Sulfidation of Zero-valent Iron Nanoparticles for Environmental Remediation

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Abstract

The ability of nano-sized zero-valent iron (nZVI) to remove environmental contaminants, from heavy metals to polyhalogenated hydrocarbons, has been well established. However, the reactivity of nZVI towards contaminants is hampered due to competing side reactions with oxygen and water. Sulfide-modified nZVI (S-nZVI) has become a viable option as S-nZVI has been shown to reduce organic compounds such as trichloroethylene faster than nZVI while also maintaining an increased resistance to oxidation by water. The Fulton group has established that nZVI supported on a naturally occurring microsilicate (Microsilica600, or “misi”), from a Rotorua geothermal deposit, is capable of removing nitrates from water. This material, or nZVI@misi, minimises the potential bioaccumulation path that nZVI has, and is easier to handle than unsupported nZVI. This research investigated the effect of sulfidation of nZVI@misi (or S-nZVI@misi) on the reactivity towards the degradation of a variety of different potential contaminants.

S-nZVI@misi was synthesised using sodium thiosulfate for sulfidation. Increasing the concentration of the reagent and sulfidation time from 3 hours to 24 hours resulted in high percentages of sulfur-to-iron (S/Fe) for each material. This increase in S/Fe had a significant impact on the removal of cadmium and chromium as with higher the percentage of S/Fe, the faster the removal of these species occurred. Compared to pristine nZVI@misi, S-nZVI@misi was significantly faster at removing both cadmium and chromium. However, sulfidation of nZVI@misi proved to reduce the rate of 4-nitrophenol reduction and prevent nitrate reduction from occurring. Experimental analysis also showed that cadmium removal was faster with S-nZVI supported by FeOOH-coated microsilica, compared to material supported by un-coated microsilica. Therefore, we have synthesised supported S-nZVI that quickly removes cadmium and chromium from solution compared to standard supported nZVI.

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List of Abbreviations

2,4-DCP	2,4-dichlorophenol
4-AP	4-aminophenol
4-NP	4-nitrophenol
CCA	Copper chromium arsenic
CMC	Carboxymethylcellulose
COMPO	Composite image
DCE	Dichloroethylene
DI	De-ionised
DLVO	Derjaguin, Landau, Verwey and Overbeek
DO	De-oxygenated
DPC	Diphenylcarbazine
EDS	Energy Dispersive Spectroscopy
FAAS	Flame Atomic Absorption Spectroscopy
FeO	Iron oxide (generic term)
FeS	Iron sulfide (generic term)
IC	Ion Chromatography
MAV	Maximum acceptable value
misi600	Microsilica600, provided by Golden Bay Cement
misi	Microsilica600, calcined and coated by FeOOH
misiUC	Microsilica600, calcined and un-coated by FeOOH
mZVI	micro/macro Zero-valent iron
NRD	Natural reductive demand
nZVI	Nano Zero-Valent Iron un-supported by misi
nZVI@misi	Nano Zero-Valent Iron supported by misi
ppm	Parts Per Million (mg/L)
S/Fe	Sulfur-to-iron
SEM	Scanning Electron Microscope
S-nZVI	Sulfide-coated nano zero-valent iron
STEM	Scanning Transmission Electron Microscope
TCE	Trichloroethylene
TEL	Tetraethyl lead
TEM	Transmission Electron Microscope
TNT	Trinitrotoluene
UV/Vis	Ultraviolet/Visible spectroscopy
WHO	World Health organisation
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Powder Diffraction
ZVI	Zero-valent iron

Chapter 1

Introduction

1.1 Overview

Technological advances during the 20th century cannot be denied as being advantageous to human development. Advances in medicine, agriculture and industrial processes have all contributed to global population growth and longer life expectancy.¹ However, these same advances have also generated contaminants which decrease water and soil quality.² Heavy metals, prescription antibiotics, inorganic anions, halogenated organic compounds and nitroaromatics are some examples of contaminants that have been identified as harmful.²

Nano-sized zero-valent iron (nZVI) has been applied in the removal of many pollutants including heavy metals, inorganic anions and nitroaromatic compounds. Research at Victoria University of Wellington by the Fulton group has focused on modifications to microsilica (misi600, provided by Golden Bay cement) as a support for nZVI, and the synthesis of bimetallic nZVI for the reduction of nitrate and heavy metals. While these advances have shown significant improvement in reactivity for the reduction of nitrate and heavy metals such as lead or cadmium, sulfidation of nZVI has been touted in research to significantly enhance the reactivity of nZVI. Therefore, the aim of this research was to synthesise sulfide-modified nZVI supported by microsilica, prepared

using the method developed within the Fulton group (S-nZVI@misi). Variations of S-nZVI@misi were synthesised using different concentrations of the sulfidation reagent and sulfidation times. These materials were then applied in the removal of contaminants such as nitrate (NO_3^-) 4-nitrophenol (4-NP), cadmium (Cd(II)) and chromium (Cr(VI)) to determine if sulfidation increases nZVI reactivity towards these contaminants.

