

**ASSESSMENT OF PERMEABLE REACTIVE BARRIERS  
ALTERNATIVE MEDIA FOR THE REMEDIATION OF  
NITRATE-CONTAMINATED GROUND-WATERS**

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**2013**  
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# DECLARATION

As the candidate's Supervisor I agree to the submission of this thesis:

Name: Prof. Cristina Trois

Date: 17/Jan/2012

Signed ..... *Cristina Trois* .....

I, ABDULMUTALEB E.ZORGANI, declare that

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## ABSTRACT

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The increase in the contamination of ground-water (GW) with nitrates in both developing and developed countries mainly results from agricultural activities and improper sanitation systems, and is a recent phenomenon that has become a source of great health concern, particularly in regions where people rely on the ground-water as their primary water source.

Due to the advantages of using Permeable Reactive Barriers (PRB) including its cost-effectiveness as well as its capability to remove or mitigate the spread of large spectrum of contaminants (including nitrates), a significant increase has been observed in the use of this subsurface treatment technology compared to other methods. However, identifying more economic and reliable reactive media to be used instead of the costly conventional PRB materials is now of key importance.

Two local soils namely Berea Red Sand (BRS) and Umgeni Sand (US) were the main focus of this research. In addition to these soils, Zero Valent Iron (ZVI) was also used in this study. Through the use of batch experiments the feasibility of the nitrate reduction was investigated by five substrates including 100% ZVI, 100% BRS, 100% US, mix of 75% ZVI + 25% BRS, and mix of 50% ZVI + 50% BRS. Five concentrations of nitrate synthetic solution including 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l were used to simulate nitrate-contaminated ground-water. All the batch experiments were performed under semi-aerobic and uncontrolled pH conditions, and only one solid/liquid ratio of 1:10 was used.

The two mixes (mix of 75% ZVI + 25% BRS, and mix of 50% ZVI + 50% BRS) exhibited a nitrate removal efficiency of 100%, with all the different initial concentrations that were used with it; besides these two mixes, none of the other substrates showed this performance. 100% ZVI; however, managed complete nitrate reduction when the 10 mg/l and 25 mg/l concentrations were used.

Finally, it was concluded that the benefits of using BRS in combination with other materials such as ZVI in the PRB field are promising.

## DEDICATION

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I would lovingly like to dedicate this dissertation to the following valuable persons:

to The most honest and faithful human being, who was sent as a mercy to the worlds, as a beacon of science, our Prophet and Master Mohamed (P.B.U.H).

to The great Imam of this time Alladden Madi Abu Al-azaem.

to My virtuous teacher Ahmed Alazab, and his wife, the mother of Ameera, for their constant motivation and encouragement to reach my dreams.

to My brothers the elder Abdurraouf, the younger Abdurraouf and Faisal, and my best friends Mohamed Al-kafrawi, and Mustafa Al-margani for instilling the importance of hard work and higher education, and for their patience as well.

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### INTRODUCTION

Nitrogen, the most profuse species in the atmosphere, can occur in a number of forms (Galloway, 2003). Nitrate, whose molecular formula is  $\text{NO}_3^-$ , is the most oxidized form of nitrogen, and is one of the prime nitrogen forms that occur in soils and seawaters. Through biological processes nitrate could occur from various forms of gaseous nitrogen including  $\text{N}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NH}_3$  (Galloway, 2003).

The nitrate ion is an essential component in various organic and inorganic compounds (Braunwald et al., 2002; Zhang et al., 2010). These compounds have advantages and disadvantages. Some of the nitrate compounds are used as medications to prevent and relieve chest ache (angina) caused by coronary artery disease (Braunwald et al., 2002). Moreover, nitrogen fertilizers and nitrogen pesticides are used to strengthen crops and protect them from insects (NADP, 2000). On the other hand, the exposure to high levels of nitrate can be unsafe particularly in the long term (WHO, 2011).

In spite of the fact that there are several nitrate sources (natural and man-made) that could possibly cause contamination in ground-waters with nitrate, the anthropogenic sources are the main and the most dangerous ones (Choe et al., 2000). Of these sources, the most common are: animal wastes, septic systems, landfill waste materials, and atmospheric deposition (Zhang et al., 2010). Even though, nitrogen fertilizers and nitrogen pesticides are used for beneficial purposes, their intensive use contributes to the contamination of ground-water (GW) (Suzuki et al., 2012).

All over the world, nitrate is a very common chemical pollutant in ground-water aquifers (Suzuki et al., 2012). Because nearly all inorganic nitrate salts are dissolved and do not evaporate, they, once reaching water, probably stay in it until they are used up by vegetation or other organisms (U.S. EPA, 2006b).

Ground-water pollution is becoming a severe environmental matter across the world (Suzuki et al., 2012). Nitrate, which is one of the most common contaminants in ground-water aquifers, can severely affect human health (ASTDR, 2007; Suzuki et al., 2012). In fact, due to the possible conversion of nitrate to nitrite, which could occur in the ground-

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water or in the human body especially in infants, nitrate is regarded as a toxic contaminant (Rivett et al., 2006). In addition to methaemoglobinemia that occur as result of the ingestion of food contaminated with high levels of nitrate ( $> 50$  mg/l ), anoxia and death can also occur when drinking water containing high nitrate and high nitrite levels is consumed. A guideline value of 50 ppm for the discharge of nitrate in the natural environment was established by the World Health Organization (WHO) in 2004 (Rivett et al., 2006).

Since pollution of ground-water with nitrate has become a health and an environmental issue in predominately industrialized and unindustrialized countries, the remediation of these contaminated ground-waters has been of great importance, particularly, to the affected population in various parts of the world (Della Rocca et al., 2007).

In fact, there is a number of remediation techniques that can remove nitrate from waters (surface and ground-water) and/or soils with varying degrees of efficiency, ease of operation, and cost (Archna et al., 2012). In recent years, industry has focused in improving existing treatment techniques or establishing new ones that can be easily operated, reliable and cost-effective (Virikutyte et al., 2002).

Permeable Reactive Barriers (PRB), which is the focus of this research, is one of the techniques that are used to treat contaminated ground-water (Powell et al., 1998). The PRB is defined as a subsurface barrier containing reactive material which serves as remediating medium for contaminated ground-water. It allows water to move through but not contaminants. The reactive media immobilize or degrade contaminants (both organic and inorganic) into innocuous species (Powell et al., 1998). Processes through which ground-water remediation occurs in the PRB can be redox reactions, precipitation, chemical dehalogenation, biodegradation, and/or adsorption (ITRC, 2005).

This research is aimed at evaluating the efficiency of PRB system in the treatment of nitrate contaminated ground-water in relation to the type of reactive media used. Lab batch trials are adopted in this study in order to simulate the processes that occur in the PRB system, whereas the nitrate contaminated ground-waters are simulated by the use of

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synthetic solutions at various nitrate concentrations including 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l.

The reactive media applied in this study are Zero Valent Iron (ZVI), and two local soils including Berea Red Sand (BRS) and Umgeni Sand (US). ZVI is a very common material in PRBs' field applications whereas the other two materials are not used in this field. In fact, US, which mainly consists of quartz, is selected in this study only as a control substrate due to its expected passivity. BRS, on the other hand, is chosen to be part of this investigation due to its low cost, easy availability, and its active composition, particularly due to its hematite content (Fanni, 2007).

Since ZVI has been successfully applied in a number of sites to treat various contaminants including nitrate (Powell et al., 1998), BRS alone or in combination with ZVI is expected to give good results due to the iron oxides it is composed of.

The objectives of this research are:

- To investigate the performance of the reactive media in relation to contaminant's concentration and time (reaction rate);
- To assess the interactions dynamics that occur among reactants involved in batch tests.

The methodological approaches to accomplish these objectives are:

- Setting up batch tests under certain environmental conditions;
- Analysis of the parameters that are considered as indicators of the interactions occurring during batch experiments;
- Comparison and discussion of the results obtained.

The dissertation is subdivided into five chapters, two of which are the literature review as presented in Figure 1, below.

INTRODUCTION

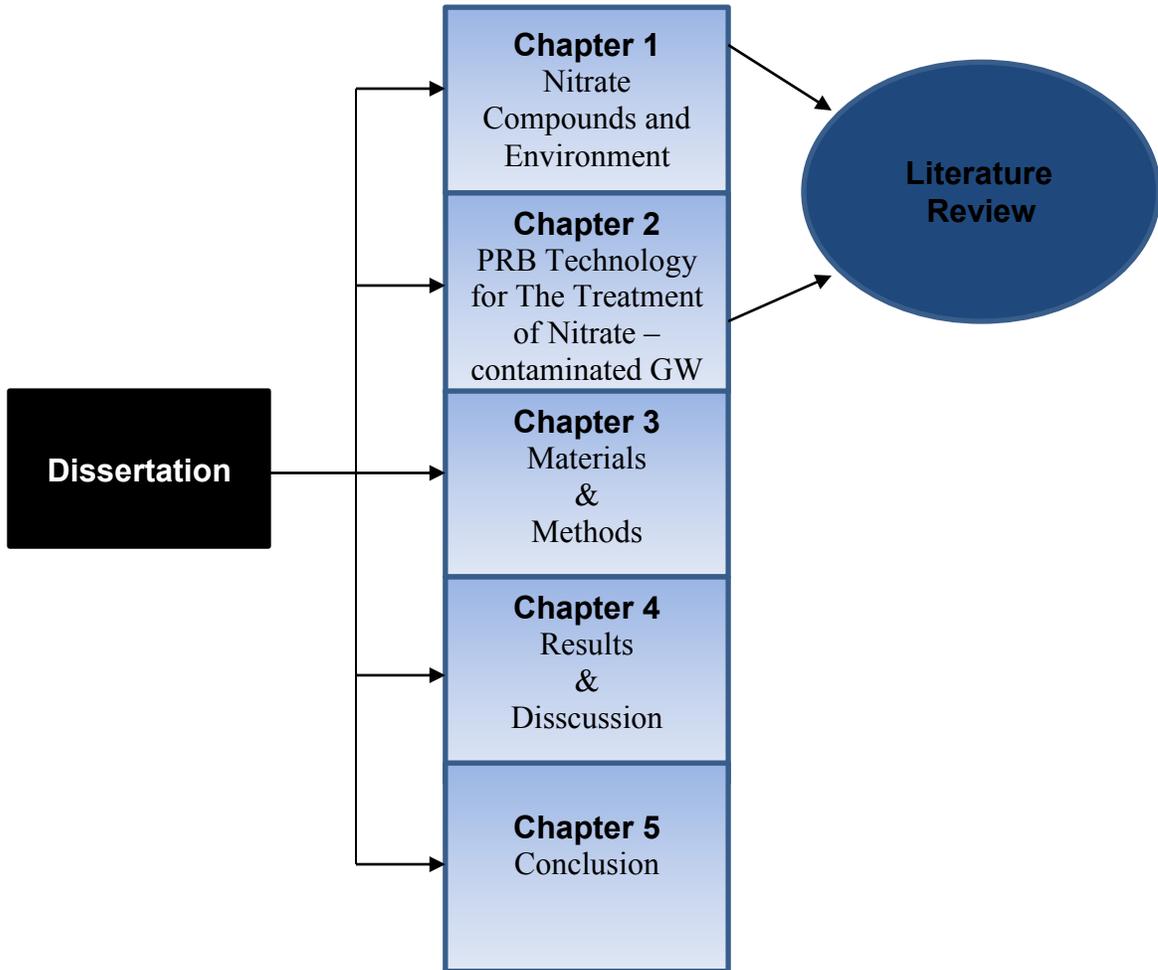


Figure 1 Dissertation components and literature review breakdown

**CHAPTER 1**  
**NITRATE COMPOUNDS AND ENVIRONMENT**

## **INTRODUCTION**

Nitrate is a nitrogen-oxygen chemical compound that naturally occurs in our environment (Galloway, 2003). It contributes to the formation of various species (both organic and inorganic) that can be beneficially used. Some nitrate compounds are widely applied in agriculture or used in medicine.

In some cases nitrate can potentially lead to serious health risks when excessively used (Rivett et al., 2006). In fact, soluble contaminants such as nitrate are of great concern due to their identified severe consequences for the human beings who may consume drinking water that is heavily contaminated with them.

It is necessary for researchers when they address contamination issues in environments such as water, air or soil to understand the properties of target contaminants due to their importance in the treatment of these contaminated environments.

This chapter also addresses the fate and transport of nitrate in the environment, its effects on human health, and treatment techniques.

## 1.1 General Chemical and Physical Properties of Nitrate Compounds

Nitrate is a non-metallic inorganic pollutant with the molecular formula  $\text{NO}_3^-$  and molecular weight (Mw) of 62.0049 g/mol (Simon & Meggyes, 2000). It is a stable and highly soluble constituent that naturally occurs (Archna et al., 2012).  $\text{NO}_3^-$  is the most oxidized nitrogen form with valence state of (+5) (Galloway, 2003). Although some properties such as physical state, density, melting point, decomposition point, and solubility degree in water could differ among the nitrate compounds, almost all inorganic nitrate salts are soluble, non-evaporable, odorless, and colorless with briny taste. In addition, inorganic nitrates solutions are usually of pH that ranges between 5 to 8 (IPCS, 1999).

## 1.2 Sources and Uses of Nitrate Compounds

As shown in Figure 1.1, nitrate could form from various gaseous nitrogen components through biological processes. Nitrification is one of these processes and through which ammonium ( $\text{NH}_4^+$ ) is transformed to nitrite, and subsequently to nitrate. Nitrate was also found to be a metabolite in mammals by the oxidation of nitric oxide (Tamme et al., 2006).

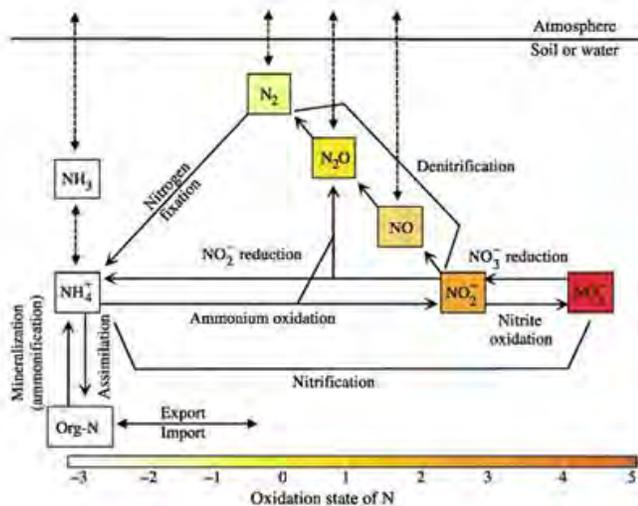


Figure 1.1 Nitrogen cycle illustrating the processes through which various nitrogen forms may transform (Galloway, 2003)

The existence of nitrate in ground and surface water as well as in land is due to several sources and activities including (NADP, 2000; Zhang et al., 2010):

- Atmospheric deposition
- Combustion of fossil fuels
- Septic systems
- Unreasonable disposal of domestic, industrial, and animal wastes
- Use of nitrogenous fertilizers and nitrogenous pesticides

Although the increase in nitrate concentrations in ground-water is mostly brought about by human activities such as sanitation and agriculture, natural sources can contribute to high levels of nitrate concentration reaching to more than 100 mg/l (Rivett et al., 2006). According to the Toxics Release Inventory, discharges to land as well as water were in total over 246 million kilograms during a period of 3 years only (from 1991 to 1993) (WQA, 2005). Most of the inorganic nitrates discharges took place in California and Georgia.

Nitrate is a structural component of various organic compounds such as glyceryl trinitrate (GTN), and inorganics such as potassium nitrate and ammonium nitrate. GTN is used in medicine to prevent and relieve chest ache caused by coronary artery disease (Braunwald et al., 2002), whereas potassium nitrate and ammonium nitrate are broadly used as fertilizers (Choe et al., 2000; U.S. EPA, 2006b).

### **1.3 Risks for Human and Environmental Health**

Nitrate is a highly common chemical pollutant in the ground-water aquifers of this world (Suzuki et al., 2012). There are many subjects across the world who rely on ground-water as their main drinking-water supply. In the United States, for example, the percentage of those people found to be 42% of the country population; in Japan, the corresponding percentage is in the order of 25% (Suzuki et al., 2012). Extreme levels of nitrate in drinking water can result in serious sickness and occasionally death (Rivett et al., 2006).

Another way of exposure to nitrate is eating foods containing nitrate which also has serious impacts on human health particularly when the nitrate is in excess of around 50 mg/l

## CHAPTER 1 – NITRATE COMPOUNDS AND ENVIRONMENT

(Rivett et al., 2006). In fact, it has been estimated that vegetables contribute approximately over 80% of the average daily intake of nitrate (Tamme et al., 2006).

Exposure to nitrate through inhalation of nitrate polluted dust can also occur, though insignificantly, compared to the exposure through ingestion (IPCS, 1999). In addition, overdose of medications that are prepared from nitrate compounds, can be another way of exposure to nitrate posing serious health problems.

Considering nitrate as a toxic chemical is mainly owing to its reduction to nitrite (Rivett et al., 2006). *Methaemoglobinemia*, a blood disorder condition, occurs through ingestion of food and/or water that are contaminated with high amounts of nitrate (ASTDR, 2007). This in fact occurs due to the enzymatic transformation of nitrate, when it comes into contact with human saliva, to nitrite which in turn causes a chemical reaction that can result in the occurrence of *methaemoglobinemia* (Rivett et al., 2006). Moreover, because of the high pH status in the stomachs of the children who are under age of one year (infants) bacteria in their stomachs can also increase the transformation of nitrate to nitrite causing the same condition (ASTDR, 2011).

It was observed that up to 100% of nitrate is converted to nitrite in infants whereas in human beings who are over the age of one year, only up to 10% of nitrate is reduced (Rivett et al., 2006). Therefore, in addition to pregnant women, infants represent a high-risk group from exposure to nitrate. Pregnant women are at risk due to the high levels of *methaemoglobin* during the pregnancy period (ASTDR, 2011). Trouble in breath, drowsiness, and a bluish skin colour are of the *methaemoglobinemia* symptoms (Rivett et al., 2006).

Other possible serious effects that could occur from the exposure to high levels of nitrate include liver damage, cancer, anoxia, and sometimes death as well (Rivett et al., 2006). Additionally, since nitrate is a nutrient for microorganisms, its excessive presence in water systems such as lakes and estuaries can lead to eutrophication of water (Galloway, 2003).

## 1.4 Discharge Standards for Nitrate

In many parts of the world such as the United States, Japan, Australia, and north Africa, nitrate levels in some water supply sources have noticed to be in exceedance of United States Environmental Protection Agency maximum contaminant level (USEPA MCL) of 10 mg/l (Rivett et al., 2006; Suzuki et al., 2012).

In fact, before about 8 years ago, USEPA maximum contaminant level for nitrate in drinking water had been 45 mg/l (Raghu Prasad et al., 2005). However, because of the constant increase in nitrate pollution of ground-water which can subsequently lead to an increase in human health risks the USEPA has developed the maximum level for nitrate in potable water to 10 mg/l, and this value is the latest published limit (Fan et al., 2009).

On the other hand, the World Health Organization (WHO) standard as well as the European Union (EU) maximum contaminant level for nitrate in drinking water are 50 mg/l (Mamba et al., 2008). As for South Africa, Department of Water Affairs and Forestry (DWAF) in 2004 has established a limit of 15 mg/l to be the maximum contaminant level for nitrate in potable water (DWAF, 2004).

## 1.5 Transport and Fate of Nitrate in the Environment

Brusseau et al. (2004) indicated that “*The term (fate) refers to the disposition of a contaminant as it is transported through the environment*”. Even though, there are many processes that affect the fate of contaminants in the environment, contaminants transport and fate in the environment is governed by four general processes including the following (Brusseau et al., 2004):

- Dispersion
- Advection
- Transformation reactions (Biotic and Abiotic reactions)
- Interphase mass transfer reactions (Evaporation, Solubilization, Volatilization, and Sorption)

## CHAPTER 1 – NITRATE COMPOUNDS AND ENVIRONMENT

Nitrates, in fact, do not evaporate and therefore are mostly present in soils and ground-water (U.S. EPA, 2006b). However, due to the great solubility of nitrates in water they tend to remain in it until taken up by vegetation and other organisms.

Nitrate, which is one of nitrogen's chemical forms, can be naturally formed and transformed depending on the environment (Galloway, 2003). In the atmosphere, nitrate is formed as a result of reactions occurred by lightning, and deposited on the land (WHO, 2011). Subsequently via the runoff, nitrate could reach the surface waters such as rivers and lakes, and could also leach through the soil into the ground-water. In addition, it can reach seawaters and oceans by means of the discharge of the ground-water and river that are contaminated with it (Galloway, 2003).

Under aerobic conditions, ammonium nitrate ( $\text{NH}_4^+$ ), which can be formed from soil organic materials, is oxidized to nitrate ( $\text{NO}_3^-$ ) through the nitrification process (Rivett et al., 2006). On the other hand, under reducing conditions nitrate is biologically transformed to ammonia ( $\text{NH}_3$ ) and nitrogen gas ( $\text{N}_2$ ) through a process called denitrification. Figure 1.2 depicts some of the nitrate formation and transformation activities.

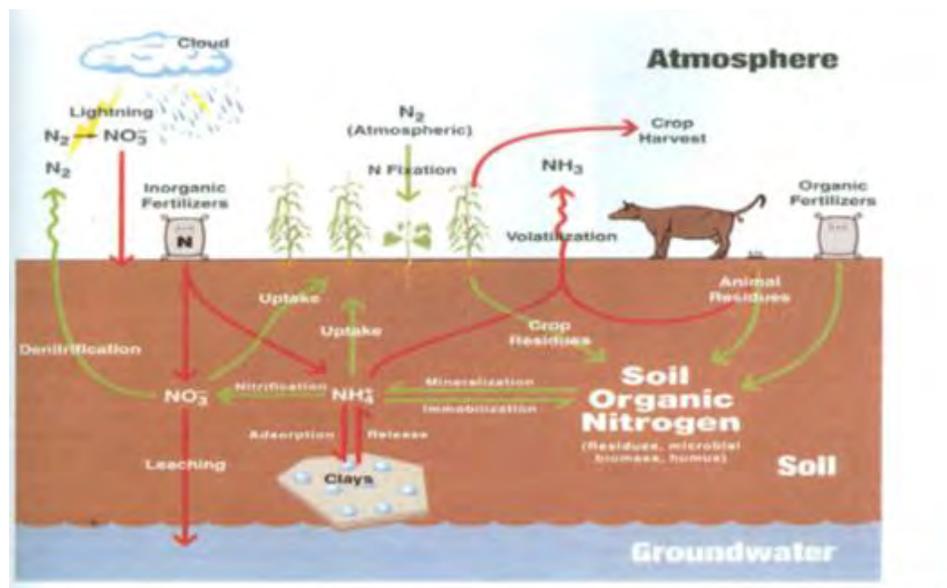


Figure 1.2 Nitrogen transformations, particularly in soil, including the formation and transformation of nitrate (Artiola et al., 2011)

## 1.6 Nitrate Treatment Technologies

As described in section 1.5, soil and ground-water are highly susceptible to contamination with nitrate. However, there is a wide variety of technologies that can be used for the remediation of nitrate contaminated soil and ground-water. Some technologies such as ion exchange and reverse osmosis are nitrate removal systems, and some others such as biological and chemical denitrification are nitrate reduction systems, while others can be a hybrid combination of the two (Seidel et al., 2011).

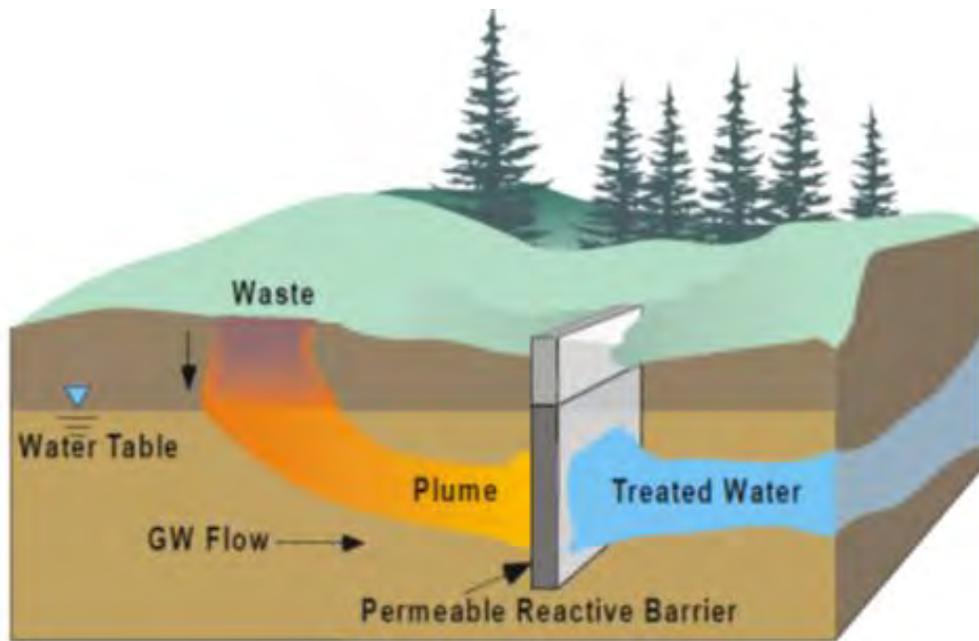
The treatment technologies that are presented in Table 1.1 are classified based on the treatment mechanisms by which the remediation is accomplished. In comparison with the excavation and ex-situ treatment systems, the in-situ treatment technologies have a number of benefits including lower costs and the treatment of deep contaminated sites (U.S. EPA, 2006a).

Table 1.1 Classification of nitrate treatment technologies based on the treatment mechanisms (after U.S. EPA, 2006a; Westerhoff & Doudrick, 2009)

Treatment Mechanism	Technology	Type of Media Treated	In situ/ Ex situ
Physical/Chemical	Solidification/Stabilization	Soil	In situ/Ex situ
	Soil Flushing	Soil	In situ
	Electrokinetic Separation	Soil	In situ
	Ion Exchange	Ground-water	Ex situ
	Membrane Separation (Reverse Osmosis)	Ground-water	Ex situ
	Chemical Denitrification (e.g. Permeable Reactive Barrier)	Ground-water	In situ
Biological	Bioremediation (Biological Denitrification)	Ground-water/Soil	In situ
Thermal	Vitrification	Soil	In situ/Ex situ

The following chapter focuses on Permeable Reactive Barrier technologies for the remediation of contaminated groundwater, with more detail for nitrate.

**CHAPTER 2**  
**PRB TECHNOLOGY FOR THE TREATMENT**  
**OF NITRATE-CONTAMINATED GROUND-WATER**



## **INTRODUCTION**

The PRB system is a physical object (porous barrier) that is placed in the path of the contaminants' plume so that flows through the barrier or the permeable part of the barrier, as is the case in the „Funnel and Gate“ configuration, in order to be treated (FRTR & ITRC, 2002). This permeable barrier contains a reactive medium that is chosen mainly according to the contaminants present in the plume (Powell et al., 1998).

PRB systems must be designed in such a way that their hydraulic conductivity is higher than the one of the surrounding aquifer (Powell et al., 1998). The rationale behind this is to allow the ground-water plume to flow through the reactive substrate rather than it bypassing the barrier. One or more processes will take place when the plume contacts the reactive media, thereby contaminants will get reduced to a harmless level, if not completely removed (ITRC, 2005).

In fact, this technology has emerged in the mid-1990s with only the use of ZVI as reactive media (FRTR & ITRC, 2002). Thereafter, there was an interest to expand the spectrum of reactive media in order to address more contaminants. Before that time, the Pump-and-Treat system was the most common used technique for remediating ground-water (Powell et al., 1998). However, since many advantages about the use of PRB system were identified, including the cost of the technique and its application, as well as its effectiveness in the removal of numerous contaminants, the technique became more implemented and favorable. Between 1995 and 2001 PRB systems have been installed at more than 40 sites in USA and Canada (U.S. EPA, 2001).

The goal of PRBs is to minimize the possibility that a contaminant plume can flow toward and imperil sensitive receptors, such as drinking water wells, or discharge into surface water bodies (Powell et al., 1998).

## 2.1 PRB Configurations

PRB system is a wall that is built in a various configurations (FRTR & ITRC, 2002). The following five configurations are the main types of PRB system:

- Continuous PRB Configuration (Powell et al., 1998; Thiruvengkatachari et al., 2008);
- Funnel-and-Gate Configuration (Thiruvengkatachari et al., 2008);
- Injection Well Configuration (ITRC, 2011);
- Caisson Configuration (Gavaskar, 1999);
- Alternative Funnel-and-Gate System (Elder, 2000).

### 2.1.1 Continuous PRB configuration

Continuous PRB is a reactive zone unit placed in the path of ground-water plume in order for it to become treated as it passes through, below its natural flow velocity. Ideally, this type of barrier is placed at a depth that allows it to contain the ground-water plume in both vertical and horizontal dimensions. The barrier thickness is determined according to factors that will be explained later in this chapter. Figure 2.1 shows an illustration of continuous barrier configuration.

This configuration is one of the most frequently used configurations in practical applications, and it has some advantages including:

- Construction cost is relatively cheap;
- Minimal disturbance is caused to the natural ground-water flow when the barrier is designed and constructed properly;
- It has proved effective for remediating a series of contaminants including organics and inorganics (Fanni, 2007);
- Simple to conceptualize and design (Fanni, 2007)

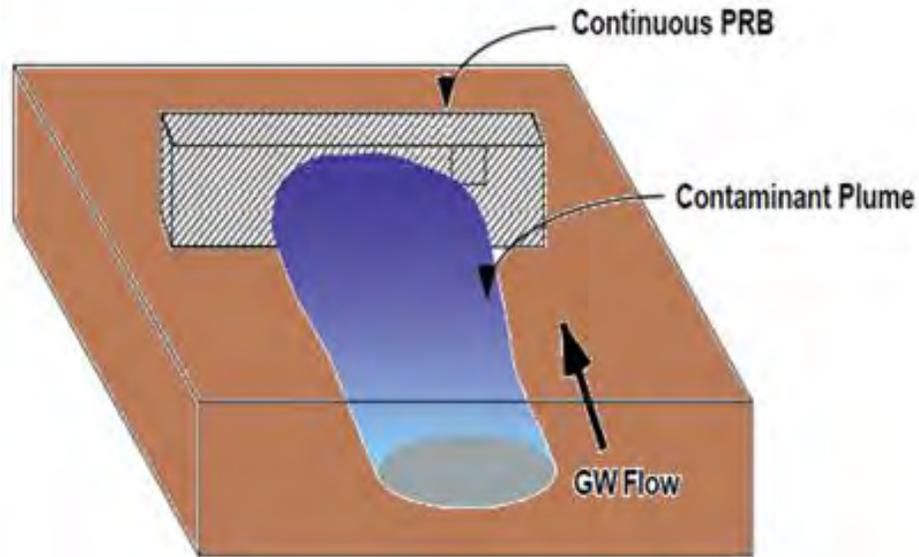


Figure 2.1 Continuous PRB configuration (after Powell et al., 1998)

### 2.1.2 Funnel-and-Gate configuration

Funnel-and-Gate system is a structure that consists of a reactive zone called 'Gate', and this reactive zone is flanked by two impermeable wings called 'Funnel'. The funnel serves as a hurdle for the plume to direct it towards the gate where the remediation of that plume occurs. Figure 2.2 shows a Funnel-and-gate system.

Reactive material cost, construction cost as well as hydrogeological characteristics of the location are three main aspects need to be considered in the selection between Funnel-and-Gate system and the Continuous system. Although the construction cost of Continuous configuration is cheaper than Funnel-and-Gate configuration, the latter was used more when costly reactive medium is applied. Therefore, a balance must be figured out between these two aspects in accordance with the contaminant of concern, and degree of remediation needs to be achieved.

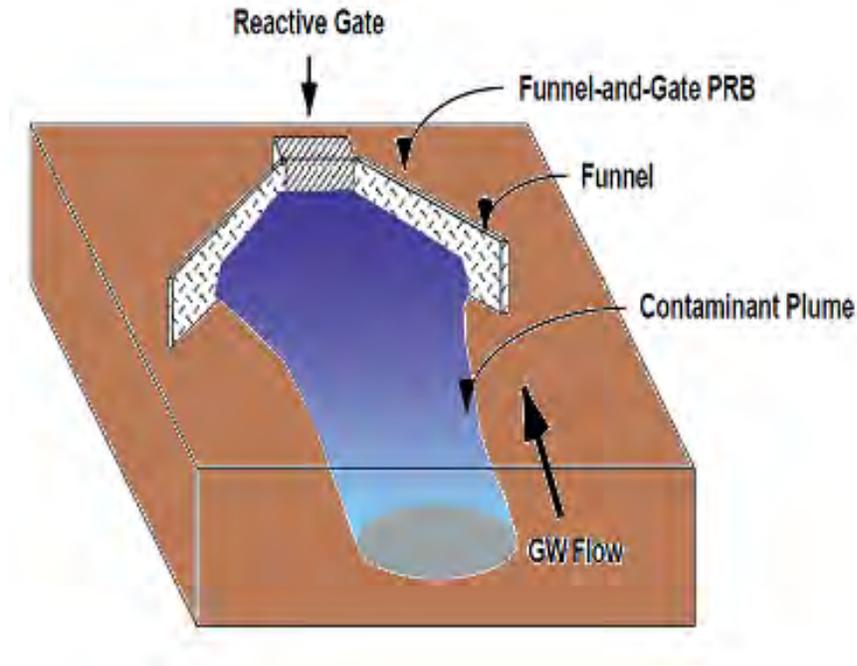


Figure 2.2 Funnel-and-Gate configuration (after Powell et al., 1998)

### 2.1.3 Injection well configuration

Injection system is configured to create a reactive treatment zone intercepting the path of ground-water contaminant plume. The reactive zones are established through drilling a number of wells and then injecting the reactive substrate under pressure into the subsurface. Figure 2.3 shows a schematic of Injection Well configuration.

Since it is difficult to control the thickness and uniformity of the reactive zone, it is necessary to make sure that the contaminant plume does not by-pass the treatment zone (Thiruvengkatachari et al., 2008). This method is preferable in some complicated cases (e.g. existing of underground utilities) where it may be costly or even difficult to manage using other configurations.

Advantages of Injection Well configuration include the following:

- No need for trenches to be installed, which makes access to aquifers deeper than 100 meter possible.
- Viable in urban areas where underground utilities and surface structure are present.

- Excavation required is very small in comparison with trenching method, which obviously has an effect in terms of application cost.

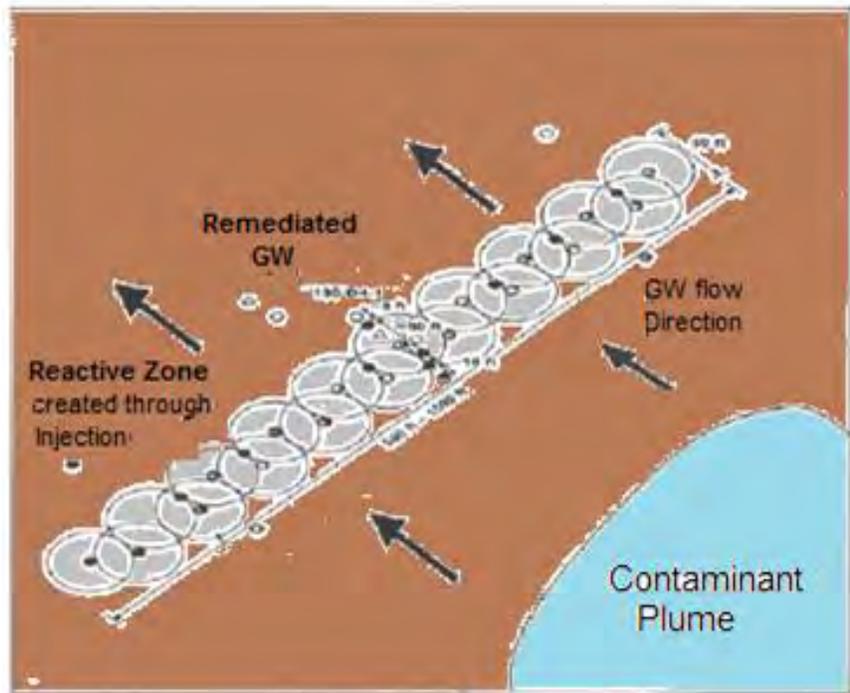


Figure 2.3 Illustration of Injection Well configuration (after ITRC, 2005)

#### 2.1.4 Caisson configuration

Caissons are hollow, load bearing enclosures that can be built in various shapes, and used instead of other methods that need excavation (Thiruvengkatachari et al., 2008). They can be prefabricated before their emplacement or they can be built in parts and then connected properly as the caisson is driven into the intended subsurface location.

