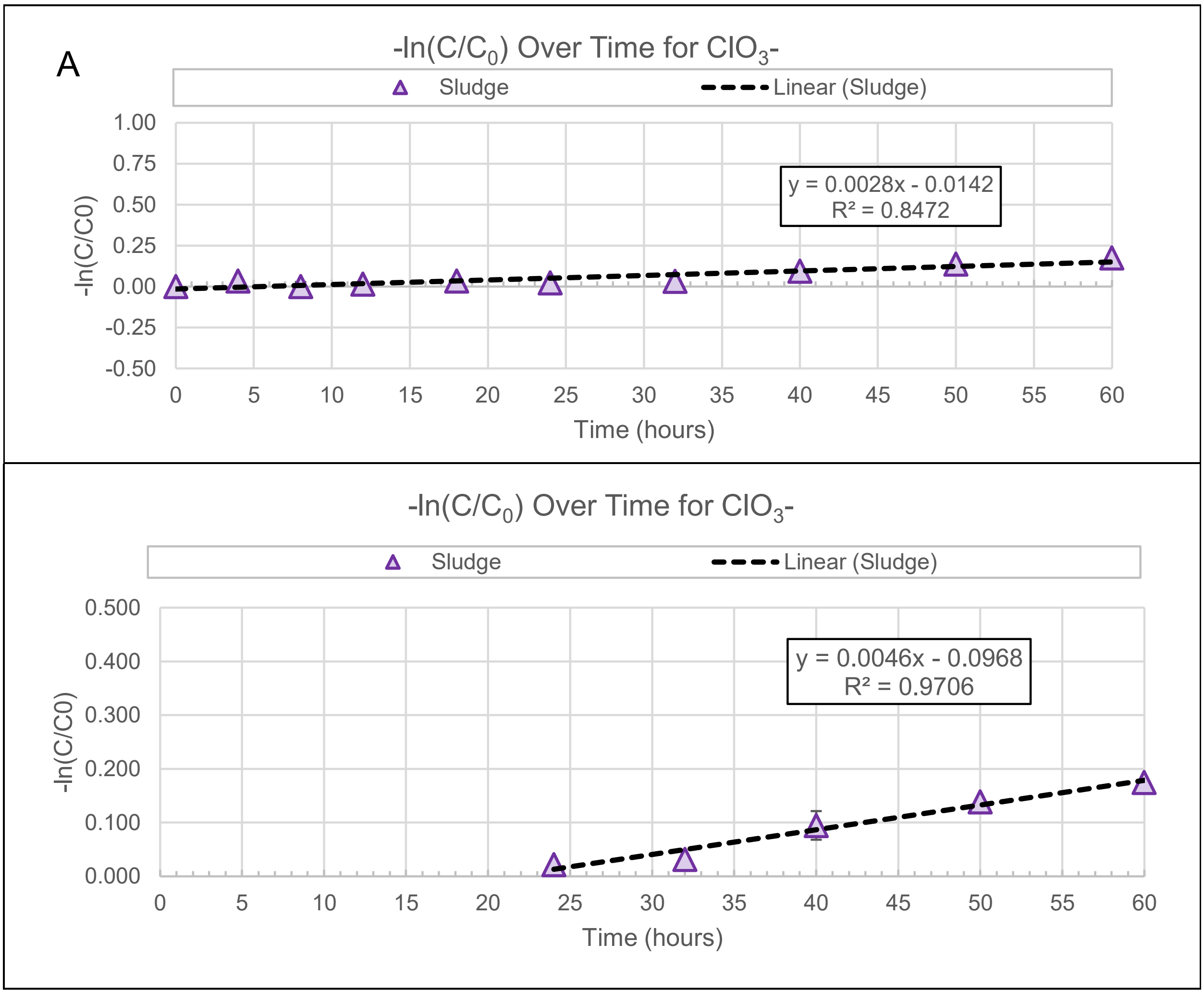


Figure C-7: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using Sludge alone in the single contaminant ClO_3^- experiment. [A] is -ln(C/C_0) from time 0 to 60 hours and [B] is from time 24 to 60 hour. Linear trend lines have been added with corresponding R^2 value and equation.

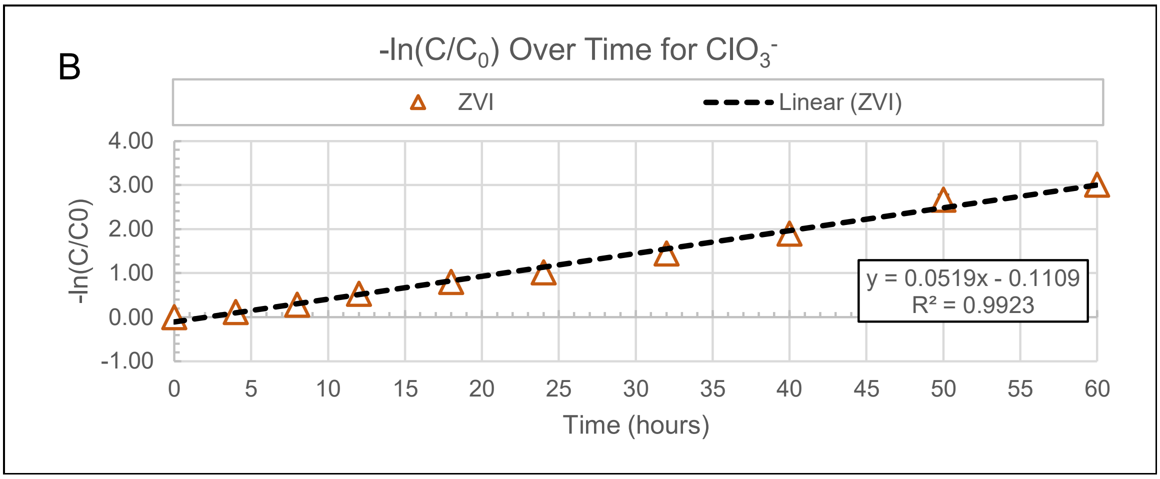


Figure C-8: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using ZVI in the single contaminant ClO_3^- experiment. Linear trend lines have been added with corresponding R^2 value and equation.

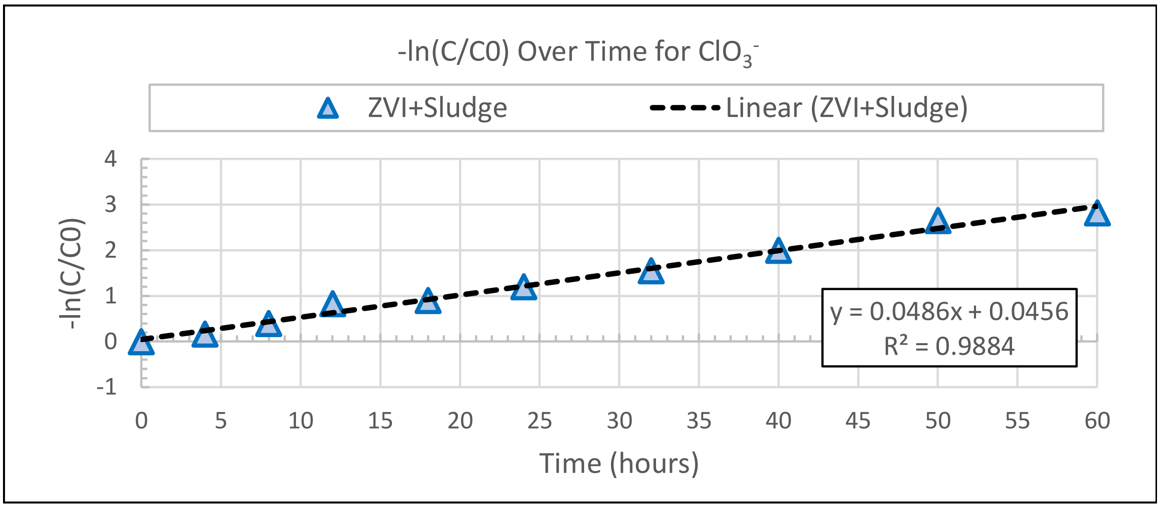


Figure C-9: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using ZVI+Sludge in the single contaminant ClO_3^- experiment. Linear trend lines have been added with corresponding R^2 value and equation.

C.3 Determination of Order and Reaction Rate for Multiple Contaminant Degradation Experiments

Graphical determination of pseudo first-order reaction rate coefficients was determined for each method in the multiple contaminant degradation experiment. As with the single contaminant Cr(VI) experiment in Section C.1, data points were reduced for several methods to limit distortion of the rates.

C.3.1 Cr(VI) Reaction Rates for Multiple Contaminant Degradation Experiment

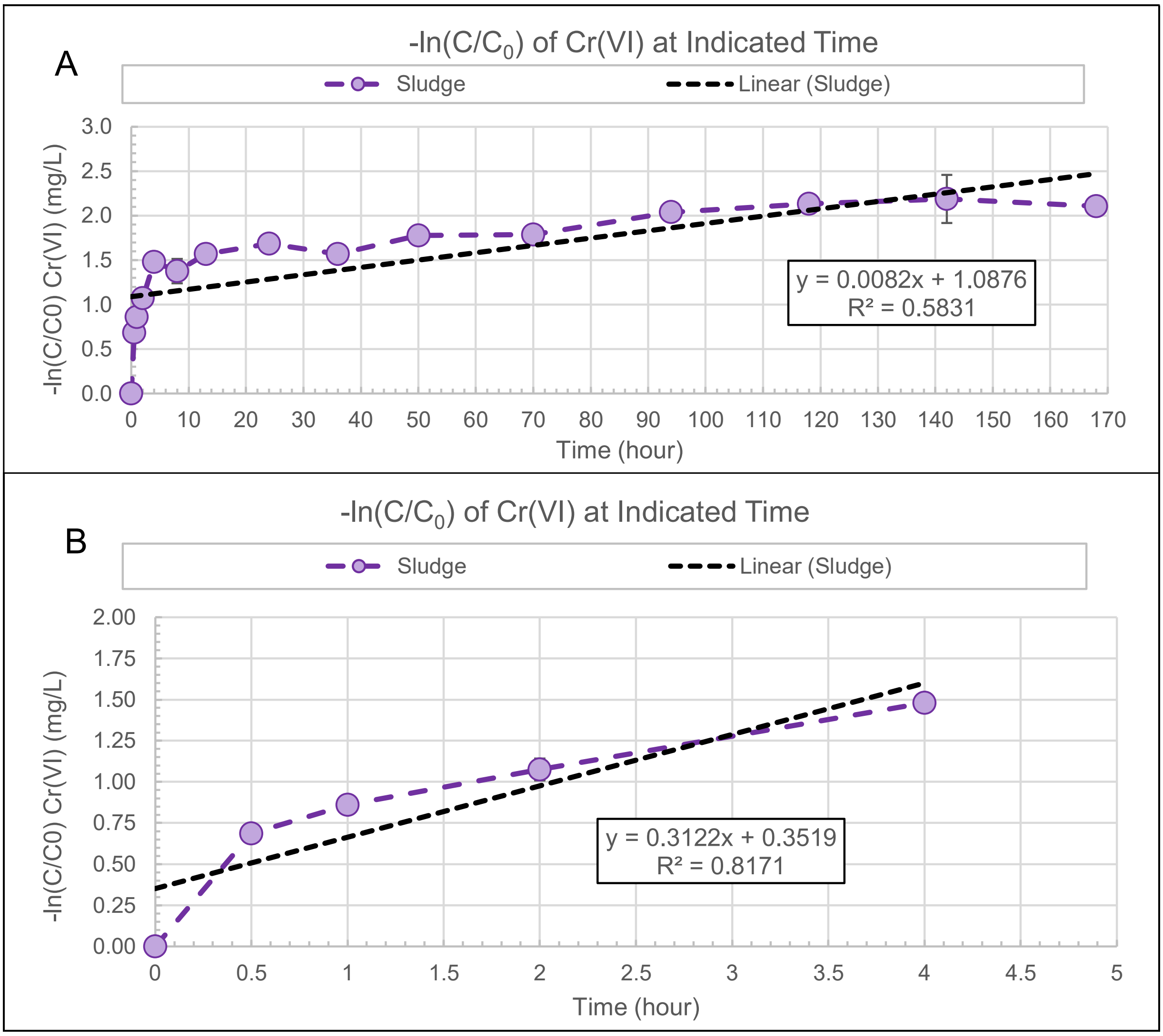


Figure C-10: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using Sludge alone in the multiple contaminant experiment. [A] is -ln(C/C_0) from time 0 to 168 hours and [B] is from time 0 to 4 hour. Linear trend lines have been added with corresponding R^2 value and equation.

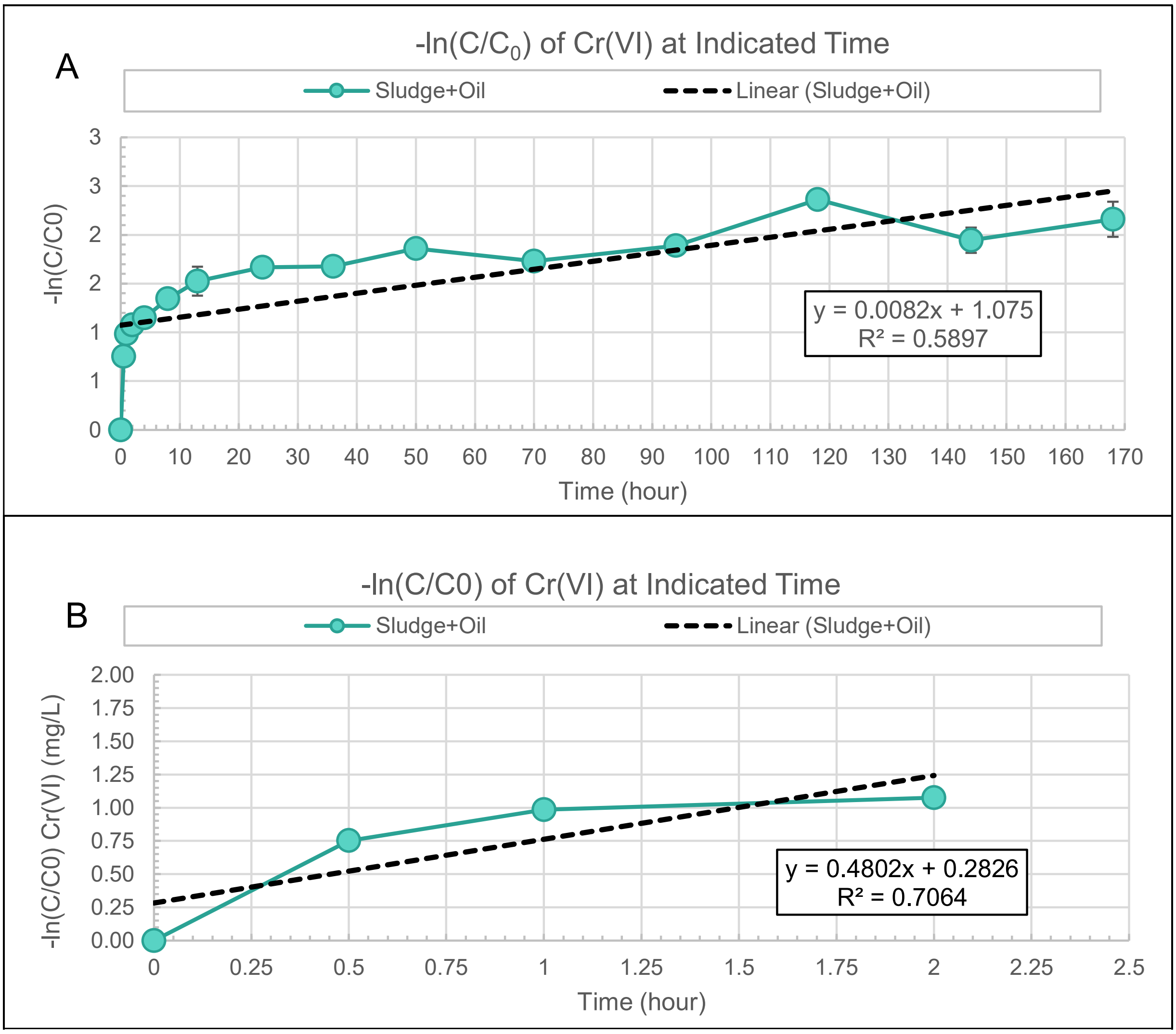


Figure C-11: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using Sludge+Oil in the multiple contaminant experiment. [A] is -ln(C/C_0) from time 0 to 168 hours and [B] is from time 0 to 2 hour. Linear trend lines have been added with corresponding R^2 value and equation.

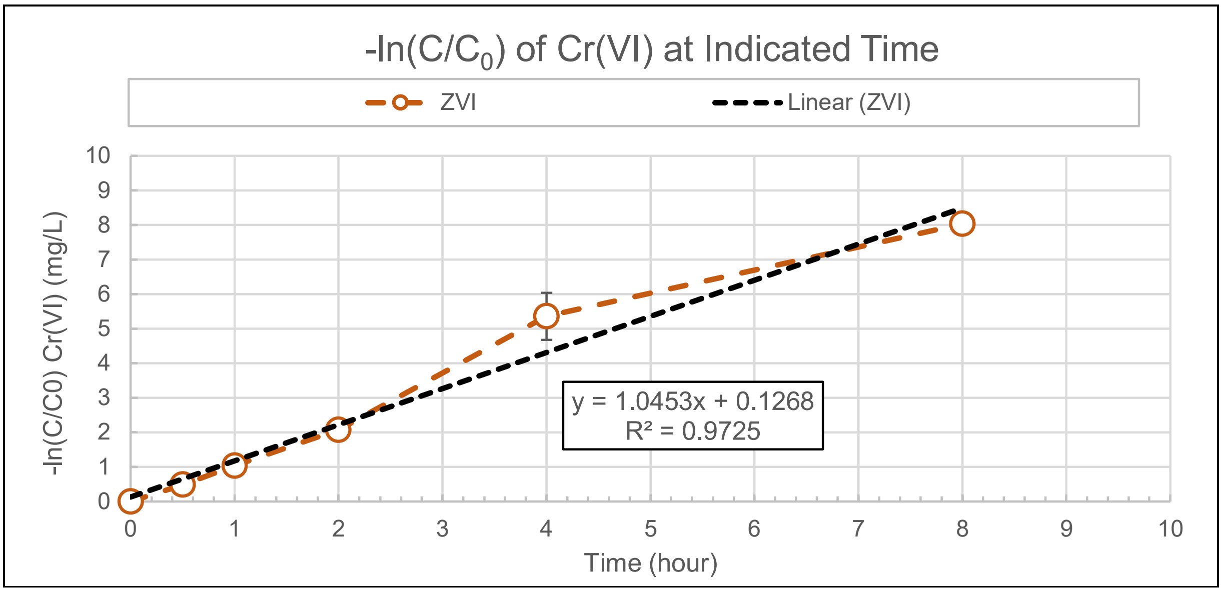


Figure C-12: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using abiotic ZVI alone in the multiple contaminant experiment. Linear trend lines have been added with corresponding R^2 value and equation.

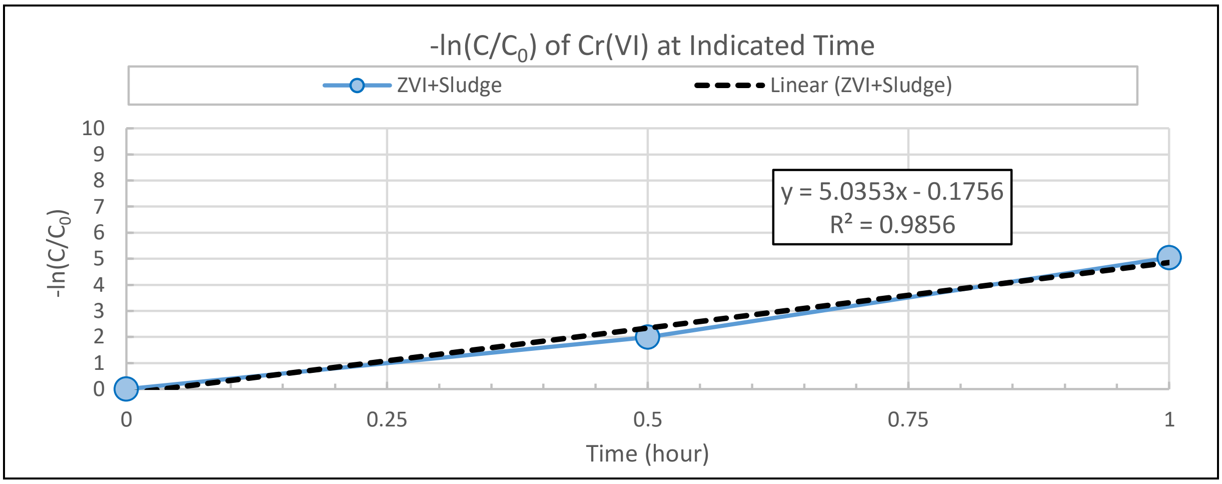


Figure C-13: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using ZVI+Sludge in the multiple contaminant experiment. Linear trend lines have been added with corresponding R^2 value and equation.