1.2 Nitrate pollution in New Zealand

Nitrate (NO_3^-) is an inorganic compound which is used as a nutrient to promote grass growth on pastoral land. However, nitrate concentrations detected in waterways have been shown to increase. Between 1994 and 2013, in 55% of monitored lakes and river systems, an increase in nitrate (as nitrogen) was detected.³ The cause of this has been identified to be due to the increase of intensive dairy farming in New Zealand as between 1994 and 2015, the cattle population increased by 69% nationally, primarily in Canterbury (+490%, 1.25 million cattle) and Southland (+539%, 731,209 cattle).³ Rapid growth in cattle numbers has increased the amount of nitrate leached into groundwater *via* both urine and the intensified application of fertilizers. This is an issue as elevated concentrations of nitrate in lakes and rivers can lead to eutrophication (an overabundance of nutrients) which can trigger the growth of toxic algae mats (cyanobacteria).⁴ Not only does this lead to eutrophication, but excessive nitrate in drinking water has significant health effects such as methemoglobinemia in infants (blue baby syndrome) and has been implicated in some forms of cancer.⁵

1.3 Heavy metals in the environment

The term 'heavy metal' refers to high-density metallic elements that have toxic properties.² While some metals such as zinc, iron and copper are considered 'heavy metals,' these species are necessary for human health. For example, iron is used in oxygen transport.⁶ The focus for environmental remediation of heavy metals are those elements that are significantly toxic to humans in small doses. For elements, such as cadmium (Cd) and mercury, the maximum acceptable values (MAV) allowed in drinking water is 0.004 ppm and 0.007 ppm respectively (Table 1.1).⁷ Cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) are contaminants of major public health concern, according to the World Health Organisation (WHO), due to their high toxicity in small doses.⁸

Element	MAV (ppm)
Antimony (Sb)	0.02
Arsenic (As)	0.01
Barium (Ba)	0.7
Cadmium (Cd)	0.004
Chromium (Cr)	0.05
Copper (Cu)	2
Lead (Pb)	0.01
Manganese (Mn)	0.4
Mercury (Hg)	0.007
Molybdenum (Mo)	0.07
Nickel (Ni)	0.08
Selenium (Se)	0.01
Uranium (U)	0.02

TABLE 1.1: Maximum acceptable value (MAV) for metal elements in drinking water.⁷

Erosion of minerals and volcanic activity can emit some heavy metals into the environment. However, the main source of heavy metals in the environment is from industrial processes.⁹ For example, cadmium has been used as a yellow pigment and in battery manufacturing.¹⁰ In biological systems, Cd(II) acts as a mimic in calcium dependant pathways due to their similar ionic radii (0.99 (Cd(II)), 0.97 (Ca(II))). In addition, Cd(II) has a high affinity for sulfur, binding

to protein thiol groups.¹¹ Itai-Itai disease is the most severe form of cadmium poisoning where cadmium attacks the kidneys, causing renal failure and vitamin D deficiency, resulting in osteomalacia and osteoporosis, respectively.¹²

Cadmium pollution in New Zealand topsoil can be traced to the use of superphosphate fertilisers during the 20th century.¹³ These fertilisers were sourced from Nauru rock phosphate, which has an average cadmium concentration of 450 mg Cd/kg P.¹⁴ Since 1997 this phosphate source has been phased out of use.¹³ Land used for dairy and Kiwifruit production have the highest levels of cadmium (>0.7 mg/kg soil), with areas of the Waikato, Taranaki and the Bay of Plenty having the highest levels of cadmium detected in soil.¹⁴

Tetraethyl lead (TEL), was added to gasoline as an anti-knocking agent until 1996 in New Zealand. Lead was also commonly used in plumbing systems and paint until the late 20th century and was only stopped being used as yellow road paint in the 2000s.¹⁵ Exposure to lead has been linked to impaired neurobehavioral and antisocial behaviour in children,⁶ as well as detrimentally impacting on the nervous system in adults.¹⁵ In recent years, events such as the Flint water crisis have highlighted the need to remove lead sources from the environment.¹⁶ However, this is a monumental task due to the prevalence of lead paint in older homes and in lead pipes in city infrastructure.¹⁶