The caisson is usually built in a cylindrical shape with a diameter of about 2.4 meters (Thiruvengkatachari et al., 2008). Through vibration process, caisson is lodged into the subsurface to the desired depth and then augered so that it provides space for the reactive material (ITRC, 2011). Pushing the caisson down into the subsurface is found to be easier than withdrawing it out.

The walls that are installed on either side of the caisson to be used as a funnel can be slurry wall or sheet piling. It is also necessary to make certain that proper installation of the

funnel is performed (i.e. No space left between funnel and caisson). This configuration can be multiple applied gates as shown in Figure 2.4.

This method is advantageous for its inexpensive installation as well as for the fact that depths greater than 18 meters can be feasible (ITRC, 2011). Furthermore, this system has the ability to treat multiple contaminants, and it is easier to construct than a Continuous PRB, and regeneration or even replacement of reactive medium is easy to perform (Elder, 2000).

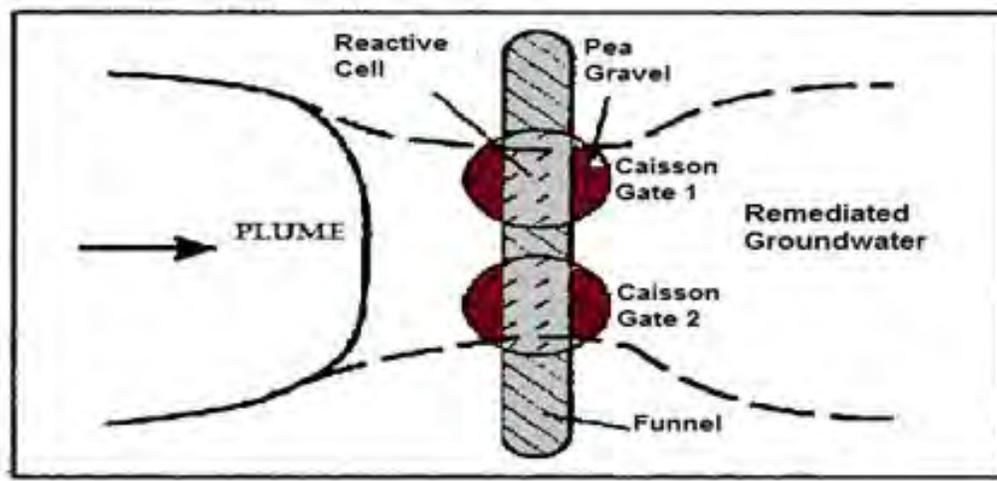


Figure 2.4 Multiple Caisson-PRB configuration (after Gavaskar, 1999)

### 2.1.5 Alternative Funnel-and-Gate system

An Alternative Funnel-and-Gate system has been designed in „X“ shape in which the reactive material is centred. The characteristic of funnel in this system is not like the funnel in Funnel-and-Gate system where it has to be less permeable than aquifer. In this system, the funnel is designed to be more permeable than the contaminated zone. Thus, it is used as a channel for the plume to pass through the center of the design which is the treatment zone, and thereafter exit through the funnel that is on the other side of the center (Fanni, 2007). Figure 2.5 shows a simplified form of Alternative Funnel-and-Gate system.

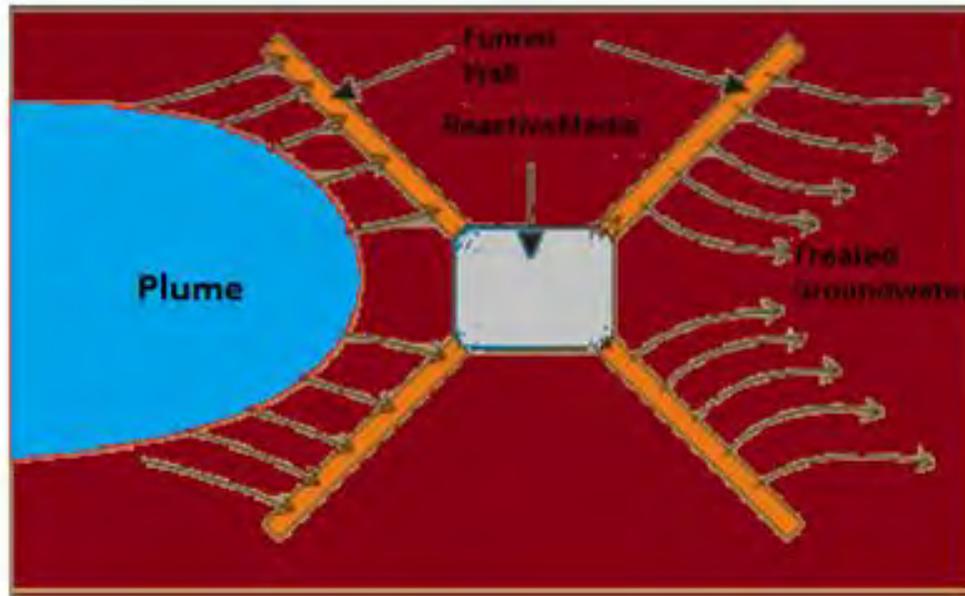


Figure 2.5 Schematic diagram of Alternative Funnel-and-Gate system (after Fanni, 2007)

## 2.2 Reactive Media and Treatment Processes

The reactive materials used in PRB system for ground-water remediation are generally characterized as follows (Thiruvengkatachari et al., 2008):

- They can change pH or redox potential
- They can cause precipitation
- They have high sorption capacity
- They release oxygen or other nutrients to boost biological degradation

Including singular and combined reactive media, reactive materials that have the potential for use in PRB technology are (Powell et al., 1998; Thiruvengkatachari et al., 2008):

- Zero valent metals (Fe, Sn, Zn, Mg, Al, Cu, In, Cd, Bi, Ag, Sb, Hg, Pb, Th, Ti, Mn, Co)
- Zero valent metalloid (e.g. Ge), and zero valent non-metal (e.g. S)
- Divalent metal cations (e.g.  $Mn^{2+}$ ,  $Fe^{2+}$ )

- Minerals such as biotite, vermiculite, bauxite, magnesite, zeolite, siderite, pyrite, and magnetite
- Bimetallic walls such as Pd-Cu, Pd-Zn, Pd-Fe, Ni-Fe, Fe-S, and Fe-FeS<sub>2</sub>
- Colloidal iron
- Dithionite
- Iron and non-iron compounds such as ferric oxides and oxyhydroxides, ferrous hydroxide, ferrous sulfide, calcium chlorid, and barium chloride
- Biomedia such as anaerobic bacteria, methanogenic bacteria, iron-reducing microbes, and sulfate-reducing bacteria
- Other substrates including activated carbon, activated alumina, peat, lignite, and coal

The main processes that may occur when contaminants plume comes into contact with reactive materials are (ITRC, 2005):

- Reductive or oxidative degradation of organic contaminants
- Sorption of contaminants
- Biological degradation of organic contaminants
- Precipitation and/or reduction of some inorganic contaminants such as heavy metals

Despite the fact that up to few years ago ZVI was the most widely used reactive substrate in full-scale PRBs, research for newer, more effective reactive media is still ongoing (ITRC, 2005). In the following subsections that fall under section 2.2, the physical-chemical properties as well as the treatment mechanisms of Zero Valent Iron, Berea Red Sand, and Umgeni Sand are addressed though with more detail for ZVI.

### **2.2.1 Zero Valent Iron (ZVI)**

ZVI (Fe<sup>0</sup>) is the most common material that has been emplaced in PRBs (Muegge, 2008). The advantages of chemical reactions that occur at the surface of ZVI are taken in consideration in order to develop In Situ treatment technologies (National Technical University of Athens, 2002). This material has been used as a reactive media for the

removal of an array of contaminants include the following (Gavaskar et al., 2000; U.S. EPA, 2002; ITRC, 2005):

- Negative-charged inorganics (Anions) (e.g.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ )
- Positive-charged inorganics (Cations) (e.g. As, Cr(VI), Se, V, U, Tc, Mn)
- Organic chlorinated compounds (e.g. TCE, VC, TCA, PCE, cisDCE) and
- Aromatic hydrocarbons (BTEX – Benzene, Toluene, Ethylbenzene, Xylenes)

In fact, this technology has originated in the mid-1990s when only ZVI was used as a reactive medium (FRTR & ITRC, 2002). ZVI is comparatively the cheapest metallic medium, and usually one of the cheapest media (National Technical University of Athens, 2002). Overall, ZVI utilized in PRB system should consist of low level of carbon, safe amounts of leachable trace elements in addition to iron metal as a main component (ITRC, 2011).

In most evaluated PRB projects, the influent contaminated water has been treated to below maximum contaminant levels (MCLs) by the time it has reached monitoring wells that are placed in the center of the technique itself (Muegge, 2008).

### **2.2.1.1 Physical and chemical characteristics**

According to characterization was done on ZVI in 2002, chemical analysis demonstrated that this material consists mainly of iron (92.03% w/w Fe), low amounts of carbon and silicon (3.31% w/w C, 2.04% w/w Si), and other trace amounts of Mn, Al, S, Ni, Cr, and P (National Technical University of Athens, 2002). On the same characterization, the paste pH, which is the mixture of the solid material with distilled water as indicated by McGeorge (1945), was found to be around 5 whereas by means of sieve analysis the granules appeared to be of a diameter ranging between 0.2 and 1.2 mm (National Technical University of Athens, 2002).

In fact, ZVI is a reducing reactive medium that tends to pass its electrons (be oxidized) to pollutants, which go through reductive mechanism resulting in degradation or precipitation (Thiruvengatachari et al., 2008).

Under aerobic condition, oxygen which is the favourable electron acceptor under this condition is consumed quickly for the iron corrosion reaction (Powell et al., 1998). In the presence of oxygen, as shown in (2-1) and (2-2), ZVI would oxidize to ferrous ions and further to ferric ions if adequate amount of O<sub>2</sub> is available (Yin et al., 2012).



Eventually, under the aerobic and near-neutral condition, Fe<sup>2+</sup> and Fe<sup>3+</sup> ions would form precipitates as ferrous and ferric hydroxides as elucidated in the following two equations (Zhang et al., 2010):



Thus, hydraulic conductivity of ZVI would be diminished due to these solid formations, and hence its reactivity may get affected (Thiruvengkatachari et al., 2008). To avoid this problem in ZVI-based PRB, a mixture of 10% iron and sand is placed as pretreatment zone (PTZ) before the 100% ZVI treatment reactive zone (Gavaskar, 1999). This mixture would slow down the dissolved oxygen (DO) reaction rate due to the reduced surface area of ZVI in the mixture. Moreover, any precipitates that may form would not be an obstacle to the flow of ground-water since these precipitates would be spread over a bigger volume (Thiruvengkatachari et al., 2008).

On the other hand, in the absence of dissolved oxygen (anaerobic condition), corrosion of ZVI via hydration proceeds slowly though, reaction under both aerobic and anaerobic conditions results in elevated-pH state (Powell et al., 1998). As presented in (2-5), corrosion of ZVI under anaerobic condition would produce hydrogen gas (Fan et al., 2009).



Hydrogen gas may temporarily passivate ZVI surface (Thiruvengkatachari et al., 2008). Therefore, in order to avoid this problem, and keep ZVI reactivity up as well as GW flow rate, anaerobic H<sub>2</sub>-degrading bacteria is introduced or sometimes hydrogen bubbles are necessary to be ventilated.

### **2.2.1.2 Treatment mechanisms**

#### *Nitrate*

Nitrate NO<sub>3</sub><sup>-</sup> is an oxidant agent that can cause reduction to ZVI reactivity, affecting the system longevity (ITRC, 2011). In fact, passing water containing NO<sub>3</sub><sup>-</sup> through ZVI barrier brings about the passivation of iron. On the other hand, since iron passivation, which occurs due to the presence of nitrate, is found to be dependent on nitrate flux as well as it may be reversible. Flushing the ZVI treatment zone with nitrate-free water periodically would help in extending the lifespan of iron PRB system (ITRC, 2011).

Previous studies have proved that nitrate can be reduced completely under aerobic or anaerobic conditions by using ZVI (Hao et al., 2005). However, anaerobic reductive denitrification of nitrate has been noticed to occur faster than that under aerobic condition (Yin et al., 2012).

According to results of the batch experiments that have been conducted in Arizona state University in 2003, the presence of dissolved oxygen found to be an inhibitor factor for the nitrate reduction by ZVI in these batches (Westerhoff & James, 2003). This was attributed to the minor possible changes in any modifications in surface chemistry that occurs due to a high solid to liquid ratio in comparison with column experiments. Contrary to the batch experiments results, increasing dissolved oxygen in ZVI packed columns is found to be an enhancing measure in the nitrate reduction process (Westerhoff & James, 2003). Huang and Zhang (2005) stated that magnetite (Fe<sub>3</sub>O<sub>4</sub>) is the dominant iron corrosion product when the reaction occurs under an anaerobic and weak acid condition.

Depending on the reaction condition, different products through the reduction of nitrate by ZVI could be yielded including ammonium, ammonia and/or nitrogen, while nitrate is always formed as a by-product of this reaction (Huang et al., 2006). Under aerobic

condition, nitrogen gas (N<sub>2</sub>) is the predominant product when the condition is neutral or alkaline, whereas ammonium is the predominant under acidic conditions.

Anaerobic condition; however, promotes the formation of ammonia and/or ammonium only. Under this condition, ammonium is the predominant product when the system is in near-neutral condition (Huang et al., 2006), whereas ammonia is the main product when the system pH is high (Hao et al., 2005).

Figure 2.6 represents the relationship between pH, Pe, and (E<sub>h</sub>) for Fe-N-H<sub>2</sub>O system.

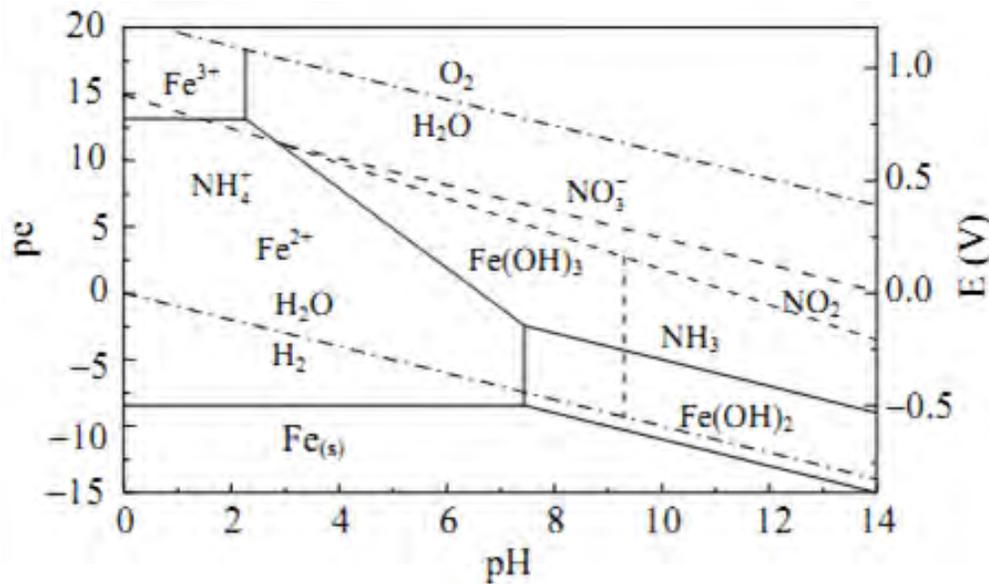
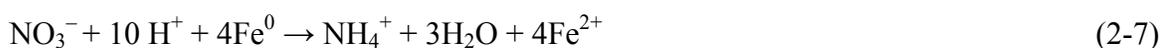


Figure 2.6 Pe-pH-E<sub>h</sub> diagram for Fe-N-H<sub>2</sub>O system (Pe is concentration of electrons in aque sol, E<sub>h</sub> is redox potential) (Solid lines are the boundaries for Fe species and dashed lines for N species) (Hao et al., 2005)

Also, as (2-6) and (2-7) indicate, the end products of the denitrification reaction by ZVI could vary according to the number of the protons involved in the reaction (ITRC, 2011).



Kinetics of nitrate reduction by ZVI under initial acidic condition can be described in a number of statements as follows:

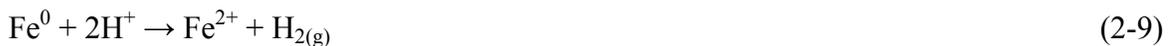
In the presence of dissolved oxygen, iron oxide coating (lepidocrocite [ $\gamma$ -FeOOH], outer layer, magnetite [ $\text{Fe}_3\text{O}_4$ ], inner layer) would form on the ZVI surface (Huang & Zhang, 2005). While the formation of lepidocrocite layer on the iron grains surface (2-8) may impede electron transfer from ZVI to  $\text{NO}_3^-$  as it is a semi-conducting material, magnetite layer as a highly reactive layer does not hinder the reductive denitrification process.



Also under this condition, ferrous ions  $\text{Fe}^{2+}$  and hydroxyl ions  $\text{OH}^-$  are released as (2-1) illustrates, and ferric ions are further formed (2-2) if adequate  $\text{O}_2$  is available (Yin et al., 2012). As elucidated in (2-3) and (2-4), in the presence of DO and under neutral or near-neutral condition, passive layers such as ferrous hydroxides  $\text{Fe}(\text{OH})_2$  and ferric hydroxides  $\text{Fe}(\text{OH})_3$  could form on the iron surface and; as a result, there could be a lag time before nitrate reduction takes place (Hao et al., 2005; Zhang et al., 2010).

The lag time could also be caused due to two other reasons including the existence of iron impurities or, the accumulation of hydrogen molecules on ZVI surface which would stay bound to the iron surface till their sizes become large enough to overcome the surface tensional force and release to the aqueous solution (Hao et al., 2005).

Once DO is depleted, lepidocrocite would gradually transform to magnetite (2-10) (Huang & Zhang, 2005). Also, ZVI will continue consuming hydrogen ions ( $\text{H}^+$ ) resulting in more ferrous ions being released (Fan et al., 2009). Meanwhile, due to the consumption of ( $\text{H}^+$ ) ions (2-9) and the release of ( $\text{OH}^-$ ) ions (2-5) that occur as result of the corrosive reaction, pH value would increase accordingly.



In fact, Nitrate can be best reduced when the solution pH is weak acidic (Hao et al., 2005). On the other hand, the more acidic initial pH, the higher the nitrate removal percentages. It is believed that low initial pH (around 2.5) is a very favorable condition for nitrate reduction by ZVI. Therefore, it is obvious from these previous statements that initial pH and the change in pH as the reaction proceeds have a significant effect on the reaction rate.

In other words, the reduction of  $\text{NO}_3^-$  by ZVI can be considered as an acid-driven process (Hao et al., 2005).

According to (2-10),  $\text{Fe}^0$  is the responsible agent for the transformation of lepidocrocite into magnetite (Huang & Zhang, 2005). However, ferrous ions released during corrosive reaction will enhance this process, and allow more efficient electron transfer from ZVI to the nitrate. Consequently, nitrate reduction reaction, which is greatly enhanced in the presence of hydrogen ions ( $\text{H}^+$ ), will take place thereafter (2-11) (Suzuki et al., 2012). Electrons required for nitrate reduction should come from ZVI, either directly or indirectly through the corrosive reaction products, ferrous iron ( $\text{Fe}^{+2}$ ) and hydrogen (Hao et al., 2005).



(2-12) indicates that ZVI, rather than ferrous ion, is the main electron source (Huang & Zhang, 2005). However,  $\text{Fe}^{2+}$  is still an essential agent in this reaction, which results in the formation of ammonium ( $\text{NH}_4^+$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) associated with the release of  $\text{OH}^-$  ions.



According to the results of some lab tests performed by Suzuki et al. (2012) and Choe et al. (2000), it can be deduced that although the increase in ZVI content would enhance the nitrate removal rate and subsequently, the removal efficiency, the increase in the ZVI dosage to more than a certain limit (vary according to the condition of the performed experiments) would still enhance the denitrification rate but not appreciably. Subsequently, a small increase in the removal efficiency would occur.

Also the results reported in the same two previous sources as well as the results obtained by Hao et al. (2005) have revealed that iron particles of smaller sizes could exhibit performance better than the one achieved by the use of bigger sizes. This can be attributed to the availability of more iron surface area that would enhance the performance of ZVI.

***Sulfate***

Sulfate ( $\text{SO}_4^{2-}$ ) is the stable form of sulfur at high redox potential ( $E_h$ ) level whereas sulfide ( $\text{S}^{2-}$ ) is the stable form at low  $E_h$ . (2-13) reflects the reversible reaction that can occur between water and hydrogen sulfide (ITRC, 2011).



At many field sites, reduction in sulfate concentrations has been observed as ground-water containing sulfate has passed through the ZVI barrier (Wilkin & Puls, 2003). This process results in the formation of an iron sulfide layer covering the ZVI media (He et al., 2008). A study extended for a period of about 8 years found that the formation of this layer has not revealed any observable loss of performance (ITRC, 2011).

In fact, Wilkin & Puls (2003) stated that reduction in sulfate concentrations in ZVI PRBs is owed to the presence of sulfate-reducing bacteria (*Desulfovibrio Desulfuricans*). The presence of these microorganisms; however, may lead to biofouling and therefore, a decrease in the hydraulic conductivity of the barrier. Shown below are the most possible biotic reactions that might occur in the presence of sulfate (Wilkin & Puls, 2003).

***Organic compounds***

A remediation strategy of organic contaminants is somewhat distinguishable from that of inorganic contaminants (Thiruvenkatachari et al., 2008). Since organic pollutants are multi-elements molecules they are degraded into harmless compounds such as water and carbon dioxide, whereas most inorganic pollutants are themselves elements (i.e. they do not degrade). The remediation of the inorganic pollutants occurs through transforming them into non-toxic (less harmful), immobile or not bio-available forms.

Reaction between ZVI and halogenated organic compounds results in the dehalogenation of organic compounds (Powell et al., 1998). In this reaction, which occurs at the iron metal

surface, the halogen group is replaced with hydrogen ion forming hydrocarbon products if the process (dehalogenation) continues to the end (2-16).



Reductive dechlorination of chlorinated organic compounds such as TCE found to be significant when  $\text{pH} > 6$ , using pyrite ( $\text{FeS}_2$ ) as reactive media, whereas the effect of  $\text{pH} < 6$  on this process is found to be insignificant (ITRC, 2011).

## 2.2.2 Berea Red Sand (BRS) and Umgeni Sand (US)

BRS and US are local sands. They are both easily available and widely spread in the region, KwaZulu-Natal Province (Hamel, 2006). Therefore, the cost of these materials is reasonable. In addition to the abundance of BRS in KwaZulu-Natal, it is also profusely available in Mozambique (Bergh et al., 2008).

BRS and US belong to one of the strata that contribute to the formation of the Umgeni Valley (Fanni, 2007). This stratum consists of silt, dark grey clay, fine, medium and coarse sands. BRS has mineral compounds, one of which is hematite ( $\text{Fe}_2\text{O}_3$ ). As will be illustrated in the following chapter, BRS has dark red colour which is attributed to the oxidation and reduction of the iron components that this material consists of naturally. US, on the other hand, consists mainly of quartz ( $\text{SiO}_2$ ) (Fanni, 2007).

According to Fanni (2007), US has demonstrated weak potential to remove the arsenic from arsenic-contaminated effluents whereas BRS has indicated a greater arsenic removal efficiency, especially when this material was mixed with the ZVI material. In fact, Fanni (2007) found that the removal of the arsenic compounds when BRS used, was mainly through the adsorption of these contaminants onto the surface of the hematite.

## 2.3 PRB Design and Emplacement Techniques

### 2.3.1 PRB design

Designing PRB system requires a team consisting of different types of professionals (ITRC, 2005). Depending on the nature of site, team members are selected. The potential members that may be included in the team are presented in Figure 2.7.



Figure 2.7 Potential members involved in PRB design and construction team (after ITRC, 2005)

In order to commence a remediation project such as designing PRB system, various factors have to be considered in advance (Gavaskar, 1999):

- Suitability of a site for PRB application,
- Site features influencing PRB design,
- Reaction rates,
- Location, configuration, and dimensions of PRB,
- Longevity,
- Monitoring strategy,
- Cost.

The following is a brief explanation of each of these factors (Gavaskar, 1999; ITRC, 2005).

- Suitability of a site for PRB application  
Preliminary assessment of the site is the first necessary step to be addressed. Information about ground-water velocity, type of contaminants, contaminants

distribution as well as geotechnical consideration is the main part of this assessment. In fact, addressing these factors is essential in order to attain a realistic preliminary assessment for the feasibility of the technique in terms of cost, geo-technicality, and administration. Despite the fact that none of these factors are insurmountable, some of them; however, can raise the cost of the project.

Chemicals that contaminate the site need to be identified in order to know whether the available reactive media are able to remove them. Contaminants distribution and ground-water velocity are taken in consideration for barrier cost assessment. The wider or the deeper the plume is, the higher the cost expected, and the fast ground-water flow will also need a thick barrier to ensure sufficient residence time for the contaminants to be degraded. As for geotechnical considerations, the existence of highly consolidated sediments over the ground-water plume layer may hinder the installation process.

- Site features influencing PRB design

Since a PRB system is almost a permanent structure, and its modification or relocation is costly and difficult, a good-understanding of the site characteristics is important in designing and constructing a proper barrier system. Contaminants distribution, in particular, should be defined precisely as it helps greatly in selecting the right configuration and the suitable location for the barrier.

Additionally, information about depth and thickness of the various ground-water layers near the prospective barrier location has to be collected. Conventional drilling rigs have been used for collecting this information though recently, new techniques such as cone penetrometer testing (CPT) and GeoProbe, have been used for this purpose. They have the potential to sample ground-water at different depths by which a map for the plume can be depicted. Therefore, by identifying various hydrostratigraphic units in the subsurface using the new techniques, the regulators will be enabled to determine the altitude and the height of the barrier.

- Reaction rates

The main objective of identifying reaction rates or half-lives of contaminants is to design an appropriate barrier thickness in order to provide a sufficient residence time for the contaminants to be broken down.

Batch and column tests have been used to define the half-lives of contaminants. However, since column tests have been found to be a better way for estimating contaminant degradation rate, it has become more widely used and more common.

Temperature is an essential factor that needs to be taken into consideration as it may affect the reaction rate. Column experiments are usually run at room temperature. In contrast, the flow-rate through a column test may not be a critical factor. However, collecting good data about ground-water velocity is still preferable.

pH and redox potential ( $E_h$ ) are also another parameters that have to be measured periodically during the test. Ion chromatography (IC) and inductively coupled plasma (ICP) are used to measure anions and cations respectively.

- Location, configuration, and dimensions of PRB

As explained earlier in the first point (suitability of a site for PRB application), appropriate location of the barrier is determined according to geotechnical, hydrologic, and administrative considerations.

From the viewpoint of hydrologists, sandy strata is a preferable layer to place the barrier whereas from a geotechnical prospective, avoiding underground utilities is essential to be considered in selecting a suitable place for the barrier. Like the scenario at Dover site, when underground utilities are existent at hydrologically optimal location, the geo-technicians prospective would then be more significant, and it would be required that the barrier be placed away from the underground utilities.

PRB system has a number of configurations which only one of them at a given time is nominated to be used according to the site condition. Continuous reactive barrier and a Funnel-and-Gate system are the most common configurations. Funnel-and-Gate

system consists of two impermeable walls on either side of the reactive zone, whereas the Continuous one consists of a reactive cell only.

During the first time after PRB technology has emerged, Funnel-and-Gate configuration was used-more due to the high cost of granular iron (reactive cell) at that time. When the price of granular iron dropped, most of the sites started installing the Continuous system instead. However, in some cases, the use of Funnel-and-Gate system is still much better. For example, at Dover site, Funnel-and-Gate configuration was the preferred system to be used for two reasons. The first reason is that the Continuous system was difficult to install due to the existence of underground utilities in the unsaturated zone over the plume. Secondly, the plume was too deep for the use of new cost effective installation techniques.

As for determination of suitable barrier dimensions (i.e. width, thickness, and depth), a number of factors need to be taken into account. Width and thickness of barrier is partially dependent on chosen configuration.

The thickness of the barrier may vary based on many factors such as the width of the funnel, funnel-to-gate ratio (in the case of a Funnel-and-Gate configuration), reaction rate of contaminant, as well as the relative hydraulic conductivities and porosities of the aquifer and the reactive cell. This is due to the fact that the determination of the barrier thickness is dependent on the residence time as well as the ground-water velocity (the velocity through the reactive cell). The residence time required depends on the contaminant reaction rate when reactants come into contact whereas the ground-water velocity may change based on all the other factors. Moreover, the funnel-to-gate ratio and the width of the funnel (in a Funnel-and-Gate system) are based on the relative hydraulic conductivities of the proximate aquifer and the gate (reactive cell) as well.

Historical water table of the site as well as the depth of aquitard is considered in determining the depth of the barrier. The top of the barrier is normally placed above the highest water table that has ever been recorded. Nevertheless, reaching the water

table to a level lower than the top of the barrier so that the iron cell gets exposed to unsaturated zone air, is a case that is still not well understood.

- Longevity

Longevity of the PRB can be defined as the age of the reactive cell to maintain its permeability and reactivity. These two parameters can be affected mainly by inorganic precipitates that may form when ground-water passes through the reactive cell, and subsequently a decline in the barrier performance may occur. Some precipitates which are colloidal in size; however, could still pass the reactive cell with ground-water flow.

Another factor that has an effect on barrier longevity is dissolved oxygen. When the reactive medium is 100% Zero Valent Iron, DO would react quickly with iron and form precipitates that occlude the reactive cell. For this reason, pretreatment zones such as a mix of iron and sand, and/or pyrite and sand, are added in order for the plume to pass through them before it passes through the iron cell.

As the plume passes through the iron and sand mixtures, DO reaction rate will slow down due to the small iron surface area that would be made whereas the purpose of pyrite and sand mixture is to control pH for better precipitation control as well as to reduce oxygen.

Column tests and geochemical models can be used to estimate the quantity of precipitates that would be formed when the contact between reactants occurs. Using accelerated column tests through which ground-water is run at rates faster than the detected rates at the prospective site is a way of testing the long-term performance of the reactive cell.

- Monitoring strategy

Monitoring plan is a necessary step that needs to be prepared. It should start immediately after installation of PRB is done. Assessing performance and longevity is achieved through monitoring three main factors including ground-water geochemistry,

hydraulic flow characteristics around and through the barrier, and target contaminants and their breakdown products.

- **Costs**

Estimating the cost of PRB deployment is not a simple duty because of the fact that series of factors need to be assessed, many of which are not well documented. Since estimating life cycle of reactive media is difficult, replacement or replenishment of the reactive cell is considered as one of those factors. The cost factors included for assessing the overall cost of a PRB project are:

- Site characterization expenses
- Design expenses
- Construction expenses
- O&M expenses
- Miscellaneous & unexpected expenses

It is believed that among all these factors, construction is the major cost factor.

### **2.3.2 Emplacement techniques and comparisons**

Various techniques are available for the construction of the barrier (Gavaskar, 1999). However, due to some site characteristics, these methods could be limited. Characteristics which need to be considered include (Gavaskar, 1999):

- **Waste concerns**

This component is crucial to be considered in the selection of construction technique in terms of two main aspects that can affect the whole process: one is the waste handling and disposal costs, and the other is the potential impact in the high-traffic area. Obviously the one that generates less waste and avoids disruption of daily activities in these traffic areas would be preferable.

- **Geotechnical considerations**

The presence of highly solid layers such as cobbles or solid sediments may hinder construction methods selected. In addition, the presence of underground utilities or aboveground structures, such as buildings may also limit the techniques used.

- Installation Depth

Installation depth, which is another contributor to construction cost, is the depth to aquitard. Deeper installations cost more than shallower ones. This component is considered to be significant in the selection of construction technique used. In addition to the higher cost and the longer construction time that deeper installations take, they require more specialized equipment.

- Health and safety

Commonly, environmentally toxic substances are not allowed during construction. Techniques that entail entry of workers into excavations may demand quite more precautionary measures, and observation.

Conventional and innovative techniques that could be involved in PRB installations are summarized in Table 2.1.

Table 2.1 Summary of several techniques for barrier construction (after Gavaskar et al., 2000)

Construction Techniques	Vender-Quoted Cost <sup>(*)</sup>	Maximum Depth (m)
<b>Sheet Pile and Slurry Wall Installation</b>		
Cement – Bentonite slurry wall		
➤ Standard backhoe excavation	\$43.6 – 239.6/ m <sup>2</sup>	9.1
➤ Modified backhoe excavation	\$43.6 – 239.6/ m <sup>2</sup>	24.2
➤ Clamshell excavation	\$174.2 – 599/ m <sup>2</sup>	60.6
Soil – Bentonite slurry wall		
➤ Standard backhoe excavation	\$21.8 – 108.9/ m <sup>2</sup>	9.1
➤ Modified backhoe excavation	\$21.8 – 108.9/ m <sup>2</sup>	24.2
➤ Clamshell excavation	\$65.3 – 185.1/ m <sup>2</sup>	45.5
Steel sheet piles	\$163.4 – 326.7/ m <sup>2</sup>	18.2
Sealable – Joint piles	\$163.4 – 326.7/ m <sup>2</sup>	18.2
Composite slurry wall	Not Applicable	30.3 +
Geomembrane barrier	\$413.8/ m <sup>2</sup>	12.1 – 15.2
<b>PRB Installation</b>		
Continuous trenching	\$54.5 – 130.7/ m <sup>2</sup>	7.6
Caisson – based construction	\$165 – 990/ vertical m	15.2 +
Mandrel – based construction	\$108.9 – 272.3/ m <sup>2</sup>	12.1 – 15.2

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Jetting	\$435.6 – 2178/ m <sup>2</sup>	60.6
Deep soil mixing	\$104.5 – 261.2/ m <sup>3</sup>	45.5
Hydraulic fracturing	\$2,300 per fracture	24.2 – 36.4
Vibrating beam	\$87.1/ m <sup>2</sup>	30.3

(\*) does not include mobilization cost

**CHAPTER 3**  
**MATERIALS & METHODS**

## **INTRODUCTION**

This chapter explains in detail the methodological approach by which the objectives of this study were achieved. Batch experiments were set up, and essential variables had to be analyzed. These batch trials were performed in order to simulate the processes that occur in the PRB system. The main components of the batch experiments are the solid and liquid reactants. Three different main solid reactants (ZVI, BRS, US), and two liquids (distilled water, nitrate synthetic solution) were involved in this study.

As mentioned in the introduction, BRS was involved in this study for several reasons including: its reasonable cost, its abundance, and its active components, hematite in particular. The presence of hematite could contribute to the removal of the nitrate through adsorption processes.

US, on the other hand, was selected in this study to be used as a control substrate since it is not expected to cause any change in the nitrate concentration.

In addition to distilled water, a synthetic solution was used in this study in order to simulate nitrate-contaminated ground-water. Since this research aimed at evaluating the efficiency of different substrates in the nitrate removal process, five nitrate concentrations were investigated.

All the experiments and tests conducted for this research were undertaken at the UKZN Environmental Engineering Laboratory. Repeatability was ensured by performing all the tests in triplicate.

### 3.1 Solid Reactants

#### 3.1.1 Zero Valent Iron

ZVI ( $\text{Fe}^0$ ) is the most commonly used material in PRBs. It has multiple advantages in terms of ease of availability, the potential to treat a series of contaminants (organics and inorganics) efficiently, and cost efficiency amongst others, which have resulted in its common usage (Powell et al., 1998).

This type of granular ZVI was imported from Gotthart Maier Metallpulver GmbH (Germany), hence its name GmbH ZVI. It is characterized by coarse particles with a size of 1 to 2 mm (Fanni, 2007). Figure 3.1 shows the type of the ZVI that was used in our batch experiments.



Figure 3.1 Sample of GmbH Zero Valent Iron

#### 3.1.2 Berea Red Sand and Umgeni Sand

As was indicated in Chapter 2, both BRS and US are locally available materials, and belong to one of the strata that contribute to the formation of the Umgeni Valley. BRS has mineral compounds, one of which is hematite ( $\text{Fe}_2\text{O}_3$ ), whereas US consists mainly of quartz ( $\text{SiO}_2$ ) (Fanni, 2007). Figure 3.2 shows samples of both BRS and US.