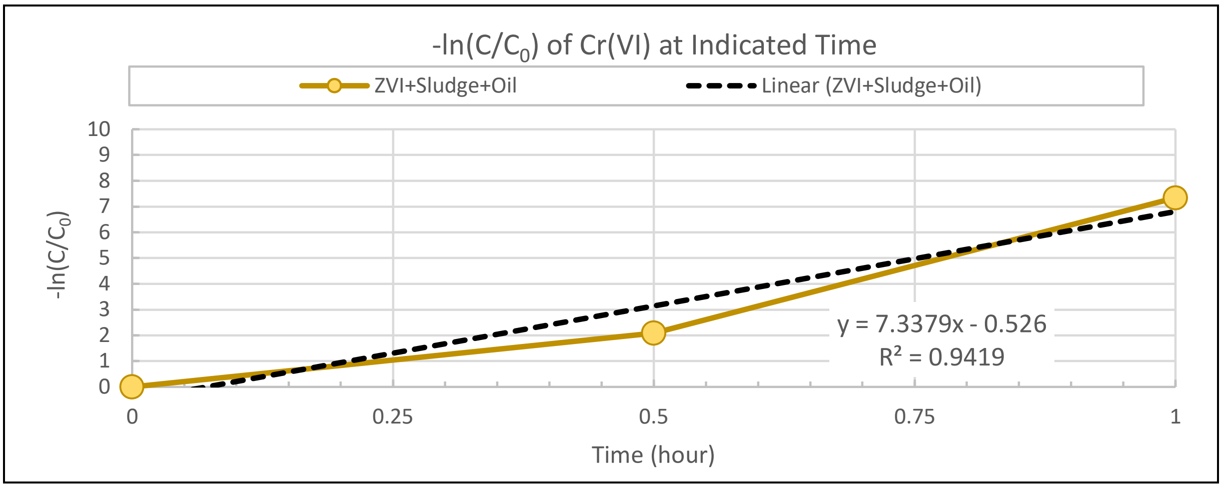


Figure C-14: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using ZVI+Sludge+Oil in the multiple contaminant experiment. Linear trend lines have been added with corresponding R^2 value and equation.

C.3.2 ClO_3^- Reduction in Multiple Contaminant Experiment

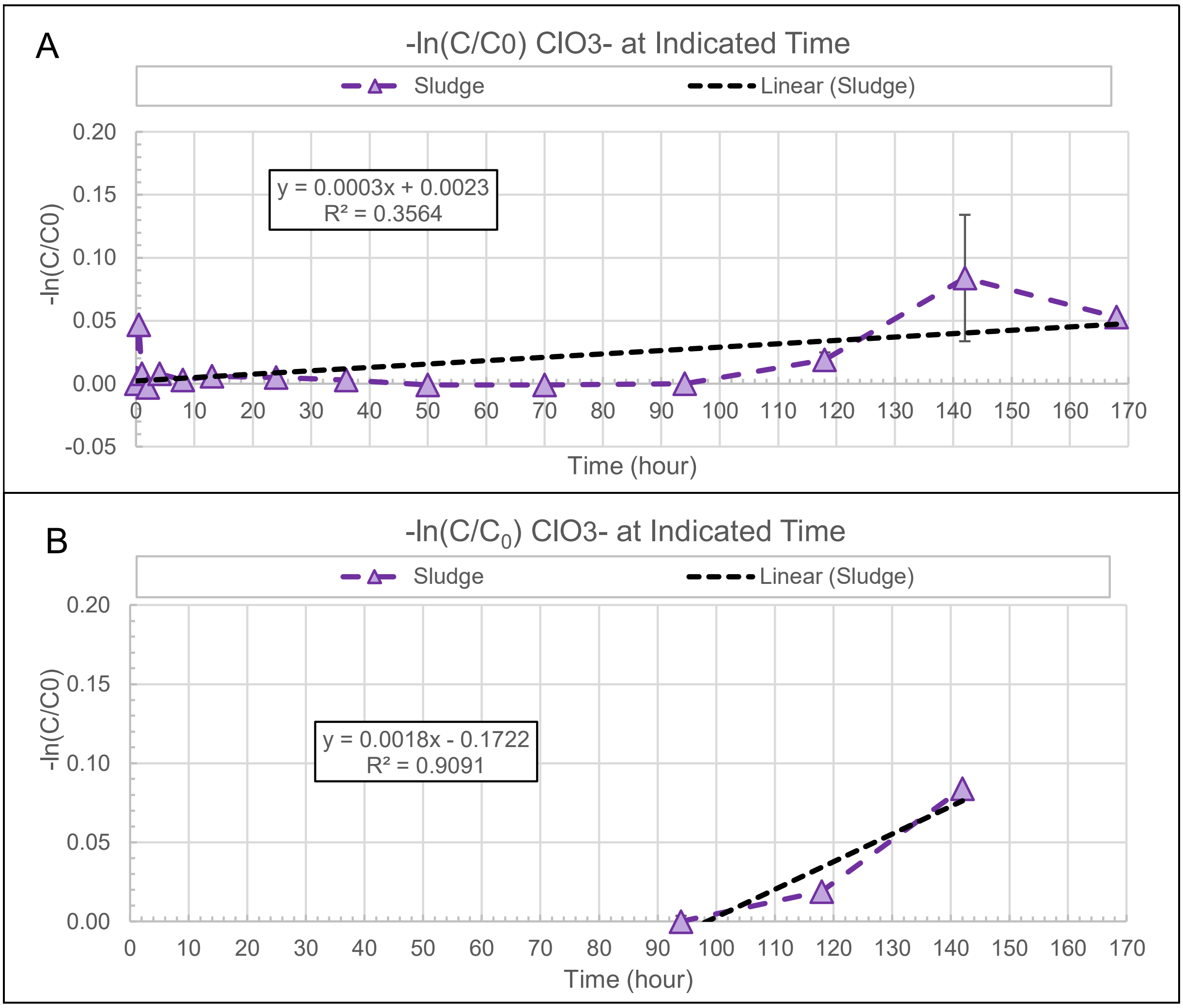


Figure C-15: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using Sludge alone in the multiple contaminant experiment. [A] is $-\ln(C/C_0)$ from time 0 to 168 hours and [B] is from time 94 to 142 hour. Linear trend lines have been added with corresponding R^2 value and equation.

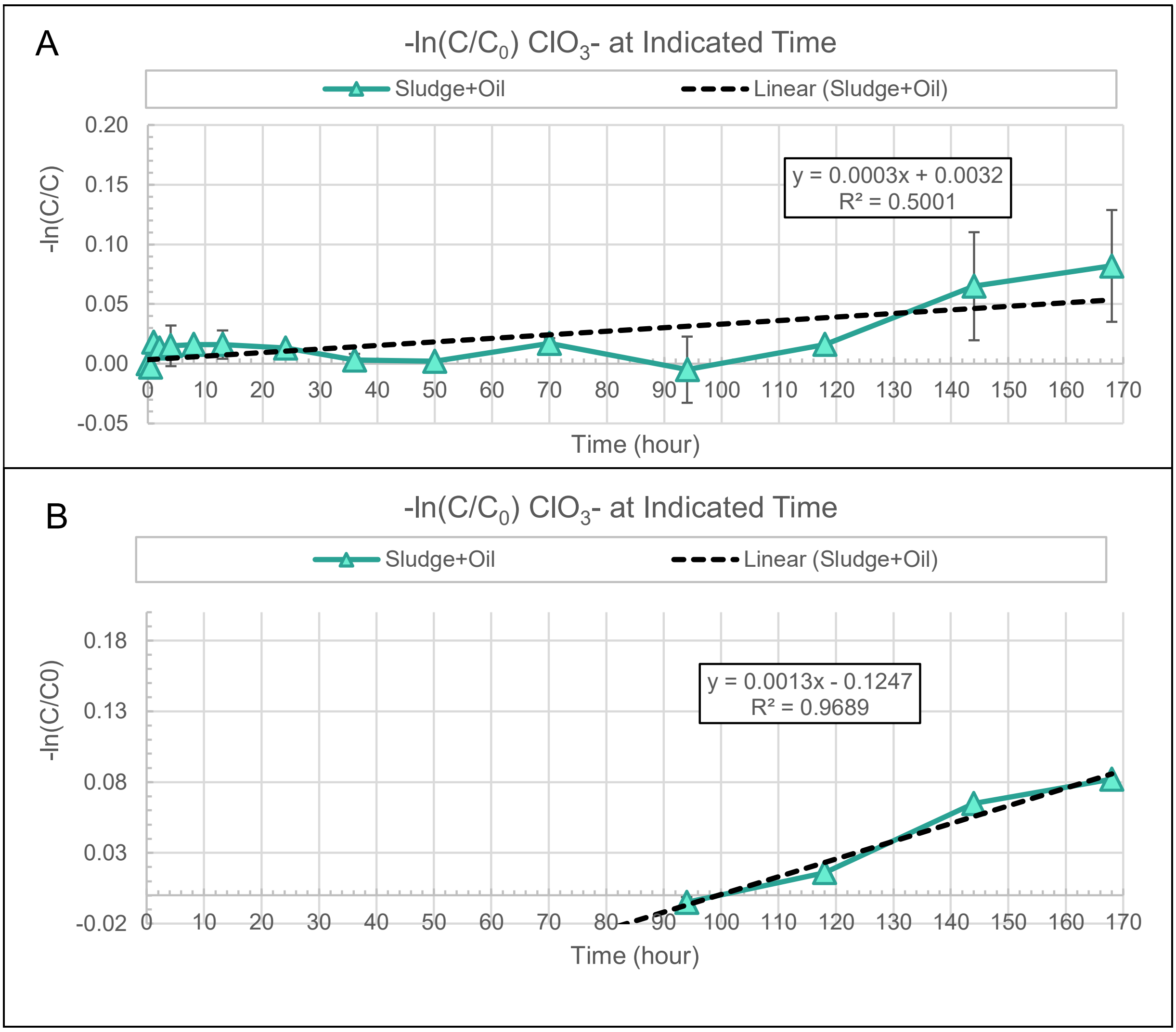


Figure C-16: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using Sludge+Oil in the multiple contaminant experiment. [A] is -ln(C/C_0) from time 0 to 168 hours and [B] is from time 94 to 168 hour. Linear trend lines have been added with corresponding R^2 value and equation.

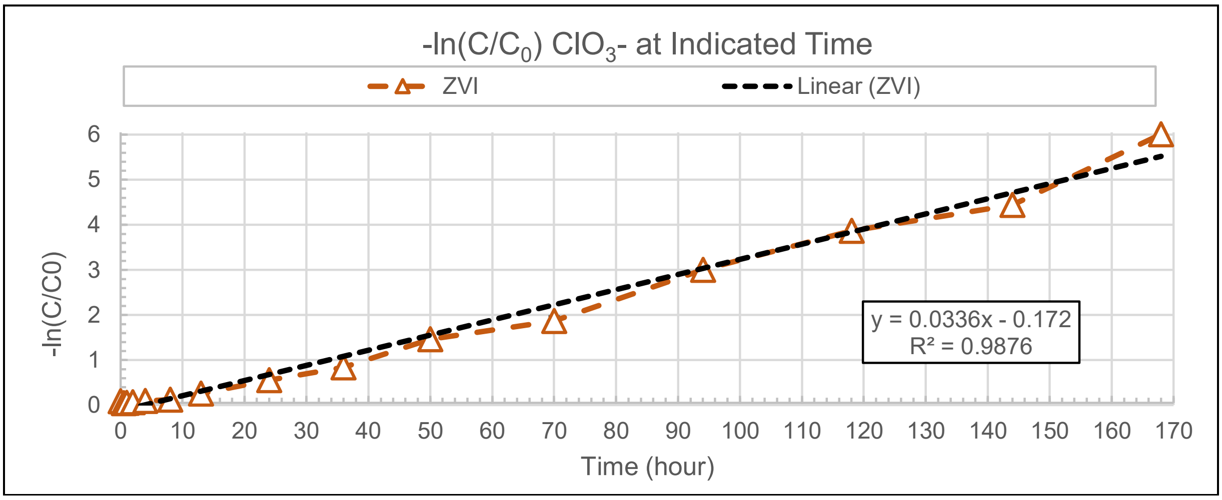


Figure C-17: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using abiotic ZVI alone in the multiple contaminant experiment. Linear trend lines have been added with corresponding R^2 value and equation.

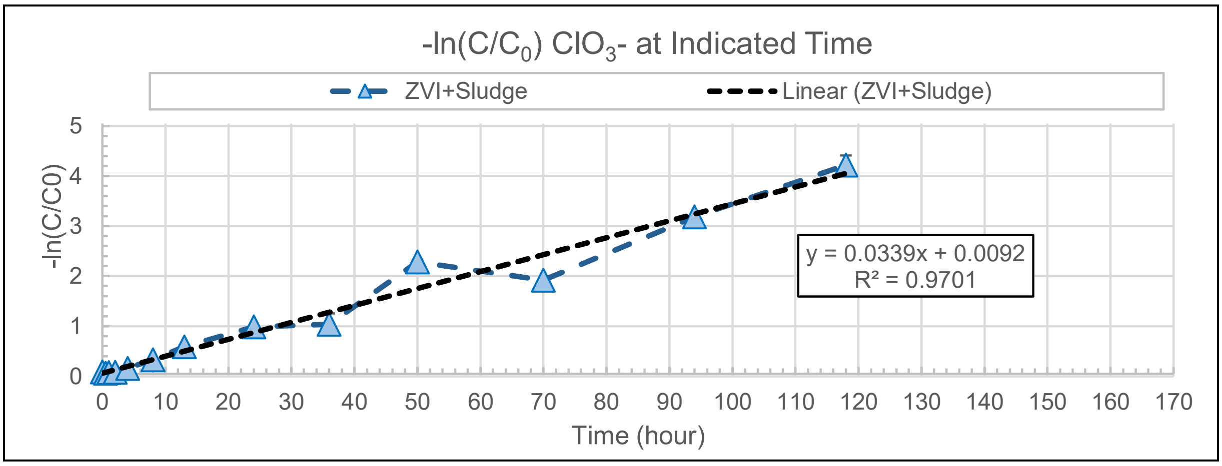


Figure C-18: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using ZVI+Sludge in the multiple contaminant experiment. Linear trend lines have been added with corresponding R^2 value and equation.

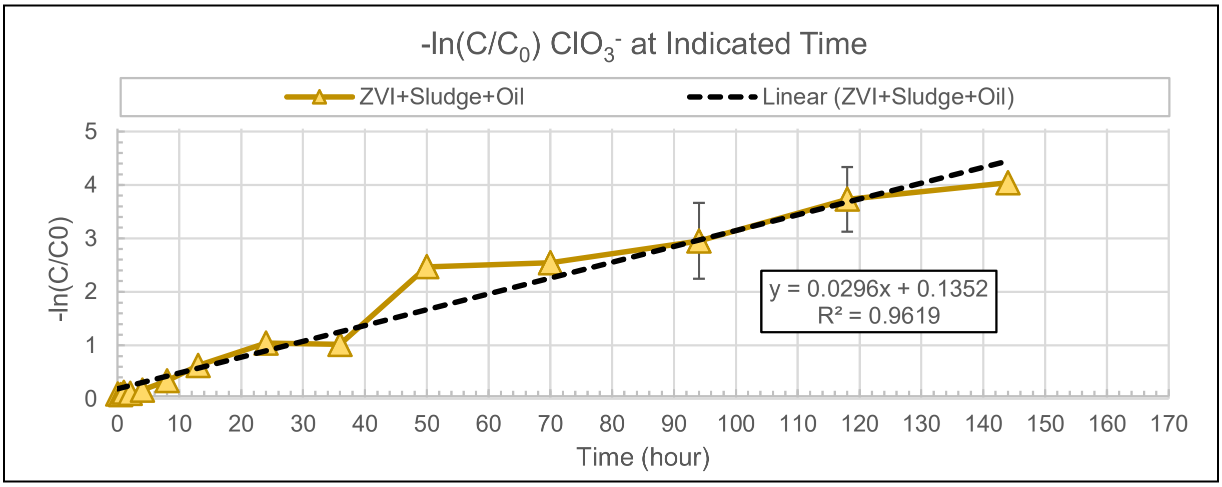


Figure C-19: Graphical determination for pseudo first-order reaction for the reduction of ClO3- using ZVI+Sludge+Oil in the multiple contaminant experiment. Linear trend lines have been added with corresponding R2 value and equation.

C.4 Determination of Reaction Order and Reaction Rate for ZVI+Sludge using Increasing and Decreasing Stoichiometric Ration

Graphical determination of the pseudo first-order reaction rate coefficients was determined for each method in the increasing and decreasing stoichiometric ratio experiment. As with the single contaminant Cr(VI) experiment in Section C.1, data points were reduced for several methods to limit distortion of the rates.

C.4.1 Cr(VI) Reduction in Sludge+ZVI with Varying Stoichiometric Ratio

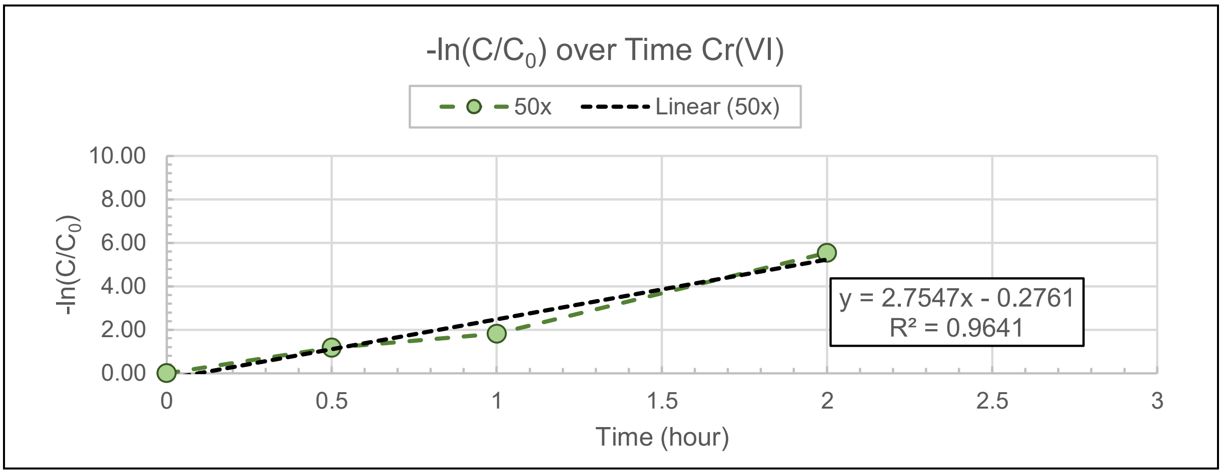


Figure C-20: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using 50X stoichiometric ratio ZVI+Sludge in the increasing and decreasing stoichiometric ratio experiment. Linear trend lines have been added with corresponding R^2 value and equation.

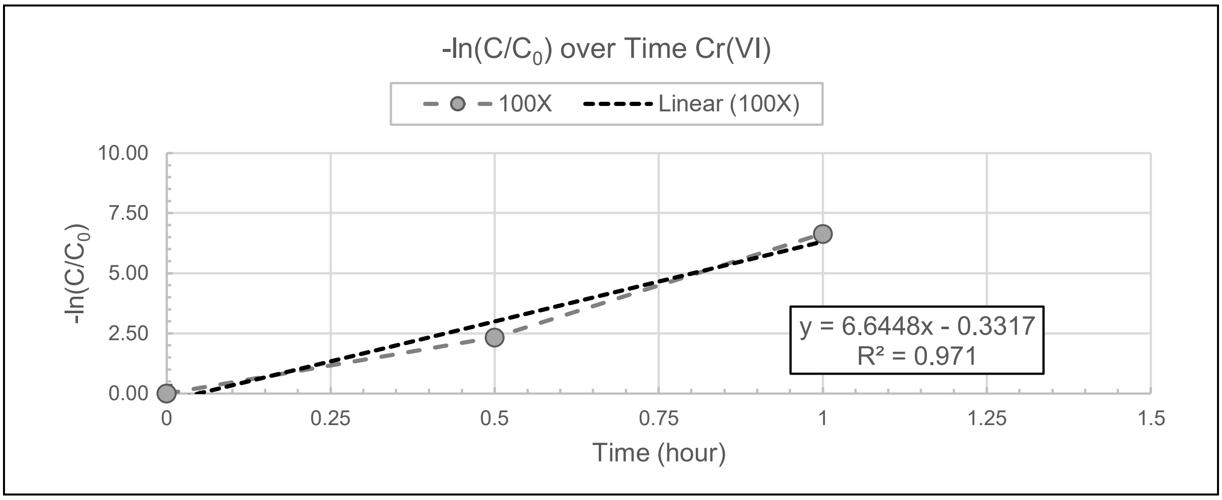


Figure C-21: Graphical determination for pseudo first-order reaction for the reduction of Cr(VI) using 100X stoichiometric ratio ZVI+Sludge in the increasing and decreasing stoichiometric ratio experiment. Linear trend lines have been added with corresponding R^2 value and equation.