Arsenic is known for its carcinogenic properties. Exposure to arsenic has been linked to skin, lung and bladder cancers, as well as liver and prostate cancers and is linked to other conditions such as diabetes, cardiac disorders and neurological effects.¹⁷ In New Zealand, lead arsenate, calcium arsenate and copper arsenate were used as pesticides for orchards until the 1960s.¹⁸ Arsenic was also used for the treatment of parasites on sheep and cattle until the 1980s.¹⁹ As the risks associated with arsenic were unknown at the time, waste was dumped into waterways and sheep were allowed to dry in open fields.¹⁹ Currently, copper chromium arsenic (CCA) is used as a wood treatment and

studies have demonstrated that leaching can occur if CCA-treated posts come into contact with groundwater.²⁰ However, the main path way for arsenic (and chromium) exposure is through the burning of CCA-treated wood.²¹ High levels of arsenic have also been detected in the Waikato river due to effluent from geothermal waste, and from Central Otago gold mines such as the historic Barewood mine.²²

Toxicity of heavy metals can be dependent on the oxidation state. Hexavalent chromium Cr(VI) (as CrO_4^{2-}) in drinking water increases the risk of stomach cancer.⁶ However, trivalent chromium Cr(III), is essential in protein, fat and glucose metabolism and Cr(III) deficiencies have been linked to adult-onset diabetes.²³ Chromium is emitted into the environment from tannery wastewater, electroplating, pigment synthesis and wood treatment.^{20,24}

1.4 Zero-valent iron technology (ZVI)

1.4.1 Macro-sized Zero-valent iron

The use of metallic iron or zero-valent iron (ZVI) for the remediation of polluted groundwater has been investigated for two decades. Iron metal has a reduction potential of -0.44 V, therefore, will directly reduce a variety of pollutants with positive reduction potentials.²⁵ This includes organohalides (trichloroethylene,²⁶ chlorinated methanes²⁷), inorganic compounds (nitrate and nitrite),²⁸ heavy metals (Cr(VI)),²⁸ nitroaromatics (trinitrotoluene (TNT))²⁹ and azo dyes.³⁰ Indirect reduction by the Fe(II), formed by the oxidation of Fe(0) by water, can also occur and has been attributed to the reduction of chlorinated methane compounds.²⁷

Non-reductive processes by ZVI, such as oxidative Fenton processes, can occur in the presence of dissolved oxygen. ZVI reduces O_2 to H_2O_2 . H_2O_2 will then

FIGURE 1.1: Mechanisms of contaminant removal by Zero-valent iron (ZVI)

react with Fe(II) , to form hydroxyl radicals which oxidise contaminants such as AsO_3^{3-} .³¹ Other proposed removal mechanisms for contaminants by ZVI include adsorption of contaminants such as cadmium, and co-precipitation of metal cations, such as zinc.²⁵ The mechanisms for the above reactions described can be found in Figure 1.1.

The use of ZVI *in situ* has focused on macro- or granular sized and micro-sized or powder sized ZVI (mZVI). However, in solution the outer surface of mZVI will oxidise creating a thick outer layer of iron oxides and hydroxides. This thick outer layer inhibits electron transfer from the core to the outer surface, thus, becoming less reductive towards contaminants.²⁹ While pre-treatment methods, such as acid washing,²⁹ or ultrasonic techniques,³² have been employed to improve the performance of ZVI, the most significant development has been in the use of nano-sized zero-valent iron (nZVI).

FIGURE 1.2: Increasing surface area as particle size decreases

1.4.2 Nanosized zero-valent iron (nZVI)

Nanosized zero-valent iron (nZVI) has proven to be more reactive than macro or micro-sized ZVI because of its smaller particle size. As particle size decreases, the surface to volume ratio increases. Therefore, for the same mass of iron, there is an increased number of active sites on the surface of nZVI, compared to mZVI (Figure 1.2). Increased reactivity for nZVI, compared to the same mass of mZVI, was investigated for the removal of phosphate, with nZVI removing phosphate from solution 13.9 times faster than mZVI.³³ Other comparative studies have shown that nZVI was more effective than mZVI in the removal of arsenic³⁴ and pyrene.³⁵

The impact on the morphology of nZVI is dependent on the synthesis route. Top/down approaches, such as ball-milling lead to inconsistent size distribution and morphology.^{36,37} However, bottom-up approaches, such as chemical reduction, using reducing agents like sodium borohydride (NaBH₄), produce homogeneous, spherical nanoparticles.³⁸ Chemical reduction is the most popular method to synthesise nZVI as it is simple and generates highly reactive nanoparticles.