Figure 3.2 Samples of BRS (right) and US (left)

## 3.2 Liquid Reactants

### 3.2.1 Synthetic nitrate solution

Potassium nitrate ( $\text{KNO}_3$ ) solution was one of the liquids that used in batch tests. This solution was prepared in the lab by dissolving a certain mass of potassium nitrate into a certain volume of distilled water, depending on what nitrate concentration and what solution volume needed to be prepared.

In the preparation of the solution the molar mass of  $\text{KNO}_3$  and  $\text{NO}_3$  considered were 101.1 g/mol and 62 g/mol respectively. Therefore, the formula used in the solution preparation was as follows:

$$\begin{aligned} X (\text{NO}_3, \text{mg/l}) & \dots\dots\dots 62 \text{ g/mol} \\ Y (\text{KNO}_3, \text{mg/l}) & \dots\dots\dots 101.1 \text{ g/mol} \end{aligned}$$

Where,

- X: required solution concentration with respect to nitrate (known), mg/l
- Y: calculated solution concentration with respect to potassium nitrate (unknown), mg/l

Rather than using real contaminated ground-water, a synthetic potassium nitrate solution of various concentrations was used as a nitrate-contaminated ground-water simulator.

Concentrations prepared in this study were 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l.

### 3.2.2 Distilled water

Distilled water was the other liquid part used in this study. Since this liquid is almost free of impurities, it was used, in eluate tests, with each substrate that was used in the batch experiments in order to have a clear understanding of the potential effects of each substrate on the synthetic solution that it mixed with. This was assessed by means of measuring the physical and chemical properties of distilled H<sub>2</sub>O before and after mixing with the substrates.

## 3.3 Solid Reactants Characterization

Characterization conducted on solid substrates included porosity test, physical characterization, sieve analysis, and chemical and mineralogical characterization.

### 3.3.1 Porosity test (Fanni, 2007)

Porosity ( $n$ ) is defined as the ratio of the volume of the voids of a sample to the bulk or total volume of that sample.

$$n = \left( \frac{V_v}{V_{\text{tot}}} \right) * 100 \quad (3-1)$$

Since soil consists of voids and solid particles, total volume is expressed as follows:

$$V_{\text{tot}} = V_s + V_v \quad (3-2)$$

Where,

$V_s$  : volume of solids

Generally, fluid saturation in a sample is defined as the volume of the fluid to the volume of the voids, and it is expressed as follows:

$$S_f = \frac{V_f}{V_v} \quad (3-3)$$

Where,

$S_f$ : fluid saturation in a sample

$V_f$ : volume of fluid in the sample

Saturation and porosity are both expressed as percentages.  $S_f$  is equal to 100% when the sample measured is completely saturated.

Void ratio ( $e$ ) is a parameter that defined as the ratio of the volume of voids to the volume of solids, and it is expressed as follows:

$$e = \frac{V_v}{V_s} \quad (3-4)$$

It is also related to porosity through this equation

$$e = \frac{n}{1-n} \quad (3-5)$$

Porosity can also be determined using (3-6):

$$n = 1 - \frac{D_r}{G_s} \quad (3-6)$$

Where,

$$D_r \text{ (Relative Density)} = \frac{M_s}{V_{tot}} \quad (3-7)$$

$$G_s \text{ (Specific Gravity)} = \frac{M_s}{V_s} \quad (3-8)$$

$M_s$ : mass of solids

Note that  $V_{tot}$  is the total volume of the same sample whose mass was considered in the equation.

In this study, as will be explained in the following paragraphs, porosity was determined using (3-1) whereas  $V_{tot}$  was calculated from (3-7), and  $V_v$  was calculated from the following equation.

$$V_v = V_{\text{tot}} - V_s \quad (3-9)$$

Because  $V_s$  and  $D_r$  are two unknown parameters, and they are both involved in the determination of porosity, the determination of each parameter was achieved in separate experiment as follows:

***Determination of the volume of solids ( $V_s$ )***

Materials involved in this experiment include:

- Air Pump
- Volumetric flask of 250 ml capacity
- Vacuum desiccator
- Two valves for the inlet of air and de-oxygenated water
- Rubber tubes for the connection

A schematic view for the determination of the volume of solids is illustrated in Figure 3.3.

The experiment was performed following these procedures:

1. Weigh the volumetric flask and record the mass ( $M_f$ ).
2. De-oxygenate 1 L of de-ionized water by diffusing nitrogen for half an hour.
3. Pass a representative sample through a 4.75 mm sieve, oven-dry it for 24 hours at 105°C and then weigh it (this will be mass of solid,  $M_s$ ).
4. After the sample cools, place it inside the flask and put the flask inside the desiccator.
5. Create vacuum in the desiccator (valve 1 opened, valve 2 is closed).
6. Inject de-oxygenated water into the flask (valve 1 closed, valve 2 opened), followed by pumping air in order to get rid of any air bubbles trapped inside the voids (valve 1 opened, valve 2 closed).
7. Repeat step 6 until all trapped bubbles have escaped.
8. Fill the volumetric flask with the de-oxygenated water up to its full capacity (250 ml), and then weigh it (this will be considered the total mass,  $M_{\text{tot}}$ ).

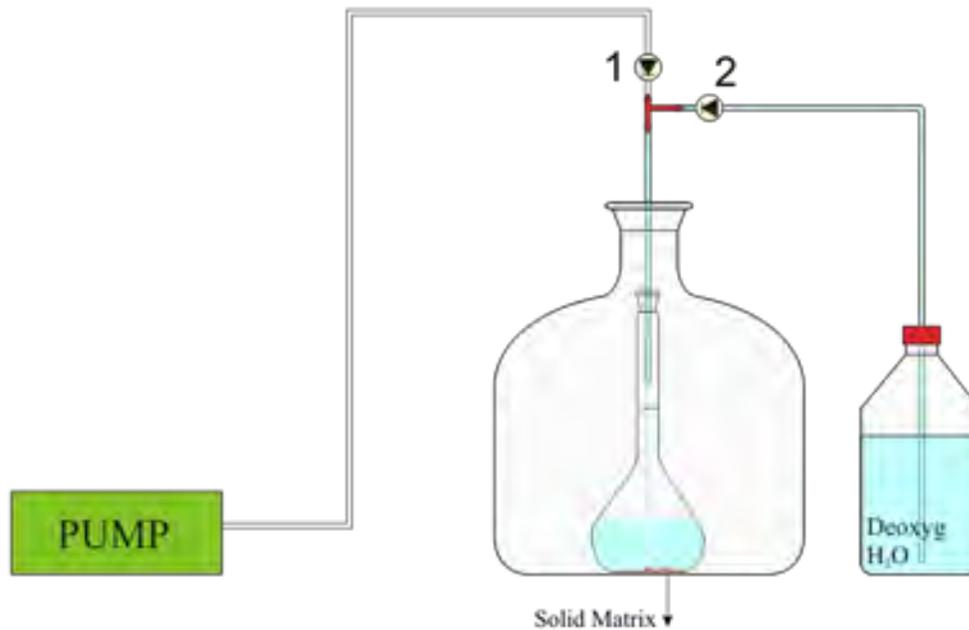


Figure 3.3 An illustration for the procedures of solids volume determination (Fanni, 2007)

9. Determine the water mass ( $M_w$ ) present in the flask as follows:

$$V_w = M_w = M_{\text{tot}} - M_f - M_s \quad (3-10)$$

10. Determine the volume of solids ( $V_s$ ):

$$V_s = 250 \text{ ml} - V_w \quad (3-11)$$

#### ***Determination of relative density ( $D_r$ )***

A 500 cm<sup>3</sup> capacity cylinder was weighed and filled with the sampled soil that was already oven-dried and sieved through a 4.75 mm sieve. This filling was done gradually, with occasional soft tamping.

The full cylinder was weighed neglecting approximations, and then by subtracting the cylinder mass from the full cylinder mass, the mass of solid (soil) was determined. Since  $M_s$  was now known, and total volume was 500 cm<sup>3</sup>,  $D_r$  was then determined using (3-7). The procedures for determining  $M_s$  was repeated 5 times and an arithmetic mean of these values was considered in order to get a better estimation for relative density.

After the determination of both  $V_s$  and  $D_r$ , porosity of the soil was determined as follows:

Using the mass of solid ( $M_s$ ) determined in step 3, and ( $D_r$ ), total volume ( $V_{tot}$ ) is determined through (3-7). Thereafter, considering volume of solids ( $V_s$ ) determined in step 10, and  $V_{tot}$ , the volume of voids is calculated and thus, all parameters needed to determine porosity by (3-1) become known.

### 3.3.2 Physical characterization

#### 3.3.2.1 Moisture content (MC)

The moisture content of a sample is defined as the ratio of the mass of water in the sample to the total mass of that sample. Therefore, it is a dimensionless parameter and is expressed only in percentage. In this study, the moisture content characterization was done for both BRS and US as they are the only substrates that had moisture content. This characterization was performed in order to consider the moisture content values in the set-up of the batch and eluate experiments that contain BRS or US.

Four crucibles were used for the measurement of moisture content in order for results to be more precise. After weighing the four empty crucibles, each of them was filled to one third with a sample of the wet substrate, weighed and then placed in oven at 105 °C overnight. Thereafter, the four crucibles (with dry sample) were taken out the oven and weighed again.

The moisture content of each sample was calculated, and the average was considered to represent the moisture content of the whole substrate. The following equation was used to calculate the moisture content:

$$MC (\%) = \frac{(M_w - M_d)}{M_w} * 100 \quad (3-12)$$

Where,

$M_w$ : Mass of a wet sample (before putting in the oven), (g)

$M_d$ : Mass of a dry sample (after putting in the oven), (g)

### 3.3.2.2 Total solids (TS)

Total solids of a sample can be defined as the ratio of the solid mass to the total mass of the sample. The same procedure as the one used for MC, is performed in drying the sample. (3-13) was used to calculate TS:

$$TS (\%) = \frac{M_d}{M_w} * 100 \quad (3-13)$$

Because MC and TS are complementary parameters, and together sum up to 100, MC can be calculated from TS and vice versa. (3-14) demonstrates the relation between MC and TS.

$$MC (\%) = 100 - TS \quad (3-14)$$

### 3.3.2.3 Volatile Solids (VS)

Volatile solids are defined as the solids that are volatilized on ignition of the dry solids at 1,022°F (Baxter & Rexing, 2005). Measuring VS is a step that comes after the steps followed in measuring TS or MC. In other words, after the dry samples were taken out the oven to weigh them for TS or MC calculations, the same samples were placed into a furnace (Figure 3.4) for two hours at 550°C. Thereafter, the samples were taken out and weighed after they became cool enough. The mass of these samples were used in the following equation to calculate VS.

$$VS (\%) = \frac{(M_d - M_{\text{fired}})}{M_d} * 100 \quad (3-15)$$

Where,

$M_{\text{fired}}$ : Mass of dry samples after they are taken out the furnace, (g)



Figure 3.4 Furnace used in evaporating volatile solids in dry samples

### 3.3.3 Sieve analysis

Sieve analysis, which is also called gradation analysis, involves a column of sieves with various diameters used to evaluate the particle size distribution of a solid substrate. Consequently, this would enable a better understanding of the hydraulic conductivity of the analysed substrate. In fact, well-graded soil may have a lower permeability than poorly-graded soil.

These are the procedures that were followed to perform this test (Fanni, 2007):

- A representative amount of the investigated soil was divided into four quarters, as illustrated in Figure 3.5, two of which were taken out, and the other two were mixed and quartered again. This step was repeated until two quarters of the four became of a size that similar to the sample size required for the analysis (more than 500 grams).
- The two quarters were then mixed together and placed into the oven for 24 hours at 105°C.
- Thereafter, a sample of 500 grams (initial total mass) of the oven-dried soil was washed inside a 4.75 mm sieve, while a 0.063 mm sieve is placed underneath, until any cohesive particles that might be present in the sample have broken into individual particles.

### CHAPTER 3 – MATERIALS AND METHODS

- The masses retained in both sieves were poured into a pan together, and placed back into the oven for 24 hours again.
- The oven-dried sample was then poured into 9.5 mm sieve while the following different sizes of sieves are placed in descending order underneath: 6.7 mm, 4.75 mm, 2 mm, 1.18 mm, 0.6 mm, 0.425 mm, 0.3 mm, 0.15 mm, 0.075 mm, 0.063 mm, and a pan at the bottom.
- These sieves were then put on the shaker, which was switched on thereafter for  $\pm$  5min.
- The retained mass on each sieve was weighed and recorded.
- The mass of the soil that passes the 0.063 mm sieve was determined by subtracting the summation of the masses retained on all the sieves from the initial total mass of the soil.



Figure 3.5 Representative sample preparation

- The cumulative mass of retained soil on each sieve as well as the mass of the soil passed through each sieve was then calculated.
- The mass of soil passed through each sieve was then calculated in percentage.
- By using a semi-logarithmic scale and plotting the diameters of the used sieves on the X axis and the masses of the soils passed through each sieve in percentage on the Y axis, the grading curves, as shown in Chapter 4, were obtained.

These plots are used to determine the uniformity coefficient ( $C_u$ ) of the analysed soils through this equation:

$$C_u = \frac{D_{60}}{D_{10}} \quad (3-16)$$

Where,

$D_{60}$ : diameter corresponding to 60% finer.

$D_{10}$ : diameter corresponding to 10% finer.

The  $C_u$  of a well-graded soil is greater than 4 for gravels and 6 for sands whereas it can be close to the unit if the soil is poorly-graded (Fanni, 2007). In addition to the degree of the soil particles gradation,  $D_{10}$  could also be used as a measure of the hydraulic conductivity of soil.

### 3.3.4 Chemical and mineralogical characterization

Since the ZVI material used in this research is from the very same source that was used in research carried out by Fanni (2007), the chemical and certain granulometric characterizations of the ZVI were not performed again as the results would be the same as those received in 2007.

As for the mineralogical characterization of BRS as well as US, it was re-conducted at UKZN rather than using the same results received in 2007. This was due to the potential changes that may occur in the substrates' characteristics as a result of their exposure to the atmosphere. XRD - X-ray Diffractometer was the technique used for this scope. Figure 3.6 shows a simple illustration of the XRD technique.

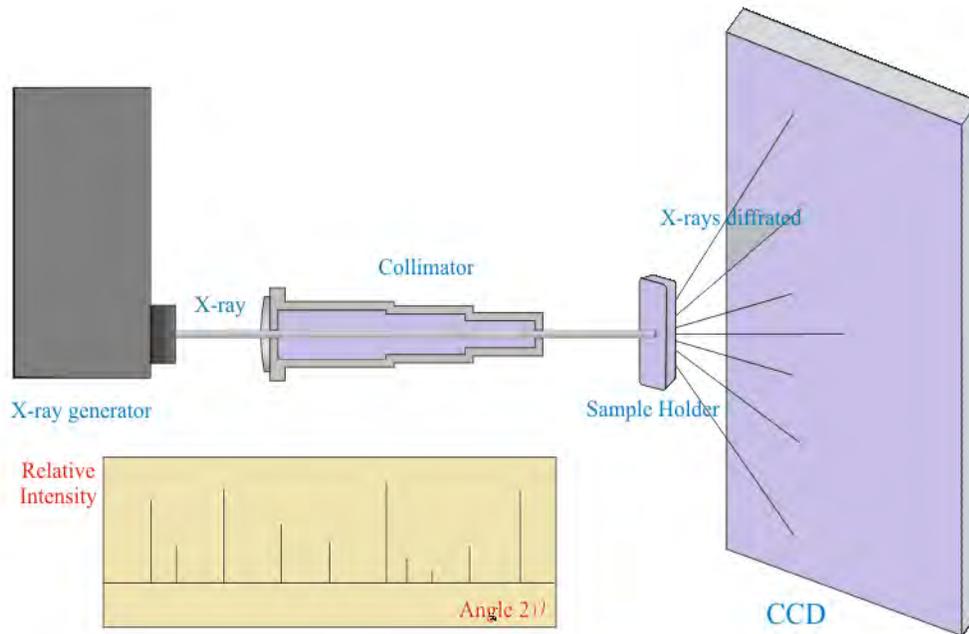


Figure 3.6 Illustration of XRD - X-ray Diffractometer (after Fanni, 2007)

### 3.4 Liquid Characterization

Liquid characterization was performed for the eluate and the batch tests as well as for each liquid (synthetic solution and distilled water) on its own. This characterization included the measurement of variables such as pH, dissolved oxygen (DO), conductivity (C), total dissolved solids (TDS), redox potential ( $E_h$ ), total dissolved iron (Fe) concentration, and nitrate concentration ( $\text{NO}_3$ ).

#### 3.4.1 pH

Two ranges of calibrations were used for pH measurement, (4 – 7) and (7 – 10). The pH meter was calibrated only at one range a time, and this range was chosen depending on in what status (acidic or basic) the sample might be. The calibration did not need to be done before each reading unless the next sample was in a state different to the preceding one. Samples drawn for pH analysis were about 5 ml each.

Measuring pH was done via the use of:

- ORION Model 410 A (Figure 3.7) with

- Probe: Orion 9107 BN Low Maintenance pH Triode

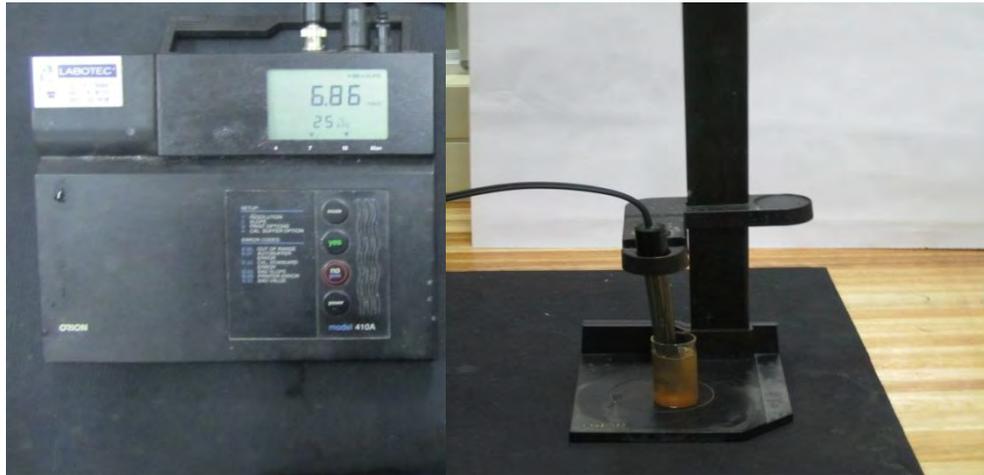


Figure 3.7 pH-Meter and measurement of the pH

### 3.4.2 Dissolved oxygen (DO)

Measuring dissolved oxygen was done by plunging the DO probe directly into the bottle that contains the tested sample, and covering it up with parafilm as soon as possible afterwards. Once the reading stabilizes for 1 minute, the measurement was taken. DO is measured in (mg/l). Figure 3.8 displays the instruments used in this process, and the way measuring DO was approached. These instruments are:

- YSI Model 50B Dissolved Oxygen Meter;
- Probe: YSI 5740



Figure 3.8 YSI Model 50B Dissolved Oxygen Meter and measurement of DO

Calibration of DO meter was done as specified in the instrument manual (YSI Model 50B Dissolved Oxygen Meter Instructions Manual).

### 3.4.3 Conductivity (C) and total dissolved solids (TDS)

The conductivity of a solution is an explanation of its ability to pass electrical current. This ability varies from one solution to another depending on what kind of ions are existent in the solution. Even though, the conductivity meter used in this study defines how conductive a solution is, it does not specify what ions are present.

The conductivity meter used in this study was a multi-range conductivity meter (0  $\mu\text{S}/\text{cm}$  – 199.9  $\mu\text{S}/\text{cm}$ , 0  $\mu\text{S}/\text{cm}$  – 1999  $\mu\text{S}/\text{cm}$ , 0  $\mu\text{S}/\text{cm}$  – 19.99  $\text{mS}/\text{cm}$ , 0  $\mu\text{S}/\text{cm}$  – 199.9  $\text{mS}/\text{cm}$ ) each of which was represented by one button made on the meter. The number of calibration solutions is as many as the ranges. However, only one solution was used at a time to calibrate the meter. The instrument manual (Multi-Range Conductivity Meters for Laboratories Instruction Manual) was followed in calibrating the meter. Recalibration is necessary if unexpected results are noticed.

Once the meter was calibrated, the probe was then placed into the sample that the top holes of the probe are immersed inside the sample (Figure 3.9). By using those four buttons and starting with a minimal range, moving from one range to another was done if the reading fell outside of the selected range. The meter then gives a stabilized reading in a few minutes.

Conductivity is a measure of the specific conductance within a given sample, and is measured in milliSiemens (mS) or microSiemens ( $\mu\text{S}$ ). The equation that relates conductivity with conductance is (Fanni, 2007):

$$C = G * \frac{L}{A} \quad (3-17)$$

Where,

C = conductivity [mS/cm]

G = conductance [mS]

L = distance between plates [cm]

$A = \text{area of 1 plate [cm}^2\text{]}$

Conductivity was measured using the following meter:

- EC 215 Conductivity Meter, Hanna Instruments (Figure 3.9)



Figure 3.9 Conductivity Meter and measurement of conductivity

As for Total Dissolved Solids (TDS), it is a parameter that can be measured indirectly from the conductivity value. It is linked to conductivity by the following equation (Fanni, 2007):

$$\text{TDS} = C * 0.5 \quad (3-18)$$

Where,

TDS is measured in (mg/l).

#### 3.4.4 Redox potential (ORP/ $E_h$ )

Redox potential and oxidation reduction potential are different terms but with the same meaning.  $E_h$  is the corrected (indirect) reading of the measured potential of platinum electrode, whereas ORP is the uncorrected (direct) potential reading of the reference electrode (Wilkin et al., 2002). The electron acceptors are arranged in terms of their oxidizing potential in descending order as follows: oxygen, nitrate, manganese, ferric iron, sulphate, and carbon dioxide (Riser-Roberts, 1998).

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Measuring redox potential in a sample was performed by magnetically stirring the sample for about 30 seconds. Thereafter, the stirring rate was lowered to about 10 rpm, and the electrode was placed into the sample that should be covered again afterwards (Figure 3.10). Once “mV” sign, that appears on the meter screen, stops flashing the reading was taken for ORP. The sample drawn for redox potential analysis must fill a vial in which the sample is placed in.

The measurement unit of these parameters is millivolt (mV). The following instruments were used to measure redox potential:

- Thermo Electron Corporation ORION 2 Star pH Benchtop (Figure 3.10);
- Probe: Orion 9179BNMD Triode Electrode (Figure 3.10)



Figure 3.10  $E_h$ -Meter and measurement of  $E_h$

$E_h$  was then calculated from the following equation (Wilkin et al., 2002):

$$E_h = \text{ORP} - \text{ORP}_{(\text{reference solution})} + E_h(\text{reference solution}) \quad (3-19)$$

Both  $\text{ORP}_{\text{reference solution}}$  and  $E_h(\text{reference solution})$  were obtained during the calibration of the redox potential meter. The difference between these two values was always around 200.

Calibration of  $E_h$ -Meter was only done once before the first use; however, if the readings started changing to unexpected values then recalibration would be necessary. Instrument manual (ORION APLUS Benchtop pH and pH/ISE Meters Instruction Manual) was followed in calibrating the meter in which the use of Orion 967901 solution was recommended.

### 3.4.5 Total dissolved iron (Fe)

For better comprehension of the nitrate reduction kinetics that occur during the batch experiments, the total dissolved iron concentration, as one of the essential indicators, was measured for the times that will be indicated later in this chapter.

An inductively coupled plasma-optical emission spectrometer (ICP-OES) (Figure 3.11) was used to determine the total dissolved iron concentration in the samples that need to be analysed. The method used for the preparation of ICP samples was from the EPA METHOD 200.7 (U.S. EPA, 1994).



Figure 3.11 Optical Emission Spectrometer OPTIMA 5300 DV Perkin Elmer

ICP samples, which were about 4 ml each, were first filtered through 0.45  $\mu\text{m}$  filter paper using Millipore Swinnex (Figure 3.12). Then 0.4 ml of nitric acid was added to each sample for proper preservation. Nitric acid was prepared by adding 500 ml of concentrated  $\text{HNO}_3$  to 400 ml reagent water, and diluted to 1000 ml. Immediately prior to ICP analysis, the samples were pH tested to ensure that it is less than 2 which is an indication of a proper preservation.

Standards that were prepared from 100 mg/l iron solution and used in this analysis are: 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, and 10 mg/l. A transfer pipette (Figure 3.12) was used to get an aliquot of the volumes required for the preparation of these six standards. A calibration curve was made before the analysis of the samples in order to ensure that the standards are prepared correctly. The calibration curve has to be made again before the analysis if different standards need to be prepared or even when the same standards need to be re-prepared.

The wavelength adopted in this study to analyse iron were 238.204 nm, 239.562 nm, and 259.939 nm respectively. The measurement unit of the total dissolved iron concentration is mg/l.

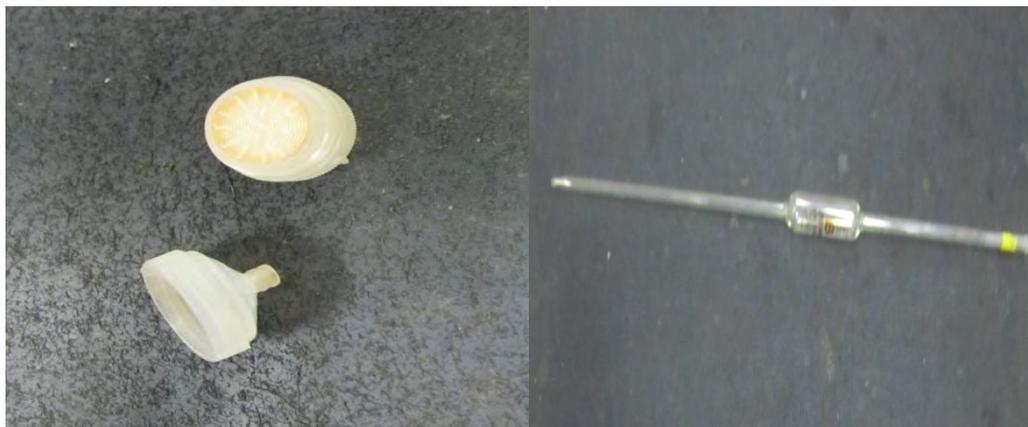


Figure 3.12 Millipore Swinnex (left) and transfer pipette (right)

#### **3.4.6 Nitrate concentration (NO<sub>3</sub>)**

Measuring nitrate concentration was the main indicator of the efficiency of the various substrates. The better substrate in performance is the one that reduces the same or higher nitrate concentration to the maximum allowable limit (15 mg/l) in less time. In other words, the better substrate in performance is the one that demonstrates higher nitrate removal rate.

Periodically, one millilitre of the aqueous solution was withdrawn by a syringe into a small vial (Figure 3.13). The concentration of nitrate is then determined via nitrate test sticks.



Figure 3.13 The manner of sample collection (Fanni, 2007)

The nitrate test stick was dipped into the sample for a moment, and then after one minute the colour, that appears on the stick and which represents the nitrate concentration in that sample, was compared with the colours made on the nitrate test sticks container (Figure 3.14). When the measuring stick appeared in a colour that is not clearly identifiable, the drawn sample was then filtered, and the concentration was measured again. Also, if the stick detects any presence of nitrite, a few drops of sulphamic acid will then have to be added to the sample, and the nitrate reading is taken again.



Figure 3.14 Nitrate stick and sticks container with the various concentrations reference on it

In measuring concentrations higher than 100 mg/l in a sample, the certainty about the nitrate concentration in that sample by the naked eye was impossible. Therefore, the sample was to be diluted. 0.4 ml of the sample was mixed with 3.6 ml of distilled water,

and the same previous procedures for measuring concentration were followed. Since the dilution was to ten times of the concentration, the reading obtained was multiplied by ten.

### **3.5 Batch Tests**

In the batch tests a set of experiments were conducted under semi-aerobic and uncontrolled pH conditions using various substrates along with potassium nitrate synthetic solution, and distilled water. The substrates involved in these batch tests are:

- Zero Valent Iron (ZVI)
- Berea Red Sand (BRS)
- Umgeni Sand (US)
- Mix of 75% ZVI + 25% BRS
- Mix of 50% ZVI + 50% BRS

As indicated previously in this chapter, the synthetic solution was of various concentrations including 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l. The purpose of these batch tests was to investigate the efficiency of the five substrates in the removal of nitrate starting at those different concentrations.

The batch tests were performed in 1 L Schott Duran glass bottles (Figure 3.15). In each batch experiment four bottles were used, three of which were used as replicates and one as a control. Each of the three contained one synthetic solution concentration mixed with one substrate in the ratio of (10: 1). The fourth bottle (control) contained the same substrates mixed with distilled water considering the same ratio.

The choice of the ratio was based on batch trials that were carried out by Fanni (2007), which examined the arsenic removal efficiency of various substrates including the substrates used in this study.



Figure 3.15 Schott Duran glass bottle with the plastic caps

ZVI was used with all concentrations including the 500 mg/l solution whereas US was only used with the 25 mg/l solution. In fact, since using only one concentration with US is expected to be enough for the investigation of its nitrate removal efficiency, the other concentrations were not used with it.

On the other hand, the rest of substrates were used with all concentrations other than 500 mg/l. In fact, after using the 500 mg/l with ZVI, we realized that using only four different concentrations (10 mg/l, 25 mg/l, 50 mg/l, and 100 mg/l) with the rest of substrates is enough to compare the nitrate removal efficiencies of these substrates.

A total liquid volume of 750 ml and a substrate mass of 75 g was used for each bottle. However, when BRS or US was used, the volume of the liquid and the mass of the substrate were adjusted due to the moisture content of the two substrates. Table 3.1 presents the exact amount of each substrate mass, and the corresponding liquid volume used.

## CHAPTER 3 – MATERIALS AND METHODS

Table 3.1 Quantities of solid mass and liquid volume employed in each batch

Type of batch	Solid mass	Liquid volume
100% ZVI	75 g	750 ml
100% BRS	85 g	740 ml
100% US	79 g	746 ml
75% ZVI + 25% BRS	56.25 g of ZVI + 21.35 g of BRS	747.4 ml
50% ZVI + 50% BRS	37.5 g of ZVI + 42.7 g of BRS	744.8 ml

Each bottle was then flushed with nitrogen for 2 minutes (Figure 3.16) in order to expel free oxygen, and change the condition to a semi-aerobic condition.



Figure 3.16 Nitrogen flushing process in batch bottles

The bottle was closed tightly with the caps immediately after the flushing process and then placed on the shaker at a speed of around 160 rpm (Figure 3.17). Thereafter, the analysis was done as explained in the following paragraphs.



Figure 3.17 Scientific shaker operating at around 160 rpm

Various parameters including: pH, conductivity (C), total dissolved solids (TDS), redox potential ( $E_h$ ), and total dissolved iron (Fe), were measured in triplicate for the purpose of accuracy, and at three different stages for all the batch tests other than the US and BRS batches.

In the US and BRS batches, these parameters were measured only at the beginning and at the end. The three stages were as follows: one at the beginning - immediately after the experiment is set up, one at the middle - when initial nitrate concentration drops to half (if possible) and one at the end - when initial nitrate concentration drops to zero (if possible).

In similar way, dissolved oxygen (DO) was also measured but only done with the 10 mg/l batch experiments due to the late delivery of the dissolved oxygen meter. In addition, nitrate concentration ( $\text{NO}_3$ ) was measured frequently in the three replicates and in the control bottle for all the batch experiments, until complete denitrification in the three replicates is achieved (if possible).

Average values for all these parameters were calculated from the replicate samples. In fact, one separate batch was required to be set up for the measurement of those parameters for each stage. The reason for that was to not disturb the liquid to solid ratio.

The purpose of measuring all the previous mentioned parameters is to be used as indicators of the reactions that occur in batch experiments, particularly the iron corrosive process, and also to assess the system performance.

### 3.6 Eluate Tests

Eluate is the solution that results from the process of elution. In this study, the eluate was the liquid solution that obtained from mixing distilled water with a substrate for a period of 24 hours (Fanni, 2007). Eluate tests in this study, which were performed under semi-aerobic conditions, were to determine the leaching capacity of each substrate in distilled water over the 24 hours.

Procedures followed in setting up the eluate tests were the same as in the batch tests (section 3.5). Also, substrates used as well as the liquid to solid ratio (L: S) applied in these tests were the same as in batch tests. MC was considered in preparing eluate test mixture and therefore, the quantities used in the eluate tests were the same as the ones used in the batch tests (see Table 3.1).

Parameters measured after the 24 hours included:

- pH
- Conductivity (C)
- Total dissolved solids (TDS)
- Nitrate concentration (NO<sub>3</sub>)
- Total dissolved iron (Fe)

Each of these parameters was measured in triplicate for accuracy, and in a separate vial in order to avoid contamination.

In both batch and eluate tests, standard deviation (SD) for the replicates of nitrate concentration readings, and for the multiple calibrations of total dissolved iron concentration readings, was calculated using (3-20) (Pisano, 2007):

$$\sqrt{\frac{\sum_{i=0}^n (C_i - \bar{C})^2}{n-1}} \quad (3-20)$$

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Where,

$C_i$ : concentration of sample i

$\bar{C}$ : arithmetic average of concentrations involved in the calculation  
of standard deviation

SD: standard deviation

Relative standard deviation (RSD) for both tests was also calculated using the following equation:

$$RSD = \frac{SD}{\bar{C}} * 100 \quad (3-21)$$

All the SD and RSD values are presented in the Appendices section. In addition, for each batch test, error bars were used to represent the standard deviation for nitrate concentration readings as shown in Chapter 4.

**CHAPTER 4**  
**RESULTS & DISCUSSION**

## 4.1 Solid Substrates Characteristics

### 4.1.1 Sieve analysis

In this research the gradation test was not performed for the ZVI material due to the fact that this material was purchased with specifications provided by the manufacturer (particle size distribution was ranging from 1 to 2 mm).

For the BRS and US, the particle size distribution of these substrates is illustrated on the gradation curves graph (Figure 4.1).

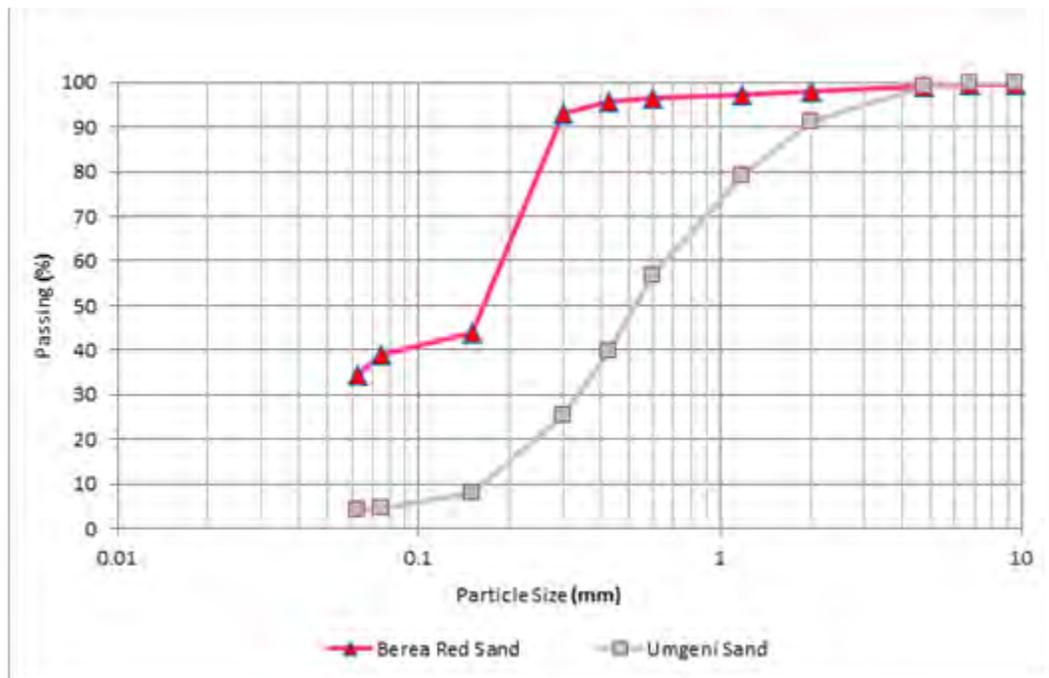


Figure 4.1 Gradation curves for Berea Red Sand and Umgeni Sand

From the above graph,  $D_{10}$  and  $D_{60}$  of Berea Red Sand and Umgeni Sand were determined, and by which the uniformity coefficient of both substrates was also calculated.  $D_{10}$  of Berea Red Sand was determined by extrapolation. Table 4.1 illustrates these various parameters for both substrates.