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C.4.2 ClO_3^- Reduction in Sludge+ZVI with Varying Stoichiometric Ratio

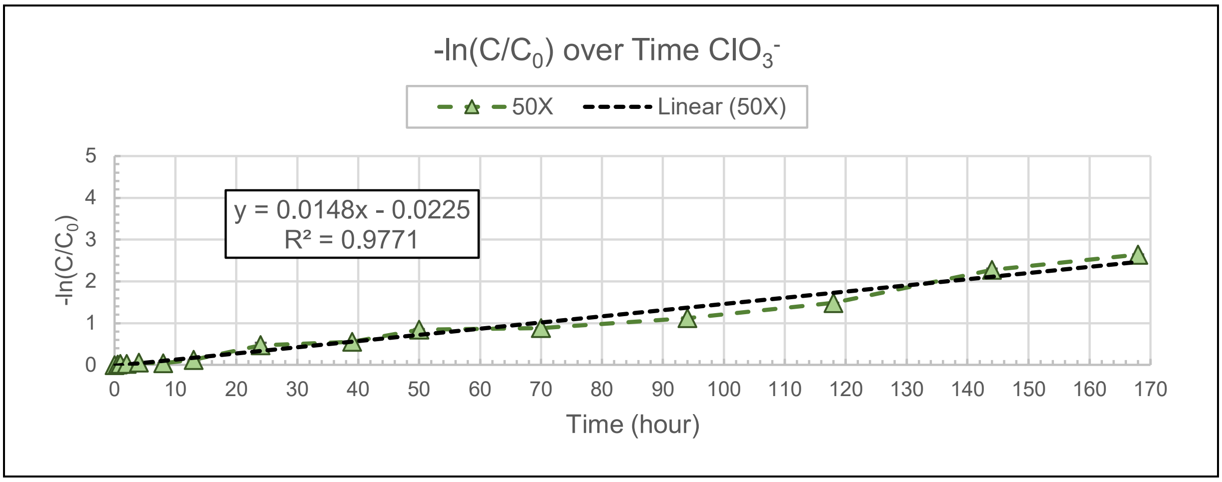


Figure C-22: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using 50X stoichiometric ratio ZVI+Sludge in the increasing and decreasing stoichiometric ratio experiment. Linear trend lines have been added with corresponding R^2 value and equation.

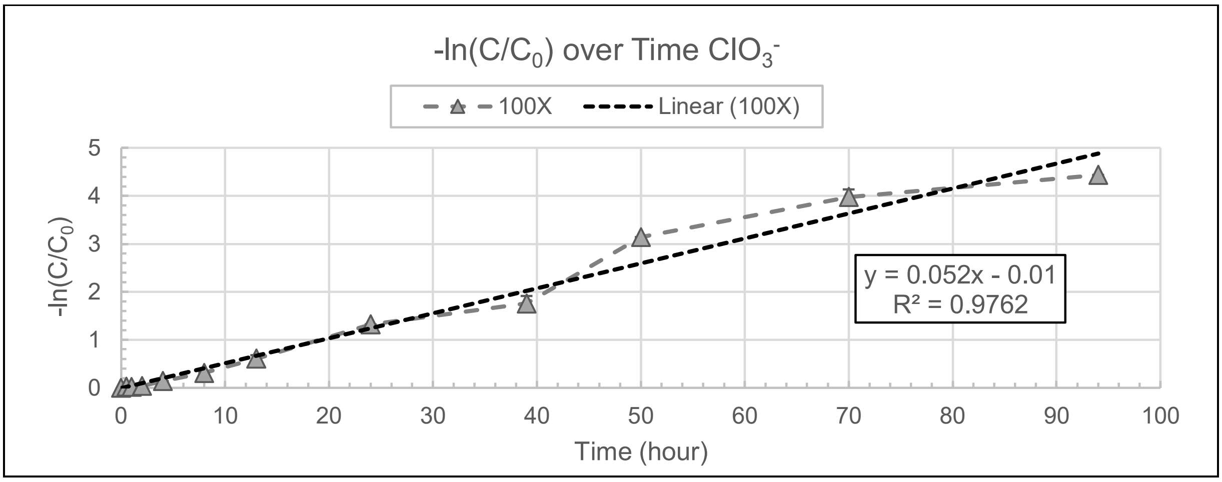


Figure C-23: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using 100X stoichiometric ratio ZVI+Sludge in the increasing and decreasing stoichiometric ratio experiment. Linear trend lines have been added with corresponding R^2 value and equation.

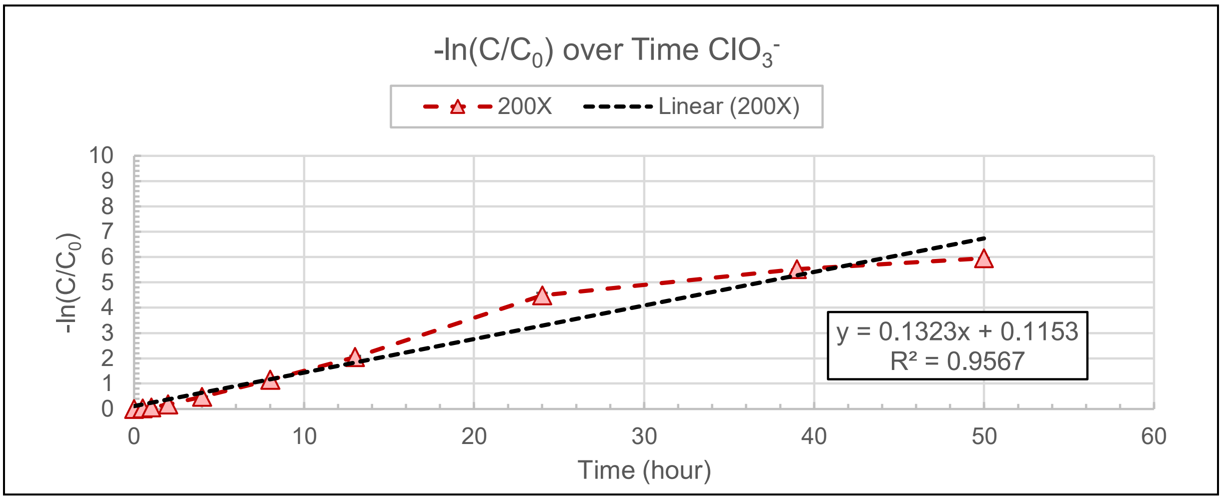


Figure C-24: Graphical determination for pseudo first-order reaction for the reduction of ClO_3^- using 200X stoichiometric ratio ZVI+Sludge in the increasing and decreasing stoichiometric ratio experiment. Linear trend lines have been added with corresponding R^2 value and equation.

Appendix D: Experimental Data for Batch Tests

D.1 Testing of Major Parameters: Selection of ZVI Size

Table D-1: Results for selection of ZVI size batch test. Iron filings and iron powder were tested. Initial Cr(VI) concentration was 10 mg/L. ZVI dose was 40g/L. Batch tests were performed using 30 mL glass vials.

Time (min)	Filings		Powder	
	Conc. (mg/L)	% removed	Conc. (mg/L)	% removed
0	11.00	0	11.00	0
20	5.00	54.55	4.86	55.82
40	2.40	78.18	3.10	71.82
60	1.30	88.18	1.00	90.91
80	2.60	76.36	0.80	92.73

D.2 Testing of Major Parameters: ZVI Dosage

Table D-2: Results for initial ZVI dosage batch test using Cr(VI). Initial Cr(VI) concentration was 10 mg/L. ZVI dose was 10 g/L. Batch tests were performed using 30 mL glass vials.

Time (min)	Conc. (mg/L)	% Cr(VI) Removed
0	10	0
10	5.7	43
20	2.2	78
30	1.1	89
40	0.48	95.2
45	0.16	98.4

Table D-3: Initial set-up and results for second ZVI dosage batch test utilizing Cr(VI). Initial Cr(VI) concentration was 20 mg/L. ZVI dosage was 2 g/L. Batch tests performed using 30 mL glass vials.

					$Cr(VI)_f$		% Removed		pH	
Time (hour)	ZVI_0 (g/L)	$Cr(VI)_0$ (mg/L)	READING (mg/L)	DF (-)	each (mg/L)	AVG (mg/L)	each (%)	AVG (%)	each (-)	AVG (-)
0.0	2.0	19.25	0.38 0.39	50	19 19.5	19.25	1.3 -1.3	0.0	6.85 6.88	6.87
0.5	2.0	19.25	0.32 0.33	50	16 16.5	16.25	16.9 14.3	15.6	7.29 7.4	7.35
1.0	2.0	19.25	0.3 0.31	50	15 15.5	15.25	22.1 19.5	20.8	7.45 7.49	7.47
1.5	2.0	19.25	0.32 0.3	50	16 15	15.5	16.9 22.1	19.5	7.52 7.56	7.54
2.0	2.0	19.25	0.28 0.32	50	14 16	15	27.3 16.9	22.1	7.59 7.61	7.60
2.5	2.0	19.25	0.31 0.29	50	15.5 14.5	15	19.5 24.7	22.1	7.63 7.67	7.65
3.0	2.0	19.25	0.31 0.29	50	14.5 13.5	14	24.7 29.9	27.3	7.66 7.66	7.66
3.5	2.0	19.25	0.27 0.31	50	13.5 15.5	14.5	29.9 19.5	24.7	7.64 7.66	7.65
4.0	2.0	19.25	0.27 0.32	50	13.5 16	14.75	29.9 16.9	23.4	7.63 7.6	7.62
4.5	2.0	19.25	0.3 0.27	50	15 13.5	14.25	22.1 29.9	26.0	7.62 7.7	7.66
36.5	2.0	19.25	0.27 0.23	50	13.5 11.5	12.5	29.9 40.3	35.1	7.52 7.57	7.55
62	2.0	19.25	0.22 0.22	50	11 11	11	42.9 42.9	42.9	7.79 7.62	7.71

Table D-4: Results for ZVI dosage using chlorate. Initial ClO_3^- concentrations were 10 mg/L and 100 mg/L. ZVI doses were 4 g/L and 10 g/L. 40 mL glass vials were used.

	ZVI			ClO_3^-	Stoichiometric	Results		**pH**
CT (hour)	Theo. (g)	Meas. (g)	Dose (g/L)	Concentration (mg/L)	Ratio (X)	ClO_3-_f mg/L	%Removed (%)	Avg. (-)
0	-	-	-	10	-	10.5	0	7.63
14	0.16	0.1648	4.12	10	205.3	8.61	18	7.76
36	0.16	0.1758	4.4	10	219	1.66	84.2	7.93
60	0.16	0.1627	4.07	10	202.6	0	100	-
86	0.16	0.1705	4.26	10	212.4	0	100	-
0	-	-	-	100	-	10.5	0	7.61
14	0.16	0.1693	4.23	100	21.1	86.4	15.3	7.77
36	0.16	0.1983	4.96	100	24.4	47.2	53.7	7.96
60	0.16	0.1667	4.17	100	20.8	3.79	96.3	-
86	0.16	0.1702	4.26	100	21.2	2.89	97.2	-
0	-	-		10	-	102	0	7.63
14	0.4	0.6207	15.62	10	773.1	5.84	44.4	7.85
36	0.4	0.4089	10.22	10	509.3	0	100	8.07
60	0.4	0.4498	11.25	10	560.2	0	100	-
86	0.4	0.4129	10.32	10	514.3	0	100	-
0	-	-		100	-	102	0	7.91
14	0.4	0.4202	10.51	100	52.3	69	32.4	7.72
36	0.4	0.4202	10.51	100	52.3	27.2	73.3	8.16
60	0.4	0.4014	10.04	100	50	1.82	98.2	-
86	0.4	0.4072	10.18	100	50.7	1.13	98.9	-

D.3 Testing of Major Parameters: ZVI+Sludge vs. ZVI

Table D-5: ZVI (blue) vs. ZVI+Sludge (green) results. Initial Cr(VI) concentration was 5 mg/L. ZVI dose was 10 g/L. Sludge dose was 360mg SS/L. EOS-PRO was used as an additional carbon source. 40 mL glass vials were used.

					$Cr(VI)_f$		**% Removed**		**pH**	
Time (hour)	ZVI_0 (g/L)	$Cr(VI)_0$ (mg/L)	Sludge (mL)	EOS-PRO (mL/L)	each (mg/L)	AVG (mg/L)	each (%)	AVG (%)	each (-)	AVG (-)
0.0	10	5	0	0		5	0	0		
0.3	10	5	0	0	0.3 0.1	0.2	94.0 98.0	96.0	7.49 7.61	7.55
0.5	10	5	0	0	0 0	0	100 100	100	7.67 7.69	7.68
1.0	10	5	0	0	0 0	0	100 100	100	7.70 7.71	7.71
1.5	10	5	0	0	0 0	0	100 100	100	7.71 7.73	7.72
2.0	10	5	0	0	0 0	0	100 100	100	7.71 7.70	7.71
2.5	10	5	0	0	0 0	0	100 100	100	7.69 7.68	7.69
0.0	10	5	1.0	8.3	5	5	0	0		
0.3	10	5	1.0 1.0	8.3 8.3	0.03 0.01	0.02	99.4 99.8	99.6	7.25 7.40	7.33
0.5	10	5	1.0 1.0	8.3 8.3	0.01 0	0.01	99.8 100	99.9	7.43 7.53	7.48
0.8	10	5	1.0 1.0	8.3 8.3	0 0	0	100 100	100	7.52 7.45	7.49
1.0	10	5	1.0 1.0	8.3 8.3	0 0	0	100 100	100	7.56 7.68	7.62
1.3	10	5	1.0 1.0	8.3 8.3	0 0	0	100 100	100	7.56 7.53	7.55
1.5	10	5	1.0 1.0	8.3 8.3	0 0	0	100 100	100	7.53 7.49	7.51

Table D-6: ZVI (yellow) vs. ZVI+Sludge (purple) results. Initial Cr(VI) concentration was 10 mg/L. ZVI dose was 10 g/L. Sludge dose was 360mg SS/L. EOS-PRO was added as an additional carbon source. 40 mL glass vials were used.

					$Cr(VI)_f$		**% Removed**		**pH**	
Time (hour)	ZVI_0 (g/L)	$Cr(VI)_0$ (mL)	Sludge (mL/L)	EOS-PRO (mL/L)	each (mg/L)	AVG (mg/L)	each (%)	AVG (%)	each (-)	AVG (-)
0.00		10	0	0	10	10	0	0		
0.25	10	10	0	0	2.8	1.7	72 94	83	7.22 7.42	7.32
0.50	10	10	0	0	0.9	0.95	91 90	90.5	7.60 7.68	7.64
1.00	10	10	0	0	0	0.25	100 95	97.5	7.77 7.83	7.80
1.50	10	10	0	0	0	0	100 100	100	7.88 7.92	7.90
2.00	10	10	0	0	0	0	100 100	100	7.95 7.99	7.97
2.50	10	10	0	0	0	0	100 100	100	7.98 8.00	7.99
0.00		10	1.0	12.1	10	10		0		
0.25	10	10	1.0	12.1	0.02 0.13	0.075	99.8 98.7	99.3	7.78 7.84	7.81
0.50	10	10	1.0	12.1	0.02 0	0.01	99.8 100	99.9	7.84 7.81	7.83
0.75	10	10	1.0	12.1	0 0	0	100 100	100	7.77 7.79	7.78
1.00	10	10	1.0	12.1	0 0	0	100 100	100	7.85 7.81	7.83
1.25	10	10	1.0	12.1	0 0	0	100 100	100	7.67 7.64	7.66
1.50	10	10	1.0	12.1	0 0	0	100 100	100	7.58 7.55	7.57

Table D-7: ZVI (green) vs. ZVI+Sludge (orange) results. Initial Cr(VI) concentration was 20 mg/L. ZVI dose was 10 g/L. Sludge dose was 360mg SS/L. EOS-PRO was added as an additional carbon source. 40 mL glass vials were used.

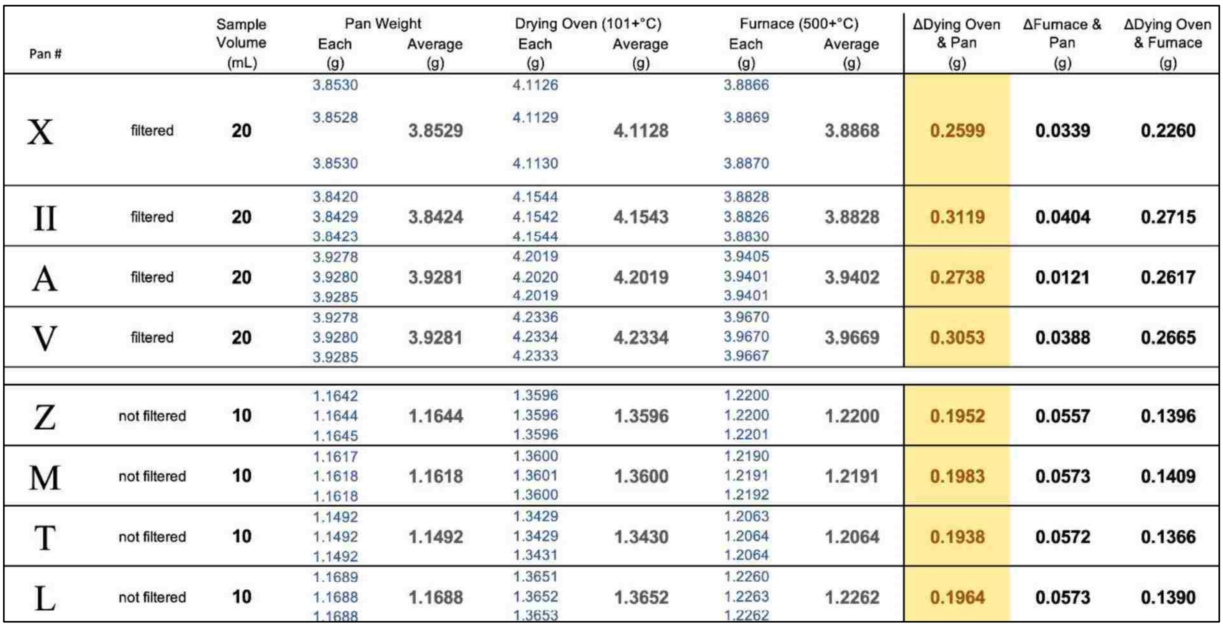
					$Cr(VI)_f$		% Removed		pH	
Time (hour)	ZVI_0 (g/L)	$Cr(VI)_0$ (mg/L)	Sludge (mL)	EOS-PRO (mL/L)	each (mg/L)	AVG (mg/L)	each (%)	AVG (%)	each (-)	AVG (-)
0.00		20	0	0	20	20	0	0		
0.25	10	20	0	0	11.6 12.2	11.9	42 39	40.5	5.88 6.02	5.95
0.50	10	20	0	0	10.0 11.0	10.5	50 45	47.5	7.23 7.50	7.37
1.00	10	20	0	0	10.0 6.0	8.0	50 70	60	7.78 7.91	7.85
1.50	10	20	0	0	8.0 5.0	6.5	60 75	67.5	8.14 8.21	8.18
2.00	10	20	0	0	6.0 5.0	5.5	70 75	72.5	8.28 8.33	8.31
3.00	10	20	0	0	5.0 3.0	4.0	75 85	80	8.13 8.22	8.18
4.00	10	20	0	0	2.0 0.4	1.2	90 98	94	8.29 8.36	8.33
5.00	10	20	0	0	0 0	0	100 100	100	8.39 8.41	8.40
6.00	10	20	0	0	0 0	0	100 100	100	8.39 8.38	8.39
0.00		20	1.0	19.6	20	20	0	0		
0.25	10	20	1.0	19.6	5.6 0.8	3.2	72 96	84	8.07 8.07	8.07
0.50	10	20	1.0	19.6	0.04 0.16	0.1	99.8 99.2	99.5	8.09 8.06	8.08
0.75	10	20	1.0	19.6	0 0	0	100 100	100	8.26 8.32	8.29
1.00	10	20	1.0	19.6	0 0	0	100 100	100	8.06 8.24	8.15
1.25	10	20	1.0	19.6	0 0	0	100 100	100	8.07 8.29	8.18
1.50	10	20	1.0	19.6	0 0	0	100 100	100	8.06 8.17	8.12
1.75	10	20	1.0	19.6	0 0	0	100 100	100	8.13 8.06	8.10
2.00	10	20	1.0	19.6	0 0	0	100 100	100	8.14 8.22	8.18
2.25	10	20	1.0	19.6	0 0	0	100 100	100	8.24 8.09	8.17

Table D-8: ZVI (blue) vs. ZVI+Sludge (yellow) results. Initial Cr(VI) concentration was 20 mg/L. ZVI dose was 50 g/L. Sludge dose was 360mg SS/L. EOS-PRO was added as an additional carbon source. 40 mL glass vials were used.