While nZVI can remove a number of contaminants, issues such as agglomeration and oxidation will decrease reactivity. Agglomerations of nZVI results

in the appearance of long nZVI chains, not only decreasing the overall particle surface area, but also decreasing reactivity of particles towards contaminants (Figure 1.3(a)). Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory for nanomaterial synthesis predicts agglomeration will occur due to attractive Van der Waals forces.³⁹ The agglomeration of nZVI chains is further enhanced by the magnetic properties of iron which promote particle agglomeration.⁴⁰ However, agglomeration can be minimised by using stabilising agents or supports such as carboxymethyl cellulose (CMC). Materials such as activated carbon, silicates and zeolites have also been used to help stabilise nZVI.⁴¹ Supported nZVI shows increased reactivity towards contaminants compared to unsupported nZVI. For example, in the reduction of 40 ppm Cr(VI), nZVI supported by silica fume removed 88% of chromium in 120 minutes, compared to unsupported nZVI which only removed 65% in the same period of time (Fe(0) loading; 0.4 g/L).⁴²

Research at Victoria University of Wellington by the Fulton group, focused on the selection and preparation of silicate materials as supports for nZVI. Microsilica600, a geothermally sourced silicate from the central north island region, was determined to improve dispersion of nZVI when activated by calcination (600 °C) and acid washing.⁴³ SEM, showed that nZVI dispersion on the support was significantly improved after the microsilica underwent these pre-treatment steps prior to formation of nZVI by chemical reduction (Figure 1.3(b)).

Bimetallic nZVI, which comprises catalytic amounts of 'noble' metals deposited on the surface of nZVI can improve the reactivity of nZVI. For instance, nZVI doped with copper reduced nitrate faster than standard nZVI.⁴⁴ Other examples of 'noble' metal dopants on nZVI, include palladium Pd-nZVI is able to successfully reduce organohalides, whereas, standard nZVI is slow at reducing this class of compounds. Specifically, palladium-doped nZVI supported by

FIGURE 1.3: (a) Agglomerated and (b) nZVI stabilised by misi (nZVI@misi)

vermiculite, a phyllosilicate, was faster in the reduction of 2,4-dichlorophenol (2,4-DCP) than un-doped nZVI.⁴⁵

1.4.3 Current knowledge by the Fulton group

The research in the Fulton group has focused on the pretreatment of silicate supports for nZVI stabilisation. H. Putri Fraser,⁴³ found that the pre-treatment of Microsilica600 was important in the adsorption of nZVI to the silicate surface. These treatments include calcination at 600 °C and acid washing to regenerate silanol sites. However other modifications, such as activation through boiling in water or coating the surface with FeOOH, did not improve adsorption. The latter modification did, however, improve the efficiency of nitrate reduction by nZVI.

Research by Loc Tran into bimetallic nZVI@misi has shown that the addition of catalytic amounts of nickel, copper and copper/palladium increased the efficiency of nitrate reduction over 30 minutes.⁴⁶ Ni- and Cu-doped nZVI@misi (using 5 mol % Ni and Cu) will reduce 10 ppm nitrate (as nitrogen) within 5

and 15 minutes respectively. In comparison, the reduction of nitrate by undoped nZVI@misi was slow, with ~ 2 ppm nitrate still in solution at 30 minutes. The inhibition of reactivity by other ions such as PO_4^{3-} , is a problem for the reduction of nitrate by nZVI, however, nitrate reduction by Ni-doped nZVI supported by FeOOH-coated misi (5Ni-nZVI@misi) was shown to not be inhibited by the presence of these ions. The reduction of nitrate by 5Ni-nZVI@misi was also shown to occur in the presence of air indicating stability in oxygen rich conditions.