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.1 Uniformity coefficients ( $C_u$ ),  $D_{10}$  and  $D_{60}$  of BRS and US

	$D_{60}$	$D_{10}$	$C_u$
	mm	mm	-
B R S	0.2	0.027	7.4
U S	0.65	0.16	4

From Table 4.1, it is clearly observed that the BRS exhibits a greater degree of uniformity, and also has finer particles than the US. Moreover, given the value of  $D_{10}$  of both substrates, BRS is expected to have a lower hydraulic conductivity than the US (Fanni, 2007).

### 4.1.2 Porosity

As was described in Chapter 3, subsection 3.3.1, porosity was calculated using (3-1). The porosity test was accomplished for the following substrates:

- Zero Valent Iron
- Berea Red Sand
- Umgeni Sand
- Mix of 75% ZVI + 25% BRS
- Mix of 50% ZVI + 50% BRS

Porosity value of each substrate as well as all the other parameters that were involved in the calculation of the porosity are presented in Table 4.2.

Table 4.2 Porosity ( $n$ ), void ratio ( $e$ ), relative density ( $D_r$ ), solid mass ( $M_s$ ), total volume ( $V_{tot}$ ), solid volume ( $V_s$ ), and void volume ( $V_v$ ) for all the above mentioned substrates

	$D_r$	$M_s$	$V_{tot}$ ( $M_s / D_r$ )	$V_s$ ( $250 - V_w$ )	$V_v$ ( $V_{tot} - V_s$ )	$e$	$n$
	$g/cm^3$	<b>g</b>	<b>cm<sup>3</sup></b>	<b>cm<sup>3</sup></b>	<b>cm<sup>3</sup></b>	-	<b>%</b>
Zero Valent Iron	3.51	60	17.09	5.8	11.29	1.95	66.12
Berea Red Sand	1.42	60	42.25	18	24.25	1.35	57.4
Umgeni Sand	1.66	60	36.14	25.27	10.87	0.43	30.08
75% ZVI + 25% BRS	3	60	20	9.19	10.81	1.18	54.03
50% ZVI + 50% BRS	2.49	60	24.1	12.8	11.30	0.88	46.9

### 4.1.3 Chemical and mineralogical characterization

#### Zero Valent Iron - chemical characterization

The results of the chemical characterization of the ZVI used in this study are shown in Table 4.3. As mentioned in Chapter 3, since the ZVI material used in this study is the same one that was used in the study carried out by Fanni (2007), the chemical characterization of this material was not performed again in this study, and the results presented in Table 4.3 are derived from Fanni (2007).

Table 4.3 Chemical components of ZVI (Fanni, 2007)

<b>Zero Valent Iron</b>	
Chemical Component	%
Carbon	2.8 – 3.2
Silica	1.8 – 2.1
Chromium	0.05 – 0.4
Nickel	0.05 – 0.3
Phosphorous	0.04 – 0.4
Aluminium	0.01 – 0.1
Iron	92 Typical

#### Berea Red Sand and Umgeni Sand - mineralogical characterization

The results of the mineralogical characterization of BRS and US have demonstrated that both substrates consist mainly of quartz ( $\text{SiO}_2$ ). In addition, the other components of BRS were found to be ilmenite ( $\text{FeTiO}_3$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), and rutile ( $\text{TiO}_2$ ) (Figure 4.2). Instead, US was found to be consisting of microcline ( $\text{KAlSi}_3\text{O}_8$ ), and albite ( $\text{NaAlSi}_3\text{O}_8$ ) (Figure 4.3).

CHAPTER 4 – RESULTS AND DISCUSSION

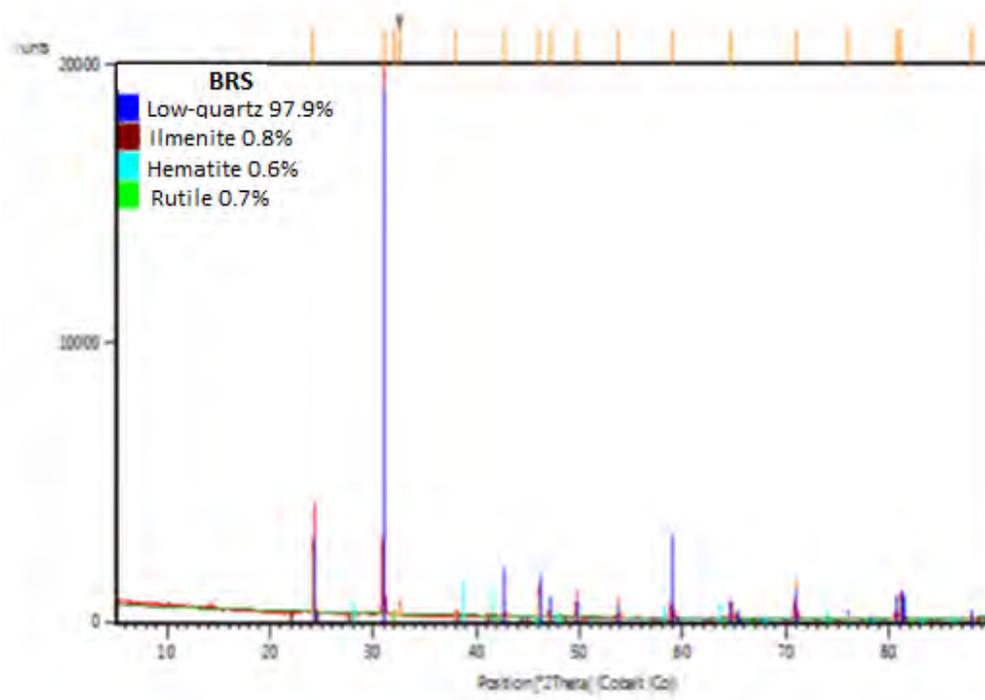


Figure 4.2 Mineralogical characterization of Berea Red Sand

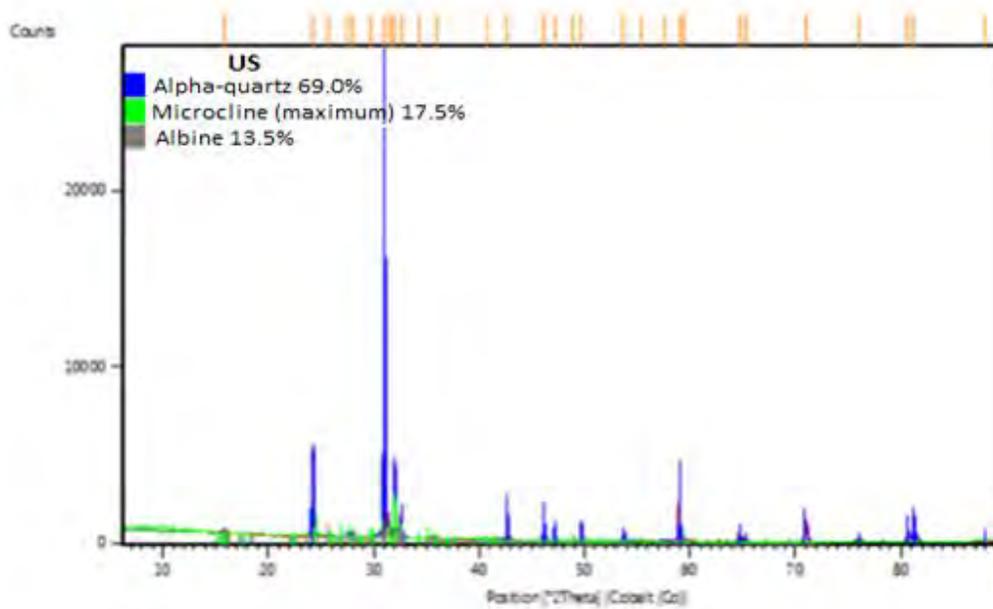


Figure 4.3 Mineralogical characterization of Umgeni Sand

## 4.2 Liquid Characteristics

The liquids used in all batch experiments are either potassium nitrate synthetic solution being of five different concentrations or distilled water. The following table displays a number of parameters that have been measured for quality characterization of each liquid, which has been used in batch experiments, on its own before setting up the experiments.

Table 4.4 Quality characterization of the liquids involved in the batch experiments

	pH	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
	-	µS/cm	mg/l	mV	mg/l	mg/l
Distilled H <sub>2</sub> O	5.61	1.5	1	289	0	0.1
10mg/l KNO <sub>3</sub>	5	23.6	12	410	10	0.3
25mg/l KNO <sub>3</sub>	5.28	58.9	30	321	25	0.2
50mg/l KNO <sub>3</sub>	5.58	101.5	51	293	50	0.4
100mg/l KNO <sub>3</sub>	5.57	202	101	265	100	0.2
500mg/l KNO <sub>3</sub>	4.84	989	495	294	500	0.2

## 4.3 Eluate Tests

The purpose of eluate tests was to investigate the leaching capacity of the substrates that are described in Table 4.5. These tests were performed under semi-aerobic conditions. The following table shows the parameters that represent the eluate characteristics for each substrate.

Table 4.5 Eluate characteristics

	pH	C	TDS	NO <sub>3</sub>	Fe
	-	µS/cm	mg/l	mg/l	mg/l
Blank (Distilled H <sub>2</sub> O)	5.61	1.5	1	0	0.1
Zero Valent Iron	5.87	11.8	6	0	0.5
Berea Red Sand	6.50	123.6	62	25-45	0.5
Umgeni Sand	5.11	40.2	20	0	0.4
75% ZVI + 25% BRS	6.91	51.8	26	7-15	0.7
50% ZVI + 50% BRS	6.58	69.8	35	10-20	0.7

From Table 4.5 it is clear that among the five substrates the highest total dissolved iron concentration was detected when the mix of 50% ZVI + 50% BRS was applied whereas the lowest concentration identified was when the US was investigated.

On the other hand, BRS eluate has exhibited the highest values for conductivity, TDS, and nitrate concentration whereas the release of nitrate from ZVI and US was nil. As the amount of BRS reduced in the analysed substrate the eluate became less conductive, and less nitrate concentration was detected. As reported by Fanni (2007), the increment of conductivity in the presence of BRS could be due to the increase of the ions released from this substrate.

Increasing pH values in most substrates to values higher than the blank pH value could be imputed to the consumption of hydrogen ions ( $H^+$ ) and the production of hydroxyl ions ( $OH^-$ ) that occur during the iron corrosion process (Yin et al., 2012).

### **4.4 Batch Tests**

The purpose of batch tests was to investigate the nitrate removal efficiency of different substrates at different initial nitrate concentrations, and under semi-aerobic and uncontrolled pH conditions.

In these batch tests a set of experiments was conducted using five substrates along with varying concentrations of the potassium nitrate synthetic solution. For each test a control (substrate and distilled water) was performed.

As indicated in Chapter 3 the solid substrates that were involved in batch tests are:

- Zero Valent Iron (ZVI)
- Berea Red Sand (BRS)
- Umgeni Sand (US)
- Mix of 75% ZVI + 25% BRS
- Mix of 50% ZVI + 50% BRS

Initial concentrations of the synthetic solution used were 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l. ZVI was used with all concentrations including the 500 mg/l whereas

US was only used with 25 mg/l solution. The rest of substrates were used with all concentrations except 500 mg/l.

#### 4.4.1 Zero Valent Iron (ZVI)

As described in the previous paragraph, ZVI ( $\text{Fe}^0$ ) was mixed with each of the previous-mentioned concentrations in separate batches. Results of the required parameters obtained during the three stages of each batch experiment are presented separately in Tables 4.6, 4.8, 4.10, 4.12, and 4.14. Also in each of these tables the readings of the same parameters for each of the solutions before mixing are presented.

From these results, it was observed that pH values have demonstrated an increase throughout all the batch experiments other than the 25 mg/l and 50 mg/l batches in which pH readings dropped in the final stage after they had elevated in the middle stage. The pH increase was due to the production of hydroxyl ions ( $\text{OH}^-$ ), and the consumption of hydrogen ions ( $\text{H}^+$ ) that were used for the oxidation of ZVI (see also Chapter 2). Higher initial pH has demonstrated higher final pH. However, the more nitrate reduced the greater the change in pH noticed.

Although the release of the total dissolved ions such as dissolved iron into the solution contributes to the increase in the solution conductivity, in the final stage of the five experiments it was noted that the conductivity decreased when the solution pH increased even if the total dissolved iron concentration (including ferrous ions) increased. This is attributable to the fact that when hydroxyl ions were released into the solution more precipitates such as  $\text{Fe}(\text{OH})_2$  were formed resulting in depletion in the total dissolved solids in the solution.

Since TDS was calculated from conductivity by using the factor (0.5), it demonstrated the same scenario of conductivity. As for redox potential, it was decreasing due to the consumption of dissolved oxygen.

Total dissolved iron concentration detected in the middle stage of each batch experiment was found to be lower than that of the initial stage. On the other hand, the total dissolved iron concentration detected in the final stages of the 50 mg/l, 100 mg/l, and 500 mg/l

batches was higher than that of the initial stages. Contrary to these results, total dissolved iron concentration detected in the final stage of the 10 mg/l and 25 mg/l batches was lower than that of the initial stage but still higher than the one detected in the middle stage.

The reduction in total dissolved iron concentration could be explained by the fact that some of the OH<sup>-</sup> ions have bonded to some of the ferrous ions (Fe<sup>2+</sup>), which were released during the oxidation of Fe<sup>0</sup>, forming iron solids such as ferrous hydroxides. Presumably some of the ferrous ions have been consumed for the nitrate reduction by Fe<sup>0</sup>, while some others could have enhanced the transformation of iron oxides into more reactive material such as magnetite (Fe<sub>3</sub>O<sub>4</sub>).

Among all the 100% ZVI batches, it was noticed that the higher the initial nitrate-concentration solution used, the higher the final total dissolved iron concentration detected. As clearly illustrated in Figures 4.4, 4.6, 4.8, 4.10, and 4.12, there was a large change in nitrate concentration at the initial interval of the experiments (first 3 to 7 days). This change was increasing with the increase of the initial nitrate concentration.

Also, as illustrated in the Appendices 4, 12, 22, 30, and 38, in all the 100% ZVI batch experiments there had been a lag time of various intervals before nitrate reduction took place. This can be attributed to one or more of the causative factors that were reported previously in Chapter 2, subsection 2.2.1.2.

#### **Zero Valent Iron – 10 mg/l KNO<sub>3</sub> solution**

Major parameters for the 10 mg/l KNO<sub>3</sub> solution before and after mixing with ZVI for batch test are presented in Table 4.6, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test is presented in Figure 4.4.

Table 4.6 Major parameters of 10 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.15	1.9	37.2	19	304	10	0.6
Middle	3	9.05	0	43.8	22	164	4.3	0.5
Final	8	9.80	0	39.97	20	140	0	0.5
10 mg/l KNO <sub>3</sub> (Before mixing)		5	3.6	23.6	12	410	10	0.3

## CHAPTER 4 – RESULTS AND DISCUSSION

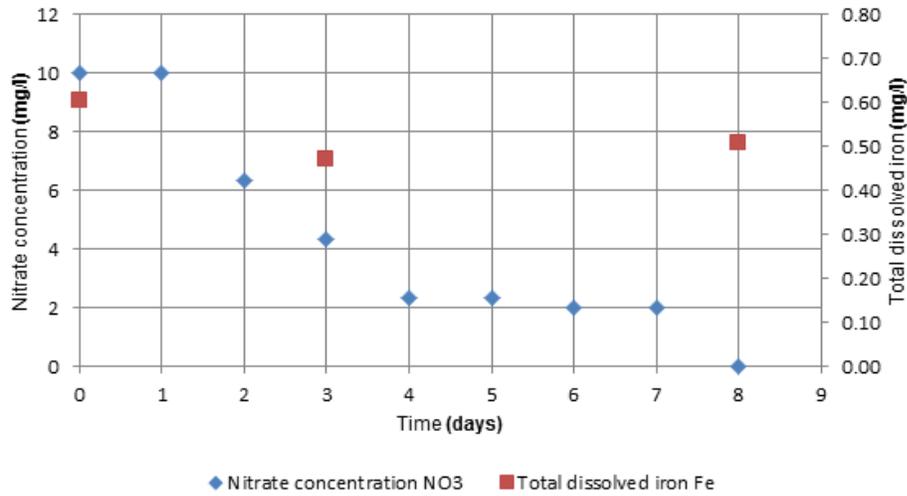


Figure 4.4 Evolution of nitrate and total dissolved iron concentrations during the ZVI batch tests – 10 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of ZVI in terms of the change in nitrate concentration throughout the batch test is of first-order as shown in Figure 4.5 and Table 4.7

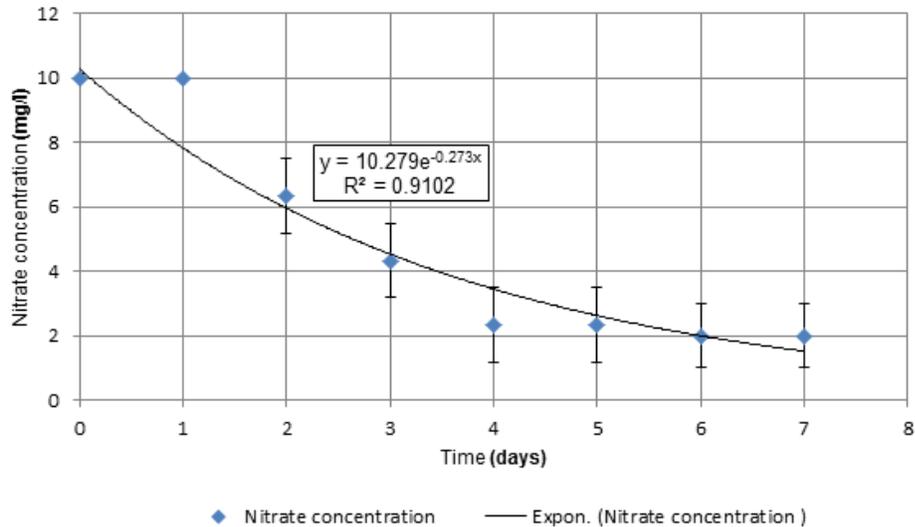


Figure 4.5 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 10 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.7 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.273	1	2.54	0.9102

### Zero Valent Iron – 25 mg/l KNO<sub>3</sub> solution

Major parameters for the 25 mg/l KNO<sub>3</sub> solution before and after mixing with ZVI for batch test are presented in Table 4.8, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.6.

Table 4.8 Major parameters of 25 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	5.68	-	60.4	30	319	25	1.3
Middle	11	9.48	-	64.5	32	226	12	0.4
Final	27	9.37	-	74.7	37	174	0	0.5
25 mg/l KNO <sub>3</sub> (Before mixing)		5.28	-	58.9	30	321	25	0.2

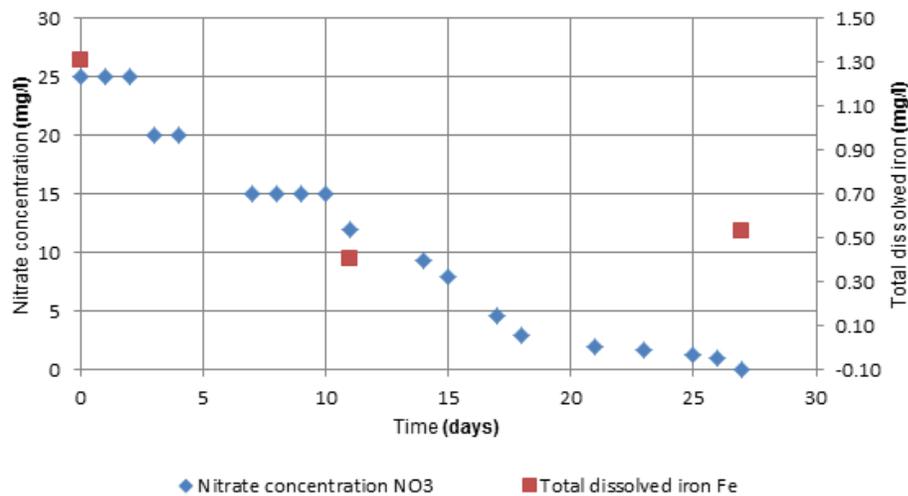


Figure 4.6 Evolution of nitrate and total dissolved iron concentrations during the ZVI batch tests – 25 mg/l KNO<sub>3</sub> solution

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The kinetic model used to describe the performance of ZVI in terms of the change in nitrate concentration throughout the batch test is of first-order as elucidated in Figure 4.7 and Table 4.9.

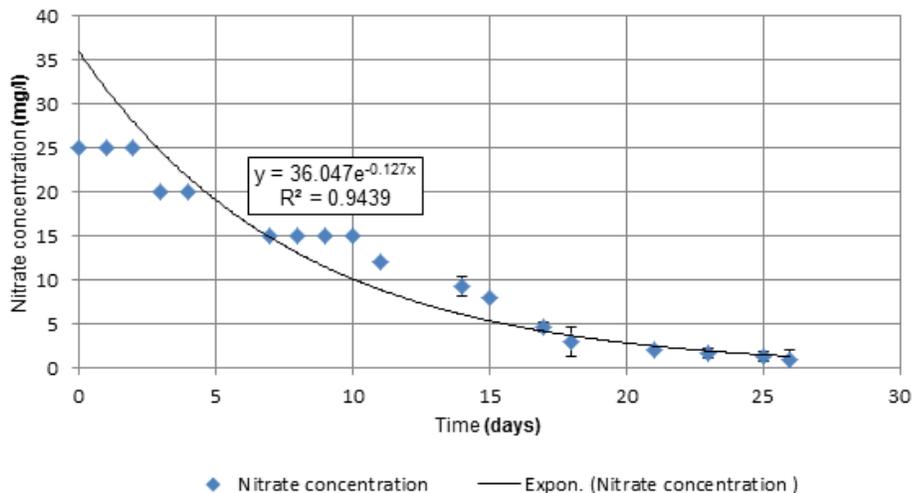


Figure 4.7 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 25 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.9 Values of first-order kinetic parameters

First-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
1/day	-	day	-
0.127	1	5.46	0.9439

**Zero Valent Iron – 50 mg/l KNO<sub>3</sub> solution**

Major parameters for the 50 mg/l KNO<sub>3</sub> solution before and after mixing with ZVI for batch test are presented in Table 4.10, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.8.

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Table 4.10 Major parameters of 50 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	5.94	-	110.03	55	294	50	2
Middle	6	9.92	-	130.6	65	224	23.3	0.6
Final	18	9.77	-	134.2	67	210	10.7	3.3
50 mg/l KNO <sub>3</sub> (Before mixing)		5.58	-	101.5	51	293	50	0.4

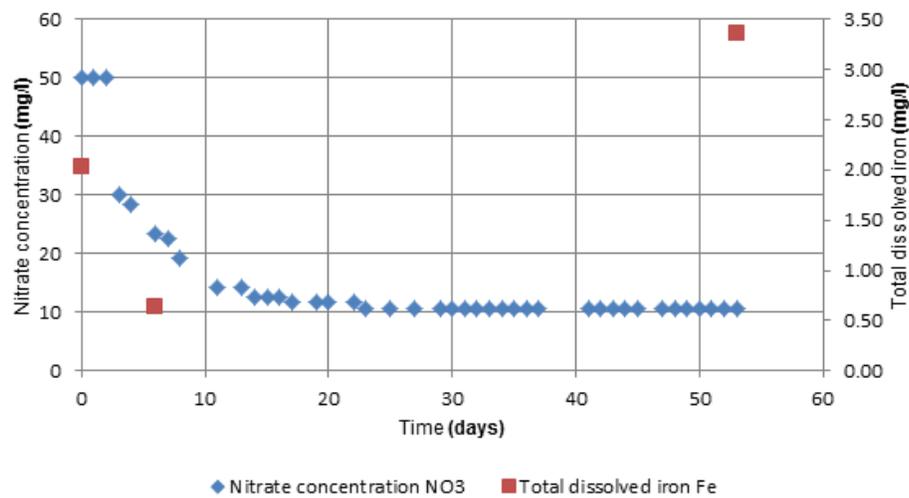


Figure 4.8 Evolution of nitrate and total dissolved iron concentrations during the ZVI batch tests – 50 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of ZVI in terms of the change in nitrate concentration throughout the batch test is of first-order as shown in Figure 4.9 and Table 4.11.

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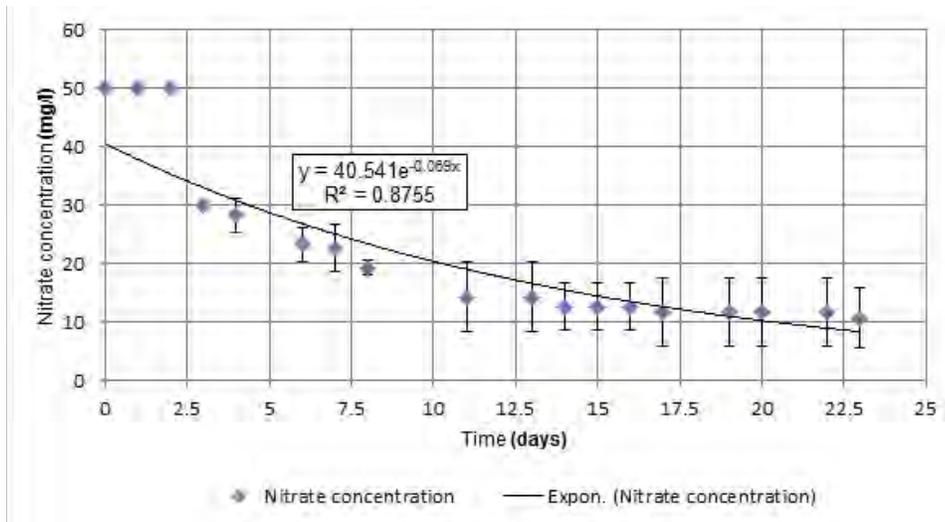


Figure 4.9 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 50 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.11 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.069	1	10.05	0.8755

### Zero Valent Iron – 100 mg/l KNO<sub>3</sub> solution

Major parameters for the 100 mg/l KNO<sub>3</sub> solution before and after mixing with ZVI for batch test are presented in Table 4.12, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.10.

Table 4.12 Major parameters of 100 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	<b>days</b>	-	<b>mg/l</b>	<b>µS/cm</b>	<b>mg/l</b>	<b>mV</b>	<b>mg/l</b>	<b>mg/l</b>
Initial	0	6.24	-	213	107	289	100	2
Middle	5	9.96	-	254	127	220	60	0.4
Final	34	10.24	-	252.7	126	189	28.3	4.1
100 mg/l KNO <sub>3</sub> (Before mixing)		5.57	-	202	101	265	100	0.2

## CHAPTER 4 – RESULTS AND DISCUSSION

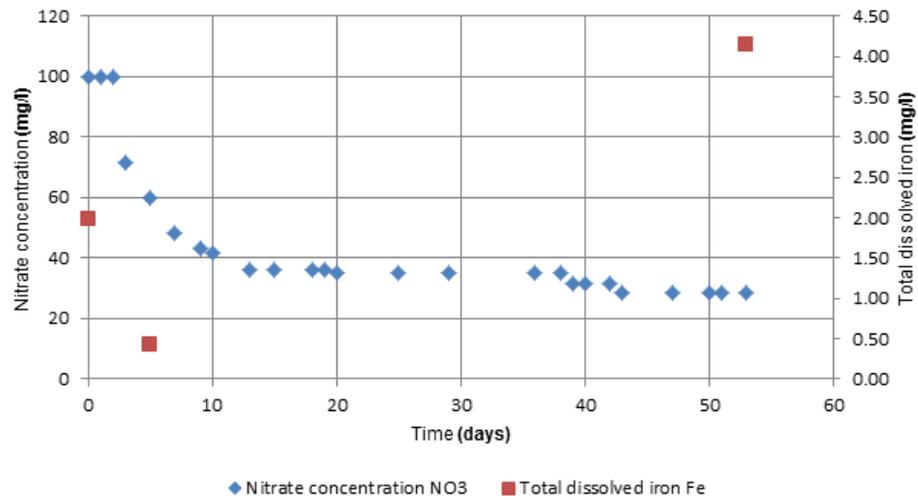


Figure 4.10 Evolution of nitrate and total dissolved iron concentrations during the ZVI batch tests – 100 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of ZVI in terms of the change in nitrate concentration throughout the batch test is of first-order as illustrated in Figure 4.11 and Table 4.13.

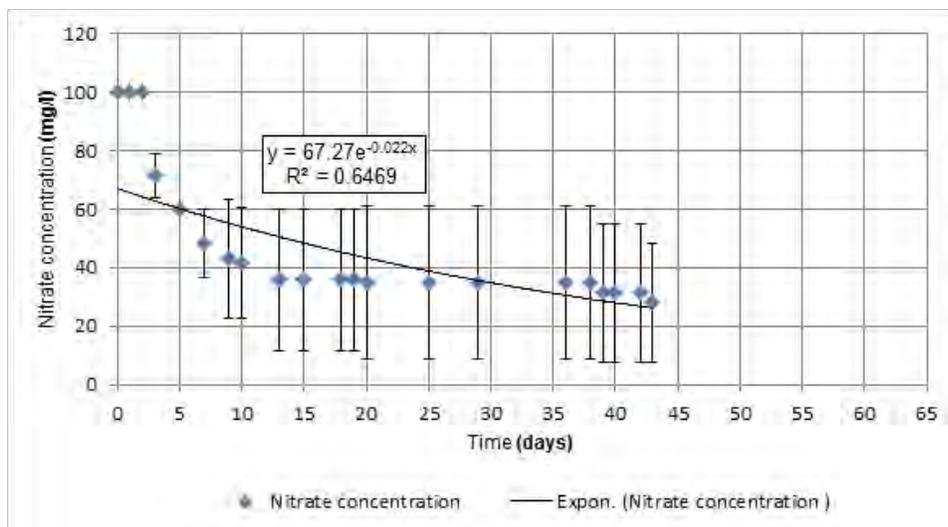


Figure 4.11 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 100 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.13 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.022	1	31.51	0.6469

### Zero Valent Iron – 500 mg/l KNO<sub>3</sub> solution

Major parameters for the 500 mg/l KNO<sub>3</sub> solution before and after mixing with ZVI for batch test are presented in Table 4.14, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.12.

Table 4.14 Major parameters of 500 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.35	-	1001.7	501	280	500	0.9
Middle	6	10.67	-	1220.7	610	190	320	0.6
Final	75.5	11	-	1197.7	599	176	210	10.1
500 mg/l KNO <sub>3</sub> (Before mixing)		4.84	-	989	495	294	500	0.2

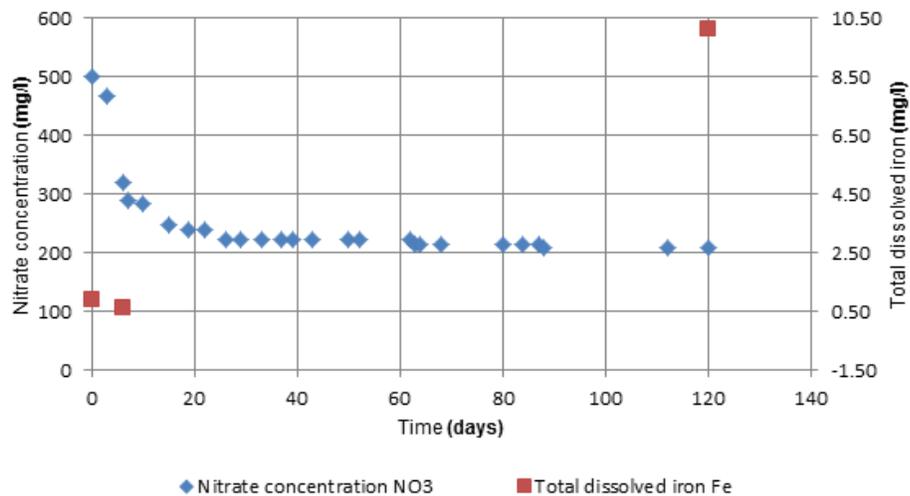


Figure 4.12 Evolution of nitrate and total dissolved iron concentrations during the ZVI batch tests – 500 mg/l KNO<sub>3</sub> solution

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From Figure 4.12, it is clear that the denitrification process could be divided into 2 phases as illustrated in Figures 4.13a and 4.13b. The kinetic model used to describe the performance of ZVI in terms of the change in nitrate concentration throughout the batch test is of first-order as described in Table 4.15.

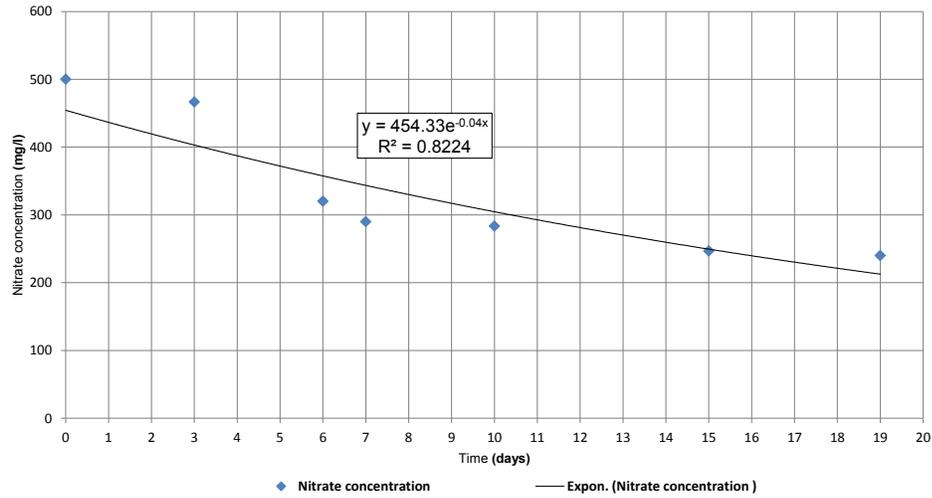


Figure 4.13a Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 500 mg/l KNO<sub>3</sub> solution (phase 1)

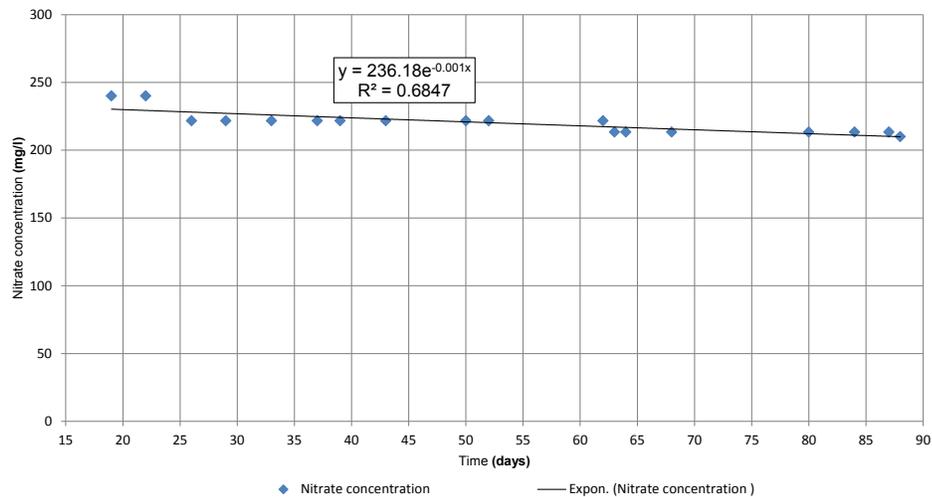


Figure 4.13b Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the ZVI batch tests using 500 mg/l KNO<sub>3</sub> solution (phase 2)

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Table 4.15 Values of first-order kinetic parameters

<b>First-order</b>				
Phase	Reaction rate constant (k)	n	$t_{1/2}$	$R^2$
-	<b>1/day</b>	-	<b>day</b>	-
1	0.04	1	17.33	0.8224
2	0.001	1	693.15	0.6847

Although the higher initial nitrate concentration resulted in greater change in nitrate concentration at the initial interval of the experiment, considering the total courses of those five experiments the reaction rate was decreasing as the initial nitrate concentration increased. Also, as presented in Table 4.16, besides the 10 mg/l and 25 mg/l batches in which nitrate was reduced completely, the percentage of nitrate removal in the other batches decreased as the initial nitrate concentration increased.