					$Cr(VI)_f$		**% Removed**		**pH**	
Time (hour)	ZVI_0 (g/L)	$Cr(VI)_0$ (mg/L)	Sludge (mL/L)	EOS-PRO (mL/L)	each (mg/L)	AVG (mg/L)	each (%)	AVG (%)	each (-)	AVG (-)
0.00		50	0	0	50.0	50	0	0		
0.50	10	50	0	0	33.0 39.0	36	34 22	28	7.07 7.01	7.04
1.00	10	50	0	0	31.0 36.0	33.5	38 28	33	7.14 7.10	7.12
2.00	10	50	0	0	28.0 37.0	32.5	44 26	35	7.61 7.46	7.54
3.00	10	50	0	0	35.0 29.0	32	30 42	36	7.42 7.37	7.40
4.00	10	50	0	0	26.0 36.0	31	48 28	38	7.39 7.34	7.37
5.00	10	50	0	0	31.0 30.0	30.5	38 40	39	7.34 7.39	7.37
14.50	10	50	0	0	31.0 33.0	32	38 34	36	- -	-
17.50	10	50	0	0	31.0 32.0	31.5	38 36	37	- -	-
0.00		50	1.0	42.2	50.0	50.0	0.0	0.0		
0.25	10	50	1.0	42.2	10.5 12.0	11.3	79.0 76.0	77.5	8.40 8.36	8.38
0.50	10	50	1.0	42.2	10.5 9.5	10.0	79.0 81.0	80.0	8.26 8.25	8.36
0.75	10	50	1.0	42.2	7.0 10.0	8.5	86.0 80.0	83.0	8.56 8.28	8.42
1.00	10	50	1.0	42.2	10.5 6.0	8.3	79.0 88.0	83.2	8.61 8.51	8.56
1.50	10	50	1.0	42.2	8.5 6.0	7.3	83.0 88.0	85.5	8.26 8.27	8.27
2.00	10	50	1.0	42.2	6.0 5.0	5.5	88.0 90.0	89.0	8.27 8.27	8.27
2.50	10	50	1.0	42.2	6.2 3.6	4.9	87.6 92.8	90.2	8.28 8.48	8.38
3.00	10	50	1.0	42.2	6.4 0.6	3.5	87.2 98.8	93.0	8.45 8.39	8.42
3.50	10	50	1.0	42.2	5.6 1.2	3.4	88.8 87.6	88.2	8.53 8.56	8.55

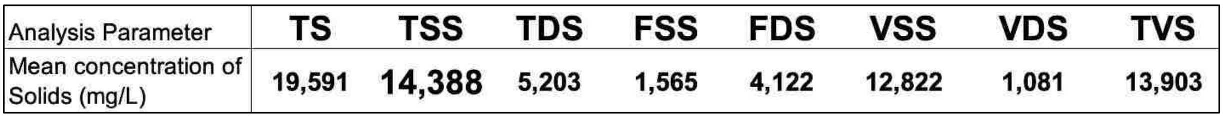
D.4 Testing of Major Parameters: Sludge Doses

Table D-9: Solids analysis for sludge.



Pan #		Sample Volume (mL)	Pan Weight		Drying Oven (101+°C)		Furnace (500+°C)		ΔDying Oven & Pan (g)	ΔFurnace & Pan (g)	ΔDying Oven & Furnace (g)
			Each (g)	Average (g)	Each (g)	Average (g)	Each (g)	Average (g)			
X	filtered	20	3.8530 3.8528 3.8530	3.8529	4.1126 4.1129 4.1130	4.1128	3.8866 3.8869 3.8870	3.8868	0.2599	0.0339	0.2260
II	filtered	20	3.8420 3.8429 3.8423	3.8424	4.1544 4.1542 4.1544	4.1543	3.8828 3.8826 3.8830	3.8828	0.3119	0.0404	0.2715
A	filtered	20	3.9278 3.9280 3.9285	3.9281	4.2019 4.2020 4.2019	4.2019	3.9405 3.9401 3.9401	3.9402	0.2738	0.0121	0.2617
V	filtered	20	3.9278 3.9280 3.9285	3.9281	4.2336 4.2334 4.2333	4.2334	3.9670 3.9670 3.9667	3.9669	0.3053	0.0388	0.2665
Z	not filtered	10	1.1642 1.1644 1.1645	1.1644	1.3596 1.3596 1.3596	1.3596	1.2200 1.2200 1.2201	1.2200	0.1952	0.0557	0.1396
M	not filtered	10	1.1617 1.1618 1.1618	1.1618	1.3600 1.3601 1.3600	1.3600	1.2190 1.2191 1.2192	1.2191	0.1983	0.0573	0.1409
T	not filtered	10	1.1492 1.1492 1.1492	1.1492	1.3429 1.3429 1.3431	1.3430	1.2063 1.2064 1.2064	1.2064	0.1938	0.0572	0.1366
L	not filtered	10	1.1689 1.1688 1.1688	1.1688	1.3651 1.3652 1.3653	1.3652	1.2260 1.2263 1.2262	1.2262	0.1964	0.0573	0.1390

Table D-10: Mean concentration of solids from solids analysis for sludge.



Analysis Parameter	TS	TSS	TDS	FSS	FDS	VSS	VDS	TVS
Mean concentration of Solids (mg/L)	19,591	14,388	5,203	1,565	4,122	12,822	1,081	13,903

Table D-11: Results for sludge dosage batch tests. Sludge doses were 36mg SS/L, 72mg SS/L, 180mg SS/L, and 360mg SS/L. EOS-PRO was used as an additional carbon source. No ZVI was added.

Contact	Sludge	EOS-PRO	Hexavalent Chromium [Cr(VI)]				
Time (hour)	Dose (mL)	10^3 dil. (mL/L)	$Cr(VI)_0$ (mL)	$Cr(VI)_F$ (mL)	AVG_F (mL)	% Removed (%)	pH
30	0.5	2.0	10	4.2	4.2	58.0	7.06
30	0.5	2.0	20	13.0 13.0	13.0	35.0	7.46
30	0.5	4.3	50	34.0	34.0	32.0	7.48
30	0.5	6.1	75	62.0	62.0	17.3	7.30
30	0.5	8.0	100	78.0	75.0	22.0	7.25
30	1.0	12.0	10	0.7	0.7	93.3	7.63
30	1.0	18.8	20	7.2	7.2	64.0	7.84
30	1.0	4.3	50	34.0	34.0	32.0	7.79
30	1.0	6.0	75	47.0	47.0	37.3	7.64
30	1.0	8.0	100	66.0 68.0	67.0	33.0	7.61
30	0.2	1.3	10	6.8	6.8	32.0	7.70
30	0.2	2.0	20	17.0 17.5	17.3	13.8	7.63
30	0.2	4.3	50	40.0	40.0	20.0	7.50
30	0.2	6.0	75	58.0	58.0	22.7	7.27
30	0.2	8.0	100	86.0	86.0	14.0	7.10
30	0.1	1.3	10	7.8 8.0	7.9	21.0	7.67
30	0.1	2.0	20	18.0	18.0	10.0	7.65
30	0.1	4.3	50	45.0	45.0	10.0	7.43
30	0.1	6.0	75	62.0	62.0	17.3	7.17
30	0.1	8.0	100	84.0	84.0	16.0	7.04

D.5 Testing of Major Parameters: ClO_3^- Concentration

Table D-12: Results for initial ClO_3^- concentrations tests using ZVI. Initial ClO_3^- concentrations were 10mg/L and 100mg/L ClO_3^- ZVI doses ranged from 4g/L to 15.6g/L. No Sludge was used.

CT (hour)	ZVI Theo. (g)	Meas. (g)	Dose (g/L)	ClO_3^- Concentration (mg/L)	Stoichiometric Ratio (X)	Results ClO_3-_f mg/L	%Removed (%)	pH Avg. (-)
0	-	-	-	10	-	10.5	0	7.63
14	0.16	0.1648	4.12	10	205.3	8.61	18	7.76
36	0.16	0.1758	4.4	10	219	1.66	84.2	7.93
60	0.16	0.1627	4.07	10	202.6	0	100	-
86	0.16	0.1705	4.26	10	212.4	0	100	-
0	-	-	-	100	-	10.5	0	7.61
14	0.16	0.1693	4.23	100	21.1	86.4	15.3	7.77
36	0.16	0.1983	4.96	100	24.4	47.2	53.7	7.96
60	0.16	0.1667	4.17	100	20.8	3.79	96.3	-
86	0.16	0.1702	4.26	100	21.2	2.89	97.2	-
0	-	-		10	-	102	0	7.63
14	0.4	0.6207	15.62	10	773.1	5.84	44.4	7.85
36	0.4	0.4089	10.22	10	509.3	0	100	8.07
60	0.4	0.4498	11.25	10	560.2	0	100	-
86	0.4	0.4129	10.32	10	514.3	0	100	-
0	-	-		100	-	102	0	7.91
14	0.4	0.4202	10.51	100	52.3	69	32.4	7.72
36	0.4	0.4202	10.51	100	52.3	27.2	73.3	8.16
60	0.4	0.4014	10.04	100	50	1.82	98.2	-
86	0.4	0.4072	10.18	100	50.7	1.13	98.9	-

D.6 Molar Ratio Batch Tests

Table D-13: Results for abiotic ZVI molar ratio test. Initial Cr(VI) concentration was 10mg/L.

Contact	ZVI			$Cr(VI)_0$		Molar Ratio		Hexavalent Chromium				pH	
Time (hour)	theoretical (g)	measured (g)	DOSE (g/L)	Concentration (mg/L)	mass (mg)	Theoretical (mol ZVI:mol Cr(VI))	Actual (mol ZVI:mol Cr(VI))	$Cr(VI)_f$ (mg/L)	$Cr(VI)_{f\ avg}$ (mg/L)	% Removed (%)	% $Removed_{avg}$ (%)	pH (-)	pH_{avg} (-)
0	0	0	0	10	0.4	0	0	10	10	0	0.0	7.09	7.09
30	0.04	0.0725	1.8	10	0.4	100	169	9.00	9.00	10	10.0	7.79	7.79
30	0.09	0.1162	2.9	10	0.4	200	271	7.50	7.45	25	25.5	7.78	7.69
		0.1317	3.3				307	7.40		26		7.60	
30	0.17	0.2266	5.7	10	0.4	400	528	5.50	5.50	45	45.0	7.77	7.77
30	0.26	0.2592	6.5	10	0.4	600	604	5.00	4.90	50	51.0	7.76	7.73
		0.2734	6.8				637	4.80		52		7.69	
30	0.34	0.3789	9.5	10	0.4	800	883	3.00	3.00	70	70.0	7.79	7.79
30	0.43	0.4766	11.9	10	0.4	1000	1110	1.10	0.95	89	90.5	7.71	7.82
		0.4555	11.4				1061	0.80		92		7.93	
30	0.52	0.5238	13.1	10	0.4	1200	1220	0.45	0.45	95.5	95.5	7.63	7.63
30	0.60	0.5961	14.9	10	0.4	1400	1389	0.04	0.04	99.6	99.6	7.59	7.59
30	0.69	0.6981	17.5	10	0.4	1600	1626	0.00	0.00	100	100.0	7.55	7.55
30	0.77	0.8004	20.0	10	0.4	1800	1865	0.00	0.00	100	100.0	7.43	7.43

Table D-14: Results for abiotic ZVI molar ratio test. Initial Cr(VI) concentration was 20mg/L.

Contact	ZVI			$Cr(VI)_0$		Molar Ratio		Hexavalent Chromium				pH	
Time	theoretical	measured	DOSE	Concentration	mass	Theoretical	Actual	$Cr(VI)_f$	$Cr(VI)_{f\ avg}$	% Removed	% $Removed_{avg}$	pH	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mg/L)	(mg)	(mol ZVI:mol Cr(VI))	(mol ZVI:mol Cr(VI))	(mg/L)	(mg/L)	(%)	(%)	(-)	(-)
0	0	0	0	20	0.8	0	0	20	20.00	0	0.0	6.99	6.99
30	0.09	0.0885	2.2	20	0.8	100	103	18.00	18.50	10	7.5	7.79	7.68
		0.0907	2.3				106	19.00		5		7.57	
30	0.17	0.1728	4.3	20	0.8	200	201	15.00	15.00	25	25.0	7.66	7.66
30	0.34	0.3619	9.0	20	0.8	400	422	11.40	11.40	43	43.0	7.77	7.77
30	0.52	0.5705	14.3	20	0.8	600	665	9.40	9.40	53	53.0	7.77	7.77
30	0.69	0.6876	17.2	20	0.8	800	801	7.60	7.30	62	63.5	7.82	7.83
		0.7034	17.6				819	7.00		65		7.83	
30	0.86	0.8706	21.8	20	0.8	1000	1014	3.20	3.20	84	84.0	7.86	7.86
30	1.03	1.0329	25.8	20	0.8	1200	1203	1.90	1.90	90.5	90.5	7.87	7.87
30	1.20	1.2072	30.2	20	0.8	1400	1406	0.36	0.18	98.2	99.1	7.86	7.81
		1.4032	35.1				1635	0.00		100		7.75	
30	1.37	1.3748	34.4	20	0.8	1600	1601	0.03	0.03	99.85	99.9	7.81	7.81
30	1.55	1.5656	39.1	20	0.8	1800	1824	0.00	0.00	100	100.0	7.74	7.74

Table D-15: Results for abiotic ZVI molar ratio test. Initial Cr(VI) concentration was 50mg/L.

Contact	ZVI			$Cr(VI)_0$		Molar Ratio		Hexavalent Chromium				pH	
Time	theoretical	measured	DOSE	Concentration	mass	Theoretical	Actual	$Cr(VI)_f$	$Cr(VI)_{f\ avg}$	% Removed	% $Removed_{avg}$	pH	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mg/L)	(mg)	(mol ZVI:mol Cr(VI))	(mol ZVI:mol Cr(VI))	(mg/L)	(mg/L)	(%)	(%)	(-)	(-)
0	0	0	0	50	2	0	0	50.00	50.00	0	0.0	6.65	6.65
30	0.21	0.2152	5.4	50	2	100	100	45.00	45.00	10	10.0	7.00	7.00
30	0.43	0.4375	10.9	50	2	200	204	38.00	38.00	24	24.0	7.21	7.21
30	0.86	0.8867	22.2	50	2	400	413	32.00	33.00	36	34.0	7.35	7.37
		0.8858	22.1				413	34.00		32		7.39	
30	1.29	1.3291	33.2	50	2	600	619	23.00	23.00	54	54.0	7.68	7.68
30	1.72	1.8056	45.1	50	2	800	841	16.00	16.00	68	68.0	7.90	7.90
30	2.15	2.1495	53.7	50	2	1000	1002	7.00	7.00	86	86.0	8.03	8.03
30	2.58	2.5894	64.7	50	2	1200	1207	3.00	3.60	94	92.8	7.97	7.78
		2.5834	64.6				1204	4.20		91.6		7.59	
30	3.00	3.0177	75.4	50	2	1400	1406	0.00	0.00	100	100.0	7.75	7.75
30	3.43	3.4664	86.7	50	2	1600	1615	0.02	0.02	100.0	100.0	7.54	7.54
30	3.86	3.8702	96.8	50	2	1800	1803	0.00	0.00	100	100.0	7.46	7.37
		3.8804	97.0				1808	0.00		100		7.27	

Table D-16: Results for abiotic ZVI molar ratio test. Initial Cr(VI) concentration was 75mg/L.

Contact	ZVI			$Cr(VI)_0$		Molar Ratio			Hexavalent Chromium			pH	
Time (hour)	theoretical (g)	measured (g)	DOSE (g/L)	Concentration (mg/L)	mass (mg)	Theoretical (mol ZVI:mol Cr(VI))	Actual (mol ZVI:mol Cr(VI))	$Cr(VI)_f$ (mg/L)	$Cr(VI)_{f\ avg}$ (mg/L)	% Removed (%)	% $Removed_{avg}$ (%)	pH (-)	pH_{avg} (-)
0	0	0	0	75	3	0	0	75	75.00	0	0	6.46	6.46
30	0.32	0.3292	8.2	75	3	100	102	68	67.50	9.3	10.0	6.89	6.96
		0.4867	12.2				151	67		10.7		7.03	
30	0.64	0.6458	16.1	75	3	200	201	56	56.00	25.3	25.3	7.15	7.15
30	1.29	1.2895	32.2	75	3	400	401	51	52.00	32.0	30.7	7.42	7.44
		1.3764	34.4				428	53		29.3		7.45	
30	1.93	1.9483	48.7	75	3	600	605	35	35.00	53.3	53.3	7.28	7.28
30	2.58	2.5801	64.5	75	3	800	801	27.5	27.50	63.3	63.3	7.27	7.27
30	3.22	3.2338	80.8	75	3	1000	1005	13	16.25	82.7	78.4	7.80	7.65
		3.2953	82.4				1024	19.5		74.0		7.49	
30	3.86	3.8953	97.4	75	3	1200	1210	9.4	9.40	87.5	87.5	7.63	7.63
30	4.51	4.5088	112.7	75	3	1400	1401	0.04	0.04	99.9	99.9	7.16	7.16
30	5.15	5.1937	129.8	75	3	1600	1613	0	0.00	100.0	100.0	7.28	7.28
30	5.79	5.7961	144.9	75	3	1800	1800	0	0.00	100.0	100.0	7.21	7.21

Table D-17: Results for abiotic ZVI molar ratio test. Initial Cr(VI) concentration was 100mg/L.