1.5 Contaminant remediation by nZVI

1.5.1 Nitrate reduction by nZVI

nZVI removes nitrate from solution by reducing it to first nitrite (NO_2^-), and then ammonium (NH_4^+) (Eq. 1.1 and 1.2). Although other nitrogen products are feasible, including NO and N_2O , the only product typically observed is ammonium, although nitrite can be observed as a transient intermediate.^{29,47} The holy grail of nitrate reduction is conversion to dinitrogen (N_2); however, although postulated, N_2 is rarely observed.^{47,48} Instead, over-reduction to ammonia/ammonium is common. In soils, ammonium can be trapped by the negatively charged soil silicates and other technology exists for the removal of ammonium from water.⁴⁹

A comparison of unsupported versus supported nZVI, shows that supported nZVI was faster at removing pollutants compared to unsupported nZVI.^{50,51}

The reduction of nitrate by zeolite-supported nZVI was shown to be more efficient than unsupported nZVI.⁵¹ However, the supporting material can enhance reactivity due to mediation of nitrate reduction by nZVI. For example, pillared-clay-supported nZVI was shown to remove all nitrate from solution compared to plain nZVI which only removed 62.3% in 120 minutes. This is believed to be because the pillared clay mediates adsorption of nitrate to the surface of nZVI, thus, an increased efficiency towards nitrate is observed.⁵² Enhancement of the rate of nitrate reduction due to the supporting agent is shown in the reduction of nitrate by nZVI supported by FeOOH-coated misi (nZVI@misi). Almost 90% of the nitrate in solution was reduced by nZVI supported by FeOOH-coated misi in 60 minutes, whereas only 65% was removed on nZVI supported by un-coated microsilica within the same amount of time. This is because FeOOH acts as a catalyst, and decreases the reduction potential of Fe(II) which can then reduce nitrate.⁴³

Experimental results have shown that doping nZVI with noble metals improves selectivity and reactivity. For example, kaolinite-supported Ni-doped nZVI demonstrated improved removal efficiency towards both nitrate and Pb(II) in solution compared to undoped kaolinite-supported nZVI.⁵³ Improved removal efficiency by nickel-doped misi-supported nZVI has also been shown to remove all nitrate (10 ppm) from solution within 5 minutes..⁴⁶ Nitrate reduction by Cu-doped nZVI was also found to remove 80% of nitrate within 20 minutes compared to 20% by pristine nZVI.⁵

1.5.2 Cadmium removal by nZVI

The mechanism for cadmium removal (Cd(II)) by nZVI, is accepted to be adsorption to the particle surface. Techniques, such as X-ray photoelectron spectroscopy (XPS) and electron dispersive spectroscopy (EDS) which is used in

conjunction with scanning transmission electron microscopy (STEM), have provided evidence of Cd(II) on the surface of nZVI. For instance, STEM-EDS mapping confirmed the presence of cadmium on the surface of nZVI that had reacted with nZVI.⁵⁴ The oxidation state of the adsorbed cadmium was confirmed using XPS with a peak at 404-405 eV. This is consistent for Cd(II) being absorbed onto the surface of nZVI.⁵⁵⁻⁵⁷ The morphology of nZVI changed post Cd(II) removal. STEM analysis of nZVI after cadmium adsorption revealed nanofibres, comprising of a mix of iron oxides and cadmium ferrite (CdFe_2O_4) formed on the surface (Figure 1.4).⁵⁸

Supported nZVI has been shown to increase the efficiency of cadmium removal. Different nZVI-supporting agents have been tested, including industrial coal fly ash,⁵⁹ and ascorbic acid.⁶⁰ In these studies it was found that control of solution acidity was important for Cd(II) removal. As pH increased, the rate of Cd(II) removal increased,^{55,56} with the optimal pH for Cd(II) removal between 8.0 - 8.6 although this might be due to the precipitation of $\text{Cd}(\text{OH})_2$.⁵⁶ Increased temperature was found to improve the rate of Cd(II) removal, consistent with an endothermic process.⁵⁴ Oxidised nZVI decreased the efficiency of Cd(II) removal when compared to freshly synthesised nZVI.⁵⁶ It was postulated that the presence of a thick iron oxide layer decreases reactivity.

Cadmium removal with nZVI was found to have decreased efficiency in the

FIGURE 1.4: Adsorption of Cd(II) and formation of CdFe_2O_4 nanofibres

presence of competing cations such as Zn(II), Co(II), Mg(II), Mn(II), Cu(II), Ca(II), Na(I) and K(I) as well as chloride.⁵⁵ For, example, in the simultaneous removal of Cd(II) and Pb(II), the removal of Pb(II) decreased slightly in the presence of Cd(II), from 93.8% to 91.0%. The removal of Cd(II) was significantly affected by the presence of Pb(II), as Cd(II) removal efficiency decreased from 41.7% to 31.4%.⁶¹ Cd(II) removal, in the presence of >30 ppm nitrate, had an increase in removal efficiency.⁶² However, initial quantities of Cd (<30ppm Cd) did not improve nitrate removal.