Table 4.16 illustrates the performance of ZVI in the removal of nitrate for different initial nitrate concentration batches.

Table 4.16 The performance of ZVI in nitrate reduction during different initial nitrate concentration batches

<b>Zero Valent Iron</b>					
KNO <sub>3</sub> solution conc.	Removal efficiency	Elapsed time	n	k	$R^2$
<b>mg/l</b>	<b>%</b>	<b>days</b>	-	<b>1/day</b>	-
10	100	8	1	0.273	0.9102
25	100	27	1	0.127	0.9439
50	79	18	1	0.069	0.8755
100	72	34	1	0.022	0.6469
500	58	75.5	1	0.021*	0.7536*

(\*) : The average value for both phases.

As clearly illustrated in Figure 4.12 and reported in Appendix 58, nitrate concentration in the 500 mg/l ZVI batch experiment plateaued around 210 mg/l after 63 days. The

performance of ZVI during the different-concentration batches is also shown in Figure. 4.14.

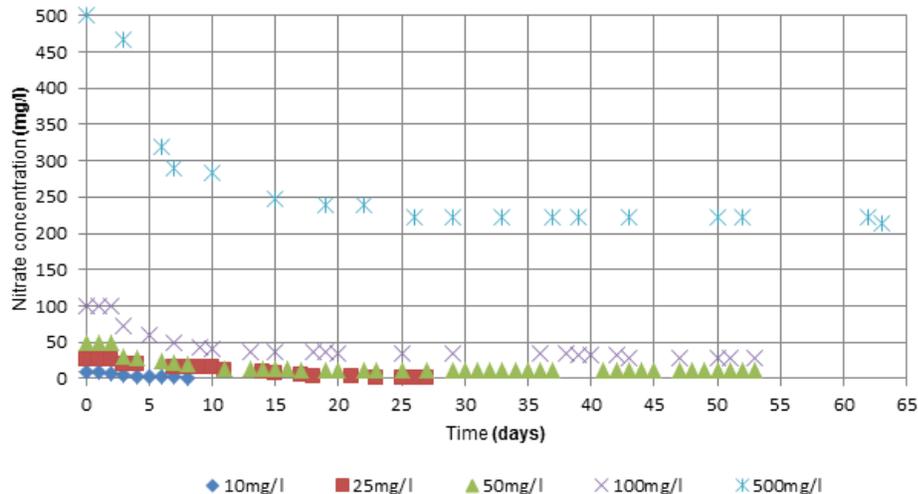


Figure 4.14 Nitrate reduction profiles for different initial nitrate concentrations batches using ZVI

#### 4.4.2 Berea Red Sand (BRS)

As referred to previously in this chapter, this substrate was used with only four different initial nitrate-concentration solutions in four separate batch experiments including 10 mg/l, 25 mg/l, 50 mg/l, and 100 mg/l.

Almost all the major parameters were measured only twice: first at the beginning and again at the end. Tables 4.17, 4.19, 4.21, and 4.23 display the readings of the required parameters that were obtained during the two stages for each batch experiment separately. Also, in each of these tables the readings of the same parameters for each of the solutions before mixing are presented.

pH in the four batches found to be stable around weak acidic condition ( $6 \leq \text{pH} < 6.40$ ). In fact, as revealed in the same four previous mentioned tables, readings of each parameter were exhibiting similar results in the four BRS experiments. In other words, pH readings of the four experiments have all declined. In addition, redox potential and total dissolved

## CHAPTER 4 – RESULTS AND DISCUSSION

iron concentration readings have all also decreased. Conductivity and TDS have elevated in all the batches. Increase in conductivity throughout these batches could be due to the solubilisation of ions, as suggested by (Fanni, 2007).

As confirmed by the slight decrease in the  $E_h$  values in all the batches, the dissolved oxygen was totally consumed during the experiments periods. Depletion in pH values, and minor decreases in  $E_h$  values in all the batches indicates that the main nitrate removal mechanism was adsorption (ITRC, 2011).

Comparing the total amount of the nitrate removed in each batch to the initial nitrate concentration for the synthetic solution used, would render the BRS as the sole material regarded as a good medium in treating nitrate. From this comparison, it is evident that the nitrate removal efficiency of BRS is more than 65% in all the batches, even in the 25 mg/l batch it was 100%.

However, because the nitrate removal efficiency is determined upon the nitrate concentration that was detected at the beginning of the experiments rather than the original nitrate concentration for the synthetic solution, the percentage removal of nitrate was noticed to be lower in all the different-concentration batches.

The nitrate removal efficiency was calculated only for the period that demonstrated depletion in the nitrate concentration, starting from the initial concentration detected, otherwise if the results of the entire course for each experiment were considered, the removal efficiency will be lower, if not zero, in all the batch experiments other than the 50 mg/l one.

In fact, in the four BRS batches, the nitrate concentration increased initially. However, this concentration decreased to levels below the original synthetic solution concentration, except for the 10 mg/l batch in which the nitrate concentration decreased slightly. Thereafter, the nitrate concentration again started elevating during all the batches other than the 50 mg/l batch. The nitrate concentration in the 10 mg/l and 100 mg/l batches eventually became higher than the original synthetic solution concentration while it was 25 mg/l in the 25 mg/l batch.

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As was confirmed by the eluate experiments results (section 4.3), the increase in the nitrate concentration during the BRS batch tests is due to the contamination of this substrate with nitrate.

**Berea Red Sand – 10 mg/l KNO<sub>3</sub> solution**

Major parameters for the 10 mg/l KNO<sub>3</sub> solution before and after mixing with BRS for batch test are presented in Table 4.17, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.15.

Table 4.17 Major parameters of 10 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.23	2.1	104.6	52	411	50	0.9
Final	63	6.22	0	214.1	107	403	56.7	0.4
10 mg/l KNO <sub>3</sub> (Before mixing)		5	3.6	23.6	12	410	10	0.3

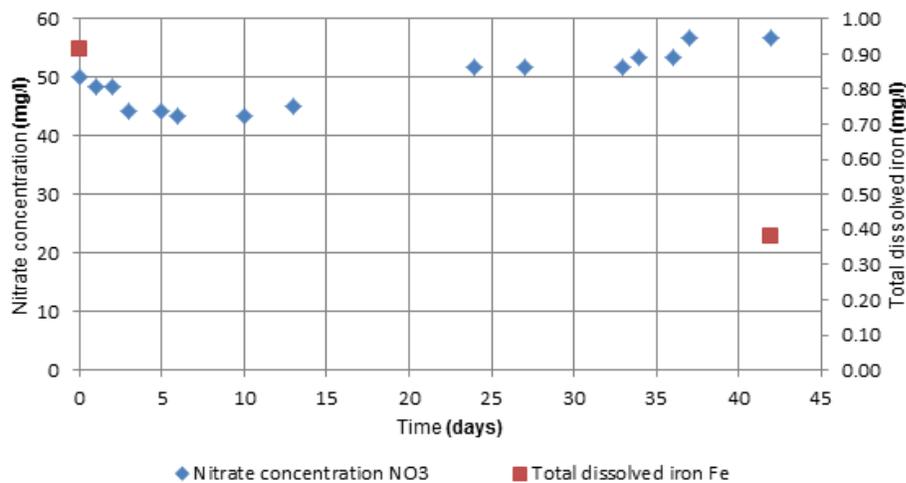


Figure 4.15 Evolution of nitrate and total dissolved iron concentrations during the BRS batch tests – 10 mg/l KNO<sub>3</sub> solution

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The kinetic model used to describe the performance of BRS in terms of the nitrate removal throughout the batch test is of first-order as shown in Figure 4.16 and Table 4.18.

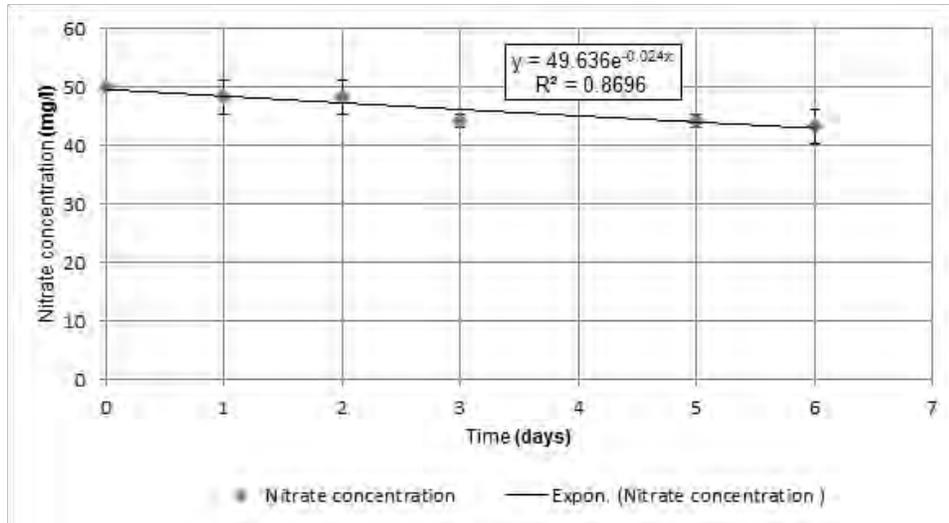


Figure 4.16 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the BRS batch tests using 10 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.18 Values of first-order kinetic parameters

First-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
1/day	-	day	-
0.024	1	28.88	0.8696

**Berea Red Sand – 25 mg/l KNO<sub>3</sub> solution**

Major parameters for the 25 mg/l KNO<sub>3</sub> solution before and after mixing with BRS for batch test are presented in Table 4.19, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.17.

Table 4.19 Major parameters of 25 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.35	-	109.3	55	340	50	1.1

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Final	69	6.28	-	304	144	326	25	0.5
25 mg/l KNO <sub>3</sub> (Before mixing)		5.28	-	58.9	30	321	25	0.2

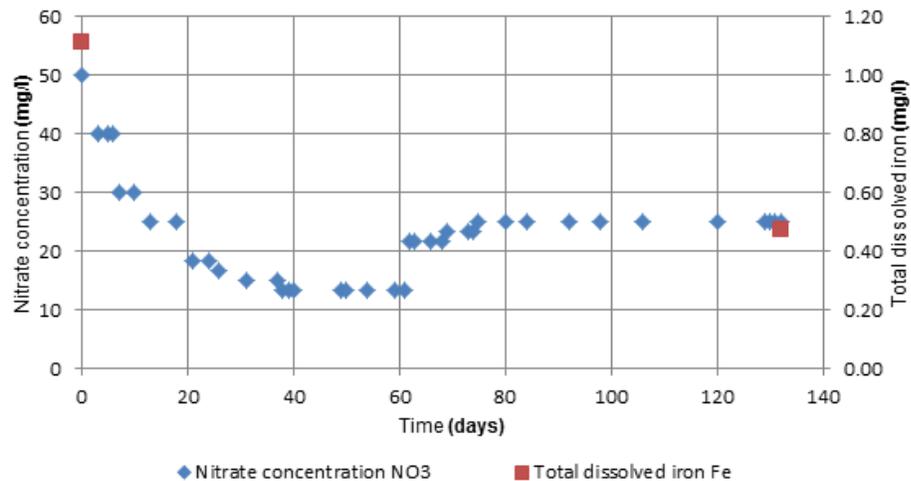


Figure 4.17 Evolution of nitrate and total dissolved iron concentrations during the BRS batch tests – 25 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of BRS in terms of the nitrate removal throughout the batch test is of first-order as illustrated in Figure 4.18 and Table 4.20.

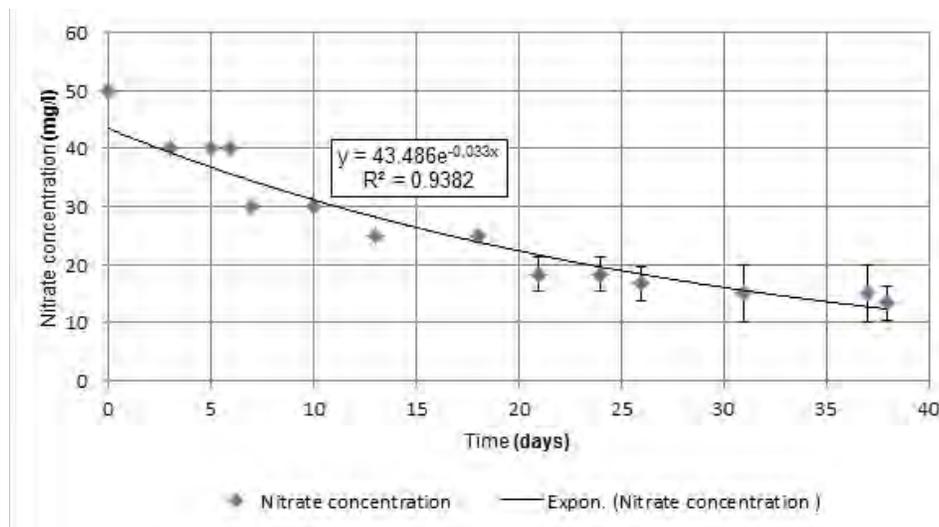


Figure 4.18 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the BRS batch tests using 25 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.20 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.033	1	21	0.9382

### Berea Red Sand – 50 mg/l KNO<sub>3</sub> solution

Major parameters for the 50 mg/l KNO<sub>3</sub> solution before and after mixing with BRS for batch test are presented in Table 4.21, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.19.

Table 4.21 Major parameters of 50 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	<b>days</b>	-	<b>mg/l</b>	<b>µS/cm</b>	<b>mg/l</b>	<b>mV</b>	<b>mg/l</b>	<b>mg/l</b>
Initial	0	6.29	-	153.5	77	350	81.7	1.4
Final	54	6.12	-	253.7	127	303	48.3	0.6
50 mg/l KNO <sub>3</sub> (Before mixing)		5.58	-	101.5	51	293	50	0.4

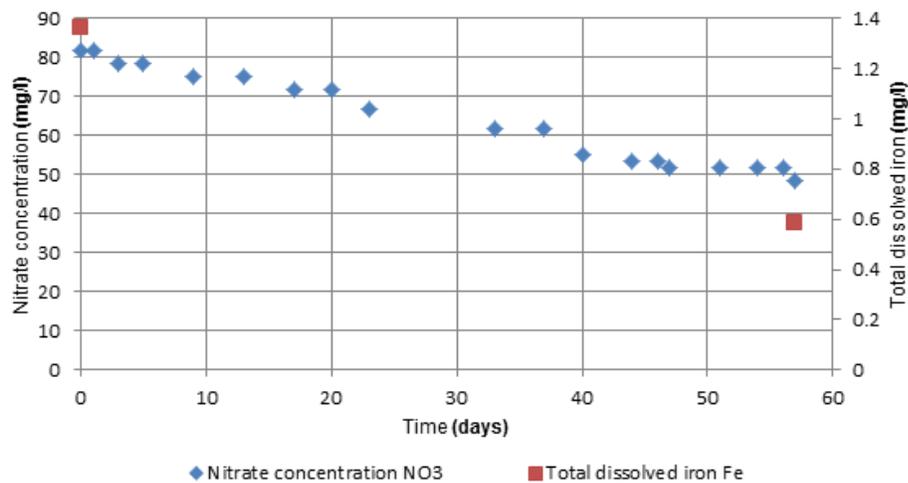


Figure 4.19 Evolution of nitrate and total dissolved iron concentrations during the BRS batch tests – 50 mg/l KNO<sub>3</sub> solution

CHAPTER 4 – RESULTS AND DISCUSSION

The kinetic model used to describe the performance of BRS in terms of the change in nitrate concentration throughout the batch test is of first-order as shown in Figure 4.20 and Table 4.22.

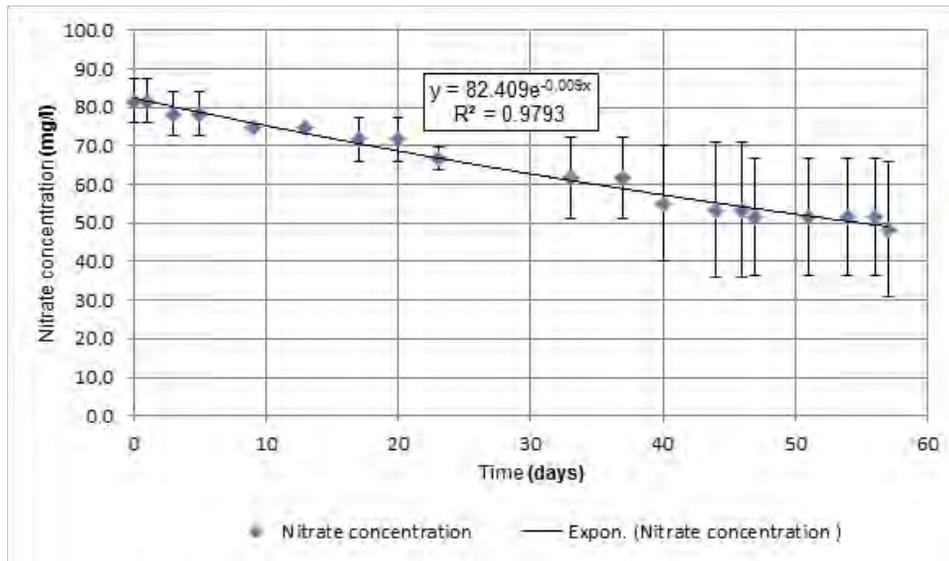


Figure 4.20 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the BRS batch tests using 50 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table.4.22 Values of first-order kinetic parameters

First-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
1/day	-	day	-
0.009	1	77.02	0.9793

**Berea Red Sand – 100 mg/l KNO<sub>3</sub> solution**

Major parameters for the 100 mg/l KNO<sub>3</sub> solution before and after mixing with BRS for batch test are presented in Table 4.23, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.21.

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Table 4.23 Major parameters of 100 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.33	-	260.3	130	327	140	1.8
Final	81	6	-	375.3	188	319	146.7	0.5
100 mg/l KNO <sub>3</sub> (Before mixing)		5.57	-	202	101	265	100	0.2

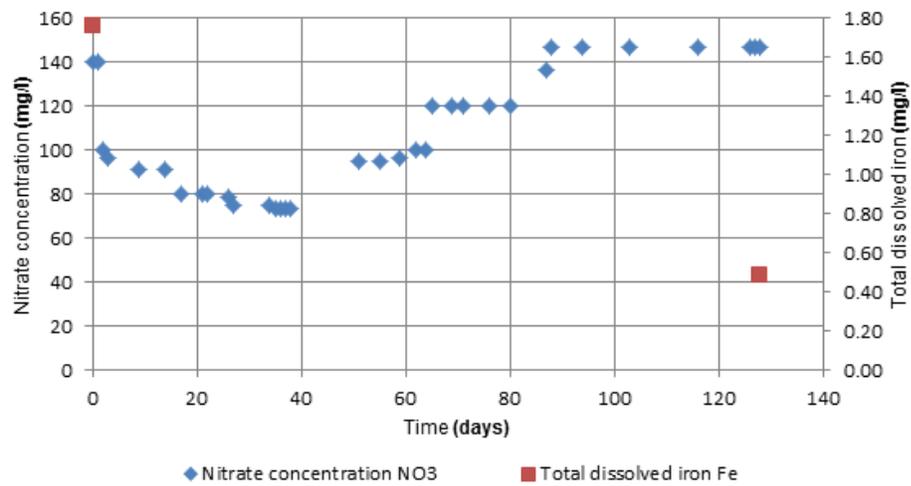


Figure 4.21 Evolution of nitrate and total dissolved iron concentrations during the BRS batch tests – 100 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of BRS in terms of the nitrate removal throughout the batch test is of first-order as elucidated in Figure 4.22 and Table 4.24.

## CHAPTER 4 – RESULTS AND DISCUSSION

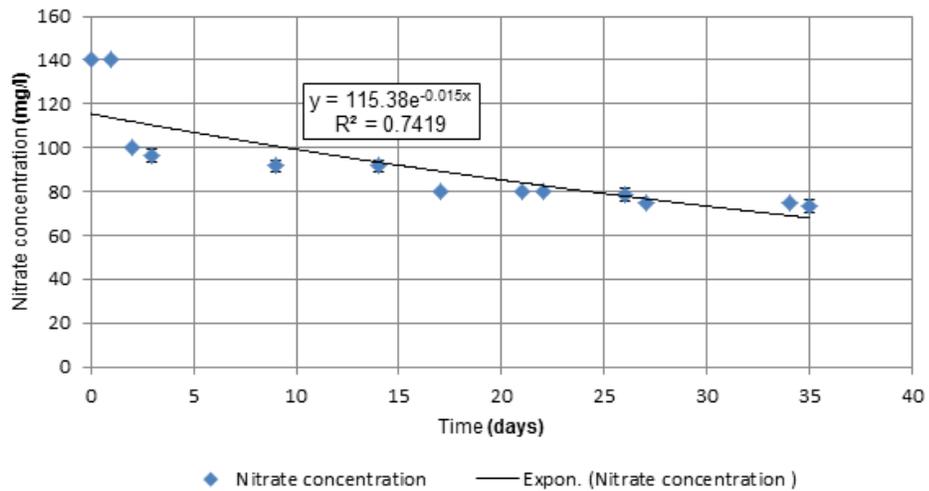


Figure 4.22 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the BRS batch tests using 100 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table.4.24 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.015	1	46.21	0.7419

Table 4.25 shows the performance of BRS in the removal of nitrate for different initial nitrate concentration batches. The nitrate removal efficiencies as well as the reaction rate constants presented in Table 4.25 were calculated only for the interval that demonstrated depletion in the nitrate concentration, starting from the initial concentration detected in each batch experiment.

From the results presented in the following table, it is noticed that there is no relation between the initial nitrate concentration for the synthetic solution and removal efficiency, and also no relation between the initial nitrate concentration for the synthetic solution and reaction rate.

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.25 The performance of BRS in nitrate reduction during different initial nitrate concentration batches

<b>Berea Red Sand</b>					
KNO <sub>3</sub> solution conc.	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
mg/l	%	days	-	1/day	-
10	13	4	1	0.024	0.8696
25	73	46	1	0.033	0.9382
50	41	54	1	0.009	0.9793
100	48	30	1	0.015	0.7419

As clearly shown in Figures 4.17 and 4.21, and reported in Appendices 22 and 49, nitrate concentration in the 25 mg/l BRS batch experiment plateaued at 25 mg/l after 75 days whereas in the 100 mg/l one, it plateaued around 140 mg/l after 88 days. The performance of BRS during the different-concentration batches is also illustrated in Figure. 4.23.

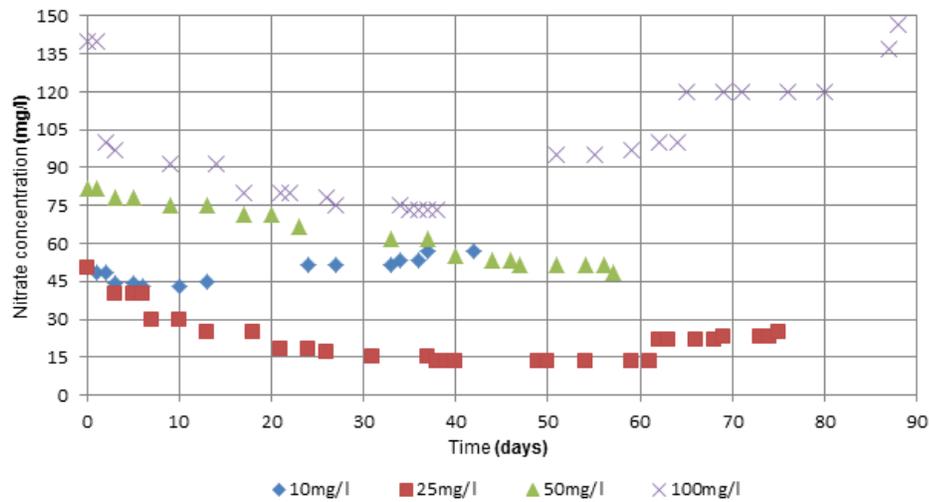


Figure 4.23 Nitrate reduction profiles for different initial nitrate concentrations batches using BRS

### 4.4.3 Umgeni Sand (US)

This substrate was used only with the 25 mg/l  $\text{KNO}_3$  solution, and as with the BRS batch experiments almost all the major parameters were measured only twice: once at the beginning and once at the end.

Table 4.26 presents the readings of the required parameters that were obtained during the two stages of this batch. The readings of the same parameters for the 25 mg/l solution before mixing are presented in the same table.

pH readings have demonstrated that the batch solution stay in an acidic condition throughout the experiment. In fact, similar to the results of the BRS batches, the pH has slightly decreased, and redox potential and total dissolved iron concentration have also declined. Conductivity and TDS; however, have both slightly increased.

The following graph clearly illustrates that the nitrate removal efficiency of this substrate is nil. This implies that the change in the nitrate concentration that occurred in all the other batch experiments is solely brought about by the presence of the used substrates.

#### Umgeni Sand – 25 mg/l $\text{KNO}_3$ solution

Major parameters for the 25 mg/l  $\text{KNO}_3$  solution before and after mixing with US for batch test are presented in Table 4.26, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.24.

Table 4.26 Major parameters of 25 mg/l  $\text{KNO}_3$  solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	$E_h$	$\text{NO}_3$	Fe
-	days	-	mg/l	$\mu\text{S/cm}$	mg/l	mV	mg/l	mg/l
Initial	0	5.12	-	72.8	36	382	25	1.6
Final	-	5.07	-	76.7	38	299	25	1
25 mg/l $\text{KNO}_3$ (Before mixing)		5.28	-	58.9	30	321	25	0.2

## CHAPTER 4 – RESULTS AND DISCUSSION

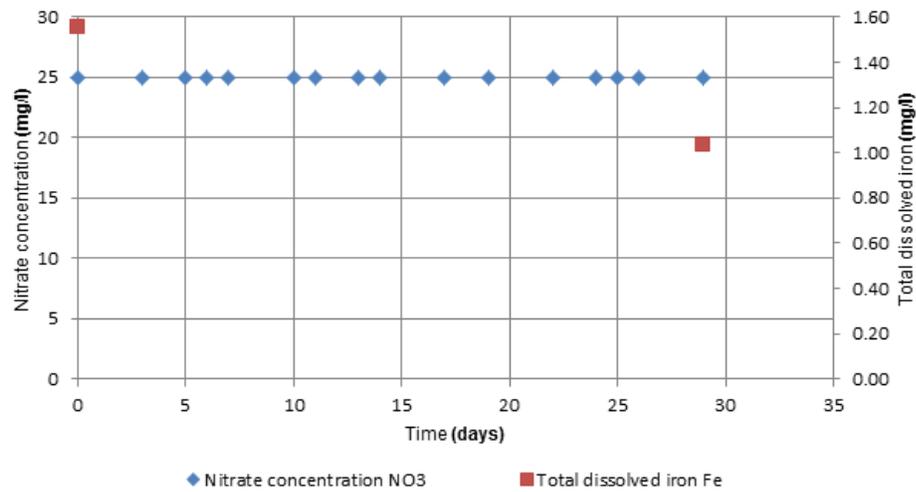


Figure 4.24 Evolution of nitrate and total dissolved iron concentrations during the US batch tests – 25 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of US in terms of the change in nitrate concentration throughout the batch test is of zero-order as shown in Figure 4.25 and Table 4.27.

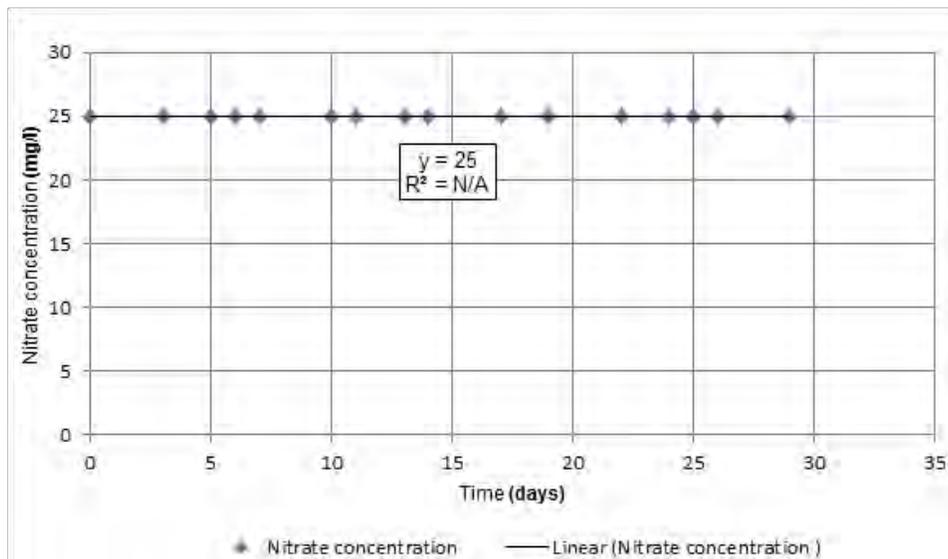


Figure 4.25 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the US batch tests using 25 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table.4.27 Values of zero-order kinetic parameters

<b>Zero-order</b>			
Reaction rate constant (k)	n	$t_{1/2}$	$R^2$
<b>mg/l.day</b>	-	<b>day</b>	-
0	0	NA	NA

#### 4.4.4 Mix of 75% Zero Valent Iron (ZVI) + 25% Berea Red Sand (BRS)

As mentioned previously in this chapter, this mix of substrates was used with the same four different-concentration solutions that BRS was used with.

Tables 4.28, 4.30, 4.32, and 4.34 present the readings of the required parameters that were obtained during the three stages for each batch experiment apart. Also in each of these tables the readings of the same parameters for each of the solutions before mixing are presented.

Similar to the pH scenario of the 100% ZVI batch experiments, pH readings obtained from the 75% ZVI + 25% BRS batches were demonstrating an increase throughout all the batches other than the 25 mg/l batch in which pH decreased in the final stage after it had increased in the middle stage.

Similar to what was observed in all BRS and US batches as well as some ZVI batches. In the 25 mg/l batch for the 75% ZVI + 25% BRS batches, the final conductivity improved when the final pH decreased. Conductivity readings of the 50 mg/l and 100 mg/l batches were decreasing throughout the experiments. Since TDS results are always exhibiting the same scenario as conductivity results do, TDS readings were dropping throughout those two experiments.

Reduction in conductivity and TDS could be explained by some conductive dissolved ions in the solution having bonded to hydroxyl ions released during corrosive reaction forming precipitates such as iron oxides/hydroxides. As for redox potential, there was a continuous dropping in  $E_h$  readings throughout the four batches.

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As presented in the tables in the first paragraph of this section, total dissolved iron concentrations exhibited two scenarios. In other words, for the 10 mg/l and 25 mg/l batches, total dissolved iron concentrations reflected an increase in both the middle and the final stages whereas for the 50 mg/l and 100 mg/l batches, total dissolved iron concentrations had reduced in the middle stages followed by an increase in the final stages.

Nevertheless, given the change in the total dissolved iron concentration throughout each batch experiment course, the four batch experiments could have had a similar evolution approach for total dissolved iron concentration. In fact, in the four batches the total dissolved iron concentration of the final stages was higher than those of the initial stages.

Although nitrate concentration detected at the first stage of each batch experiment was found to be more than the initial nitrate concentration used, this mix of substrates, as shown in Figures 4.26, 4.28, 4.30, and 4.32, and Tables 4.28, 4.30, 4.32, and 4.34, has performed a complete nitrate removal in all batches.

Not only that, in comparison with ZVI particularly for the 10 mg/l and 25 mg/l batches in which the nitrate removal efficiency of both substrates (the mix of 75% ZVI + 25% BRS and the 100% ZVI) were 100%, the mix of 75% ZVI + 25% BRS, as noticed in Tables 4.7, 4.9, 4.29, and 4.31, reflected a greater denitrification rate.

### **Mix of 75% ZVI + 25% BRS – 10 mg/l KNO<sub>3</sub> solution**

Major parameters for the 10 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 75% ZVI + 25% BRS for batch test are presented in Table 4.28, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.26.

Table 4.28 Major parameters of 10 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.29	1.5	48.7	24	349	17	1.1
Middle	4	8.27	0	59.1	30	85	7.3	1.2
Final	6.7	8.59	0	56.8	28	59	0	1.2
10 mg/l KNO <sub>3</sub> (Before mixing)		5	3.6	23.6	12	410	10	0.3

## CHAPTER 4 – RESULTS AND DISCUSSION

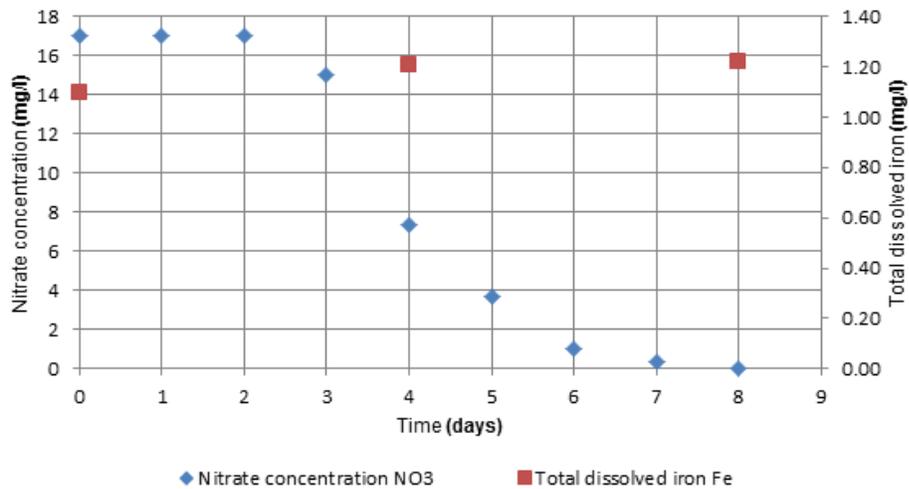


Figure 4.26 Evolution of nitrate and total dissolved iron concentrations during the 75% ZVI + 25% BRS batch tests – 10 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of first-order as shown in Figure 4.27 and Table 4.29.

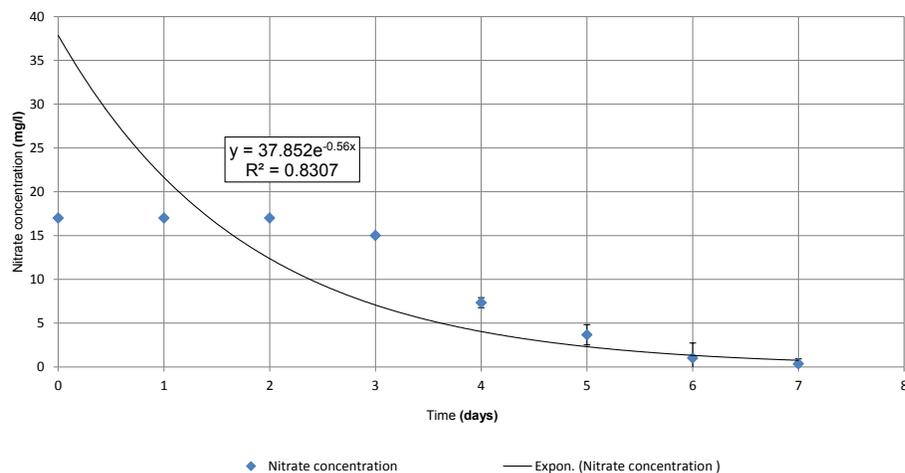


Figure 4.27 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the 75% ZVI + 25% BRS batch tests using 10 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.29 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	$t_{1/2}$	$R^2$
<b>1/day</b>	-	<b>day</b>	-
0.56	1	1.24	0.8307

**Mix of 75% ZVI + 25% BRS – 25 mg/l KNO<sub>3</sub> solution**

Major parameters for the 25 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 75% ZVI + 25% BRS for batch test are presented in Table 4.30, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.28.