Contact	ZVI			$Cr(VI)_0$		Molar Ratio			Hexavalent Chromium			pH	
Time (hour)	theoretical (g)	measured (g)	DOSE (g/L)	Concentration (mg/L)	mass (mg)	Theoretical (mol ZVI:mol Cr(VI))	Actual (mol ZVI:mol Cr(VI))	$Cr(VI)_f$ (mg/L)	$Cr(VI)_{f\ avg}$ (mg/L)	% Removed (%)	% $Removed_{avg}$ (%)	pH (-)	pH_{avg} (-)
0	0	0	0	100	4	0	0	100	100.00	0	0	6.33	6.33
30	0.43	0.4378	10.9	100	4	100	102	86	86.00	14	14	6.85	6.85
30	0.86	0.8659	21.6	100	4	200	202	80	82.00	20	18	6.91	6.92
		0.8698	21.7				203	84		16		6.93	
30	1.72	1.7238	43.1	100	4	400	402	60	60.00	40	40	7.43	7.43
30	2.58	2.5930	64.8	100	4	600	604	53	53.00	47	47	7.48	7.48
30	3.43	3.4351	85.9	100	4	800	800	43	42.50	57	57.5	7.42	7.37
		3.4298	85.7				799	42		58		7.32	
30	4.29	4.2974	107.4	100	4	1000	1001	20	20.00	80	80	7.54	7.54
30	5.15	5.1578	128.9	100	4	1200	1202	5.6	5.60	94.4	94.4	7.47	7.47
30	6.01	6.0140	150.4	100	4	1400	1401	0.02	0.02	99.8	99.8	7.52	7.52
30	6.87	6.8757	171.9	100	4	1600	1602	0	0.00	100	100	7.41	7.22
		6.9006	172.5				1608	0		100		7.03	
30	7.73	7.7398	193.5	100	4	1800	1803	0	0.00	100	100	7.30	7.30

Table D-18: Results for ZVI+Sludge molar ratio tests. Initial Cr(VI) concentration was 10mg/L. Sludge dose was 180mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio				$Cr(VI)_f$			
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	10	0	0	10	10	0	0.0	0	7.09
30	0.04	0.0546	1.4	0.5	0.482	10	100	127	2.10	1.85	79	82.0	8.15	7.50
		0.0747	1.9					174	1.60		84			
30	0.09	0.1118	2.8	0.5	0.482	10	200	260	2.00	2.00	80	80.0	8.00	7.93
30	0.17	0.1807	4.5	0.5	0.482	10	400	421	1.20	1.20	88	88.0	8.80	7.99
30	0.26	0.2997	7.5	0.5	0.482	10	600	698	0.40	0.40	96	96.0	9.60	7.97
30	0.34	0.3654	9.1	0.5	0.482	10	800	851	0.00	0.01	100	100.0	9.99	7.94
		0.3765	9.4					877	0.01		99.9			
30	0.43	0.5391	13.5	0.5	0.482	10	1000	1256	0.00	0.00	100	100.0	10.00	7.65
30	0.52	0.5722	14.3	0.5	0.482	10	1200	1333	0.00	0.00	100	100.0	10.00	7.77
30	0.60	0.6072	15.2	0.5	0.482	10	1400	1415	0.00	0.00	100	100.0	10.00	7.59

Table D-19: Results for ZVI+Sludge molar ratio test. Initial Cr(VI) concentration was 10mg/L. Sludge dose was 360mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio				$Cr(VI)_f$			
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	10	0	0	10	10	0	0	9.97	7.09
30	0.04	0.0543	1.4	1.0	0.482	10	100	127	0.30	0.03	97	97	9.94	7.87
30	0.09	0.1038	2.6	1.0	0.482	10	200	242	0.06	0.06	99.4	99.4	10.00	7.95
30	0.17	0.2127	5.3	1.0	0.482	10	400	496	0	0	100	100	10.00	7.98
		0.1918	4.8					447	0		100			
30	0.26	0.2666	6.7	1.0	0.482	10	600	621	0	0	100	100	10.00	8.03
30	0.34	0.3458	8.6	1.0	0.482	10	800	806	0	0	100	100	10.00	7.97
30	0.43	0.4359	10.9	1.0	0.482	10	1000	1016	0	0	100	100	10.00	7.86
		0.4421	11.1					1030	0		100			
30	0.52	0.5191	13.0	1.0	0.482	10	1200	1209	0	0	100	100	10.00	7.51
30	0.60	0.5993	15.0	1.0	0.482	10	1400	1396	0	0	100	100	10.00	7.68

Table D-20: Results for ZVI+Sludge molar ratio test. Initial Cr(VI) concentration was 100mg/L. Sludge dose was 180mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio		$Cr(VI)_f$					
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	100	0	0	100	100	0	0	0	6.33
30	0.43	0.4312	10.8	0.5	0.320	100	100	100	84.0	84.0	16	16	16.0	7.65
30	0.86	0.8675	21.7	0.5	0.320	100	200	202	74.0	75.0	26	25	25.0	7.48
		0.8828	22.1					206	76.0		24			
30	1.72	1.7615	44.0	0.5	0.320	100	400	410	60.0	60.0	40	40	40.0	7.82
30	2.58	2.5834	64.6	0.5	0.320	100	600	602	41.0	41.0	59	59	59.0	7.76
30	3.43	3.4319	85.8	0.5	0.320	100	800	800	28.0	28.0	72	72	72.0	8.02
30	4.29	4.3046	107.6	0.5	0.320	100	1000	1003	6.5	6.5	93.5	93.5	93.5	8.21
30	5.15	5.1636	129.1	0.5	0.320	100	1200	1203	1.0	1.0	99	99	99.0	7.43
30	6.01	6.0152	150.4	0.5	0.320	100	1400	1401	0.0	0.0	100	100	100.0	7.51
		6.0175	150.4					1402	0.0		100			

Table D-21: Results for ZVI+SLudge molar ratio test. Initial Cr(VI) concentration was 100mg/L. Sludge dose was 360mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio		$Cr(VI)_f$					
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	100	0	0	100	100	0	0	0	6.33
30	0.43	0.4560	11.4	1.0	0.320	100	100	106	74.0	74.0	26.0	26.0	26.0	7.68
30	0.86	0.8602	21.5	1.0	0.320	100	200	200	70.0	70.0	30.0	30.0	30.0	8.11
30	1.72	1.7219	43.0	1.0	0.320	100	400	401	51.0	50.5	49.0	49.5	49.5	8.21
		1.7230	43.1					401	50.0		50.0			
30	2.58	2.5817	64.5	1.0	0.320	100	600	601	33.0	33.0	67.0	67.0	67.0	8.30
30	3.43	3.4312	85.8	1.0	0.320	100	800	799	18.5	15.3	81.5	84.8	84.8	8.35
		3.4327	85.8					800	12.0		88.0			
30	4.29	4.2901	107.3	1.0	0.320	100	1000	999	0.2	0.2	99.8	99.8	99.8	8.34
30	5.15	5.1551	128.9	1.0	0.320	100	1200	1201	0.0	0.0	100	100	100.0	8.22
30	6.01	6.0148	150.4	1.0	0.320	100	1400	1401	0.0	0.0	100	100	100.0	8.08

Table D-22: Results for ZVI+Sludge molar ratio test. Initial Cr(VI) concentration was 20mg/L. Sludge dose was 180mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio		$Cr(VI)_f$					
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	20	0	0	20.0	20.0	0	0	0	6.99
30	0.09	0.0942	2.4	0.5	0.482	20	100	110	11.0	11.0	45.0	45.0	9.0	7.40
30	0.17	0.1743	4.4	0.5	0.482	20	200	203	8.0	8.0	60.0	60.0	12.0	7.66
30	0.34	0.3518	8.8	0.5	0.482	20	400	410	7.2	7.1	64.0	64.5	12.9	7.79
		0.3457	8.6					403	7.0		65.0			
30	0.52	0.5238	13.1	0.5	0.482	20	600	610	4.0	4.0	80.0	80.0	16.0	7.92
30	0.69	0.6987	17.5	0.5	0.482	20	800	814	1.5	1.5	92.5	92.5	18.5	7.73
30	0.86	0.8858	22.1	0.5	0.482	20	1000	1032	0.2	0.3	99.0	98.5	19.7	7.83
		0.8718	21.8				1000	1016	0.4		98.0			
30	1.03	1.0452	26.1	0.5	0.482	20	1200	1218	0	0	100	100	20.0	7.83
30	1.20	1.2075	30.2	0.5	0.482	20	1400	1407	0	0	100	100	20.0	7.79

Table D-23: Results for ZVI+Sludge molar ratio test. Initial Cr(VI) concentration was 50mg/L. Sludge dose was 180mg SS/L.

Contact	ZVI			Bacteria	EOS-Pro	$Cr(VI)_0$	Molar Ratio		$Cr(VI)_f$					
Time	theoretical	measured	DOSE	Sludge	10,000x dil	Concentration	Theoretical	Actual	Concentration	$Cr(VI)_{f\ avg}$	% Removed	% Removed $_{avg}$	Mass Removed	pH_{avg}
(hour)	(g)	(g)	(g/L)	(mL)	(mL)	(mg/L)	(mol ZVI:mol Cr(VI))		(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	0	0	50	0	0	50.0	50.0	0	0	0	6.65
30	0.21	0.2759	6.9	0.5	0.482	50	100	129	36.0	36.0	28.0	28.0	14.0	7.56
		0.2152	5.4					100	36.0		28.0			
30	0.43	0.4396	11.0	0.5	0.482	50	200	205	30.5	30.5	39.0	39.0	19.5	7.73
30	0.86	0.8678	21.7	0.5	0.482	50	400	404	24.0	24.0	52.0	52.0	26.0	7.90
30	1.29	1.2991	32.5	0.5	0.482	50	600	605	17.5	17.5	65.0	65.0	32.5	7.99
30	1.72	1.7365	43.4	0.5	0.482	50	800	809	7.6	7.7	84.8	84.6	42.3	8.07
		1.7531	43.8					817	7.8		84.4			
30	2.15	2.1603	54.0	0.5	0.482	50	1000	1007	2.0	2.0	96.0	96.0	48.0	8.06
30	2.58	2.6664	66.7	0.5	0.482	50	1200	1242	0	0	100	100	50.0	7.97
30	3.00	3.0104	75.3	0.5	0.482	50	1400	1403	0	0	100	100	50.0	7.88

D.7 Single Contaminant Cr(VI) Reduction Batch Tests

Table D-24: Results for Blank samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. No ZVI or sludge was added.

Contact Time (hour)	ZVI theoretical (g)	ZVI measured (g)	ZVI DOSE (g/L)	$Cr(VI)_0$ Concentration (mg/L)	Molar Ratio Theoretical (mol ZVI:mol Cr(VI))	Molar Ratio Actual (mol ZVI:mol Cr(VI))	Sludge (mL)	EOS-PRO (mL)	Results $Cr(VI)_f$ (mg/L)	Results $Cr(VI)_{f\_avg}$ (mg/L)	Results % Removed (%)	Results % $Removed_{AVG}$ (%)	Results Mass $Removed_{AVG}$ (mg/L)	pH Avg. Meas. (-)
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0	0	0	30	0	0	0	0	31.0	31.0	-5.1	-5.1	-1.5	7.13
1	0	0	0	30	0	0	0	0	30.0	30.0	-1.7	-1.7	-0.5	7.27
		0	0	30	0	0	0	0	30.0		-1.7			
1.5	0	0	0	30	0	0	0	0	30.0	30.0	-1.7	-1.7	-0.5	7.24
		0	0	30	0	0	0	0	30.0		-1.7			
2	0	0	0	30	0	0	0	0	30.0	30.0	-1.7	-1.7	0.0	7.21
3	0	0	0	30	0	0	0	0	32.0	32.0	-8.5	-8.5	-2.0	7.19
4	0	0	0	30	0	0	0	0	31.0	29.5	-5.1	0	0	7.22
		0	0	30	0	0	0	0	28.0		5.1			
5	0	0	0	30	0	0	0	0	32.0	32.0	-8.5	-8.5	-2.0	7.14
6	0	0	0	30	0	0	0	0	34.0	32.0	-15.3	-8.5	-2.5	7.24
		0	0	30	0	0	0	0	30.0		-1.7			

Table D-25: Results for Sludge (with no EOS-PRO) samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. No ZVI was added. Sludge dose was 180mg SS/L.

Contact Time (hour)	ZVI theoretical (g)	ZVI measured (g)	ZVI DOSE (g/L)	$Cr(VI)_0$ Concentration (mg/L)	Molar Ratio Theoretical (mol ZVI:mol Cr(VI))	Molar Ratio Actual (mol ZVI:mol Cr(VI))	Sludge (mL)	EOS-PRO (mL)	Results $Cr(VI)_f$ (mg/L)	Results $Cr(VI)_{f\_avg}$ (mg/L)	Results % Removed (%)	Results % Removed$_{AVG}$ (%)	Results Mass Removed$_{AVG}$ (mg/L)	pH Avg. Meas. (-)
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0	0	0	30	0	0	0.5	0.48	15.0	14.5	49.2	50.9	15.0	8.13
		0	0	30	0	0	0.5	0.48	14.0		52.5			
1	0	0	0	30	0	0	0.5	0.48	15.0	16.0	49.2	49.2	13.5	8.11
1.5	0	0	0	30	0	0	0.5	0.48	14.0	14.0	52.5	52.5	15.5	8.19
2	0	0	0	30	0	0	0.5	0.48	14.0	13.5	52.5	54.2	16.0	8.18
		0	0	30	0	0	0.5	0.48	13.0		55.9			
3	0	0	0	30	0	0	0.5	0.48	13.0	13.0	55.9	55.9	16.5	8.26
4	0	0	0	30	0	0	0.5	0.48	11.0	11.0	62.7	62.7	18.5	8.32
		0	0	30	0	0	0.5	0.48	11.0		62.7			
5	0	0	0	30	0	0	0.5	0.48	13.0	13.0	55.9	55.9	16.5	8.33
		0	0	30	0	0	0.5	0.48	13.0		55.9			
6	0	0	0	30	0	0	0.5	0.48	9.0	9.0	69.5	69.5	20.5	8.27

Table D-26: Results for Sludge (with EOS-PRO) samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. No ZVI was added. Sludge dose was 180mg SS/L.

Contact Time (hour)	ZVI theoretical (g)	ZVI measured (g)	ZVI DOSE (g/L)	$Cr(VI)_0$ Concentration (mg/L)	Molar Ratio Theoretical (mol ZVI:mol Cr(VI))	Molar Ratio Actual (mol ZVI:mol Cr(VI))	Sludge (mL)	EOS-PRO (mL)	Results $Cr(VI)_f$ (mg/L)	Results $Cr(VI)_{f\_avg}$ (mg/L)	Results % Removed (%)	Results % Removed$_{AVG}$ (%)	Results Mass Removed$_{AVG}$ (mg/L)	pH Avg. Meas. (-)
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0	0	0	30	0	0	0.5	0.48	15.0	15.0	49.2	49.2	14.5	8.14
1	0	0	0	30	0	0	0.5	0.48	15.0	15.0	49.2	49.2	14.5	8.16
		0	0	30	0	0	0.5	0.48	15.0		49.2			
1.5	0	0	0	30	0	0	0.5	0.48	14.0	14.0	52.5	52.5	15.5	8.18
2	0	0	0	30	0	0	0.5	0.48	15.0	14.5	49.2	50.9	15.0	8.19
		0	0	30	0	0	0.5	0.48	14.0		52.5			
3	0	0	0	30	0	0	0.5	0.48	14.0	14.0	52.5	52.5	15.5	8.24
4	0	0	0	30	0	0	0.5	0.48	12.0	12.5	59.3	57.6	17.0	8.26
		0	0	30	0	0	0.5	0.48	13.0		55.9			
5	0	0	0	30	0	0	0.5	0.48	14.0	14.0	52.5	52.5	15.5	8.25
6	0	0	0	30	0	0	0.5	0.48	14.0	14.0	52.5	52.5	15.5	8.26
		0	0	30	0	0	0.5	0.48	14.0		52.5			

Table D-27: Results for abiotic ZVI samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. ZVI dose was 6.25g/L. No sludge was added.

Contact Time (hour)	ZVI			$Cr(VI)_0$ Concentration (mg/L)	Molar Ratio		Sludge (mL)	EOS-PRO (mL)	Results					pH Avg. Meas. (-)
	theoretical (g)	measured (g)	DOSE (g/L)		Theoretical (mol ZVI:mol Cr(VI))	Actual (mol ZVI:mol Cr(VI))			$Cr(VI)_f$ (mg/L)	$Cr(VI)_{f\_avg}$ (mg/L)	% Removed (%)	% $Removed_{AVG}$ (%)	Mass $Removed_{AVG}$ (mg/L)	
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0.25	0.2500	6.250	30	200	197.88	0	0	24.0	24.0	18.6	18.6	5.5	7.46
1	0.25	0.2591	6.478	30	200	205.08	0	0	21.0	21.0	28.8	28.8	8.5	7.58
		0.2623	6.558	30	200	207.61	0	0	21.0		28.8			
1.5	0.25	0.2531	6.328	30	200	200.33	0	0	21.0	21.0	28.8	28.8	8.5	7.69
2	0.25	0.2543	6.358	30	200	201.28	0	0	20.0	19.0	32.2	35.6	10.5	7.62
		0.2525	6.313	30	200	199.86	0	0	18.0		39.0			
3	0.25	0.2514	6.285	30	200	198.99	0	0	18.0	19.0	39.0	35.6	10.5	7.83
		0.2589	6.473	30	200	204.92	0	0	20.0		32.2			
4	0.25	0.2569	6.423	30	200	203.34	0	0	19.0	19.0	35.6	35.6	10.5	8.07
5	0.25	0.2528	6.320	30	200	200.10	0	0	19.0	19.0	35.6	35.6	10.5	7.97
		0.2545	6.363	30	200	201.44	0	0	19.0		35.6			
6	0.25	0.2591	6.478	30	200	205.08	0	0	17.0	17.0	42.4	42.4	12.5	8.03

Table D-28: Results for ZVI+Sludge (with EOS-PRO) samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. ZVI dose was 6.25g/L. Sludge dose was 180mg SS/L.

Contact Time (hour)	ZVI			$Cr(VI)_0$ Concentration (mg/L)	Molar Ratio		Sludge (mL)	EOS-PRO (mL)	Results					pH Avg. Meas. (-)
	theoretical (g)	measured (g)	DOSE (g/L)		Theoretical (mol ZVI:mol Cr(VI))	Actual (mol ZVI:mol Cr(VI))			$Cr(VI)_f$ (mg/L)	$Cr(VI)_{f\_avg}$ (mg/L)	% Removed (%)	% $Removed_{AVG}$ (%)	Mass $Removed_{AVG}$ (mg/L)	
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0.25	0.2644	6.610	30	200	209.28	0.5	0.48	7.0	8.5	76.3	71.2	21.0	8.27
		0.2540	6.350	30	200	201.05	0.5	0.48	10.0		66.1			
1	0.25	0.2538	6.345	30	200	200.89	0.5	0.48	7.0	7.0	76.3	76.3	22.5	8.46
1.5	0.25	0.2671	6.678	30	200	211.41	0.5	0.48	3.0	3.5	89.8	88.1	26.0	8.51
		0.2708	6.770	30	200	214.34	0.5	0.48	4.0		86.4			
2	0.25	0.2603	6.508	30	200	206.03	0.5	0.48	3.5	3.5	88.1	88.1	26.0	8.52
3	0.25	0.2506	6.625	30	200	198.35	0.5	0.48	1.0	1.3	96.6	95.8	28.2	8.61
		0.2545	6.363	30	200	201.44	0.5	0.48	1.5		94.9			
4	0.25	0.2603	6.508	30	200	206.03	0.5	0.48	0.2	0.2	99.3	99.3	29.3	8.54
5	0.25	0.2598	6.495	30	200	205.64	0.5	0.48	0	0	100	100	29.5	8.52
6	0.25	0.2609	6.523	30	200	206.51	0.5	0.48	0	0	100	100	29.5	8.46
		0.2546	6.365	30	200	201.52	0.5	0.48	0		100			

Table D-29: Results for ZVI+Sludge (with no EOS-PRO) samples in the Cr(VI) single contaminant test. Initial Cr(V) concentration was 30mg/L. ZVI dose was 6.25g/L. Sludge dose was 180mg SS/L.

Contact	ZVI			$Cr(VI)_0$	Molar Ratio				Results					pH
Time	theoretical	measured	DOSE	Concentration	Theoretical	Actual	Sludge	EOS-PRO	$Cr(VI)_f$	$Cr(VI)_{f\_avg}$	% Removed	% $Removed_{AVG}$	Mass $Removed_{AVG}$	Avg. Meas.
(hour)	(g)	(g)	(g/L)	(mg/L)	(mol ZVI:mol Cr(VI))		(mL)	(mL)	(mg/L)	(mg/L)	(%)	(%)	(mg/L)	(-)
0	0	0	0	30	0	0	0	0	30.0	29.5	-1.7	0	0	7.15
		0	0	30	0	0	0	0	29.0		1.7			
0.5	0.25	0.2615	6.538	30	200	206.98	0.5	0.48	11.0	10.0	62.7	66.1	19.5	8.34
		0.2499	6.248	30	200	197.80	0.5	0.48	9.0		69.5			
1	0.25	0.2556	6.390	30	200	202.31	0.5	0.48	5.0	5.0	83.1	83.1	24.5	8.46
1.5		0.2534	6.335	30	200	200.57	0.5	0.48	5.0	5.0	83.1	83.1	24.5	8.59
2	0.25	0.2559	6.398	30	200	202.55	0.5	0.48	4.0	4.0	86.4	86.4	25.5	8.54
3	0.25	0.2536	6.340	30	200	200.73	0.5	0.48	2.0	1.5	93.2	94.9	28.0	8.58
		0.2554	6.385	30	200	202.15	0.5	0.48	1.0		96.6			
4	0.25	0.2532	6.330	30	200	200.41	0.5	0.48	0.2	0.3	99.3	99.0	29.2	8.54
		0.2554	6.385	30	200	202.15	0.5	0.48	0.4		98.6			
5	0.25	0.2596	6.490	30	200	205.48	0.5	0.48	0.3	0.3	99.0	99.0	29.2	8.55
6	0.25	0.2547	6.368	30	200	201.60	0.5	0.48	0	0	100	100	29.5	8.47

D.8 Single Contaminant ClO_3^- Reduction Batch Tests

Table D-30: Results for Blank samples in the ClO_3^- single contaminant test. Initial ClO_3^- concentration was 30mg/L. No ZVI or sludge was added.

Contact	Bacteria	ZVI			ClO_3^- Concentration		Stoichiometric Ratio				Avg.	Mass		pH
Time (hour)	Dose (mL)	theoretical (g)	measured (g)	DOSE (g/L)	Theo. Conc. (mg/L)	Theo. mass (mg)	Theo. (X)	Actual (X)	$ClO_{3\ final}^-$ (mg/L)	% Removed (%)	% Removed (%)	Removed (mg/L)	COD $_{avg}$ (mg/L COD)	Avg. Meas. (-)
0	0	0	0	0	100	4	0	0	98.4	-0.2	0	0	6.0	7.97
			0	0				0	98.1	0.2				
4	0	0	0	0	100	4	0	0	101	-2.8	-1.4	-1.3	---	7.92
		0	0	0				0	98.2	0.1				
8	0	0	0	0	100	4	0	0	98.9	-0.7	-0.7	-0.7	---	7.97
12	0	0	0	0	100	4	0	0	99.4	-1.2	-1.2	-1.2	---	7.93
18	0	0	0	0	100	4	0	0	97.8	0.5	0.6	0.6	---	7.72
			0	0				0	97.6	0.7				
24	0	0	0	0	100	4	0	0	99.1	-0.9	-0.9	-0.8	---	7.69
32	0	0	0	0	100	4	0	0	97.0	1.3	0.5	0.5	---	7.77
			0	0				0	98.6	-0.4				
40	0	0	0	0	100	4	0	0	97.9	0.4	0.4	0.3	---	7.77
50	0	0	0	0	100	4	0	0	96.4	1.9	1.9	1.8	---	7.88
60	0	0	0	0	100	4	0	0	98.1	0.2	0.6	0.6	7.0	7.82
			0	0				0	97.2	1.1				

Table D-31: Results for Sludge samples in the ClO_3^- single contaminant test. Initial ClO_3^- concentration was 30mg/L. Sludge dose was 180mg SS/L. No ZVI was added.

Contact Time (hour)	Bacteria Dose (mL)	ZVI			ClO_3^- Concentration		Stoichiometric Ratio				Avg.	Mass		pH
		theoretical (g)	measured (g)	DOSE (g/L)	Theo. Conc. (mg/L)	Theo. mass (mg)	Theo. (X)	Actual (X)	$ClO_{3\ final}^-$ (mg/L)	% Removed (%)	% Removed (%)	Removed (mg/L)	COD_{avg} (mg/L COD)	Avg. Meas. (-)
0	0	0	0	0	100	4	0	0	98.4	-0.15	0	0	---	7.97
			0	0				0	98.1	0.15				
4	0.5	0	0	0	100	4	0	0	95.1	3.21	3.2	3.2	17.0	7.58
8	0.5	0	0	0	100	4	0	0	96.3	1.98	0.1	0.1	18.0	7.23
			0	0				0	100	-1.78				
12	0.5	0	0	0	100	4	0	0	97.6	0.66	1.4	1.4	14.5	6.90
			0	0				0	96.1	2.19				
18	0.5	0	0	0	100	4	0	0	95.1	3.21	3.2	3.2	---	6.70
24	0.5	0	0	0	100	4	0	0	97.6	0.66	2.1	2.1	---	6.35
			0	0				0	94.7	3.61				
32	0.5	0	0	0	100	4	0	0	95.2	3.10	3.1	3.1	23.0	6.79
40	0.5	0	0	0	100	4	0	0	89.4	9.01	9.0	8.8	---	6.91
50	0.5	0	0	0	100	4	0	0	85.6	12.88	12.9	12.7	15.0	6.51
			0	0				0	85.5	12.98				
60	0.5	0	0	0	100	4	0	0	82.5	16.03	16.0	15.8	12.0	6.58

Table D-32: Results for abiotic ZVI samples in the ClO_3^- single contaminant test. Initial ClO_3^- concentration was 30mg/L. ZVI dose was 14g/L. No sludge was added.

Contact Time (hour)	Bacteria Dose (mL)	ZVI theoretical (g)	ZVI measured (g)	ZVI DOSE (g/L)	ClO_3^- Concentration Theo. Conc. (mg/L)	ClO_3^- Concentration Theo. mass (mg)	Stoichiometric Ratio Theo. (X)	Stoichiometric Ratio Actual (X)	$ClO_{3\ final}^-$ (mg/L)	% Removed (%)	Avg. % Removed (%)	Mass Removed (mg/L)	COD_{avg} (mg/L COD)	pH Avg. Meas. (-)
0	0	0	0	0	100	4			98.4	-0.15	0	0	---	7.97
			0	0					98.1	0.15				
4	0	0.54	0.5518	14	100	4	67	69	86.9	11.55	11.5	11.3	24.0	7.36
			0.5432	14				68	87	11.45				
8	0	0.54	0.5401	14	100	4	67	67	74.1	24.58	24.6	24.2	---	7.52
12	0	0.54	0.5528	14	100	4	67	69	58.4	40.56	41.2	40.5	---	7.64
			0.5408	14				67	57.2	41.78				
18	0	0.54	0.5487	14	100	4	67	68	44.3	54.91	54.9	54.0	---	7.60
24	0	0.54	0.5418	14	100	4	67	68	35.5	63.87	63.9	62.8	20.0	7.61
32	0	0.54	0.5529	14	100	4	67	69	23.6	75.98	76.5	75.2	---	7.88
			0.5572	14				69	22.6	77.00				
40	0	0.54	0.5420	14	100	4	67	68	15.1	84.63	84.9	83.5	---	7.82
			0.5426	14				68	14.5	85.24				
50	0	0.54	0.5529	14	100	4	67	69	6.25	93.64	93.0	91.4	---	7.88
			0.5411	14				67	7.41	92.46				
60	0	0.54	0.5588	14	100	4	67	70	4.86	95.05	95.1	93.4	18.0	7.75

Table D-33: Results for ZVI+Sludge samples in the ClO_3^- single contaminant test. Initial ClO_3^- concentration was 30mg/L. Sludge dose was 180mg SS/L. ZVI dose was 14g/L.

Contact Time	Bacteria Dose	ZVI			ClO_3^- Concentration		Stoichiometric Ratio				Avg.	Mass		pH
		theoretical	measured	DOSE	Theo.Conc.	Theo. mass	Theo.	Actual	$ClO_3^-{}_{final}$	% Removed	% Removed	Removed	COD $_{avg}$	Avg. Meas.
(hour)	(mL)	(g)	(g)	(g/L)	(mg/L)	(mg)	(X)	(X)	(mg/L)	(%)	(%)	(mg/L)	(mg/L COD)	(-)
0	0	0	0	0	100	0	0	0	98.4	-0.15	0	0	---	7.97
			0	0				0	98.1	0.15				
4	0.5	0.54	0.5544	14	100	4	67	69.1	83.3	15.22	15.2	15.0	30.0	7.29
8	0.5	0.54	0.5408	14	100	4	67	67.4	66.9	31.91	32.7	32.1	---	7.31
			0.5550	14				69.1	65.4	33.44				
12	0.5	0.54	0.5592	14	100	4	67	69.6	42.9	56.34	56.3	55.4	---	7.48
18	0.5	0.54	0.5492	14	100	4	67	68.4	41.6	57.66	59.2	58.2	30.0	7.53
			0.5806	15				72.3	38.5	60.81				
24	0.5	0.54	0.5672	14	100	4	67	70.6	28.9	70.59	70.1	68.9	---	7.66
			0.5523	14				68.8	29.9	69.57				
32	0.5	0.54	0.5516	14	100	4	67	68.7	20.8	78.83	78.8	77.5	29.0	7.86
40	0.5	0.54	0.5491	14	100	4	67	68.4	13.5	86.26	86.5	85.0	---	8.03
			0.5672	14				70.6	13	86.77				
50	0.5	0.54	0.5601	14	100	4	67	69.8	6.96	92.92	92.9	91.3	---	8.06
60	0.5	0.54	0.5566	14	100	4	67	69.3	5.41	94.49	94.0	92.4	30.0	7.96
		0.54	0.5432	14				67.7	6.32	93.57				

D.9 Multiple Contaminants Reduction Batch Tests

Table D-34: Results for Blank samples in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. No Sludge was used.

	ZVI		Bacteria	Oil	Stoichiometric Ratio		Cr(VI) Results				ClO_3^- Results				pH
Total (hour)	measured (g)	DOSE (g/L)	Dose (mL)	EOS-PRO (mL)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	$Cr(VI)_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	$ClO3_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	0	30.5	30.75	0	0	96.8	96.55	0	0	6.74
	0	0		0		0	31.0				96.3				
0.5	0	0	0	0	0	0	31.0	31.00	-0.8	-0.3	96.4	96.40	0.2	0.1	7.13
4	0	0	0	0	0	0	30.5	30.50	0.8	0.3	96.1	96.10	0.5	0.5	7.29
24	0	0	0	0	0	0	30.0	30.00	2.4	0.8	97.0	97.00	-0.5	-0.5	6.99
70	0	0	0	0	0	0	30.5	30.50	0.8	0.3	98.2	98.20	-1.7	-1.7	7.58
168	0	0	0	0	0	0	30.5	30.50	0.8	0.3	96.2	96.20	0.4	0.3	7.06

Table D-35: Results for Sludge samples with no addition carbon source in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. Sludge dose was 180mg SS/L. No EOS-PRO was added.

Total	ZVI		Bacteria	Oil	Stoichiometric Ratio		Cr(VI) Results				ClO_3^- Results				pH
(hour)	measured (g)	DOSE (g/L)	Dose (mL)	EOS-PRO (mL)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	$Cr(VI)_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	$ClO3_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	0	30.5	30.75	0	0	96.8	96.55	0	0	6.74
	0	0		0		0	31.0				96.3				
0.5	0	0	0.5	0	0	0	15.5	15.50	49.6	15.3	92.1	92.10	4.6	4.5	8.06
1	0	0	0.5	0	0	0	13.0	13.00	57.7	17.8	95.8	95.80	0.8	0.8	8.44
2	0	0	0.5	0	0	0	10.0	10.50	65.9	20.3	97.1	96.80	-0.3	-0.3	8.49
		0				0	11.0				96.5				
4	0	0	0.5	0	0	0	7.0	7.00	77.2	23.8	95.8	95.80	0.8	0.8	8.37
8	0	0	0.5	0	0	0	8.5	7.75	74.8	23.0	96.4	96.30	0.3	0.3	8.45
		0				0	7.0				96.2				
13	0	0	0.5	0	0	0	6.4	6.40	79.2	24.4	96.0	96.00	0.6	0.5	8.13
24	0	0	0.5	0	0	0	6.0	5.70	81.5	25.1	96.3	96.05	0.5	0.5	8.05
		0				0	5.4				95.8				
36	0	0	0.5	0	0	0	6.4	6.40	79.2	24.4	96.3	96.30	0.3	0.3	7.26
50	0	0	0.5	0	0	0	5.2	5.20	83.1	25.6	96.6	96.60	-0.1	0	7.43
70	0	0	0.5	0	0	0	5.1	5.15	83.3	25.6	96.7	96.65	-0.1	-0.1	7.31
		0				0	5.2				96.6				
94	0	0	0.5	0	0	0	4.0	4.00	87.0	26.8	99.8	99.80	-3.4	-3.3	7.36
118	0	0	0.5	0	0	0	3.4	3.65	88.1	27.1	95.1	94.70	1.9	1.8	7.26
		0				0	3.9				94.3				
142	0	0	0.5	0	0	0	2.8	3.45	88.8	27.3	85.6	88.75	8.1	7.8	7.01
		0				0	4.1				91.9				
168	0	0	0.5	0	0	0	3.7	3.75	87.8	27.0	91.5	91.55	5.2	5.0	6.92
		0				0	3.8				91.6				

Table D-36: Results for Sludge samples with an additional carbon source in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. Sludge dose was 180mg SS/L. EOS-PRO dose was 0.01025mL/L.

	ZVI		Bacteria	Oil	Stoichiometric Ratio		Cr(VI) Results				ClO_3^- Results				pH
Total	measured	DOSE	Dose	EOS-PRO	Theoretical	Actual	$Cr(VI)_{fin}$	$Cr(VI)_{fin\_avg}$	% Removed	Mass Removed	$ClO3_{fin}$	$ClO3_{fin\_avg}$	% Removed	Mass Removed	Avg. Meas.
(hour)	(g)	(g/L)	(mL)	(mL)	X	X	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(mg/L)	(%)	(mg/L)	(-)
0	0 0	0 0	0	0 0	0	0 0	30.5 31.0	30.75	0	0	96.8 96.3	96..55	0	0	6.74
0.5	0	0	0.5	0.41	0	0	14.5	14.50	52.8	16.3	96.8	96.80	-0.3	-0.3	8.09
1	0	0 0	0.5	0.41	0	0 0	12.0 11.0	11.50	62.6	19.3	94.9	94.85	1.8	1.7	8.52
0	0	0	0.5	0.41	0	0	10.5	10.50	65.9	20.3	95.3	95.30	1.3	1.3	8.35
4	0	0 0	0.5	0.41	0	0 0	9.5 10.0	9.75	68.3	21.0	94.0 96.3	95.15	1.5	1.4	8.33
8	0	0	0.5	0.41	0	0	8.0	8.00	74.0	22.8	95.0	95.00	1.6	1.6	8.32
13	0	0 0	0.5	0.41	0	0 0	6.0 7.4	6.70	78.2	24.1	94.2 95.8	95.00	1.6	1.6	8.17
24	0	0	0.5	0.41	0	0	5.8	5.80	81.1	25.0	95.3	95.30	1.3	1.3	8.06
36	0	0 0	0.5	0.41	0	0 0	5.7 5.8	5.75	81.3	25.0	96.6 95.9	96.25	0.3	0.3	7.10
50	0	0	0.5	0.41	0	0	4.8	4.80	84.4	26.0	96.4	96.40	0.2	0.1	7.37
70	0	0 0	0.5	0.41	0	0 0	5.3 5.6	5.45	82.3	25.3	95.2 94.6	94.90	1.7	1.6	7.09
94	0	0 0	0.5	0.41	0	0 0	4.9 4.4	4.65	84.9	26.1	98.9 95.1	97.00	-0.5	-0.5	7.09
118	0	0	0.5	0.41	0	0	2.9	2.90	90.6	27.9	95.0	95.00	1.6	1.6	6.88
144	0	0 0	0.5	0.41	0	0 0	4.8 4.0	4.40	85.7	26.4	93.4 87.6	90.50	6.3	6.1	6.83
168	0	0 0	0.5	0.41	0	0 0	3.1 4.0	3.55	88.5	27.2	88.9 83.2	88.90	7.9	7.6	6.70

Table D-37: Results for ZVI+Sludge samples with an additional carbon source in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. ZVI dose was 19.8g/L. Sludge dose was 180mg SS/L. EOS-PRO dose was 0.01025mL/L.

	ZVI		Bacteria	Oil	Stoichiometric Ratio		Cr(VI) Results				ClO_3^- Results				pH
Total (hour)	measured (g)	DOSE (g/L)	Dose (mL)	EOS-PRO (mL)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	$Cr(VI)_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	$ClO3_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	0	30.5	30.75	0	0	96.8	96.55	0	0	6.74
	0	0		0		0	31.0				96.3				
0.5	0.7928	19.8	0.5	0.41	80	79.9	3.6	3.80	87.6	27.0	94.6	94.25	2.4	2.3	7.99
	0.7953	19.9				80.1	4.0				93.9				
1	0.8008	20.0	0.5	0.41	80	80.7	0.02	0.02	99.9	30.7	89.9	89.90	6.9	6.6	8.41
2	0.7991	20.0	0.5	0.41	80	80.5	0	0	100	30.8	91.5	91.65	5.1	4.9	8.40
	0.7967	19.9				80.3	0				91.8				
4	0.7902	19.8	0.5	0.41	80	79.6	0	0	100	30.8	86.4	86.40	10.5	10.2	7.93
8	0.7901	19.8	0.5	0.41	80	79.6	0	0	100	30.8	73.0	72.35	25.1	24.2	8.15
	0.7986	20.0				80.5	0				71.7				
13	0.7913	19.8	0.5	0.41	80	79.7	0	0	100	30.8	54.4	54.40	43.7	42.2	7.99
24	0.7955	19.9	0.5	0.41	80	80.2	0	0	100	30.8	36.5	35.75	63.0	60.8	8.12
	0.7996	20.0				80.6	0				35.0				
36	0.8025	20.1	0.5	0.41	80	80.9	0	0	100	30.8	36.6	36.60	62.1	60.0	8.07
50	0.7930	19.8	0.5	0.41	80	79.9	0	0	100	30.8	8.57	8.60	91.1	88.0	7.85
	0.7945	19.9				80.1	0				8.63				
70	0.7928	19.8	0.5	0.41	80	79.9	0	0	100	30.8	7.97	7.97	91.7	88.6	8.04
94	0.7906	19.8	0.5	0.41	80	79.7	0	0	100	30.8	7.74	5.29	94.5	91.3	8.18
	0.7998	20.0				80.6	0				2.84				
118	0.7909	19.8	0.5	0.41	80	79.7	0	0	100	30.8	1.45	2.43	97.5	94.1	7.98
	0.7923	19.8				79.8	0				3.41				
144	0.7914	19.8	0.5	0.41	80	79.7	0	0	100	30.8	1.78	1.78	98.2	94.8	7.91
168	0.7960	19.9	0.5	0.41	80	80.2	0	0	100	30.8	0	0	100.0	96.6	8.25

Table D-38: Results for ZVI+Sludge samples with no additional carbon source in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. ZVI dose was 19.8g/L. Sludge dose was 180mg SS/L. EOS-PRO was not added.

	ZVI		Bacteria	Oil	Stoichiometric Ratio			Cr(VI) Results				ClO_3^- Results			pH
Total (hour)	measured (g)	DOSE (g/L)	Dose (mL)	EOS-PRO (mL)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	$Cr(VI)_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	$ClO3_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	0	31.0	30.75	0	0	96.3	96.55	0	0	6.74
0.5	0.8025	20.1	0.5	0	80	80.9	4.4	4.20	86.3	26.6	96.0	95.30	1.3	1.3	7.93
	0.7927	19.8				79.9	4.0				94.6				
1	0.7989	20.0	0.5	0	80	80.5	0.2	0.20	99.3	30.6	94.4	94.40	2.2	2.1	8.39
	0.7907	19.8				79.7	0.2				94.4				
2	0.7968	19.9	0.5	0	80	80.3	0	0	100	30.8	93.8	93.80	2.8	2.8	8.15
4	0.8007	20.0	0.5	0	80	80.7	0	0	100	30.8	87.1	86.60	10.3	10.0	8.04
	0.7994	20.0			80	80.6	0				86.1		10.8	10.5	
8	0.7964	19.9	0.5	0	80	80.3	0	0	100	30.8	73.1	73.10	24.3	23.5	8.08
13	0.7928	19.8	0.5	0	80	79.9	0.01	0.01	100	30.7	54.9	56.35	41.6	40.2	8.03
	0.8033	20.1			80	80.9	0				57.8				
24	0.7928	19.8	0.5	0	80	79.9	0	0	100	30.8	37.9	37.90	60.7	58.7	8.06
36	0.7926	19.8	0.5	0	80	79.9	0	0	100	30.8	30.5	35.90	62.8	60.7	8.09
	0.7915	19.8			80	79.8	0		100	30.8	41.3		100	96.6	
50	0.7930	19.8	0.5	0	80	79.9	0	0	100	30.8	10.6	10.30	89.3	86.3	7.93
	0.7926	19.8			80	79.9	0		100	30.8	10.0		100	96.6	
70	0.7940	19.9	0.5	0	80	80.0	0	0	100	30.8	14.9	14.90	84.6	81.7	8.26
94	0.7997	20.0	0.5	0	80	80.6	0	0	100	30.8	4.2	4.20	95.6	92.4	8.07
118	0.8030	20.1	0.5	0	80	80.9	0	0	100	30.8	1.29	1.49	98.5	95.1	7.93
	0.8050	20.1			80	81.1	0				1.69			94.9	
144	0.7939	19.8	0.5	0	80	80.0	0	0	100	30.8	0	0	100	96.6	8.17
168	0.7985	20.0	0.5	0	80	80.5	0	0	100	30.8	0	0	100	96.6	8.40

Table D-39: Results for abiotic ZVI samples in the multiple contaminant tests. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. ZVI dose was 19.8g/L. No Sludge was added. EOS-PRO was not added.