Table 4.30 Major parameters of 25 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	$E_h$	NO <sub>3</sub>	Fe
-	<b>days</b>	-	<b>mg/l</b>	<b>μS/cm</b>	<b>mg/l</b>	<b>mV</b>	<b>mg/l</b>	<b>mg/l</b>
Initial	0	6.69	-	80.3	40	303	35	1.2
Middle	7	8.87	-	87.5	44	126	11.7	1.5
Final	9	8.54	-	92.4	46	121	0	6.5
25 mg/l KNO <sub>3</sub> (Before mixing)		5.28	-	58.9	30	321	25	0.2

## CHAPTER 4 – RESULTS AND DISCUSSION

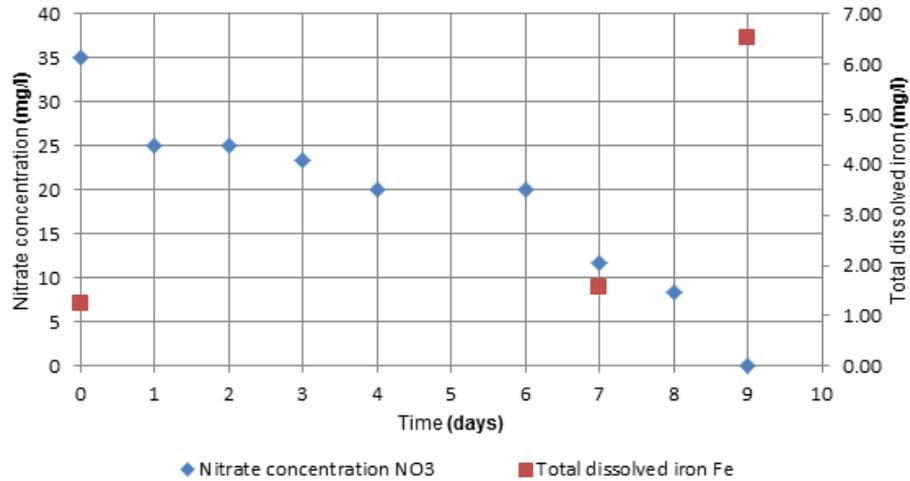


Figure 4.28 Evolution of nitrate and total dissolved iron concentrations during the 75% ZVI + 25% BRS batch tests – 25 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of zero-order as illustrated in Figure 4.29 and Table 4.31.

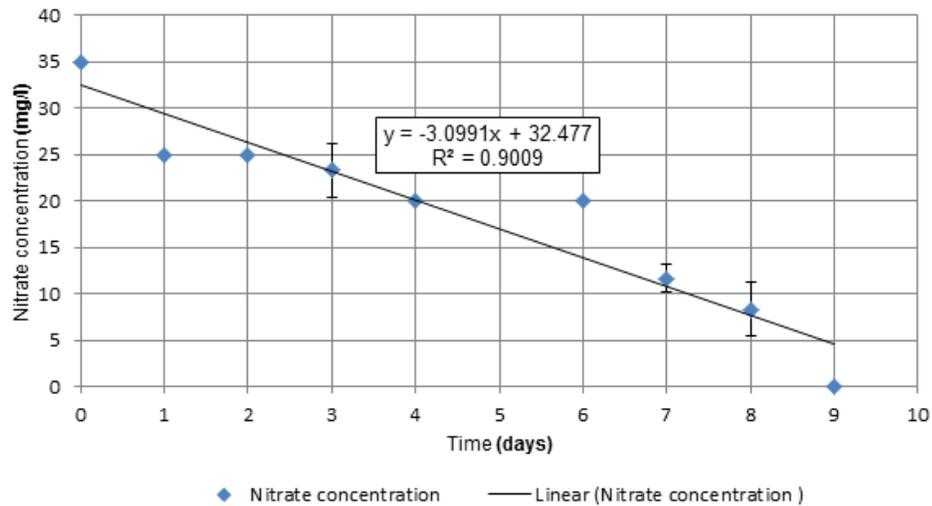


Figure 4.29 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the 75% ZVI + 25% BRS batch tests using 25 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.31 Values of zero-order kinetic parameters

<b>Zero-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>mg/l.day</b>	-	<b>day</b>	-
3.0991	0	5.65	0.9009

### **Mix of 75% ZVI + 25% BRS – 50 mg/l KNO<sub>3</sub> solution**

Major parameters for the 50 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 75% ZVI + 25% BRS for batch test are presented in Table 4.32, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.30.

Table 4.32 Major parameters of 50 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	<b>days</b>	-	<b>mg/l</b>	<b>µS/cm</b>	<b>mg/l</b>	<b>mV</b>	<b>mg/l</b>	<b>mg/l</b>
Initial	0	6.57	-	124.5	62	330	60	1.8
Middle	6	8.77	-	114.5	57	250	23.3	0.9
Final	10	9.45	-	102.3	51	162	0	5.4
<b>50 mg/l KNO<sub>3</sub> (Before mixing)</b>		5.58	-	101.5	51	293	50	0.4

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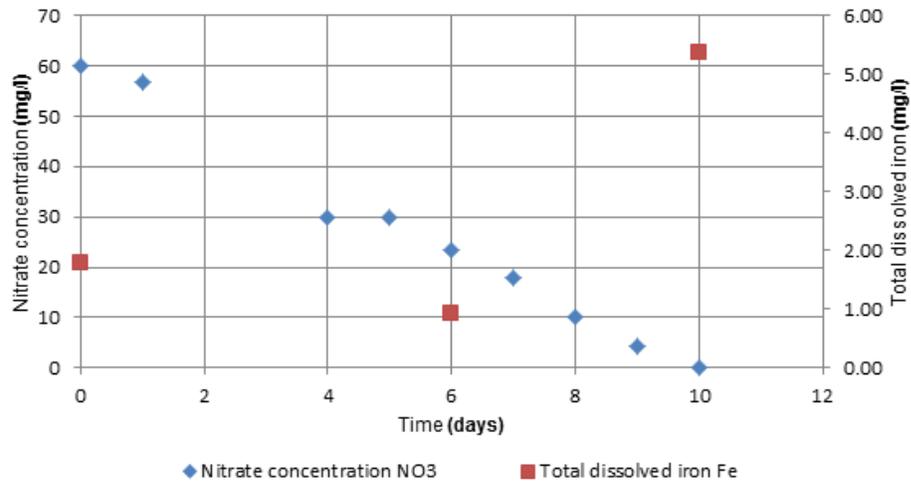


Figure 4.30 Evolution of nitrate and total dissolved iron concentrations during the 75% ZVI + 25% BRS batch tests – 50 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of zero-order as shown in Figure 4.31 and Table 4.33.

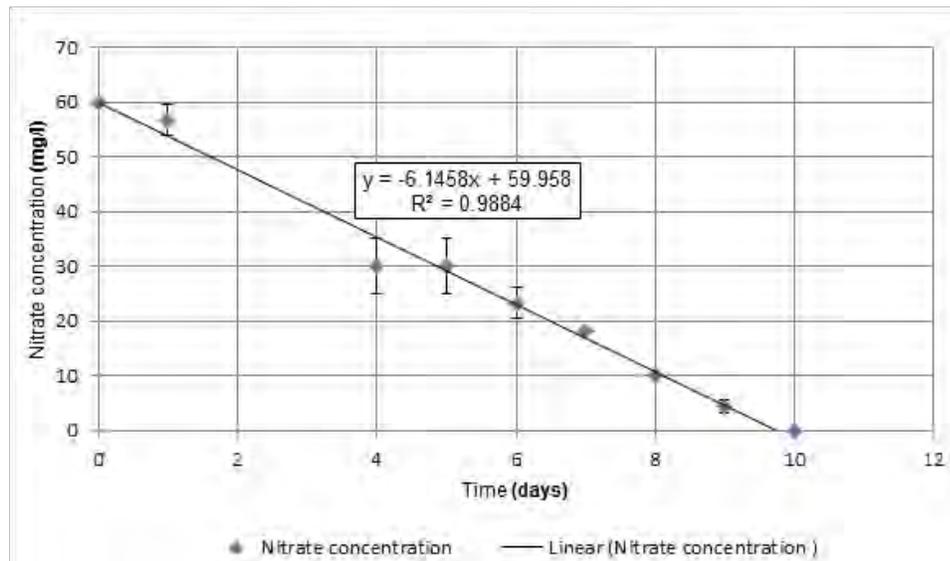


Figure 4.31 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the 75% ZVI + 25% BRS batch tests using 50 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

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Table 4.33 Values of zero-order kinetic parameters

Zero-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
mg/l.day	-	day	-
6.1458	0	4.88	0.9884

**Mix of 75% ZVI + 25% BRS – 100 mg/l KNO<sub>3</sub> solution**

Major parameters for the 100 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 75% ZVI + 25% BRS for batch test are presented in Table 4.34, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.32.

Table 4.34 Major parameters of 100 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.35	-	225	113	316	110	2.3
Middle	5	9.14	-	202	101	286	46.7	1.2
Final	20	9.98	-	188.9	95	159	0	2.7
100 mg/l KNO <sub>3</sub> (Before mixing)		5.57	-	202	101	265	100	0.2

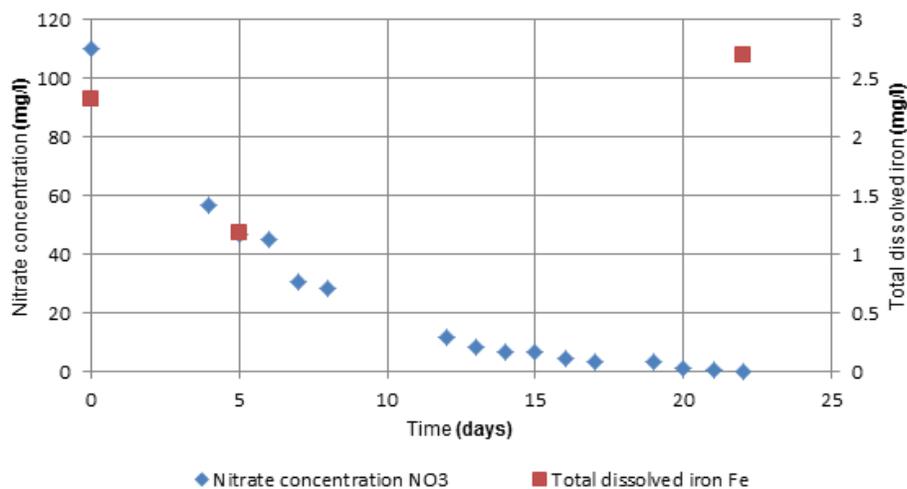


Figure 4.32 Evolution of nitrate and total dissolved iron concentrations during the 75% ZVI + 25% BRS batch tests – 100 mg/l KNO<sub>3</sub> solution

## CHAPTER 4 – RESULTS AND DISCUSSION

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of first-order as elucidated in Figure 4.33 and Table 4.35.

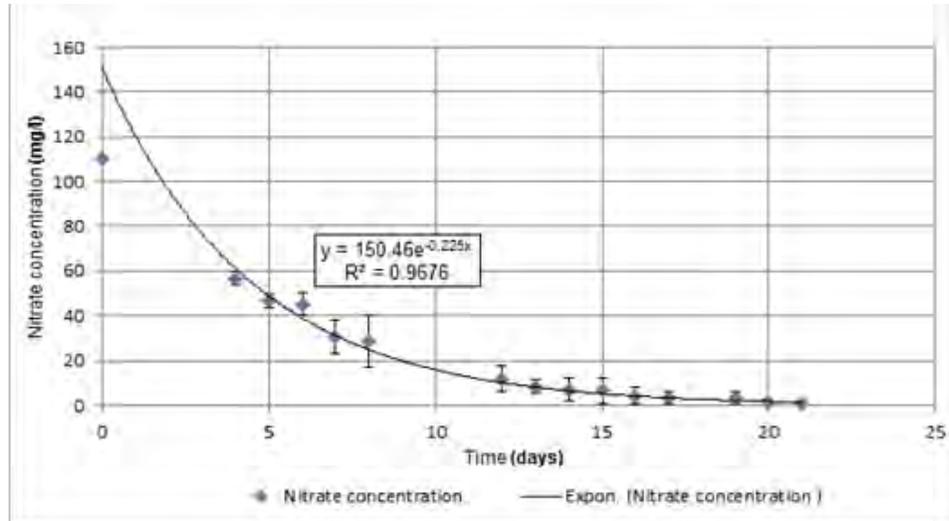


Figure 4.33 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the 75% ZVI + 25% BRS batch tests using 100 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.35 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.225	1	3.08	0.9676

Table 4.36 shows the performance of the mix of 75% ZVI + 25% BRS in the removal of nitrate for different initial nitrate concentration batches. It was observed for the mix of 75% ZVI + 25% BRS that, the reaction rate increased as the concentration of nitrate increased up to 50 mg/l (Table 4.36). When a 100 mg/l concentration was used a decline in the reaction rate was noticed. Even though, this result implies that there is no relation between the initial nitrate concentration and the reaction rate, it is still not conclusive evidence.

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Table 4.36 The performance of the mix of 75% ZVI + 25% BRS in nitrate reduction during different initial nitrate concentration batches

<b>Mix of 75% Zero Valent Iron + 25% Berea Red Sand</b>					
KNO <sub>3</sub> solution conc.	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
mg/l	%	days	-	mg/l.day Or 1/day	-
10	100	6.7	1	0.56	0.8307
25	100	9	0	3.0991	0.9009
50	100	10	0	6.1458	0.9884
100	100	20	1	0.225	0.9676

The performance of the mix of 75% ZVI + 25% BRS during the different-concentration batches is also illustrated in Figure. 4.34.

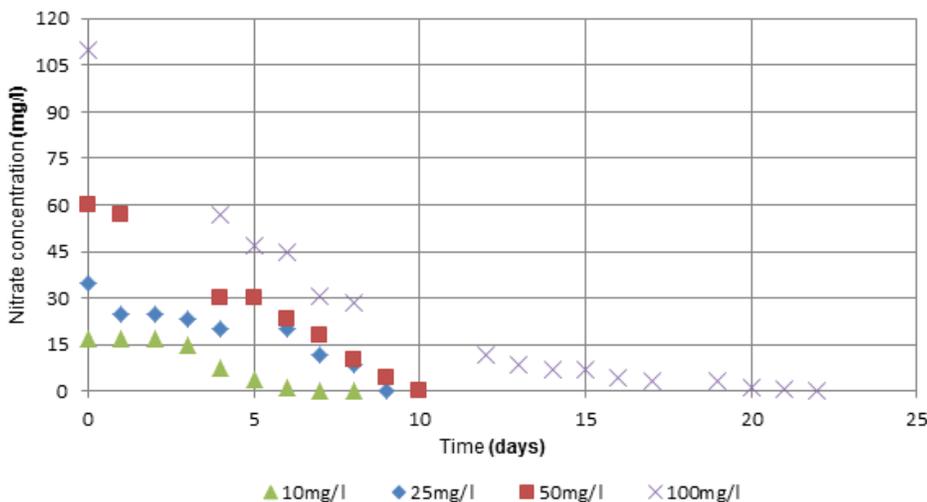


Figure 4.34 Nitrate reduction profiles for different initial nitrate concentrations batches using the mix of 75% ZVI + 25% BRS

### 4.4.5 Mix of 50% Zero Valent Iron (ZVI) + 50% Berea Red Sand (BRS)

As referred to previously in this chapter, in four separate batch experiments this mix of substrates was used with the same four different-concentration solutions that the other mix as well as BRS were used with.

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Tables 4.37, 4.39, 4.41, and 4.43 present the readings of the required parameters that were obtained during the three stages for each batch experiment apart. Also in each of these tables the readings of the same parameters for each of the solutions before mixing are presented.

For the mix of 50% ZVI + 50% BRS and the mix of 75% ZVI + 25% BRS, it was noted that similar changes, in some of the parameters measured (pH, C, TDS, and  $E_h$ ), for the same concentrations, occurred.

In the different-substrate batches including the 50% ZVI + 50% BRS batches, it was noted that initial conductivity readings were increasing as the initial applied nitrate concentration increased. Therefore, higher conductivity may be an indication of higher salinity.

The total dissolved iron concentrations that were obtained from the four 50% ZVI + 50% BRS batches, have demonstrated the same two scenarios that were observed in the 75% ZVI + 25% BRS batches.

Nitrate removal efficiency of the mix of 50% ZVI + 50% BRS was 100% in all the different-concentration batches. As noticed during the 100% ZVI batches as well as the 75% ZVI + 25% BRS batches, large change in nitrate concentration at the initial interval for the 50% ZVI + 50% BRS batch experiments (first 3-5 days) was also noticed, and this change was increasing with the increase in the initial nitrate concentration.

### **Mix of 50% ZVI + 50% BRS – 10 mg/l $KNO_3$ solution**

Major parameters for the 10 mg/l  $KNO_3$  solution before and after mixing with the combination of 50% ZVI + 50% BRS for batch test are presented in Table 4.37, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 5.35.

## CHAPTER 4 – RESULTS AND DISCUSSION

Table 4.37 Major parameters of 10 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.52	1.7	69.3	35	370	25	1.5
Middle	5	7.81	0	81.2	41	89	6.7	0.7
Final	7.7	8.03	0	73.6	37	40	0	0.9
10 mg/l KNO <sub>3</sub> (Before mixing)		5	3.6	23.6	12	410	10	0.3

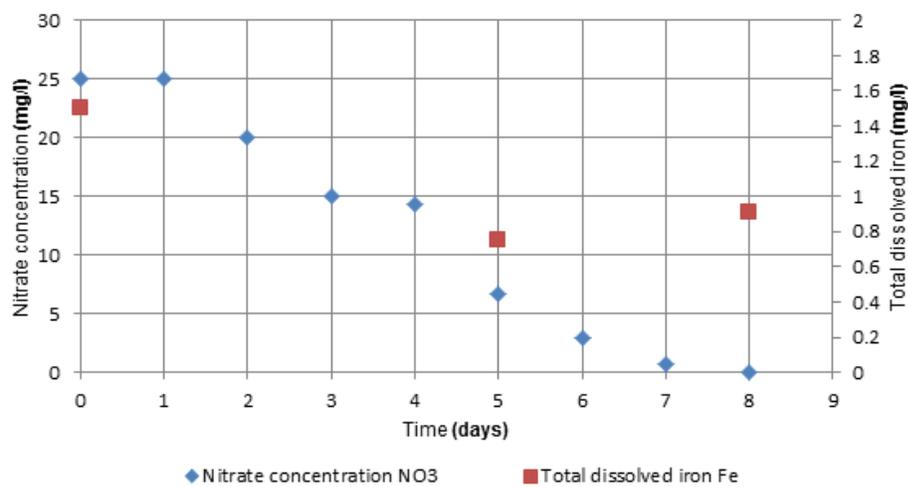


Figure 4.35 Evolution of nitrate and total dissolved iron concentrations during the 50% ZVI + 50% BRS batch tests – 10 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of zero-order as illustrated in Figure 4.36 and Table 4.38.

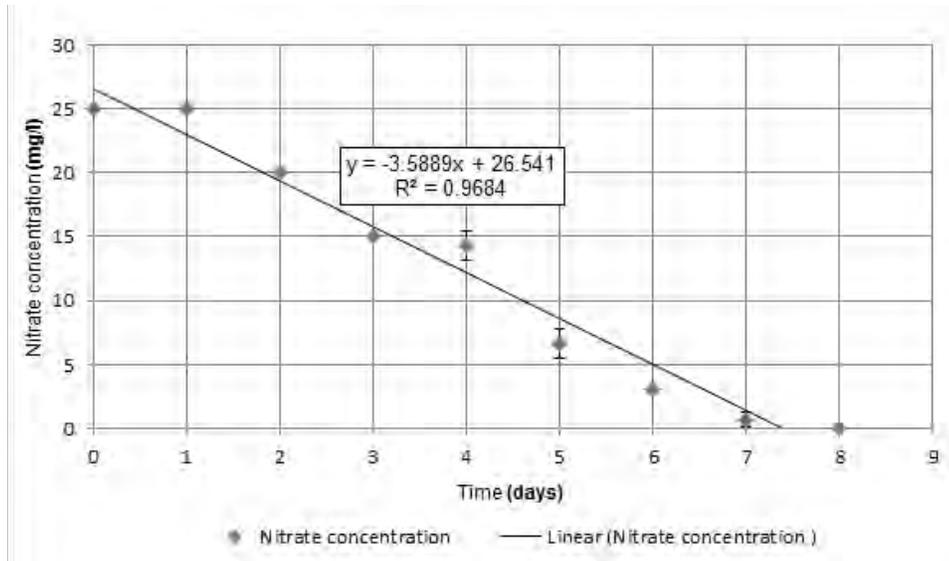


Figure 4.36 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the 50% ZVI + 50% BRS batch tests using 10 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.38 Values of zero-order kinetic parameters

Zero-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
mg/l.day	-	day	-
3.5889	0	3.48	0.9684

**Mix of 50% ZVI + 50% BRS – 25 mg/l KNO<sub>3</sub> solution**

Major parameters for the 25 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 50% ZVI + 50% BRS for batch test are presented in Table 4.39, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.37.

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Table 4.39 Major parameters of 25 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.63	-	87.3	44	306	40	1.5
Middle	7	8.16	-	99.7	50	68	15	1.3
Final	11	7.50	-	101.2	51	43	0	5
25 mg/l KNO <sub>3</sub> (Before mixing)		5.28	-	58.9	30	321	25	0.2

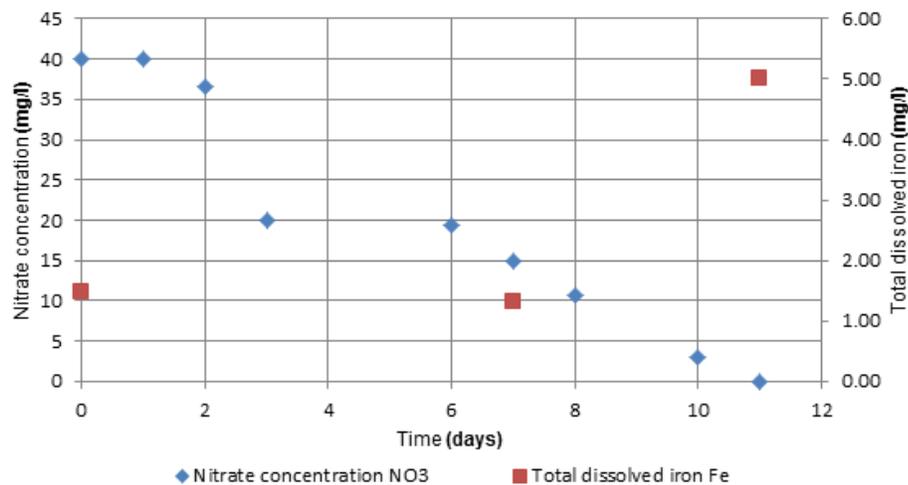


Figure 4.37 Evolution of nitrate and total dissolved iron concentrations during the 50% ZVI + 50% BRS batch tests – 25 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of zero-order as shown in Figure 4.38 and Table 4.40.

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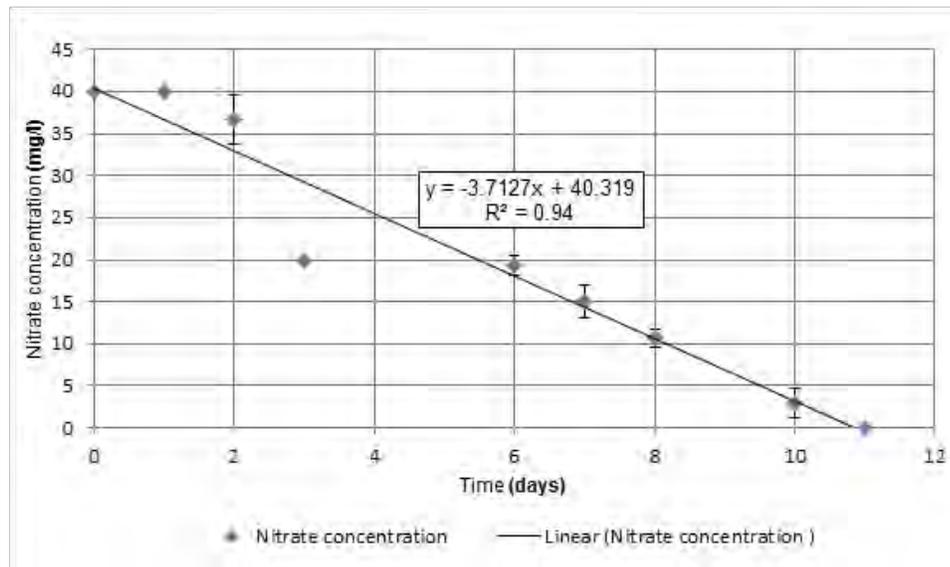


Figure 4.38 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the 50% ZVI + 50% BRS batch tests using 25 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.40 Values of zero-order kinetic parameters

Zero-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>mg/l.day</b>	-	<b>day</b>	-
3.7127	0	5.39	0.94

**Mix of 50% ZVI + 50% BRS – 50 mg/l KNO<sub>3</sub> solution**

Major parameters for the 50 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 50% ZVI + 50% BRS for batch test are presented in Table 4.41, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.39.

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Table 4.41 Major parameters of 50 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.31	-	149.1	75	326	65	0.5
Middle	6	8.31	-	141.7	71	166	25	1.1
Final	12	9.06	-	114.5	57	139	0	5.1
50 mg/l KNO <sub>3</sub> (Before mixing)		5.58	-	101.5	51	293	50	0.4

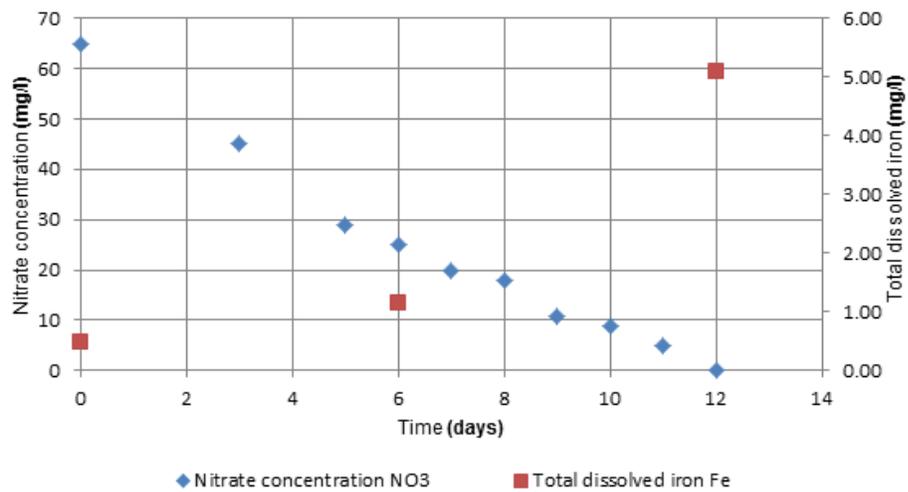


Figure 4.39 Evolution of nitrate and total dissolved iron concentrations during the 50% ZVI + 50% BRS batch tests – 50 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of zero-order as displayed in Figure 4.40 and Table 4.42.

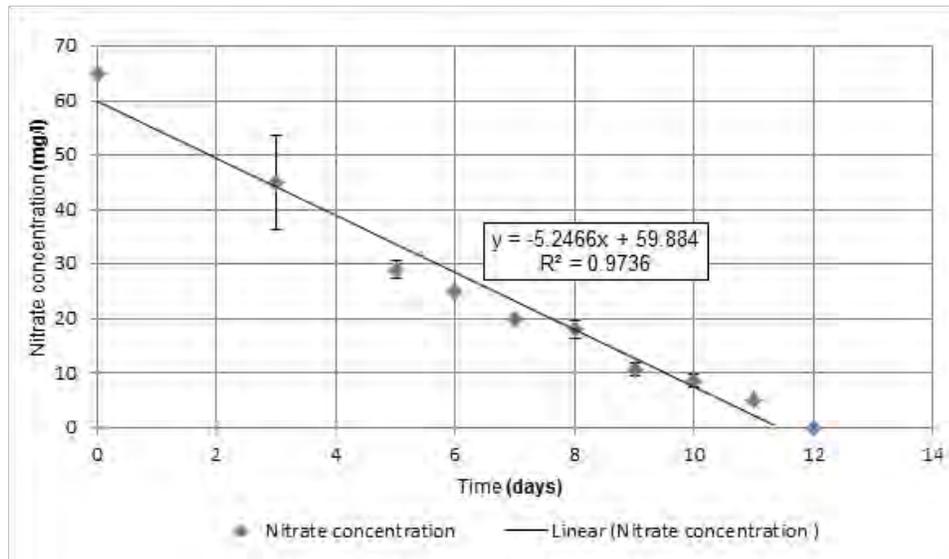


Figure 4.40 Comparison between zero-order kinetics, and the actual nitrate concentration values resulted from the 50% ZVI + 50% BRS batch tests using 50 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.42 Values of zero-order kinetic parameters

Zero-order			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
mg/l.day	-	day	-
5.2466	0	6.19	0.9736

**Mix of 50% ZVI + 50% BRS – 100 mg/l KNO<sub>3</sub> solution**

Major parameters for the 100 mg/l KNO<sub>3</sub> solution before and after mixing with the combination of 50% ZVI + 50% BRS for batch test are presented in Table 4.43, while the evolution of nitrate concentration as well as total dissolved iron (Fe) concentration during the batch test are presented in Figure 4.41.

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Table 4.43 Major parameters of 100 mg/l KNO<sub>3</sub> solution and evolution of these parameters during batch test

Stage	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
Initial	0	6.35	-	231.7	116	304	120	2.1
Middle	5	8.36	-	228	114	225	50	1.4
Final	21	9.12	-	201.6	101	166	0	3.8
100 mg/l KNO <sub>3</sub> (Before mixing)		5.57	-	202	101	265	100	0.2

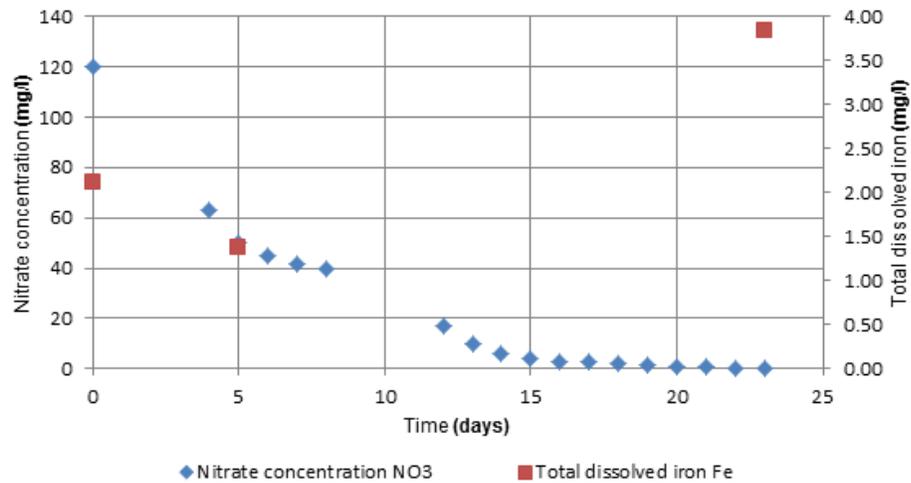


Figure 4.41 Evolution of nitrate and total dissolved iron concentrations during the 50% ZVI + 50% BRS batch tests – 100 mg/l KNO<sub>3</sub> solution

The kinetic model used to describe the performance of the mix of substrates in terms of the change in nitrate concentration throughout the batch test is of first-order as shown in Figure 4.42 and Table 4.44.

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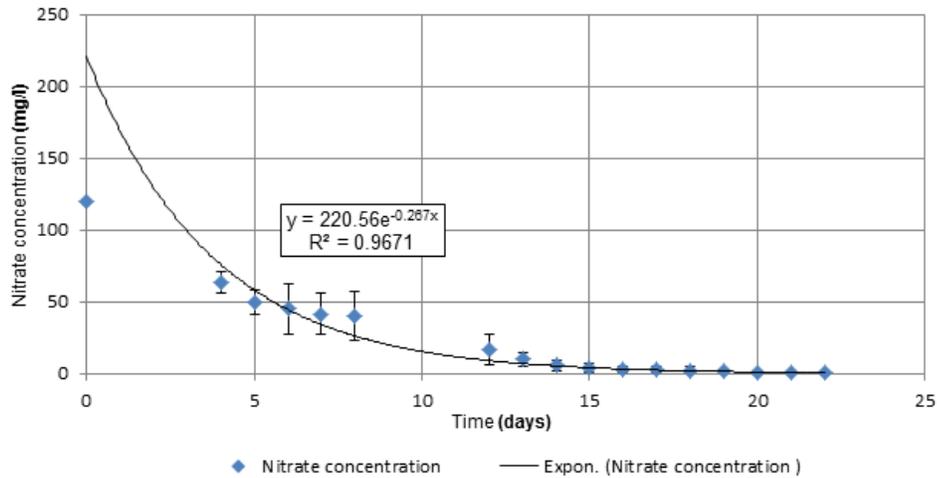


Figure 4.42 Comparison between first-order kinetics, and the actual nitrate concentration values resulted from the 50% ZVI + 50% BRS batch tests using 100 mg/l KNO<sub>3</sub> solution. Error bars represent the standard deviation

Table 4.44 Values of first-order kinetic parameters

<b>First-order</b>			
Reaction rate constant (k)	n	t <sub>1/2</sub>	R <sup>2</sup>
<b>1/day</b>	-	<b>day</b>	-
0.267	1	2.6	0.9671

Table 4.45 shows the performance of the mix of 50% ZVI + 50% BRS in the removal of nitrate for different initial nitrate concentration batches. As noticed with the mix of 75% ZVI + 25% BRS, it was observed for the mix of 50% ZVI + 50% BRS that, the reaction rate increased as the concentration of nitrate increased up to 50 mg/l (Table 4.45). When a 100 mg/l concentration was used, the reaction rate was noticed to decline. This is; however, not conclusive evidence to affirm that there is no relation between the initial nitrate concentration and the reaction rate.

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Table 4.45 The performance of the mix of 50% ZVI + 50% BRS in nitrate reduction during different initial nitrate concentration batches

<b>Mix of 50% Zero Valent Iron + 50% Berea Red Sand</b>					
KNO <sub>3</sub> solution conc.	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
mg/l	%	days	-	mg/l.day Or 1/day	-
10	100	7.7	0	3.5889	0.9684
25	100	11	0	3.7127	0.94
50	100	12	0	5.2466	0.9736
100	100	21	1	0.267	0.9671

The performance of the mix of 50% ZVI + 50% BRS during the different-concentration batches is also illustrated in Figure 4.43.

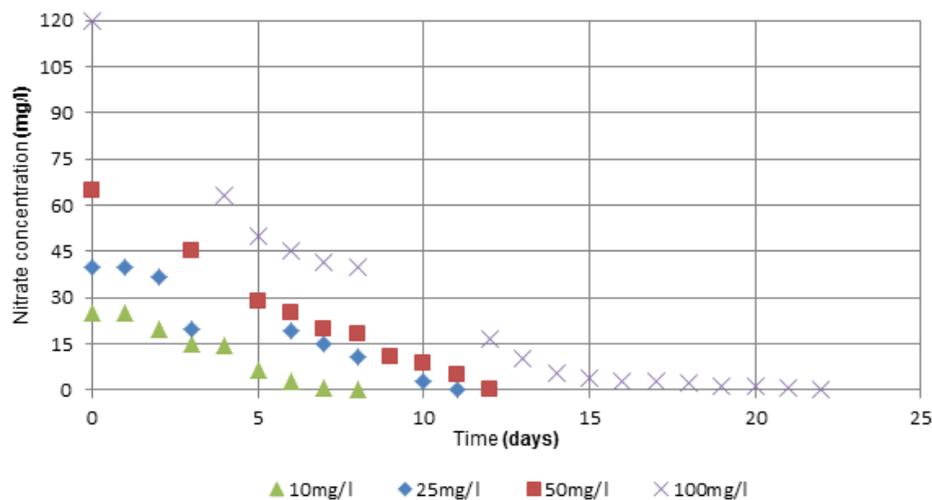


Figure 4.43 Nitrate reduction profiles for different initial nitrate concentrations batches using the mix of 50% ZVI + 50% BRS

From the results of the eluate and batch tests, it is clearly noticeable that the influence of the various substrates on the used liquid characteristics such as pH, conductivity, TDS, NO<sub>3</sub> concentration, and Fe concentration is similar between the eluate tests and the first stage of the batch tests.

#### 4.4.6 Comparison of the batch experiments

The difference between the various substrates performance for the different initial nitrate concentration batches is described in the following separate sections.

##### Comparison of the 10 mg/l KNO<sub>3</sub> solution batch trials

The performance of the various substrates in the removal of nitrate from the 10 mg/l KNO<sub>3</sub> synthetic solution is illustrated in Figure 4.44, and also described in Table 4.46.