	ZVI		Bacteria	Oil	Stoichiometric Ratio		Cr(VI) Results				ClO_3^- Results				pH
Total (hour)	measured (g)	DOSE (g/L)	Dose (mL)	EOS-PRO (mL)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	$Cr(VI)_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	$ClO3_{fin\_avg}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	0	30.5	30.75	0	0	96.8	96.55	0	0	6.74
	0	0		0		0	31.0				96.3				
0.5	0.7915	19.8	0	0	80	79.8	19.0	19.00	38.2	11.8	96.6	96.85	-0.3	-0.3	7.24
	0.7915	19.8				79.8	19.0				97.1				
1	0.7920	19.8	0	0	80	79.8	11.0	11.00	64.2	19.8	96.2	95.90	0.7	0.6	8.09
	0.7975	19.9				80.4	11.0				95.6				
2	0.7908	19.8	0	0	80	79.7	3.9	3.90	87.3	26.9	94.6	94.60	2.0	2.0	8.06
4	0.7961	19.9	0	0	80	80.2	0.08	0.15	99.5	30.6	92.6	92.60	4.1	4.0	7.92
	0.7920	19.8				79.8	0.21				92.6				
8	0.8013	20.0	0	0	80	80.7	0.01	0.01	100	30.7	89.7	89.70	7.1	6.8	7.96
13	0.7984	20.0	0	0	80	80.5	0	0.01	100	30.7	79.9	78.80	18.4	17.8	7.66
	0.8090	20.2				81.5	0.01				77.7				
24	0.7963	19.9	0	0	80	80.2	0	0.01	100	30.7	55.9	58.25	39.7	38.3	7.87
	0.8004	20.0				80.7	0.01				60.6				
36	0.8032	20.1	0	0	80	80.9	0	0	100	30.8	43.7	43.70	54.7	52.9	7.87
50	0.7979	19.9	0	0	80	80.4	0	0	100	30.8	22.3	23.50	75.7	73.4	7.00
	0.7933	19.8				79.9	0				24.7				
70	0.7955	19.9	0	0	80	80.2	0	0	100	30.8	14.5	15.70	83.7	80.9	7.74
	0.7907	19.8				79.7	0				16.9				
94	0.7981	20.0	0	0	80	80.4	0	0	100	30.8	5.06	5.06	94.8	91.5	7.35
118	0.7949	19.9	0	0	80	80.1	0	0	100	30.8	2.12	2.12	97.8	94.4	7.77
144	0.7904	19.8	0	0	80	79.6	0	0	100	30.8	1.2	1.20	98.8	95.4	8.17
168	0.7936	19.8	0	0	80	80.0	0	0	100	30.8	0.245	0.25	99.7	96.3	8.50
	0.8010	20.0				80.7	0				0.255				

D.10 Multiple Contaminants Reduction Batch Tests with Lower and Higher Stoichiometric Ratios

Table D-40: Results for Blank samples in the multiple contaminant tests at increased and decreased stoichiometric ratios. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. No Sludge was used.

Contact Time	Bacteria	Oil	ZVI			Cr(VI)	ClO_3^-	Stoichiometric Ratio		Cr(VI) Results			ClO_3^- Results			pH
Total	Dose	EOS-PRO	theo.	measured	DOSE	Theo. Conc.	Theo. Conc.	Theoretical	Actual	$Cr(VI)_{fin}$	% Removed	Mass Removed	$ClO3_{fin}$	% Removed	Mass Removed	Avg. Meas.
(hour)	(mL)	(mL)	(g)	(g)	(g/L)	(mg/L)	(mg/L)	X	X	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(-)
0	0	0	0	0	0	30	100	0	0	30.5	0	0	96.8	0	0	6.74
		0		0	0	30			0	31			96.3			
0.5	0	0	0	0	0	30	100	0	0	31.00	-0.1	-0.3	96.9	-0.4	-0.4	6.93
4	0	0	0	0	0	30	100	0	0	30.50	0.8	0.3	98.0	-1.5	-1.5	7.05
24	0	0	0	0	0	30	100	0	0	30.00	2.4	0.8	109.0	-12.9	-12.5	7.32
70	0	0	0	0	0	30	100	0	0	30.50	0.8	0.3	107.0	-10.8	-10.5	7.55
168	0	0	0	0	0	30	100	0	0	30.50	0.8	0.3	102.3	-6.0	-5.8	7.33

Table D-41: Results for 50X ZVI+Sludge samples in the multiple contaminant tests at increased and decreased stoichiometric ratios. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. Sludge dosage was 180 mg SS/L.

Contact Time	Bacteria	Oil	ZVI			Cr(VI)	ClO_3^-	Stoichiometric Ratio		Cr(VI) Results			ClO_3^- Results			pH
Total (hour)	Dose (mL)	EOS-PRO (mL)	theo. (g)	measured (g)	DOSE (g/L)	Theo. Conc. (mg/L)	Theo. Conc. (mg/L)	Theoretical X	Actual X	$Cr(VI)_{fin}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	$ClO3_{fin}$ (mg/L)	% Removed (%)	Mass Removed (mg/L)	Avg. Meas. (-)
0	0	0	0	0	0	30	100	0	0	30.50	0	0	96.8	0	0	6.74
		0		0	0	30			0	31.00			96.3			
0.5	0.5	0	0.497	0.4988	12.5	30	100	50	50.3	9.50	69.1	21.3	95.3	1.4	1.3	8.00
			0.497	0.5083	12.7	30	100		51.2	9.50			95.1			
1	0.5	0	0.497	0.4994	12.5	30	100	50	50.3	5.00	85.4	26.3	94.7	2.5	2.5	8.12
	0.5	0	0.497	0.5007	12.5	30	100	50	50.5	4.00			93.5			
2	0.5	0	0.497	0.5094	12.7	30	100	50	51.3	0.12	99.6	30.6	94.1	2.5	2.5	7.75
4	0.5	0	0.497	0.5061	12.7	30	100	50	51.0	0	100	30.8	91.4	5.3	5.1	7.49
8	0.5	0	0.497	0.5010	12.5	30	100	50	50.5	0	100	30.8	93.1	4.1	4.0	7.66
	0.5	0	0.497	0.5039	12.6	30	100	50	50.8	0			92.1			
13	0.5	0	0.497	0.4974	12.4	30	100	50	50.1	0	100	30.8	85.1	11.9	11.5	7.54
24	0.5	0	0.497	0.5014	12.5	30	100	50	50.5	0	100	30.8	63.1	37.4	36.1	7.70
	0.5	0	0.497	0.5048	12.6	30	100	50	50.9	0			57.8			
39	0.5	0	0.497	0.5018	12.5	30	100	50	50.6	0	100	30.8	55.4	42.6	41.2	7.81
50	0.5	0	0.497	0.5093	12.7	30	100	50	51.3	0	100	30.8	41.0	57.1	55.1	7.90
	0.5	0	0.497	0.5045	12.6	30	100	50	50.8	0			41.9			
70	0.5	0	0.497	0.5033	12.6	30	100	50	50.7	0	100	30.8	39.9	58.7	56.7	8.01
94	0.5	0	0.497	0.5080	12.7	30	100	50	51.2	0	100	30.8	31.7	67.4	65.1	7.78
	0.5	0	0.497	0.4983	12.5	30	100	50	50.2	0			31.2			
118	0.5	0	0.497	0.4977	12.4	30	100	50	50.2	0	100	30.8	21.8	77.4	74.8	8.10
144	0.5	0	0.497	0.5110	12.8	30	100	50	51.5	0	100	30.8	10.2	89.7	86.6	7.66
	0.5	0	0.497	0.5039	12.6	30	100	50	50.8	0			9.75			
168	0.5	0	0.497	0.5055	12.6	30	100	50	50.9	0	100	30.8	6.89	92.9	89.7	7.31

Table D-42: Results for 100X ZVI+Sludge samples in the multiple contaminant tests at increased and decreased stoichiometric ratios. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. Sludge dosage was 180 mg SS/L.

Contact Time	Bacteria	Oil	ZVI			Cr(VI)	ClO_3^-	Stoichiometric Ratio		Cr(VI) Results			ClO_3^- Results			pH
Total	Dose	EOS-PRO	theo.	measured	DOSE	Theo. Conc.	Theo. Conc.	Theoretical	Actual	$Cr(VI)_{fin}$	% Removed	Mass Removed	$ClO3_{fin}$	% Removed	Mass Removed	Avg. Meas.
(hour)	(mL)	(mL)	(g)	(g)	(g/L)	(mg/L)	(mg/L)	X	X	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(-)
0	0	0	0	0	0	30	100	0	0	30.50	0	0	96.8	0	0	6.74
		0		0	0	30			0	31.00			96.3			
0.5	**0.5**	**0**	0.995	1.0004	25	30	100	100	101	3.00	90.9	28.0	94.3	1.4	1.4	7.78
0.5	**0.5**	**0**	0.995	0.9970	25	30	100	100	100	2.60			96.1			
1	**0.5**	**0**	0.995	1.0108	25	30	100	100	102	0.04	99.9	30.7	95.6	1.9	1.8	7.95
1	**0.5**	**0**	0.995	0.9958	25	30	100	100	100	0			93.9			
2	**0.5**	**0**	0.995	0.9950	25	30	100	100	100	0	100	30.8	94.0	3.6	3.5	7.97
2	**0.5**	**0**	0.995	0.9960	25	30	100	100	100	0			92.2			
4	**0.5**	**0**	0.995	1.0177	25	30	100	100	103	0	100	30.8	83.9	13.1	12.7	8.19
8	**0.5**	**0**	0.995	1.0001	25	30	100	100	101	0	100	30.8	70.8	26.7	25.8	8.07
13	**0.5**	**0**	0.995	0.9971	25	30	100	100	100	0	100	30.8	49.9	45.7	44.1	7.80
13	**0.5**	**0**	0.995	0.9981	25	30	100	100	101	0			55			
24	**0.5**	**0**	0.995	1.0296	25	30	100	100	104	0	100	30.8	25.8	73.3	70.8	7.76
39	**0.5**	**0**	0.995	0.9969	25	30	100	100	100	0	100	30.8	14.9	82.6	79.8	8.08
39	**0.5**	**0**	0.995	0.9984	25	30	100	100	101	0			18.7			
50	**0.5**	**0**	0.995	0.9974	25	30	100	100	101	0	100	30.8	4.17	95.7	92.4	7.83
70	**0.5**	**0**	0.995	0.9970	25	30	100	100	100	0	100	30.8	2.03	98.1	94.7	7.86
70	**0.5**	**0**	0.995	0.9986	25	30	100	100	101	0			1.62			
94	**0.5**	**0**	0.995	0.9996	25	30	100	100	101	0	100	30.8	1.14	98.8	95.4	8.09
118	**0.5**	**0**	0.995	1.0015	25	30	100	100	101	0	100	30.8	0	100	96.6	7.70
144	**0.5**	**0**	0.995	1.0189	25	30	100	100	103	0	100	30.8	0	100	96.6	8.08
168	**0.5**	**0**	0.995	0.9973	25	30	100	100	100	0	100	30.8	0	100	96.6	7.99
168	**0.5**	**0**	0.995	1.0046	25	30	100	100	101	0			0			

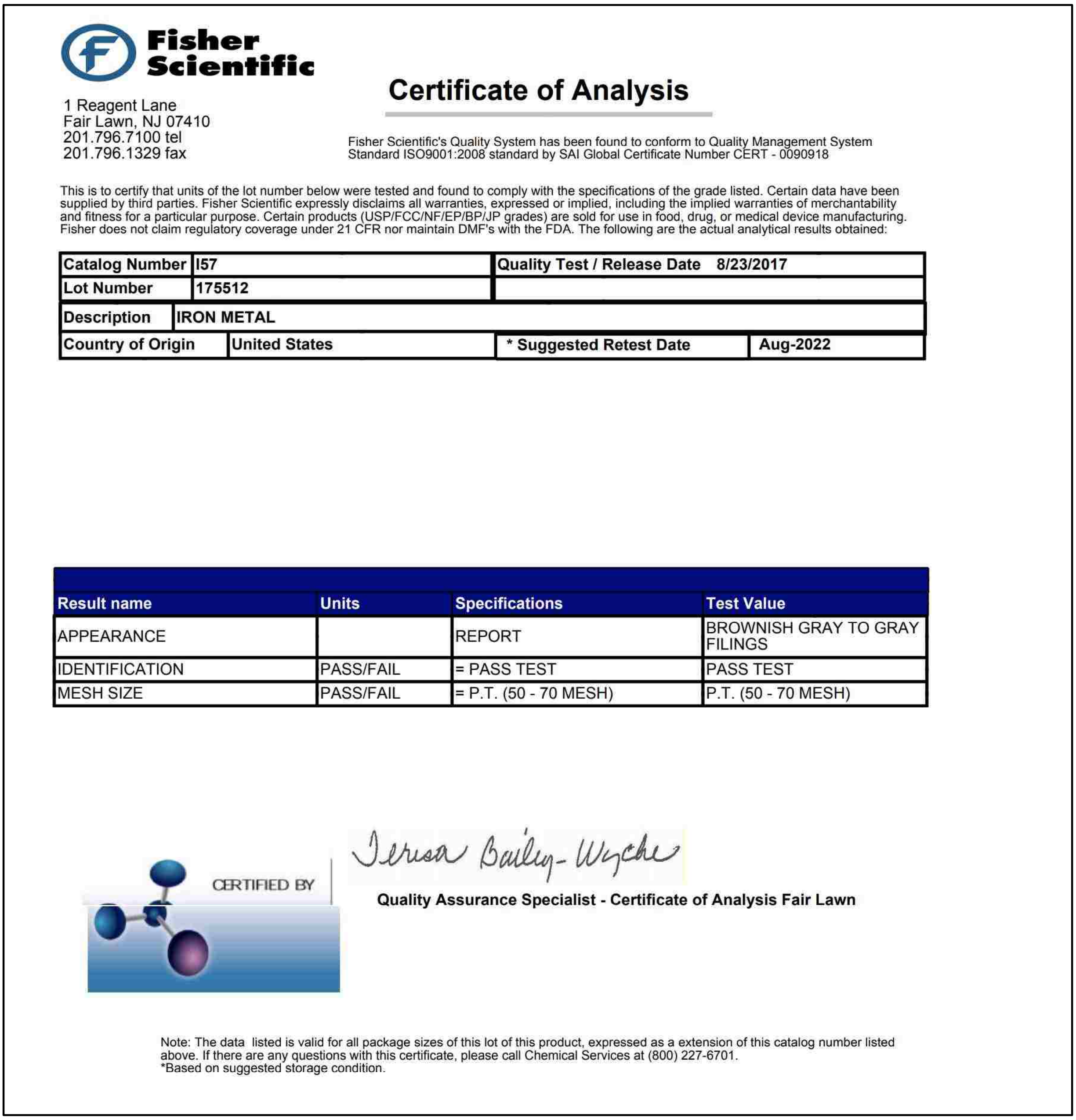
Table D-43: Results for 200X ZVI+Sludge samples in the multiple contaminant tests at increased and decreased stoichiometric ratios. Initial Cr(VI) and ClO_3^- concentrations were 30mg/L and 100mg/L, respectively. No ZVI was used. Sludge dosage was 180 mg SS/L.

Contact Time	Bacteria	Oil	ZVI			Cr(VI)	ClO_3^-	Stoichiometric Ratio		Cr(VI) Results			ClO_3^- Results			pH
Total	Dose	EOS-PRO	theo.	measured	DOSE	Theo. Conc.	Theo. Conc.	Theoretical	Actual	$Cr(VI)_{fin}$	% Removed	Mass Removed	$ClO3_{fin}$	% Removed	Mass Removed	Avg. Meas.
(hour)	(mL)	(mL)	(g)	(g)	(g/L)	(mg/L)	(mg/L)	X	X	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(-)
0	0	0	0	0	0	30	100	0	0	30.50	0	0	96.8	0	0	6.74
		0		0	0	30			0	31.00			96.3			
0.5	0.5	0	1.990	1.9935	50	30	100	200	201	0	100	30.8	94.6	2.0	1.9	7.46
0.5	0.5	0	1.990	1.9955	50	30	100	200	201	0	100	30.8	94.7			
1	0.5	0	1.990	1.9937	50	30	100	200	201	0	100	30.8	90.9	5.2	5.1	7.41
1	0.5	0	1.990	1.9954	50	30	100	200	201	0	100	30.8	92.1			
2	0.5	0	1.990	2.0154	50	30	100	200	203	0	100	30.8	80.6	16.5	16.0	7.33
4	0.5	0	1.990	2.0065	50	30	100	200	202	0	100	30.8	59.5	38.1	36.8	7.56
4	0.5	0	1.990	2.0096	50	30	100	200	203	0	100	30.8	60.1			
8	0.5	0	1.990	2.0082	50	30	100	200	202	0	100	30.8	30.5	68.4	66.1	7.85
13	0.5	0	1.990	2.0001	50	30	100	200	202	0	100	30.8	12.8	87.1	84.1	7.65
13	0.5	0	1.990	1.9900	50	30	100	200	201	0	100	30.8	12.1			
24	0.5	0	1.990	1.9967	50	30	100	200	201	0	100	30.8	1.02	98.9	95.5	7.58
24	0.5	0	1.990	2.0080	50	30	100	200	202	0	100	30.8	1.18			
39	0.5	0	1.990	1.9934	50	30	100	200	201	0	100	30.8	0.39	99.6	96.2	8.16
50	0.5	0	1.990	2.0121	50	30	100	200	203	0	100	30.8	0.251	99.7	96.3	8.19
50	0.5	0	1.990	1.9907	50	30	100	200	201	0	100	30.8	0	100	96.6	
70	0.5	0	1.990	1.9942	50	30	100	200	201	0	100	30.8	0	100	96.6	7.70
94	0.5	0	1.990	2.0073	50	30	100	200	202	0	100	30.8	0	100	96.6	8.01
118	0.5	0	1.990	2.0256	50	30	100	200	204	0	100	30.8	0	100	96.6	8.29
118	0.5	0	1.990	2.0053	50	30	100	200	202	0	100	30.8	0			
144	0.5	0	1.990	2.0472	50	30	100	200	206	0	100	30.8	0	100	96.6	8.48
168	0.5	0	1.990	2.0138	50	30	100	200	203	0	100	30.8	0	100	96.6	8.49

Appendix E: Supporting Materials

E.1 ZVI Manufacturers

E.1.1 Iron Filings



Fisher Scientific

1 Reagent Lane
Fair Lawn, NJ 07410
201.796.7100 tel
201.796.1329 fax

Certificate of Analysis

Fisher Scientific's Quality System has been found to conform to Quality Management System Standard ISO9001:2008 standard by SAI Global Certificate Number CERT - 0090918

This is to certify that units of the lot number below were tested and found to comply with the specifications of the grade listed. Certain data have been supplied by third parties. Fisher Scientific expressly disclaims all warranties, expressed or implied, including the implied warranties of merchantability and fitness for a particular purpose. Certain products (USP/FCC/NF/EP/BP/JP grades) are sold for use in food, drug, or medical device manufacturing. Fisher does not claim regulatory coverage under 21 CFR nor maintain DMF's with the FDA. The following are the actual analytical results obtained:

Catalog Number	**I57**	**Quality Test / Release Date**	**8/23/2017**
Lot Number	**175512**		
Description	**IRON METAL**		
Country of Origin	**United States**	*** Suggested Retest Date**	**Aug-2022**

Result name	Units	Specifications	Test Value
APPEARANCE		REPORT	BROWNISH GRAY TO GRAY FILINGS
IDENTIFICATION	PASS/FAIL	= PASS TEST	PASS TEST
MESH SIZE	PASS/FAIL	= P.T. (50 - 70 MESH)	P.T. (50 - 70 MESH)

CERTIFIED BY

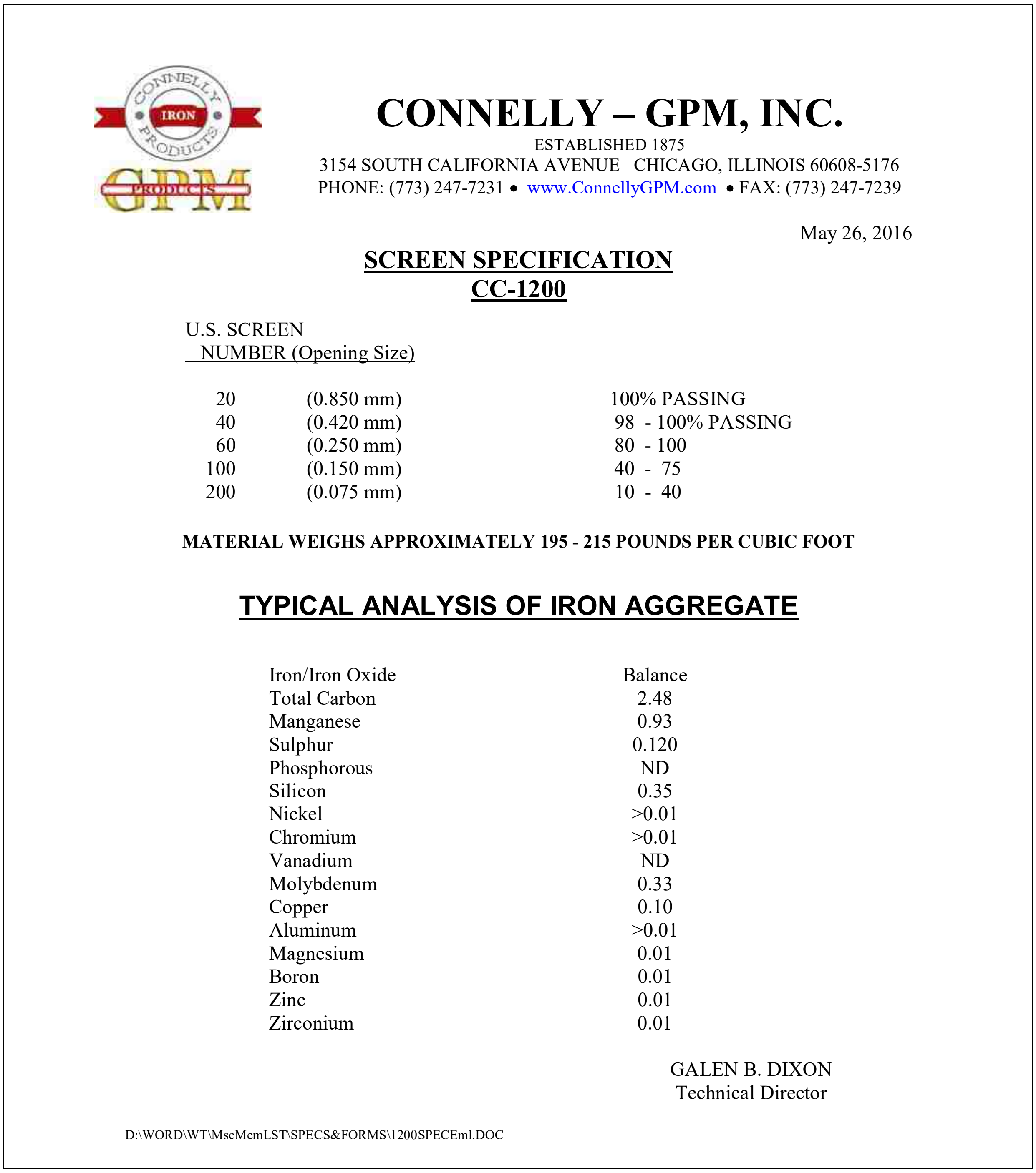
Teresa Bailey-Wyche

Quality Assurance Specialist - Certificate of Analysis Fair Lawn

Note: The data listed is valid for all package sizes of this lot of this product, expressed as a extension of this catalog number listed above. If there are any questions with this certificate, please call Chemical Services at (800) 227-6701.
*Based on suggested storage condition.

Figure E-1: Fisher Scientific iron metal filings certificate of analysis.

E.1.2 Iron Powder



CONNELLY – GPM, INC.
ESTABLISHED 1875
3154 SOUTH CALIFORNIA AVENUE CHICAGO, ILLINOIS 60608-5176
PHONE: (773) 247-7231 • www.ConnellyGPM.com • FAX: (773) 247-7239

May 26, 2016

SCREEN SPECIFICATION
CC-1200

U.S. SCREEN NUMBER (Opening Size)		
20	(0.850 mm)	100% PASSING
40	(0.420 mm)	98 - 100% PASSING
60	(0.250 mm)	80 - 100
100	(0.150 mm)	40 - 75
200	(0.075 mm)	10 - 40

MATERIAL WEIGHS APPROXIMATELY 195 - 215 POUNDS PER CUBIC FOOT

TYPICAL ANALYSIS OF IRON AGGREGATE

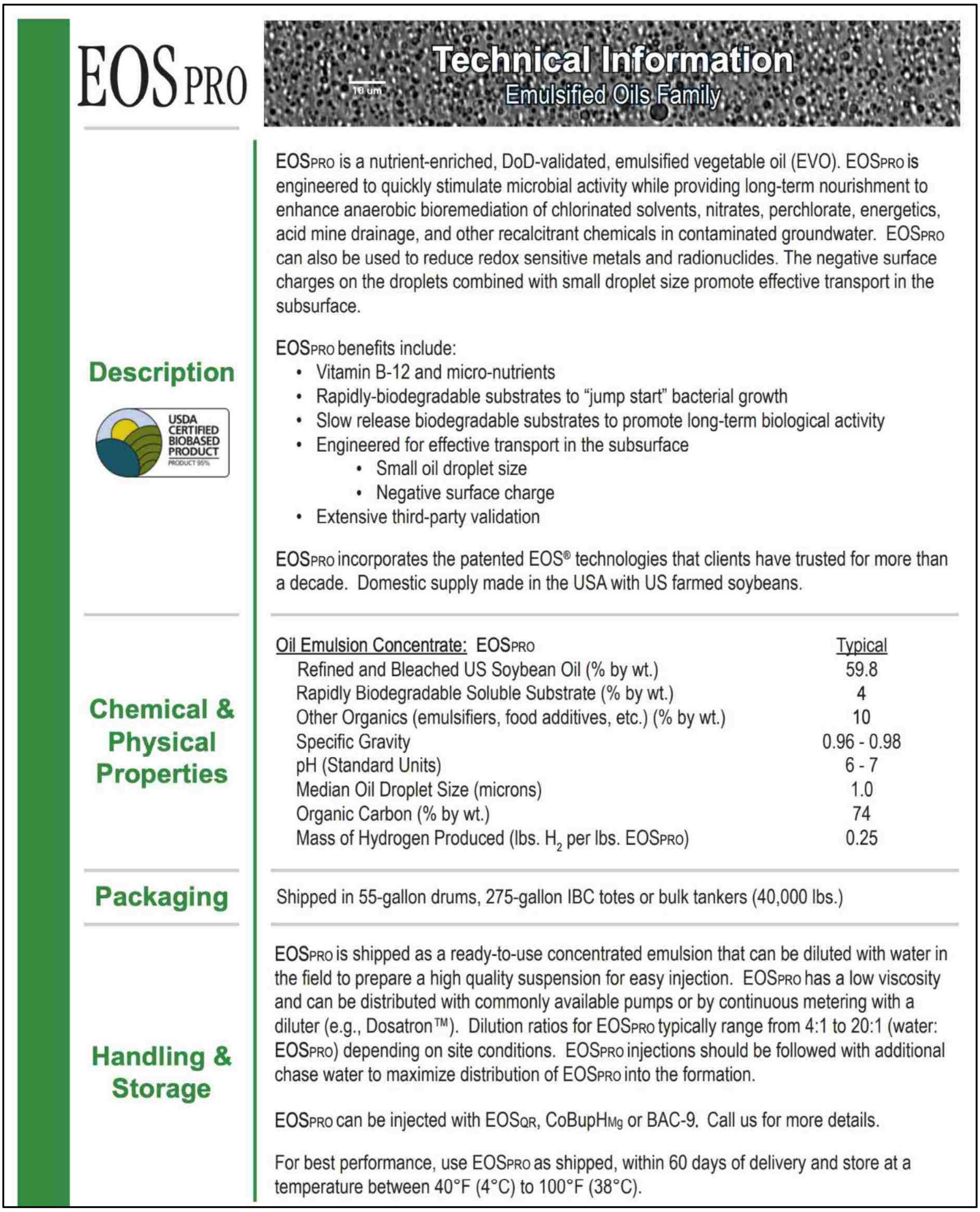
Iron/Iron Oxide	Balance
Total Carbon	2.48
Manganese	0.93
Sulphur	0.120
Phosphorous	ND
Silicon	0.35
Nickel	>0.01
Chromium	>0.01
Vanadium	ND
Molybdenum	0.33
Copper	0.10
Aluminum	>0.01
Magnesium	0.01
Boron	0.01
Zinc	0.01
Zirconium	0.01

GALEN B. DIXON
Technical Director

D:\WORD\WT\MscMemLST\SPECS&FORMS\1200SPECEml.DOC

Figure E-2: Connelly-GPM, Inc. screen specification for ZVI powder

E.2 EOS-PRO



EOSPRO

Technical Information
Emulsified Oils Family

Description

EOSPRO is a nutrient-enriched, DoD-validated, emulsified vegetable oil (EVO). EOSPRO is engineered to quickly stimulate microbial activity while providing long-term nourishment to enhance anaerobic bioremediation of chlorinated solvents, nitrates, perchlorate, energetics, acid mine drainage, and other recalcitrant chemicals in contaminated groundwater. EOSPRO can also be used to reduce redox sensitive metals and radionuclides. The negative surface charges on the droplets combined with small droplet size promote effective transport in the subsurface.

EOSPRO benefits include:
- Vitamin B-12 and micro-nutrients
- Rapidly-biodegradable substrates to “jump start” bacterial growth
- Slow release biodegradable substrates to promote long-term biological activity
- Engineered for effective transport in the subsurface
    - Small oil droplet size
    - Negative surface charge
- Extensive third-party validation

EOSPRO incorporates the patented EOS® technologies that clients have trusted for more than a decade. Domestic supply made in the USA with US farmed soybeans.

Chemical & Physical Properties

Oil Emulsion Concentrate: EOSPRO	Typical
Refined and Bleached US Soybean Oil (% by wt.)	59.8
Rapidly Biodegradable Soluble Substrate (% by wt.)	4
Other Organics (emulsifiers, food additives, etc.) (% by wt.)	10
Specific Gravity	0.96 - 0.98
pH (Standard Units)	6 - 7
Median Oil Droplet Size (microns)	1.0
Organic Carbon (% by wt.)	74
Mass of Hydrogen Produced (lbs. H_2 per lbs. EOSPRO)	0.25

Packaging

Shipped in 55-gallon drums, 275-gallon IBC totes or bulk tankers (40,000 lbs.)

Handling & Storage

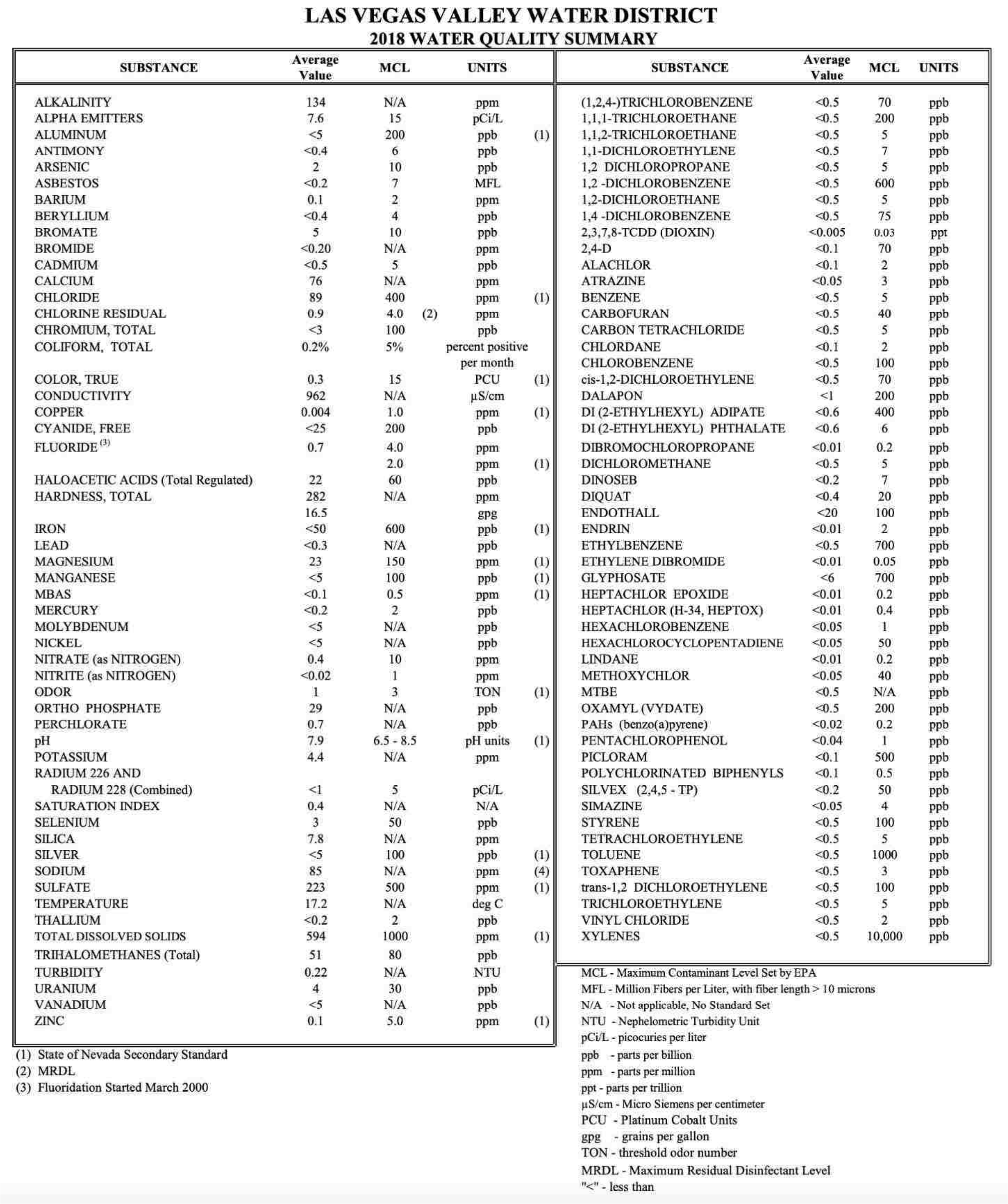
EOSPRO is shipped as a ready-to-use concentrated emulsion that can be diluted with water in the field to prepare a high quality suspension for easy injection. EOSPRO has a low viscosity and can be distributed with commonly available pumps or by continuous metering with a diluter (e.g., Dosatron™). Dilution ratios for EOSPRO typically range from 4:1 to 20:1 (water: EOSPRO) depending on site conditions. EOSPRO injections should be followed with additional chase water to maximize distribution of EOSPRO into the formation.

EOSPRO can be injected with EOSQR, CoBupHMg or BAC-9. Call us for more details.

For best performance, use EOSPRO as shipped, within 60 days of delivery and store at a temperature between 40°F (4°C) to 100°F (38°C).

Figure E-3: EOS-Pro Technical information.
www.eosremediation.com/download/product_information/eos-products/EOSPro-Product-Sheet.pdf

E.3 Water Source – LVVWD



LAS VEGAS VALLEY WATER DISTRICT

2018 WATER QUALITY SUMMARY

SUBSTANCE	Average Value	MCL	UNITS	
ALKALINITY	134	N/A	ppm	
ALPHA EMITTERS	7.6	15	pCi/L	
ALUMINUM	<5	200	ppb	(1)
ANTIMONY	<0.4	6	ppb	
ARSENIC	2	10	ppb	
ASBESTOS	<0.2	7	MFL	
BARIUM	0.1	2	ppm	
BERYLLIUM	<0.4	4	ppb	
BROMATE	5	10	ppb	
BROMIDE	<0.20	N/A	ppm	
CADMIUM	<0.5	5	ppb	
CALCIUM	76	N/A	ppm	
CHLORIDE	89	400	ppm	(1)
CHLORINE RESIDUAL	0.9	4.0 (2)	ppm	
CHROMIUM, TOTAL	<3	100	ppb	
COLIFORM, TOTAL	0.2%	5%	percent positive per month	
COLOR, TRUE	0.3	15	PCU	(1)
CONDUCTIVITY	962	N/A	µS/cm	
COPPER	0.004	1.0	ppm	(1)
CYANIDE, FREE	<25	200	ppb	
FLUORIDE (3)	0.7	4.0	ppm	
		2.0	ppm	(1)
HALOACETIC ACIDS (Total Regulated)	22	60	ppb	
HARDNESS, TOTAL	282	N/A	ppm	
	16.5		gpg	
IRON	<50	600	ppb	(1)
LEAD	<0.3	N/A	ppb	
MAGNESIUM	23	150	ppm	(1)
MANGANESE	<5	100	ppb	(1)
MBAS	<0.1	0.5	ppm	(1)
MERCURY	<0.2	2	ppb	
MOLYBDENUM	<5	N/A	ppb	
NICKEL	<5	N/A	ppb	
NITRATE (as NITROGEN)	0.4	10	ppm	
NITRITE (as NITROGEN)	<0.02	1	ppm	
ODOR	1	3	TON	(1)
ORTHO PHOSPHATE	29	N/A	ppb	
PERCHLORATE	0.7	N/A	ppb	
pH	7.9	6.5 - 8.5	pH units	(1)
POTASSIUM	4.4	N/A	ppm	
RADIUM 226 AND RADIUM 228 (Combined)	<1	5	pCi/L	
SATURATION INDEX	0.4	N/A	N/A	
SELENIUM	3	50	ppb	
SILICA	7.8	N/A	ppm	
SILVER	<5	100	ppb	(1)
SODIUM	85	N/A	ppm	(4)
SULFATE	223	500	ppm	(1)
TEMPERATURE	17.2	N/A	deg C	
THALLIUM	<0.2	2	ppb	
TOTAL DISSOLVED SOLIDS	594	1000	ppm	(1)
TRIHALOMETHANES (Total)	51	80	ppb	
TURBIDITY	0.22	N/A	NTU	
URANIUM	4	30	ppb	
VANADIUM	<5	N/A	ppb	
ZINC	0.1	5.0	ppm	(1)

(1) State of Nevada Secondary Standard
(2) MRDL
(3) Fluoridation Started March 2000

SUBSTANCE	Average Value	MCL	UNITS
(1,2,4-)TRICHLOROBENZENE	<0.5	70	ppb
1,1,1-TRICHLOROETHANE	<0.5	200	ppb
1,1,2-TRICHLOROETHANE	<0.5	5	ppb
1,1-DICHLOROETHYLENE	<0.5	7	ppb
1,2 DICHLOROPROPANE	<0.5	5	ppb
1,2 -DICHLOROBENZENE	<0.5	600	ppb
1,2-DICHLOROETHANE	<0.5	5	ppb
1,4 -DICHLOROBENZENE	<0.5	75	ppb
2,3,7,8-TCDD (DIOXIN)	<0.005	0.03	ppt
2,4-D	<0.1	70	ppb
ALACHLOR	<0.1	2	ppb
ATRAZINE	<0.05	3	ppb
BENZENE	<0.5	5	ppb
CARBOFURAN	<0.5	40	ppb
CARBON TETRACHLORIDE	<0.5	5	ppb
CHLORDANE	<0.1	2	ppb
CHLOROBENZENE	<0.5	100	ppb
cis-1,2-DICHLOROETHYLENE	<0.5	70	ppb
DALAPON	<1	200	ppb
DI (2-ETHYLHEXYL) ADIPATE	<0.6	400	ppb
DI (2-ETHYLHEXYL) PHTHALATE	<0.6	6	ppb
DIBROMOCHLOROPROPANE	<0.01	0.2	ppb
DICHLOROMETHANE	<0.5	5	ppb
DINOSEB	<0.2	7	ppb
DIQUAT	<0.4	20	ppb
ENDOTHALL	<20	100	ppb
ENDRIN	<0.01	2	ppb
ETHYLBENZENE	<0.5	700	ppb
ETHYLENE DIBROMIDE	<0.01	0.05	ppb
GLYPHOSATE	<6	700	ppb
HEPTACHLOR EPOXIDE	<0.01	0.2	ppb
HEPTACHLOR (H-34, HEPTOX)	<0.01	0.4	ppb
HEXACHLOROBENZENE	<0.05	1	ppb
HEXACHLOROCYCLOPENTADIENE	<0.05	50	ppb
LINDANE	<0.01	0.2	ppb
METHOXYCHLOR	<0.05	40	ppb
MTBE	<0.5	N/A	ppb
OXAMYL (VYDATE)	<0.5	200	ppb
PAHs (benzo(a)pyrene)	<0.02	0.2	ppb
PENTACHLOROPHENOL	<0.04	1	ppb
PICLORAM	<0.1	500	ppb
POLYCHLORINATED BIPHENYLS	<0.1	0.5	ppb
SILVEX (2,4,5 - TP)	<0.2	50	ppb
SIMAZINE	<0.05	4	ppb
STYRENE	<0.5	100	ppb
TETRACHLOROETHYLENE	<0.5	5	ppb
TOLUENE	<0.5	1000	ppb
TOXAPHENE	<0.5	3	ppb
trans-1,2 DICHLOROETHYLENE	<0.5	100	ppb
TRICHLOROETHYLENE	<0.5	5	ppb
VINYL CHLORIDE	<0.5	2	ppb
XYLENES	<0.5	10,000	ppb

MCL - Maximum Contaminant Level Set by EPA
MFL - Million Fibers per Liter, with fiber length > 10 microns
N/A - Not applicable, No Standard Set
NTU - Nephelometric Turbidity Unit
pCi/L - picocuries per liter
ppb - parts per billion
ppm - parts per million
ppt - parts per trillion
µS/cm - Micro Siemens per centimeter
PCU - Platinum Cobalt Units
gpg - grains per gallon
TON - threshold odor number
MRDL - Maximum Residual Disinfectant Level
"<" - less than

Figure E-4: 2018 LVVWD Water Quality Summary. https://www.lvvwd.com/assets/pdf/water-quality-summary-las-vegas-valley.pdf

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