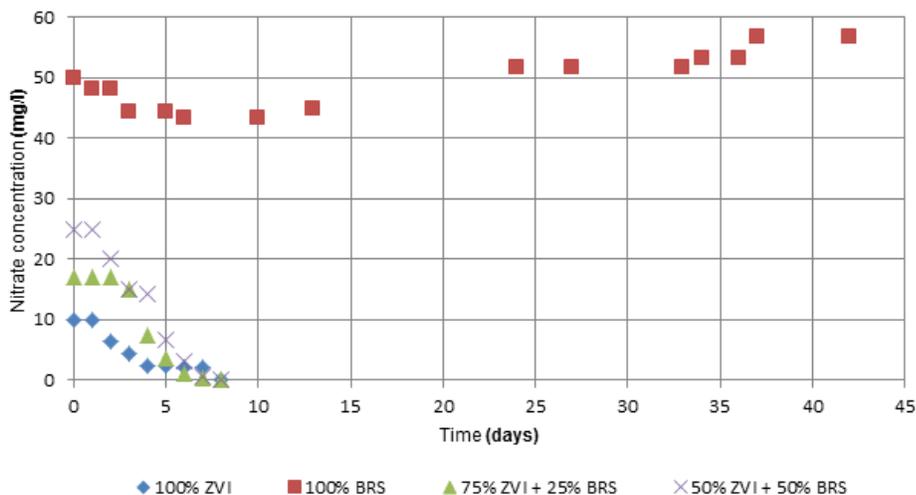


Figure 4.44 Comparison of the 10 mg/l batch tests

As illustrated in the above graph, and as shown in Table 4.46, all the substrates other than the 100% BRS had the potential to remove the nitrate completely. However, there was still a noticeable distinction between the performances of these substrates.

Although the mix of 75% ZVI + 25% BRS reduced the nitrate concentration completely in a shorter time than the mix of 50% ZVI + 50% BRS, the mix of 50% ZVI + 50% BRS exhibited a higher denitrification reaction rate. This is due to the fact that the amount of nitrate removed by the mix of 50% ZVI + 50% BRS was higher as this mix leached more nitrate into the solution, and in the same time, the time elapsed in the removal of the entire nitrate via both mixes was slightly different.

## CHAPTER 4 – RESULTS AND DISCUSSION

The following substrates are presented in order of best performance achieved:

- 1) Mix of 50% ZVI + 50 BRS;
- 2) Mix of 75% ZVI + 25% BRS;
- 3) 100% ZVI;
- 4) 100% BRS

Table 4.46 Comparison between the various substrates performance during the 10 mg/l-batch tests

<b>10 mg/l – Batch Tests</b>					
	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
	%	days	-	mg/l.day Or 1/day	-
100% ZVI	100	8	1	0.273	0.9102
100% BRS	13	4	1	0.024	0.8696
75% ZVI + 25% BRS	100	6.7	1	0.56	0.8307
50% ZVI + 50% BRS	100	7.7	0	3.5889	0.9684

### **Comparison of the 25 mg/l KNO<sub>3</sub> solution batch trials**

The performance of the various substrates in the removal of nitrate from the 25 mg/l KNO<sub>3</sub> synthetic solution is illustrated in Figure 4.45, and also described in Table 4.47. As indicated previously in subsection 4.4.2, Figure 4.17 clearly showed that nitrate concentration in the 25 mg/l BRS batch experiment plateaued at 25 mg/l after 75 days. All the substrates other than the 100% BRS and 100% US had the ability to remove the nitrate completely.

## CHAPTER 4 – RESULTS AND DISCUSSION

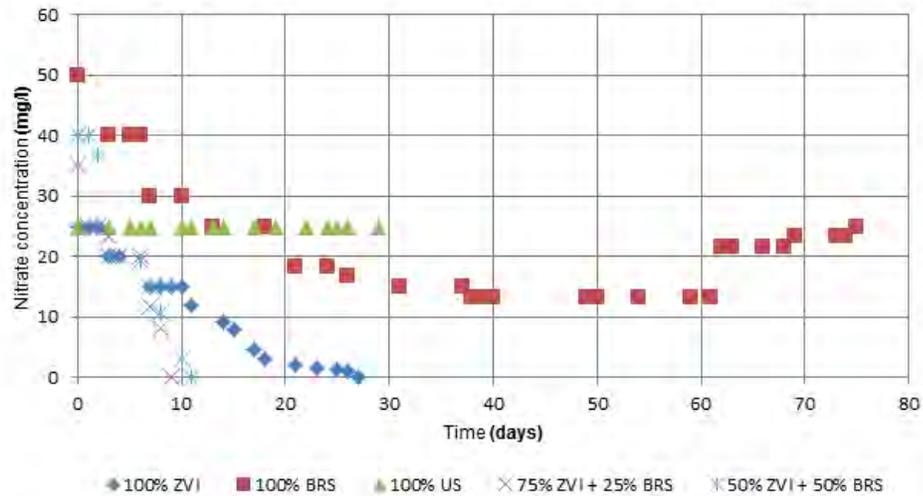


Figure 4.45 Comparison of the 25 mg/l batch tests

Similar to the 10 mg/l batch trials, the time elapsed for the complete nitrate removal via the mix of 75% ZVI + 25% BRS was the least compared with the other substrates, whereas the best denitrification reaction rate was observed when the mix of 50% ZVI + 50% BRS was used. US has exhibited removal efficiency of nil.

The following substrates are shown in order of best performance achieved:

- 1) Mix of 50% ZVI + 50% BRS;
- 2) Mix of 75% ZVI + 25% BRS;
- 3) 100% ZVI;
- 4) 100% BRS;
- 5) 100% US

Table 4.47 Comparison between the various substrates performance during the 25 mg/l-batch tests

25 mg/l – Batch Tests					
	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
	%	days	-	mg/l.day Or 1/day	-
100% ZVI	100	27	1	0.127	0.9439
100% BRS	73	46	1	0.033	0.9382

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100% US	0	-	0	0	NA
75% ZVI + 25% BRS	100	9	0	3.0991	0.9009
50% ZVI + 50% BRS	100	11	0	3.7127	0.94

**Comparison of the 50 mg/l KNO<sub>3</sub> solution batch trials**

The performance of the various substrates in the removal of nitrate from the 50 mg/l KNO<sub>3</sub> synthetic solution is illustrated in Figure 4.46, and also described in Table 4.48.

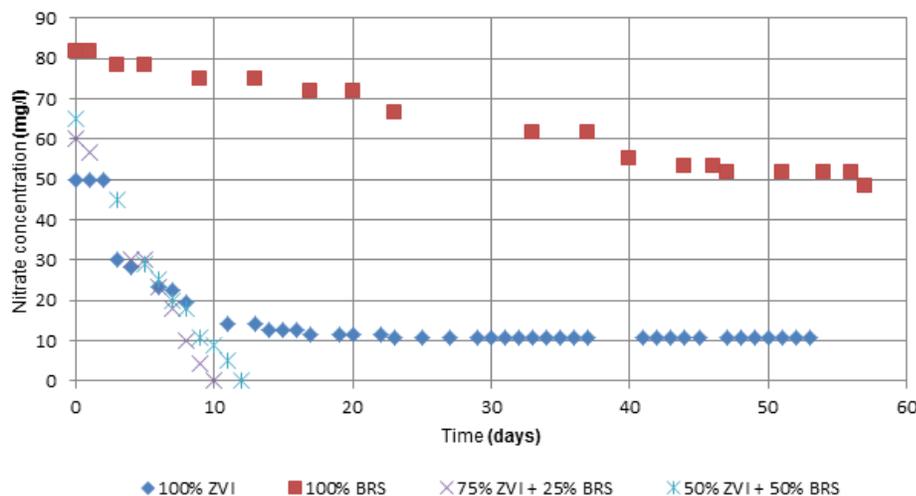


Figure 4.46 Comparison of the 50 mg/l batch tests

In the use of this concentration the removal efficiency was 100% only when the mix of 75% ZVI + 25% BRS or the mix of 50% ZVI + 50% BRS was used.

Contrary to what was noticed in the 10 mg/l and 25 mg/l batches, among the 50 mg/l batch trials as shown in Figure 4.46 and Table 4.48, the mix of 75% ZVI + 25% BRS has demonstrated the optimum performance. In other words, the best denitrification reaction rate was observed when the mix of 75% ZVI + 25% BRS was used. Also, the elapsed time for the complete nitrate removal was the shortest when this mix was used.

The following substrates are presented in order of best performance achieved:

- 1) Mix of 75% ZVI + 25% BRS;

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- 2) Mix of 50% ZVI + 50% BRS;
- 3) 100% ZVI;
- 4) 100% BRS

Table 4.48 Comparison between the various substrates performance during the 50 mg/l-batch tests

	50 mg/l – Batch Tests				
	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
	%	days	-	mg/l.day Or 1/day	-
100% ZVI	79	18	1	0.069	0.8755
100% BRS	41	54	1	0.009	0.9793
75% ZVI + 25% BRS	100	10	0	6.1458	0.9884
50% ZVI + 50% BRS	100	12	0	5.2466	0.9736

**Comparison of the 100 mg/l KNO<sub>3</sub> solution batch trials**

The performance of the various substrates in the removal of nitrate from the 100 mg/l KNO<sub>3</sub> synthetic solution is illustrated in Figure 4.47, and also described in Table 4.49. As indicated previously in subsection 4.4.2, Figure 4.21 clearly showed that nitrate concentration in the 100 mg/l BRS batch experiment plateaued around 140 mg/l after 88 days.

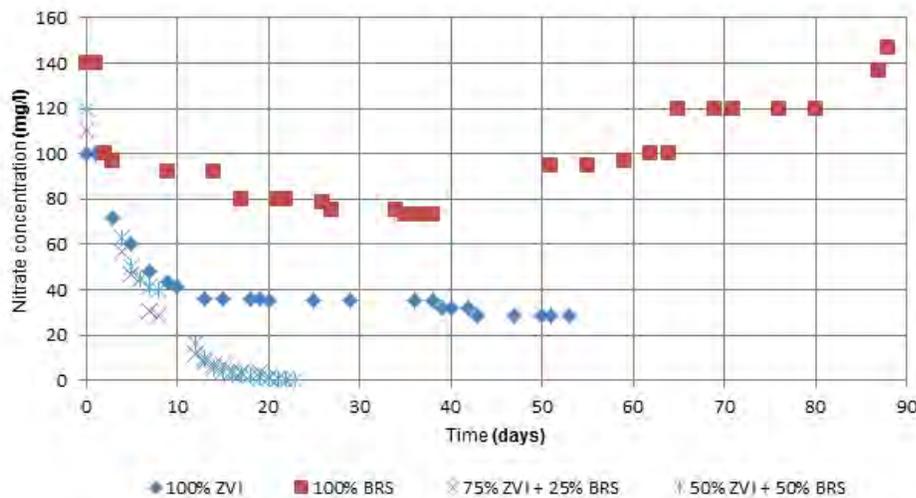


Figure 4.47 Comparison of the 100 mg/l batch tests

## CHAPTER 4 – RESULTS AND DISCUSSION

The mix of 75% ZVI + 25% BRS and the mix of 50% ZVI + 50% BRS were the only substrates that were able to remove the nitrate completely during the 100 mg/l batches.

Contrary to the 50 mg/l batches, and similar to the 10 mg/l and the 25 mg/l batches, the mix of 50% ZVI + 50% BRS has demonstrated the best performance among all the other used substrates in terms of the denitrification reaction rate. On the other hand, as observed with all the different-concentration batches, the elapsed time for the complete nitrate removal was the shortest when the mix of 75% ZVI + 25% BRS was used.

The following substrates are shown in order of best performance achieved:

- 1) Mix of 50% ZVI + 50% BRS;
- 2) Mix of 75% ZVI + 25% BRS;
- 3) 100% ZVI;
- 4) 100% BRS

Table 4.49 Comparison between the various substrates performance during the 100 mg/l-batch tests

<b>100 mg/l – Batch Tests</b>					
	Removal efficiency	Elapsed time	n	k	R <sup>2</sup>
	%	days	-	1/day	-
100% ZVI	72	34	1	0.022	0.6469
100% BRS	48	30	1	0.015	0.7419
75% ZVI + 25% BRS	100	20	1	0.225	0.9676
50% ZVI + 50% BRS	100	21	1	0.267	0.9671

**CHAPTER 5**  
**CONCLUSIONS**

## CHAPTER 5 - CONCLUSIONS

Zero Valent Iron (ZVI), Berea Red Sand (BRS), and Umgeni Sand (US) are the main objects of this research.

BRS and US, which are locally available, are not as common materials in the field of ground-water remediation via PRB technology as ZVI. Considering the low cost of BRS, its abundance, and its active composition, particularly its hematite content, which make BRS an appropriate/effective material in this field, the denitrification efficiency of the sole BRS as well as the combination of BRS with ZVI was investigated in this study through laboratory batch tests. In addition, the examination of the nitrate removal efficiency for ZVI alone as well as US through batch tests was also part of this research.

Through eighteen sets of experiments five substrates in total were investigated including 100% ZVI, 100% BRS, 100% US, mix of 75% ZVI + 25% BRS, and mix of 50% ZVI + 50% BRS. Synthetic solutions of various nitrate concentrations were employed in order to simulate nitrate-contaminated ground-water. The concentrations involved are 10 mg/l, 25 mg/l, 50 mg/l, 100 mg/l, and 500 mg/l.

Besides the 500 mg/l synthetic solution which was used only with the 100% ZVI substrate, in separate batch experiments all the different synthetic solutions were used with each of the involved substrates other than the 100% US which was used only with the 25 mg/l synthetic solution. Results of the batch tests have clearly illustrated the variance in the nitrate removal efficiency of the used substrates for each set of the batch trials.

US, which mainly consists of quartz ( $\text{SiO}_2$ ), was completely passive in the treatment of nitrate as expected.

100% ZVI substrate has revealed perfect nitrate removal efficiency when it was used in the 10 mg/l and 25 mg/l batches. The removal efficiency of this substrate when it was used with 50 mg/l, 100 mg/l, and 500 mg/l synthetic solutions; however, was only 79%, 72%, and 58% respectively.

Taking the initial nitrate concentration applied in these experiments into consideration, the failure of this substrate to remove the nitrate completely in those three batches could possibly be due to various reasons. These reasons include the possibility of the mass of

## CHAPTER 5 - CONCLUSIONS

ZVI used, having reached its reductive denitrification capacity, the possibility of the ZVI used being in improper condition (oxidized state) due to the storage of this material for extended period, or the possibility that the initial pH detected in those experiments was unsuitable for the ZVI to remove those nitrate concentrations completely.

It is recommended that additional batch experiments addressing these factors, and thus optimizing the performance of ZVI in further applications be conducted. In fact, to investigate the effect of those factors, each batch experiment would need to be repeated three times, after some changes, examining one factor at a time.

One experiment would need to be done after changing the solid to liquid ratio, one after rejuvenating the same ZVI that was allocated for this study, and another using a lower initial pH. In addition, since the more iron surface area available the better performance expected, executing other batch trials using iron particles of smaller size is also recommended.

As for BRS, the experimental results obtained from all the 100% BRS batches have demonstrated partial treatment of nitrate. These results indicated average to good nitrate removal efficiency at most batch experiments. In other words, the removal efficiency noticed in the 10 mg/l, 25 mg/l, 50 mg/l, and 100 mg/l BRS batches after 4, 32, 54, and 30 days were 13%, 73%, 41%, and 48% respectively. The incomplete nitrate removal via this substrate could be imputed to the fact that the mass of BRS used has reached its adsorption capacity.

The mix of Berea Red Sand with Zero Valent Iron exhibited 100% nitrate removal efficiency for both mixes, the mix of 50% ZVI + 50% BRS and the mix of 75% ZVI + 25% BRS. The mix of 50% ZVI + 50% BRS; however, has revealed performance better than that of the mix of 75% ZVI + 25% BRS in most batches.

The performance of the mixes of ZVI with BRS overall were better than the performance of each substrate apart. This could be attributable to two reasons. First the quantities of ZVI involved in both mixes were able to reduce the nitrate to levels that could not be reached when the sole BRS was used. Secondly, the quantities of BRS used in both mixes

## CHAPTER 5 - CONCLUSIONS

have revealed to enhance the performance of the mixes more than the same amounts of ZVI could do, when they instead of BRS were used for the 100% ZVI batches.

Since the results obtained from the mixes in the presence of 100 mg/l  $\text{NO}_3$  solution deviated from the results obtained with the other concentrations investigated, a further investigation is required with higher concentrations than 100 mg/l to determine if a similar trend is observed with regards to the initial nitrate concentration and reaction rate.

Significant increase in the nitrate concentration immediately after setting up the batch experiments that contain BRS was noticed. This could be due to the contamination of BRS with nitrate.

In conclusion, BRS as the sole treatment medium is not favorable in the treatment of nitrate, whereas it is believed that the importance of using BRS in combination with other materials such as ZVI is promising. However, since larger laboratory-scale systems allow better simulation of a real PRB system, it is recommended that the performance of both mixes (the mix of 75% ZVI + 25% BRS and the mix of 50% ZVI + 50% BRS) be investigated in column tests.

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## **APPENDICES**

Appendix 1 Sieve analysis for Berea Red Sand and Umgeni Sand

Sieve	Mass of Soil retained	Cum mass of soil retained	Mass of soil passed	Percentage of soil passed
mm	g	g	g	%
<b>Berea Red Sand</b>				
9.5	1.8	1.8	498.2	99.6
6.7	1.4	3.2	496.8	99.4
4.75	2.1	5.3	494.7	98.9
2	4.4	9.7	490.3	98.1
1.18	3.6	13.3	486.7	97.3
0.6	4.7	18	482	96.4
0.425	4.4	22.4	477.6	95.5
0.3	12.3	34.7	465.3	93.1
0.15	245.7	280.4	219.6	43.9
0.075	24.1	304.5	195.5	39.1
0.063	22.9	327.4	172.6	34.5
<b>Umgeni Sand</b>				
9.5	0	0	500	100
6.7	0	0	500	100
4.75	4.4	4.4	495.6	99.1
2	40.1	44.5	455.5	91.1
1.18	60.2	104.7	395.3	79.1
0.6	112.3	217	283	56.6
0.425	84.1	301.1	198.9	39.8
0.3	71.4	372.5	127.5	25.5
0.15	87.5	460	40	8
0.075	17.4	477.4	22.6	4.5
0.063	1.7	479.1	20.9	4.2

Appendix 2 Analysis of total solids and volatile solids for BRS and US

Sample	M <sub>w</sub>	M <sub>d</sub>	M <sub>-fired</sub>	TS	VS	MC
-	g	g	g	%	%	%
<b>Berea Red Sand</b>						
1	18.0074	15.8095	15.0738	87.7945	4.6535	12.206
2	14.999	13.0987	12.4542	87.3305	4.9203	12.67
3	19.7001	17.2754	16.4505	87.6919	4.775	12.308
4	17.5845	15.5479	14.8593	88.4182	4.4289	11.582
Average				87.8088	4.6944	12.191
<b>Umgeni Sand</b>						
1	20.1624	19.15	19.0285	94.9788	0.6345	5.0212
2	20.3088	19.2813	19.1544	94.9406	0.6582	5.0594
3	19.0921	18.1548	18.0394	95.0906	0.6356	4.9094

4	20.8225	19.7748	19.6397	94.9684	0.6832	5.0316
Average				94.9946	0.6529	5.0054

Appendix 3 Eluate test – Major parameters

Substrate	Replicate	pH	C	TDS	NO <sub>3</sub>	Fe
		-	µS/cm	mg/l	mg/l	mg/l
100% ZVI	R1	5.75	15	7.5	0	0.473
	R2	6.05	9.8	4.9	0	0.417
	R3	5.81	10.6	5.3	0	0.521
	Average	5.87	11.8	5.9	0	0.470
100% BRS	R1	6.63	123.8	61.9	25	0.391
	R2	6.44	123.5	61.75	40	0.358
	R3	6.44	123.6	61.8	45	0.766
	Average	6.50	123.6	61.82	25-45	0.505
100% US	R1	5.17	39.7	19.85	0	0.443
	R2	5.21	40.7	20.35	0	0.335
	R3	4.95	40.1	20.05	0	0.484
	Average	5.11	40.2	20.1	0	0.421
75%ZVI+25%BRS	R1	6.81	52.8	26.4	7	1.085
	R2	6.82	51.3	25.65	12	0.484
	R3	7.1	51.2	25.6	15	0.525
	Average	6.91	51.8	25.9	7-15	0.698
50%ZVI+50%BRS	R1	6.48	68.8	34.4	10	0.476
	R2	6.62	68.5	34.25	16	0.932
	R3	6.64	72.1	36.05	20	0.79
	Average	6.58	69.8	34.9	10-20	0.733

Appendix 4 Eluate test – Nitrate concentration

	Conc (Rep1)	Conc (Rep2)	Conc (Rep3)	Conc (Avg)	SD	RSD
	mg/l	mg/l	mg/l	mg/l	mg/l	-
Blank (Distilled H <sub>2</sub> O)	0	0	0	0	0	-
100% ZVI	0	0	0	0	0	-
100% BRS	25	40	45	25-45	10.41	28.39
100% US	0	0	0	0	0	-
75% ZVI + 25% BRS	7	12	15	7-15	4.04	35.65
50% ZVI + 50% BRS	10	16	20	10-20	5.03	32.80

Appendix 5 Eluate test – Iron concentration

Substrate	Replicate	Analyte Name	Conc (Calib)1	Conc (Calib)2	Conc (Calib)3	Conc (Calib)	SD	RSD
		-	mg/l	mg/l	mg/l	mg/l	mg/l	-
100% ZVI	R1	Fe 238.204	0.474	0.473	0.473	0.473	0.001	0.180
	R2	Fe 238.204	0.417	0.416	0.417	0.417	0.000	0.065
	R3	Fe 238.204	0.522	0.517	0.523	0.521	0.003	0.629
	Average						0.470	
100% BRS	R1	Fe 238.204	0.393	0.388	0.392	0.391	0.003	0.650
	R2	Fe 238.204	0.359	0.357	0.357	0.358	0.002	0.428
	R3	Fe 238.204	0.765	0.770	0.763	0.766	0.004	0.514
	Average						0.505	
100% US	R1	Fe 238.204	0.444	0.444	0.441	0.443	0.002	0.419
	R2	Fe 238.204	0.335	0.334	0.335	0.335	0.001	0.150
	R3	Fe 238.204	0.483	0.485	0.484	0.484	0.001	0.260
	Average						0.421	
75%ZVI+25%BRS	R1	Fe 238.204	1.085	1.077	1.093	1.085	0.008	0.771
	R2	Fe 238.204	0.484	0.481	0.487	0.484	0.003	0.605
	R3	Fe 238.204	0.521	0.528	0.525	0.525	0.003	0.664
	Average						0.698	
50%ZVI+50%BRS	R1	Fe 238.204	0.474	0.480	0.475	0.476	0.003	0.698
	R2	Fe 238.204	0.933	0.941	0.921	0.932	0.010	1.071
	R3	Fe 238.204	0.787	0.792	0.792	0.79	0.003	0.388
	Average						0.733	

Appendix 6 Batch test using Zero Valent Iron with 10 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	5.97	1.77	51.7	25.9	278.8	10	0.661

R2	0	6.29	1.88	32.9	16.5	311.1	10	0.564
R3	0	6.20	2.00	26.9	13.5	322.4	10	0.590
Average		6.15	1.88	37.2	18.6	304.1	10	0.605
Middle								
R1	3	9.03	0	47.1	23.55	162.8	5	0.601
R2	3	9.28	0	39.2	19.6	177.3	3	0.417
R3	3	8.83	0	45.1	22.55	150.9	5	0.404
Average		9.05	0	43.8	21.9	163.7	4.3	0.474
End								
R1	8	9.64	0	57.2	28.6	96.3	0	0.496
R2	8	9.98	0	33.4	16.7	165.7	0	0.520
R3	8	9.79	0	29.3	14.65	157.7	0	0.514
Average		9.80	0	39.97	19.98	139.9	0	0.510

Appendix 7 Batch test using Zero Valent Iron with 10 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	10	10	10	10	0	0	0
1	1	10	10	10	10	0	0	0
2	2	7	7	5	6.3	1.15	18.25	0
3	3	5	3	5	4.3	1.15	26.74	0
4	4	3	3	1	2.3	1.15	50	0
5	5	3	3	1	2.3	1.15	50	0
6	6	3	2	1	2	1	50	0
7	7	3	2	1	2	1	50	0
8	8	0	0	0	0	0	-	0

Appendix 8 Batch test using Zero Valent Iron with 10 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
Strat								
R1	0	Fe 238.204	0.664	0.657	0.662	0.661	0.003	0.529
R2	0	Fe 238.204	0.561	0.563	0.568	0.564	0.004	0.654
R3	0	Fe 238.204	0.594	0.591	0.585	0.590	0.004	0.761
Average							0.605	
Middle								
R1	3	Fe 238.204	0.605	0.612	0.586	0.601	0.013	2.239
R2	3	Fe 238.204	0.417	0.420	0.414	0.417	0.003	0.706
R3	3	Fe 238.204	0.404	0.408	0.402	0.404	0.003	0.753
Average							0.474	

End								
R1	8	Fe 238.204	0.509	0.477	0.502	0.496	0.017	3.392
R2	8	Fe 238.204	0.514	0.501	0.544	0.520	0.022	4.242
R3	8	Fe 238.204	0.509	0.523	0.509	0.514	0.008	1.625
Average						0.510		

Appendix 9 Batch test using Berea Red Sand with 10 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	6.22	1.80	112.6	56.3	414.2	50	0.986
R2	0	6.18	2.37	99	49.5	429.6	50	1.291
R3	0	6.29	2.15	102.3	51.2	387.6	50	0.465
Average		6.23	2.11	104.6	52.3	410.5	50	0.914
End								
R1	34	6.08	0	233	116.5	397.8	55	0.390
R2	37	6.50	0	189.2	94.6	399.8	60	0.363
R3	37	6.08	0	220	110	411.8	55	0.396
Average		6.22	0	214.1	107	403.1	56.7	0.383

Appendix 10 Batch test using Berea Red Sand with 10 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	50	50	50	50	0	0	40
1	1	50	50	45	48.3	2.89	5.983	40
2	2	50	50	45	48.3	2.89	5.983	40
3	3	43	45	45	44.3	1.15	2.596	35
4	5	43	45	45	44.3	1.15	2.596	35
5	6	40	45	45	43.3	2.89	6.674	35
6	10	40	45	45	43.3	2.89	6.674	30
7	13	40	45	50	45	5	11.11	40
8	24	50	55	50	51.7	2.89	5.590	40
9	27	50	55	50	51.7	2.89	5.590	40
10	33	50	55	50	51.7	2.89	5.590	40
11	34	55	55	50	53.3	2.89	5.422	50
12	36	55	55	50	53.3	2.89	5.422	50
13	37	55	60	55	56.7	2.89	5.097	50
14	42	55	60	55	56.7	2.89	5.097	50

Appendix 11 Batch test using Berea Red Sand with 10 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	0.975	0.965	1.019	0.986	0.029	2.918
R2	0	Fe 238.204	1.300	1.284	1.289	1.291	0.008	0.649
R3	0	Fe 238.204	0.466	0.466	0.464	0.465	0.001	0.217
Average						0.914		
<b>End</b>								
R1	34	Fe 238.204	0.394	0.390	0.387	0.390	0.003	0.851
R2	37	Fe 238.204	0.366	0.360	0.362	0.363	0.003	0.898
R3	37	Fe 238.204	0.394	0.397	0.398	0.396	0.002	0.567
Average						0.383		

Appendix 12 Batch test using 75% ZVI + 25% BRS with 10 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.52	1.79	47.6	23.8	352.8	17	0.982
R2	0	6.18	1.43	48.5	24.3	360.6	17	0.695
R3	0	6.18	1.26	49.9	24.95	334	17	1.622
Average		6.29	1.49	48.7	24.3	349.1	17	1.100
<b>Middle</b>								
R1	4	8.25	0	57.9	28.95	59.1	8	0.990
R2	4	8.32	0	62.1	31.1	93.7	7	0.988
R3	4	8.23	0	57.3	28.7	100.8	7	1.640
Average		8.27	0	59.1	29.6	84.5	7.3	1.206
<b>End</b>								
R1	8	8.69	0	55.9	27.95	40.1	0	1.036
R2	6	8.68	0	56.7	28.4	75	0	1.434
R3	6	8.39	0	57.9	28.95	62	0	1.194
Average		8.59	0	56.8	28.4	59.03	0	1.221

Appendix 13 Batch test using 75% ZVI + 25% BRS with 10 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	17	17	17	17	0	0	12
1	1	17	17	17	17	0	0	12
2	2	17	17	17	17	0	0	10

3	3	15	15	15	15	0	0	8
4	4	8	7	7	7.3	0.58	7.945	2
5	5	3	3	5	3.7	1.15	31.08	2
6	6	3	0	0	1	1.73	173	2
7	7	1	0	0	0.3	1	333.3	2
8	8	0	0	0	0	0	-	0

Appendix 14 Batch test using 75% ZVI + 25% BRS with 10 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	0.985	0.985	0.975	0.982	0.006	0.571
R2	0	Fe 238.204	0.695	0.693	0.698	0.695	0.003	0.406
R3	0	Fe 238.204	1.634	1.612	1.619	1.622	0.011	0.674
Average						1.100		
<b>Middle</b>								
R1	4	Fe 238.204	1.009	0.985	0.976	0.990	0.017	1.723
R2	4	Fe 238.204	1.019	0.966	0.978	0.988	0.028	2.814
R3	4	Fe 238.204	1.656	1.635	1.628	1.640	0.015	0.889
Average						1.206		
<b>End</b>								
R1	8	Fe 238.204	1.038	1.037	1.033	1.036	0.003	0.245
R2	6	Fe 238.204	1.426	1.432	1.443	1.434	0.008	0.589
R3	6	Fe 238.204	1.194	1.195	1.193	1.194	0.001	0.073
Average						1.221		

Appendix 15 Batch test using 50% ZVI + 50% BRS with 10 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.60	1.94	67.6	33.8	390.4	25	0.718
R2	0	6.30	1.74	69.3	34.7	369.8	25	1.918
R3	0	6.66	1.28	70.9	35.5	369.4	25	1.860
Average		6.52	1.65	69.3	34.7	376.5	25	1.499
<b>Middle</b>								
R1	5	7.44	0	93.8	46.9	136.9	8	0.710
R2	5	7.81	0	73.9	36.95	78.2	6	0.932
R3	5	8.17	0	76	38	53.1	6	0.602
Average		7.81	0	81.2	40.6	89.4	6.7	0.748
<b>End</b>								
R1	8	8.07	0	80.6	40.3	12.1	0	0.715
R2	7	7.99	0	66.7	33.4	41.2	0	0.690

R3	8	8.03	0	73.4	36.7	66.6	0	1.325
Average		8.03	0	73.6	36.8	40	0	0.910

Appendix 16 Batch test using 50% ZVI + 50% BRS with 10 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	25	25	25	25	0	0	20
1	1	25	25	25	25	0	0	20
2	2	20	20	20	20	0	0	17
3	3	15	15	15	15	0	0	15
4	4	15	13	15	14.3	1.15	8.042	15
5	5	8	6	6	6.7	1.15	17.16	2
6	6	3	3	3	3	0	0	1
7	7	1	0	1	0.7	0.58	82.86	0
8	8	0	0	0	0	0	-	0

Appendix 17 Batch test using 50% ZVI + 50% BRS with 10 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	0.732	0.703	0.720	0.718	0.015	2.048
R2	0	Fe 238.204	1.922	1.899	1.932	1.918	0.017	0.906
R3	0	Fe 238.204	1.892	1.845	1.844	1.860	0.027	1.477
Average							1.499	
<b>Middle</b>								
R1	5	Fe 238.204	0.705	0.711	0.714	0.710	0.005	0.687
R2	5	Fe 238.204	0.945	0.920	0.932	0.932	0.013	1.378
R3	5	Fe 238.204	0.603	0.599	0.603	0.602	0.002	0.350
Average							0.748	
<b>End</b>								
R1	8	Fe 238.204	0.720	0.712	0.713	0.715	0.004	0.610
R2	7	Fe 238.204	0.695	0.688	0.687	0.690	0.004	0.632
R3	8	Fe 238.204	1.330	1.321	1.324	1.325	0.005	0.346
Average							0.910	

Appendix 18 Batch test using Zero Valent Iron with 25 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	5.68	-	61.2	30.6	350.1	25	1.155
R2	0	5.05	-	61.4	30.7	311.3	25	1.449
R3	0	6.32	-	58.7	29.4	294.4	25	1.311
Average		5.68	-	60.4	30.2	318.6	25	1.305
<b>Middle</b>								
R1	11	9.57	-	64.9	32.5	221.2	12	0.374
R2	11	9.50	-	65.3	32.7	226.5	12	0.395
R3	11	9.36	-	63.4	31.7	231.6	12	0.439
Average		9.48	-	64.5	32.3	226.4	12	0.403
<b>End</b>								
R1	27	9.51	-	75.2	37.6	174	0	0.437
R2	26	9.35	-	76.4	38.2	186.3	0	0.318
R3	27	9.26	-	72.5	36.3	163	0	0.828
Average		9.37	-	74.7	37.4	174.4	0	0.528

Appendix 19 Batch test using Zero Valent Iron with 25 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	25	25	25	25	0	0	0
1	1	25	25	25	25	0	0	0
2	2	25	25	25	25	0	0	0
3	3	20	20	20	20	0	0	0
4	4	20	20	20	20	0	0	0
5	7	15	15	15	15	0	0	0
6	8	15	15	15	15	0	0	0
7	9	15	15	15	15	0	0	0
8	10	15	15	15	15	0	0	0
9	11	12	12	12	12	0	0	0
10	14	8	10	10	9.3	1.2	12.9	0
11	15	8	8	8	8	0	0	0
12	17	4	5	5	4.7	0.6	12.77	0
13	18	2	2	5	3	1.7	56.67	0
14	21	2	2	2	2	0	0	0
15	23	2	1	2	1.7	0.6	35.29	0
16	25	1	1	2	1.3	0.6	46.15	0
17	26	1	0	2	1	1	100	0
18	27	0	0	0	0	0	-	0

Appendix 20 Batch test using Zero Valent Iron with 25 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	1.168	1.155	1.141	1.155	0.014	1.172
R2	0	Fe 238.204	1.438	1.449	1.460	1.449	0.011	0.778
R3	0	Fe 238.204	1.298	1.302	1.332	1.311	0.019	1.415
Average						1.305		
<b>Middle</b>								
R1	11	Fe 238.204	0.376	0.372	0.374	0.374	0.002	0.619
R2	11	Fe 238.204	0.398	0.394	0.392	0.395	0.003	0.712
R3	11	Fe 238.204	0.438	0.440	0.439	0.439	0.001	0.272
Average						0.403		
<b>End</b>								
R1	27	Fe 238.204	0.434	0.438	0.438	0.437	0.002	0.470
R2	26	Fe 238.204	0.317	0.320	0.318	0.318	0.002	0.535
R3	27	Fe 238.204	0.833	0.826	0.826	0.828	0.004	0.519
Average						0.528		

Appendix 21 Batch test using Berea Red Sand with 25 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.36	-	108.3	54.2	340.8	50	2.187
R2	0	6.37	-	110.4	55.2	339.5	50	0.446
R3	0	6.31	-	109.3	54.7	339.6	50	0.708
Average		6.35	-	109.3	54.7	340	50	1.114
<b>End</b>								
R1	62	6.42	-	388	169	320.2	15	0.481
R2	69	6.23	-	295	147.5	342.6	30	0.480
R3	75	6.19	-	229	114.5	315.2	30	0.462
Average		6.28	-	304	143.7	326	25	0.474

Appendix 22 Batch test using Berea Red Sand with 25 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	50	50	50	50	0	0	40
1	3	40	40	40	40	0	0	40

2	5	40	40	40	40	0	0	40
3	6	40	40	40	40	0	0	40
4	7	30	30	30	30	0	0	35
5	10	30	30	30	30	0	0	35
6	13	25	25	25	25	0	0	35
7	18	25	25	25	25	0	0	25
8	21	20	20	15	18.3	2.89	15.79	25
9	24	20	20	15	18.3	2.89	15.79	20
10	26	15	20	15	16.7	2.89	17.31	20
11	31	15	20	10	15	5	33.33	20
12	37	15	20	10	15	5	33.33	20
13	38	15	15	10	13.3	2.89	21.73	20
14	39	15	15	10	13.3	2.89	21.73	20
15	40	15	15	10	13.3	2.89	21.73	20
16	49	15	15	10	13.3	2.89	21.73	20
17	50	10	25	5	13.3	10.41	78.27	20
18	54	10	25	5	13.3	10.41	78.27	20
19	59	10	25	5	13.3	10.41	78.27	20
20	61	10	25	5	13.3	10.41	78.27	20
21	62	15	25	25	21.7	5.77	26.59	20
22	63	15	25	25	21.7	5.77	26.59	20
23	66	15	25	25	21.7	5.77	26.59	20
24	68	15	25	25	21.7	5.77	26.59	20
25	69	15	30	25	23.3	7.64	32.79	20
26	73	15	30	25	23.3	7.64	32.79	20
27	74	15	30	25	23.3	7.64	32.79	20
28	75	15	30	30	25	8.66	34.64	20
29	80	15	30	30	25	8.66	34.64	20
30	84	15	30	30	25	8.66	34.64	20
31	92	15	30	30	25	8.66	34.64	20
32	98	15	30	30	25	8.66	34.64	20
33	106	15	30	30	25	8.66	34.64	20
34	120	15	30	30	25	8.66	34.64	20
35	129	15	30	30	25	8.66	34.64	20
36	130	15	30	30	25	8.66	34.64	20
37	131	15	30	30	25	8.66	34.64	20
38	132	15	30	30	25	8.66	34.64	20

Appendix 23 Batch test using Berea Red Sand with 25 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
Strat								
R1	0	Fe 238.204	2.183	2.208	2.171	2.187	0.019	0.875
R2	0	Fe 238.204	0.449	0.448	0.442	0.446	0.004	0.832

R3	0	Fe 238.204	0.708	0.706	0.710	0.708	0.002	0.231
Average						1.114		
End								
R1	62	Fe 238.204	0.482	0.482	0.479	0.481	0.002	0.399
R2	69	Fe 238.204	0.478	0.480	0.480	0.480	0.001	0.215
R3	75	Fe 238.204	0.462	0.464	0.461	0.462	0.002	0.377
Average						0.474		

Appendix 24 Batch test using Umgeni Sand with 25 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	5.05	-	74.3	37.2	370.7	25	1.992
R2	0	5.18	-	70.5	35.3	379.8	25	1.566
R3	0	5.14	-	73.5	36.8	394.1	25	1.100
Average		5.12	-	72.8	36.4	381.5	25	1.553
End								
R1	29	5.12	-	76.4	38.2	277.4	25	0.960
R2	29	5.05	-	77.6	38.8	310.4	25	1.070
R3	29	5.04	-	76.2	38.1	307.9	25	1.077
Average		5.07	-	76.7	38.4	298.6	25	1.036

Appendix 25 Batch test using Umgeni Sand with 25 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	25	25	25	25	0	0	0
1	3	25	25	25	25	0	0	0
2	5	25	25	25	25	0	0	0
3	6	25	25	25	25	0	0	0
4	7	25	25	25	25	0	0	0
5	10	25	25	25	25	0	0	0
6	11	25	25	25	25	0	0	0
7	13	25	25	25	25	0	0	0
8	14	25	25	25	25	0	0	0
9	17	25	25	25	25	0	0	0
10	19	25	25	25	25	0	0	0
11	22	25	25	25	25	0	0	0
12	24	25	25	25	25	0	0	0
13	25	25	25	25	25	0	0	0
14	26	25	25	25	25	0	0	0

15	29	25	25	25	25	0	0	0
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Appendix 26 Batch test using Umgeni Sand with 25 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
Strat								
R1	0	Fe 238.204	2.016	1.980	1.979	1.992	0.021	1.040
R2	0	Fe 238.204	1.579	1.558	1.560	1.566	0.012	0.736
R3	0	Fe 238.204	1.100	1.109	1.090	1.100	0.009	0.859
Average						1.553		
End								
R1	29	Fe 238.204	0.952	0.960	0.969	0.960	0.009	0.925
R2	29	Fe 238.204	1.093	1.075	1.043	1.070	0.025	2.359
R3	29	Fe 238.204	1.080	1.077	1.075	1.077	0.003	0.239
Average						1.036		

Appendix 27 Batch test using 75% ZVI + 25% BRS with 25 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	6.91	-	81.5	40.75	282.9	35	0.879
R2	0	6.55	-	83.1	41.55	312.3	35	1.412
R3	0	6.61	-	76.4	38.2	313.4	35	1.416
Average		6.69	-	80.3	40.16	302.9	35	1.236
Middle								
R1	7	9.07	-	83.5	41.8	131.9	10	1.427
R2	7	8.71	-	82.6	41.3	130.3	12	1.521
R3	7	8.84	-	96.3	48.2	116.9	13	1.692
Average		8.87	-	87.5	43.8	126.4	11.7	1.547
End								
R1	9	9.03	-	82.2	41.1	123.5	0	4.347
R2	9	8.59	-	92.3	46.15	120.9	0	7.255
R3	9	8.01	-	102.7	51.35	118.6	0	7.987
Average		8.54	-	92.4	46.2	121	0	6.530

Appendix 28 Batch test using 75% ZVI + 25% BRS with 25 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	35	35	35	35	0	0	10
1	1	25	25	25	25	0	0	10
2	2	25	25	25	25	0	0	8
3	3	25	20	25	23.3	2.89	12.4	8
4	4	20	20	20	20	0	0	5
5	6	20	20	20	20	0	0	5
6	7	10	12	13	11.7	1.53	13.08	0
7	8	10	10	5	8.3	2.89	34.82	0
8	9	0	0	0	0	0	-	0

Appendix 29 Batch test using 75% ZVI + 25% BRS with 25 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	0.882	0.884	0.872	0.879	0.006	0.710
R2	0	Fe 238.204	1.396	1.416	1.426	1.412	0.015	1.081
R3	0	Fe 238.204	1.430	1.401	1.417	1.416	0.014	1.015
Average						1.236		
<b>Middle</b>								
R1	7	Fe 238.204	1.402	1.416	1.461	1.427	0.031	2.174
R2	7	Fe 238.204	1.533	1.526	1.505	1.521	0.015	0.964
R3	7	Fe 238.204	1.660	1.717	1.701	1.692	0.029	1.726
Average						1.547		
<b>End</b>								
R1	9	Fe 238.204	4.418	4.300	4.323	4.347	0.062	1.432
R2	9	Fe 238.204	7.260	7.301	7.205	7.255	0.048	0.663
R3	9	Fe 238.204	8.046	7.987	7.928	7.987	0.059	0.741
Average						6.530		

Appendix 30 Batch Test using 50% ZVI + 50% BRS with 25 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.61	-	88.1	44.05	292.8	40	1.790
R2	0	6.71	-	88.2	44.1	306.4	40	1.658

R3	0	6.56	-	85.7	42.9	318.4	40	0.987
Average		6.63	-	87.3	43.7	305.9	40	1.478
<b>Middle</b>								
R1	7	8.33	-	92.4	46.2	64.7	17	1.536
R2	7	7.74	-	113.3	56.7	90.8	13	1.280
R3	7	8.42	-	93.3	46.7	47.5	15	1.144
Average		8.16	-	99.7	49.9	67.7	15	1.320
<b>End</b>								
R1	11	7.65	-	87.3	43.7	42.2	0	6.387
R2	11	7.59	-	121.2	60.6	46.1	0	1.320
R3	11	7.25	-	95.1	47.6	40.7	0	7.342
Average		7.50	-	101.2	50.6	43	0	5.016

Appendix 31 Batch Test using 50% ZVI + 50% BRS with 25 mg/l KNO<sub>3</sub> solution – Nitrate Concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	40	40	40	40	0	0	20
1	1	40	40	40	40	0	0	10
2	2	35	40	35	36.7	2.89	7.875	5
3	3	20	20	20	20	0	0	5
4	6	20	18	20	19.3	1.15	5.959	0
5	7	17	13	15	15	2	13.33	0
6	8	12	10	10	10.7	1.15	10.75	0
7	10	5	2	2	3	1.73	57.67	0
8	11	0	0	0	0	0	-	0

Appendix 32 Batch test using 50% ZVI + 50% BRS with 25 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	1.774	1.799	1.798	1.790	0.014	0.790
R2	0	Fe 238.204	1.679	1.644	1.650	1.658	0.019	1.149
R3	0	Fe 238.204	0.996	0.988	0.978	0.987	0.009	0.896
Average						1.478		
<b>Middle</b>								
R1	7	Fe 238.204	1.513	1.539	1.556	1.536	0.022	1.428
R2	7	Fe 238.204	1.255	1.285	1.300	1.280	0.023	1.790
R3	7	Fe 238.204	1.144	1.147	1.142	1.144	0.002	0.196
Average						1.320		

End								
R1	11	Fe 238.204	6.327	6.398	6.435	6.387	0.055	0.864
R2	11	Fe 238.204	1.329	1.325	1.307	1.320	0.012	0.895
R3	11	Fe 238.204	7.347	7.354	7.325	7.342	0.015	0.209
Average						5.016		

Appendix 33 Batch test using Zero Valent Iron with 50 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	5.63	-	110	55	294.6	50	2.226
R2	0	6.23	-	109.3	54.7	287.9	50	2.154
R3	0	5.96	-	110.8	55.4	298.6	50	1.730
Average		5.94	-	110.03	55.03	293.7	50	2.037
Middle								
R1	6	10.17	-	141.8	70.9	216.4	20	1.135
R2	6	9.88	-	123.6	61.8	228.1	25	0.411
R3	6	9.71	-	126.3	63.2	228.5	25	0.362
Average		9.92	-	130.6	65.3	224.3	23.3	0.636
End								
R1	23	9.74	-	145.1	72.6	206	12	4.261
R2	17	9.89	-	128.6	64.3	211.5	5	1.869
R3	14	9.69	-	128.8	64.4	213.4	15	3.936
Average		9.77	-	134.2	67.1	210.3	10.7	3.355

Appendix 34 Batch test using Zero Valent Iron with 50 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	50	50	50	50	0	0	0
1	1	50	50	50	50	0	0	0
2	2	50	50	50	50	0	0	0
3	3	30	30	30	30	0	0	0
4	4	30	30	25	28.3	2.89	10.21	0
5	6	20	25	25	23.3	2.89	12.4	0
6	7	18	25	25	22.7	4.04	17.8	0
7	8	18	20	20	19.3	1.15	5.959	0
8	11	15	8	20	14.3	6.03	42.17	0
9	13	15	8	20	14.3	6.03	42.17	0
10	14	15	8	15	12.7	4.04	31.81	0
11	15	15	8	15	12.7	4.04	31.81	0
12	16	15	8	15	12.7	4.04	31.81	0

13	17	15	5	15	11.7	5.77	49.32	0
14	19	15	5	15	11.7	5.77	49.32	0
15	20	15	5	15	11.7	5.77	49.32	0
16	22	15	5	15	11.7	5.77	49.32	0
17	23	12	5	15	10.7	5.13	47.94	0
18	25	12	5	15	10.7	5.13	47.94	0
19	27	12	5	15	10.7	5.13	47.94	0
20	29	12	5	15	10.7	5.13	47.94	0
21	30	12	5	15	10.7	5.13	47.94	0
22	31	12	5	15	10.7	5.13	47.94	0
23	32	12	5	15	10.7	5.13	47.94	0
24	33	12	5	15	10.7	5.13	47.94	0
25	34	12	5	15	10.7	5.13	47.94	0
26	35	12	5	15	10.7	5.13	47.94	0
27	36	12	5	15	10.7	5.13	47.94	0
28	37	12	5	15	10.7	5.13	47.94	0
29	41	12	5	15	10.7	5.13	47.94	0
30	42	12	5	15	10.7	5.13	47.94	0
31	43	12	5	15	10.7	5.13	47.94	0
32	44	12	5	15	10.7	5.13	47.94	0
33	45	12	5	15	10.7	5.13	47.94	0
34	47	12	5	15	10.7	5.13	47.94	0
35	48	12	5	15	10.7	5.13	47.94	0
36	49	12	5	15	10.7	5.13	47.94	0
37	50	12	5	15	10.7	5.13	47.94	0
38	51	12	5	15	10.7	5.13	47.94	0
39	52	12	5	15	10.7	5.13	47.94	0
40	53	12	5	15	10.7	5.13	47.94	0

Appendix 35 Batch test using Zero Valent Iron with 50 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	2.216	2.211	2.252	2.226	0.023	1.018
R2	0	Fe 238.204	2.150	2.153	2.159	2.154	0.005	0.218
R3	0	Fe 238.204	1.757	1.726	1.708	1.730	0.025	1.421
Average						2.037		
<b>Middle</b>								
R1	6	Fe 238.204	1.133	1.128	1.146	1.135	0.009	0.808
R2	6	Fe 238.204	0.413	0.409	0.413	0.411	0.002	0.597
R3	6	Fe 238.204	0.362	0.362	0.360	0.362	0.001	0.251
Average						0.636		
<b>End</b>								
R1	23	Fe 238.204	4.198	4.295	4.288	4.261	0.054	1.267

R2	17	Fe 238.204	1.880	1.861	1.865	1.869	0.010	0.540
R3	14	Fe 238.204	3.917	3.913	3.977	3.936	0.036	0.909
Average						3.355		

Appendix 36 Batch test using Berea Red Sand with 50 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
Start								
R1	0	6.41	-	153.1	76.6	336.1	85	1.089
R2	0	6.19	-	153.7	76.9	352.2	75	1.758
R3	0	6.28	-	153.6	76.3	360.3	85	1.225
Average		6.29	-	153.5	76.6	349.5	81.7	1.357
End								
R1	57	6.26	-	254	127	283.3	50	0.495
R2	57	6.10	-	235	117.5	304.5	30	0.482
R3	47	5.99	-	272	136	321.1	65	0.772
Average		6.12	-	253.7	126.8	303	48.3	0.583

Appendix 37 Batch test using Berea Red Sand with 50 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	85	75	85	81.7	5.77	7.062	35
1	1	85	75	85	81.7	5.77	7.062	35
2	3	85	75	75	78.3	5.77	7.369	30
3	5	85	75	75	78.3	5.77	7.369	30
4	9	75	75	75	75	0	0	30
5	13	75	75	75	75	0	0	30
6	17	75	65	75	71.7	5.77	8.047	30
7	20	75	65	75	71.7	5.77	8.047	30
8	23	65	65	70	66.7	2.89	4.333	30
9	33	65	50	70	61.7	10.41	16.87	18
10	37	65	50	70	61.7	10.41	16.87	18
11	40	55	40	70	55	15	27.27	18
12	44	55	35	70	53.3	17.56	32.95	18
13	46	55	35	70	53.3	17.56	32.95	18
14	47	55	35	65	51.7	15.28	29.56	18
15	51	55	35	65	51.7	15.28	29.56	18
16	54	55	35	65	51.7	15.28	29.56	18
17	56	55	35	65	51.7	15.28	29.56	18
18	57	50	30	65	48.3	17.56	36.36	15

Appendix 38 Batch test using Berea Red Sand with 50 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	1.096	1.083	1.087	1.089	0.007	0.610
R2	0	Fe 238.204	1.754	1.756	1.765	1.758	0.006	0.324
R3	0	Fe 238.204	1.220	1.229	1.226	1.225	0.005	0.375
Average						1.357		
<b>End</b>								
R1	57	Fe 238.204	0.499	0.493	0.493	0.495	0.003	0.692
R2	57	Fe 238.204	0.480	0.484	0.483	0.482	0.002	0.479
R3	47	Fe 238.204	0.769	0.779	0.768	0.772	0.006	0.792
Average						0.583		

Appendix 39 Batch test using 75% ZVI + 25% BRS with 50 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.46	-	121.9	60.95	337.6	60	1.493
R2	0	6.50	-	123.3	61.7	330.4	60	1.849
R3	0	6.75	-	128.3	64.2	323	60	2.047
Average		6.57	-	124.5	62.3	330.3	60	1.796
<b>Middle</b>								
R1	6	8.75	-	115	57.5	245.3	20	0.959
R2	6	8.84	-	114.4	57.2	254.6	25	0.791
R3	6	8.72	-	114.1	57.1	251.1	25	1.022
Average		8.77	-	114.5	57.3	250.3	23.3	0.924
<b>End</b>								
R1	10	9.40	-	100.2	50.1	140.6	0	7.395
R2	10	9.36	-	107.7	53.9	167.1	0	5.101
R3	10	9.60	-	99.1	49.6	176.7	0	3.593
Average		9.45	-	102.3	51.2	161.5	0	5.363

Appendix 40 Batch test using 75% ZVI + 25% BRS with 50 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	60	60	60	60	0	0	15

1	1	55	60	55	56.7	2.89	5.097	15
2	4	25	30	35	30	5	16.67	20
3	5	25	30	35	30	5	16.67	20
4	6	20	25	25	23.3	2.89	12.4	15
5	7	18	18	18	18	0	0	10
6	8	10	10	10	10	0	0	10
7	9	3	5	5	4.3	1.15	26.74	5
8	10	0	0	0	0	0	-	0

Appendix 41 Batch test using 75% ZVI + 25% BRS with 50 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	1.490	1.488	1.500	1.493	0.006	0.412
R2	0	Fe 238.204	1.849	1.851	1.849	1.849	0.001	0.067
R3	0	Fe 238.204	2.062	2.045	2.034	2.047	0.014	0.691
Average						1.796		
<b>Middle</b>								
R1	6	Fe 238.204	0.948	0.964	0.965	0.959	0.010	1.030
R2	6	Fe 238.204	0.792	0.793	0.787	0.791	0.003	0.413
R3	6	Fe 238.204	1.007	1.018	1.042	1.022	0.018	1.732
Average						0.924		
<b>End</b>								
R1	10	Fe 238.204	7.411	7.414	7.362	7.395	0.029	0.398
R2	10	Fe 238.204	5.144	5.100	5.058	5.101	0.043	0.844
R3	10	Fe 238.204	3.595	3.595	3.588	3.593	0.004	0.107
Average						5.363		

Appendix 42 Batch test using 50% ZVI + 50% BRS with 50 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.38	-	149.3	74.7	331.8	65	0.484
R2	0	6.27	-	154.1	77.1	319.9	65	0.511
R3	0	6.27	-	144	72	326.3	65	0.426
Average		6.31	-	149.1	74.6	326	65	0.474
<b>Middle</b>								
R1	6	8.34	-	143.6	71.8	169.9	25	1.451
R2	6	8.68	-	134.1	67.1	159.7	25	1.065
R3	6	7.92	-	147.4	73.7	166.9	25	0.910
Average		8.31	-	141.7	70.9	165.5	25	1.142

End								
R1	12	9.18	-	119.1	59.6	150	0	5.954
R2	12	8.94	-	109.2	54.6	134.2	0	2.732
R3	12	9.06	-	115.2	57.6	131.7	0	6.596
Average		9.06	-	114.5	57.3	138.6	0	5.094

Appendix 43 Batch test using 50% ZVI + 50% BRS with 50 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	65	65	65	65	0	0	20
1	3	50	50	35	45	8.66	19.24	0
2	5	30	30	27	29	1.73	5.966	0
3	6	25	25	25	25	0	0	0
4	7	20	20	20	20	0	0	0
5	8	17	17	20	18	1.73	9.611	0
6	9	10	12	10	10.7	1.15	10.75	0
7	10	8	10	8	8.7	1.15	13.22	0
8	11	5	5	5	5	0	0	0
9	12	0	0	0	0	0	-	0

Appendix 44 Batch test using 50% ZVI + 50% BRS with 50 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
Strat								
R1	0	Fe 238.204	0.482	0.488	0.483	0.484	0.003	0.716
R2	0	Fe 238.204	0.513	0.509	0.511	0.511	0.002	0.368
R3	0	Fe 238.204	0.427	0.423	0.427	0.426	0.002	0.515
Average						0.474		
Middle								
R1	6	Fe 238.204	1.454	1.441	1.459	1.451	0.009	0.631
R2	6	Fe 238.204	1.057	1.060	1.079	1.065	0.012	1.152
R3	6	Fe 238.204	0.915	0.907	0.909	0.910	0.004	0.453
Average						1.142		
End								
R1	12	Fe 238.204	5.962	5.946	5.952	5.954	0.008	0.137
R2	12	Fe 238.204	2.738	2.739	2.719	2.732	0.012	0.422
R3	12	Fe 238.204	6.650	6.621	6.517	6.596	0.070	1.061
Average						5.094		

Appendix 45 Batch test using Zero Valent Iron with 100 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	μS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.18	-	207	103.5	292.5	100	2.615
R2	0	6.34	-	217	108.5	290.1	100	1.625
R3	0	6.19	-	215	107.5	285	100	1.666
Average		6.24	-	213	106.5	289.2	100	1.969
<b>Middle</b>								
R1	5	9.93	-	251	125.5	225.9	60	0.434
R2	5	9.99	-	257	128.5	212.7	60	0.426
R3	5	9.95	-	254	127	220.1	60	0.401
Average		9.96	-	254	127	219.6	60	0.420
<b>End</b>								
R1	43	10.10	-	236	118	218.5	40	4.410
R2	20	10.61	-	295	147.5	139.5	5	1.309
R3	39	10.01	-	227	113.5	210.3	40	6.698
Average		10.24	-	252.7	126.3	189.4	28.3	4.139

Appendix 46 Batch test using Zero Valent Iron with 100 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	100	100	100	100	0	0	0
1	1	100	100	100	100	0	0	0
2	2	100	100	100	100	0	0	0
3	3	65	80	70	71.7	7.64	10.66	0
4	5	60	60	60	60	0	0	0
5	7	55	35	55	48.3	11.55	23.91	0
6	9	55	20	55	43.3	20.21	46.67	0
7	10	55	20	50	41.7	18.93	45.40	0
8	13	50	8	50	36	24.25	67.36	0
9	15	50	8	50	36	24.25	67.36	0
10	18	50	8	50	36	24.25	67.36	0
11	19	50	8	50	36	24.25	67.36	0
12	20	50	5	50	35	25.98	74.23	0
13	25	50	5	50	35	25.98	74.23	0
14	29	50	5	50	35	25.98	74.23	0
15	36	50	5	50	35	25.98	74.23	0
16	38	50	5	50	35	25.98	74.23	0
17	39	50	5	40	31.7	23.63	74.54	0
18	40	50	5	40	31.7	23.63	74.54	0
19	42	50	5	40	31.7	23.63	74.54	0
20	43	40	5	40	28.3	20.21	71.41	0

21	47	40	5	40	28.3	20.21	71.41	0
22	50	40	5	40	28.3	20.21	71.41	0
23	51	40	5	40	28.3	20.21	71.41	0
24	53	40	5	40	28.3	20.21	71.41	0

Appendix 47 Batch test using Zero Valent Iron with 100 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	2.650	2.609	2.587	2.615	0.032	1.229
R2	0	Fe 238.204	1.632	1.618	1.625	1.625	0.007	0.439
R3	0	Fe 238.204	1.646	1.677	1.674	1.666	0.017	1.037
Average						1.969		
<b>Middle</b>								
R1	5	Fe 238.204	0.429	0.429	0.444	0.434	0.009	1.969
R2	5	Fe 238.204	0.429	0.425	0.425	0.426	0.003	0.609
R3	5	Fe 238.204	0.398	0.405	0.401	0.401	0.003	0.826
Average						0.420		
<b>End</b>								
R1	43	Fe 238.204	4.422	4.394	4.414	4.410	0.015	0.334
R2	20	Fe 238.204	1.301	1.327	1.300	1.309	0.015	1.181
R3	39	Fe 238.204	6.672	6.679	6.742	6.698	0.038	0.574
Average						4.139		

Appendix 48 Batch test using Berea Red Sand with 100 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.37	-	261	130.5	315.9	140	1.648
R2	0	6.33	-	259	129.5	328.1	140	1.831
R3	0	6.30	-	261	130.5	336.1	140	1.805
Average		6.33	-	260.3	130.2	326.7	140	1.761
<b>End</b>								
R1	65	6.01	-	314	157	310	120	0.531
R2	88	5.85	-	355	177.5	320.6	150	0.516
R3	88	6.15	-	457	228.5	326.7	170	0.399
Average		6	-	375.3	187.7	319.1	146.7	0.482

Appendix 49 Batch test using Berea Red Sand with 100 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	140	140	140	140	0	0	45
1	1	140	140	140	140	0	0	45
2	2	100	100	100	100	0	0	45
3	3	95	100	95	96.7	2.89	2.989	45
4	9	90	90	95	91.7	2.89	3.152	35
5	14	90	90	95	91.7	2.89	3.152	35
6	17	80	80	80	80	0	0	35
7	21	80	80	80	80	0	0	35
8	22	80	80	80	80	0	0	35
9	26	75	80	80	78.3	2.89	3.691	35
10	27	75	75	75	75	0	0	35
11	34	75	75	75	75	0	0	30
12	35	70	75	75	73.3	2.89	3.943	30
13	36	70	75	75	73.3	2.89	3.943	30
14	37	70	75	75	73.3	2.89	3.943	30
15	38	70	75	75	73.3	2.89	3.943	30
16	51	85	100	100	95	8.66	9.116	30
17	55	85	100	100	95	8.66	9.116	30
18	59	90	100	100	96.7	5.77	5.967	25
19	62	100	100	100	100	0	0	25
20	64	100	100	100	100	0	0	25
21	65	120	120	120	120	0	0	25
22	69	120	120	120	120	0	0	25
23	71	120	120	120	120	0	0	25
24	76	120	120	120	120	0	0	25
25	80	120	120	120	120	0	0	25
26	87	120	140	150	136.7	15.28	11.18	25
27	88	120	150	170	146.7	25.17	17.16	25
28	94	120	150	170	146.7	25.17	17.16	25
29	103	120	150	170	146.7	25.17	17.16	25
30	116	120	150	170	146.7	25.17	17.16	25
31	126	120	150	170	146.7	25.17	17.16	25
32	127	120	150	170	146.7	25.17	17.16	25
33	128	120	150	170	146.7	25.17	17.16	25

Appendix 50 Batch test using Berea Red Sand with 100 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	1.645	1.646	1.655	1.648	0.005	0.316
R2	0	Fe 238.204	1.848	1.827	1.817	1.831	0.016	0.881
R3	0	Fe 238.204	1.821	1.801	1.794	1.805	0.014	0.777
Average						1.761		
<b>End</b>								
R1	65	Fe 238.204	0.530	0.533	0.529	0.531	0.002	0.410
R2	88	Fe 238.204	0.517	0.513	0.517	0.516	0.003	0.529
R3	88	Fe 238.204	0.400	0.399	0.398	0.399	0.001	0.177
Average						0.482		

Appendix 51 Batch test using 75% ZVI + 25% BRS with 100 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.45	-	226	113	308.4	110	2.051
R2	0	6.43	-	224	112	305.1	110	2.673
R3	0	6.17	-	225	112.5	335.4	110	2.238
Average		6.35	-	225	112.5	316.3	110	2.321
<b>Middle</b>								
R1	5	9.16	-	202	101	276	45	1.149
R2	5	9.04	-	205	102.5	303.3	50	1.258
R3	5	9.21	-	199	99.5	278.3	45	1.157
Average		9.14	-	202	101	285.9	46.7	1.188
<b>End</b>								
R1	15	9.82	-	199	99.5	152.4	0	1.438
R2	22	10.18	-	184.3	92.2	174.2	0	2.697
R3	21	9.95	-	183.4	91.7	149.8	0	3.960
Average		9.98	-	188.9	94.5	158.8	0	2.698

Appendix 52 Batch test using 75% ZVI + 25% BRS with 100 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	110	110	110	110	0	0	10
1	4	55	60	55	56.7	2.89	5.097	10

2	5	45	50	45	46.7	2.89	6.188	8
3	6	40	50	45	45	5	11.11	5
4	7	22	35	35	30.7	7.51	24.46	0
5	8	15	35	35	28.3	11.55	40.81	0
6	12	5	15	15	11.7	5.77	49.32	0
7	13	5	10	10	8.3	2.89	34.82	0
8	14	1	10	10	7	5.20	74.29	0
9	15	0	10	10	6.7	5.77	86.12	0
10	16	0	8	5	4.3	4.04	93.95	0
11	17	0	5	5	3.3	2.89	87.58	0
12	19	0	5	5	3.3	2.89	87.58	0
13	20	0	2	2	1.3	1.15	88.46	0
14	21	0	2	0	0.7	1.15	164.3	0
15	22	0	0	0	0	0	-	0

Appendix 53 Batch test using 75% ZVI + 25% BRS with 100 mg/l KNO<sub>3</sub> solution –Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	2.073	2.057	2.023	2.051	0.025	1.236
R2	0	Fe 238.204	2.675	2.654	2.691	2.673	0.018	0.691
R3	0	Fe 238.204	2.229	2.233	2.250	2.238	0.011	0.482
Average						2.321		
<b>Middle</b>								
R1	5	Fe 238.204	1.137	1.143	1.167	1.149	0.016	1.361
R2	5	Fe 238.204	1.256	1.253	1.264	1.258	0.006	0.447
R3	5	Fe 238.204	1.169	1.154	1.147	1.157	0.011	0.963
Average						1.188		
<b>End</b>								
R1	15	Fe 238.204	1.437	1.439	1.440	1.438	0.001	0.092
R2	22	Fe 238.204	2.696	2.705	2.689	2.697	0.008	0.294
R3	21	Fe 238.204	3.918	3.964	3.999	3.960	0.041	1.027
Average						2.698		

Appendix 54 Batch test using 50% ZVI + 50% BRS with 100 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.37	-	230	115	308.6	120	2.503
R2	0	6.45	-	233	116.5	309.6	120	2.250

R3	0	6.23	-	232	116	294.4	120	1.572
Average		6.35	-	231.7	115.8	304.2	120	2.108
<b>Middle</b>								
R1	5	8.69	-	219	109.5	201.2	40	1.271
R2	5	8.29	-	232	116	209.7	55	0.937
R3	5	8.10	-	233	116.5	263.6	55	1.937
Average		8.36	-	228	114	224.8	50	1.382
<b>End</b>								
R1	18	9.05	-	217	108.5	175	0	2.735
R2	23	9.20	-	196.6	98.3	151.8	0	4.608
R3	22	9.12	-	191.1	95.6	169.7	0	4.170
Average		9.12	-	201.6	100.8	165.5	0	3.838

Appendix 55 Batch test using 50% ZVI + 50% BRS with 100 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	120	120	120	120	0	0	20
1	4	55	65	70	63.3	7.6	12.01	10
2	5	40	55	55	50	8.7	17.4	5
3	6	25	55	55	45	17.3	38.44	0
4	7	25	50	50	41.7	14.4	34.53	0
5	8	20	50	50	40	17.3	43.25	0
6	12	5	20	25	16.7	10.4	62.28	0
7	13	5	10	15	10	5	50	0
8	14	5	2	10	5.7	4.0	70.18	0
9	15	2	2	8	4	3.5	87.5	0
10	16	1	2	5	2.7	2.1	77.78	0
11	17	1	2	5	2.7	2.1	77.78	0
12	18	0	2	5	2.3	2.5	108.7	0
13	19	0	2	2	1.3	1.2	92.31	0
14	20	0	2	1	1	1	100	0
15	21	0	1	1	0.7	0.6	85.71	0
16	22	0	1	0	0.3	0.6	200	0
17	23	0	0	0	0	0	-	0

Appendix 56 Batch test using 50% ZVI + 50% BRS with 100 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	2.521	2.502	2.485	2.503	0.018	0.711
R2	0	Fe 238.204	2.291	2.233	2.225	2.250	0.036	1.587
R3	0	Fe 238.204	1.572	1.568	1.576	1.572	0.004	0.260
Average						2.108		
<b>Middle</b>								
R1	5	Fe 238.204	1.277	1.263	1.274	1.271	0.007	0.555
R2	5	Fe 238.204	0.940	0.929	0.941	0.937	0.007	0.735
R3	5	Fe 238.204	1.924	1.952	1.935	1.937	0.014	0.720
Average						1.382		
<b>End</b>								
R1	18	Fe 238.204	2.798	2.728	2.679	2.735	0.060	2.193
R2	23	Fe 238.204	4.540	4.661	4.624	4.608	0.062	1.353
R3	22	Fe 238.204	4.186	4.178	4.144	4.170	0.022	0.530
Average						3.838		

Appendix 57 Batch test using Zero Valent Iron with 500 mg/l KNO<sub>3</sub> solution – Major parameters

Replicate	Time	pH	DO	C	TDS	E <sub>h</sub>	NO <sub>3</sub>	Fe
-	days	-	mg/l	µS/cm	mg/l	mV	mg/l	mg/l
<b>Start</b>								
R1	0	6.48	-	1003	501.5	275.2	500	0.866
R2	0	6.22	-	997	498.5	264.6	500	0.779
R3	0	6.36	-	1005	502.5	299.2	500	1.069
Average		6.35	-	1001.7	500.8	279.7	500	0.905
<b>Middle</b>								
R1	6	10.35	-	1137	568.5	197	500	0.693
R2	6	11.43	-	1409	704.5	194.4	240	0.736
R3	6	10.24	-	1116	558	177.4	220	0.384
Average		10.67	-	1220.7	610.3	189.6	320	0.604
<b>End</b>								
R1	120	10.53	-	1156	578	183.2	500	1.004
R2	63	11.14	-	1051	525.5	179.9	100	16.170
R3	88	11.32	-	1386	693	165.8	30	13.270
Average		11	-	1197.7	598.8	176.3	210	10.148

Appendix 58 Batch test using Zero Valent Iron with 500 mg/l KNO<sub>3</sub> solution – Nitrate concentration

Samples	Time	Conc (Rep 1)	Conc (Rep 2)	Conc (Rep 3)	Conc (Avg)	SD	RSD	Conc (Control)
-	days	mg/l	mg/l	mg/l	mg/l	mg/l	-	mg/l
0	0	500	500	500	500	0	0	0
1	3	500	400	500	466.7	57.74	12.37	0
2	6	500	240	220	320.0	156.2	48.81	0
3	7	500	150	220	290	185.2	63.86	0
4	10	500	150	200	283.3	189.3	66.82	0
5	15	500	120	120	246.7	219.4	88.93	0
6	19	500	120	100	240	225.4	93.92	0
7	22	500	120	100	240	225.4	93.92	0
8	26	500	110	55	221.7	242.6	109.4	0
9	29	500	110	55	221.7	242.6	109.4	0
10	33	500	110	55	221.7	242.6	109.4	0
11	37	500	110	55	221.7	242.6	109.4	0
12	39	500	110	55	221.7	242.6	109.4	0
13	43	500	110	55	221.7	242.6	109.4	0
14	50	500	110	55	221.7	242.6	109.4	0
15	52	500	110	55	221.7	242.6	109.4	0
16	62	500	110	55	221.7	242.6	109.4	0
17	63	500	100	40	213.3	250.1	117.3	0
18	64	500	100	40	213.3	250.1	117.3	0
19	68	500	100	40	213.3	250.1	117.3	0
20	80	500	100	40	213.3	250.1	117.3	0
21	84	500	100	40	213.3	250.1	117.3	0
22	87	500	100	40	213.3	250.1	117.3	0
23	88	500	100	30	210	253.6	120.8	0
24	112	500	100	30	210	253.6	120.8	0
25	120	500	100	30	210	253.6	120.8	0

Appendix 59 Batch test using Zero Valent Iron with 500 mg/l KNO<sub>3</sub> solution – Iron concentration

Replicate	Time	Analyte Name	Conc (Calib) 1	Conc (Calib) 2	Conc (Calib) 3	Conc (Calib)	SD	RSD
-	days	-	mg/l	mg/l	mg/l	mg/l	mg/l	-
<b>Strat</b>								
R1	0	Fe 238.204	0.869	0.868	0.863	0.866	0.003	0.368
R2	0	Fe 238.204	0.780	0.781	0.775	0.779	0.003	0.428
R3	0	Fe 238.204	1.074	1.069	1.064	1.069	0.005	0.436
Average							0.905	
<b>Middle</b>								
R1	6	Fe 238.204	0.702	0.691	0.685	0.693	0.009	1.295
R2	6	Fe 238.204	0.738	0.729	0.742	0.736	0.007	0.908
R3	6	Fe 238.204	0.383	0.382	0.386	0.384	0.002	0.441

Average							0.604	
End								
R1	120	Fe 238.204	0.991	1.002	1.020	1.004	0.015	1.459
R2	63	Fe 238.204	16.074	16.391	16.052	16.170	0.189	1.171
R3	88	Fe 238.204	13.465	13.177	13.173	13.270	0.167	1.260
Average							10.148	