1.5.3 Chromium removal by nZVI

Chromium(VI) can be reduced to Cr(III) by nZVI, iron oxides and Fe(II) in solution.^{63–66} In the reduction of Cr(VI) by Fe(II), the final products are Fe(III) and Cr(III). These cations have similar ionic radii and are sparingly soluble at neutral pH and room temperature. Buerge, *et al.*,⁶⁴ and Eary and Rai,⁶⁷ observed the formation of a brown amorphous precipitate when Cr(VI) was mixed with Fe(II). This precipitate had a composition of $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(s)}$ and confirmed that Fe(III) and Cr(III) will co-precipitate from solution. This is only observed at pH's greater than 4, as at more acidic pH's Fe(III) and Cr(III) remain in solution.⁶⁷ In the reduction of Cr(VI) with Fe(II), Cr(VI) is initially reduced to Cr(III) (Equation 1.3) before the ions co-precipitate out of solution (Equation 1.4):

Cr(VI) is also reduced to Cr(III) by nZVI. XPS showed that Cr(III) is present on the surface of nZVI post-reduction of Cr(VI).⁶⁸ STEM-EDS of a single nZVI

particle, after the reduction of Cr(VI), indicated a thick oxide layer compared to pure nZVI. This thick oxide layer indicated extensive oxidation of nZVI during the reduction of Cr(VI). Interestingly, STEM-EDS indicated that Cr(III) was embedded within the core of nZVI. Thus, post-Cr(VI) reduction, the Cr(III) diffuses into the core of nZVI.⁶⁹

Silicate minerals such as sepiolite,⁷⁰ bentonite,⁷¹ montmorillonite,⁷²⁻⁷⁴ and pumice,⁷⁵ have been used as supporting materials for nZVI in the remediation of Cr(VI). Supported nZVI showed improved reactivity when pH was low, but at basic pH's (> 7), the rate of reduction decreased significantly. For example, bentonite-supported nZVI reduced almost 100% Cr(VI) (20 ppm) within 20 minutes, under acidic conditions (pH = 2), whereas at pH of 8, only 27.2% was removed after 20 minutes.⁷¹ Silicate-supported nZVI was less pH dependent than unsupported nZVI. Unsupported nZVI decreased in reactivity towards Cr(VI) between pH of 3 and 6. However, montmorillonite-nZVI maintained high removal efficiency until pH of 6.57.⁷²

1.6 Oxidation of nZVI

While nZVI is effective in the remediation of many environmental contaminants, with ample research dedicated to improvement in reactivity, there are still issues that need to be addressed. Oxidation of nZVI by water and dissolved oxygen can cause the passivation by oxidising the surface of nZVI.⁷⁶ Passivation at the surface of nZVI can be explained using Cabrera-Mott theory in metal oxidation.^{77,78} Initial oxidation occurs at the surface of the metal forming a thin oxide layer. As electron transfer from the Fe(0) core to oxygen bound to the outer surface occurs, an electrical field is created (Figure 1.5).⁷⁸ This process drives diffusion of Fe(II) ions outwards, thus increasing the thickness of the iron oxide shell.

FIGURE 1.5: Cabrera-Mott theory for metal thin-film oxidation

FIGURE 1.6: Formation of Kirkendall voids from (a) the pure nanoparticle, (b) followed by the initial oxidation of the outer layer of nZVI, (c) the initial formation of a void, and (d) the hollow Fe_2O_3 particle

As the $\text{Fe}(0)$ core is depleted, the difference in diffusion rates causes the formation of voids in the centre of particles. This is called the Kirkendall effect (Figure 1.6).⁷⁷ Oxidation of $\text{Fe}(0)$ displaying these effects has been observed in analysis into the aging process in oxygen⁷⁹ and in reactions with Ni(II) .⁸⁰ Thus, oxygen and water can increase the rate of depletion for nZVI and formation of Kirkendall voids.⁸¹

The reducing capacity for nZVI, is defined as the quantifiable amount of material that acts as a reducing agent. As reactions with nZVI occur in aqueous environments, it is difficult to control the natural reductive demand (NRD) of water and oxygen, as well as other reducible species in solution, *e.g.* nitrate, phosphate. The NRD of species present in the reaction mix, for example, water, take a percentage of the reducing capacity of nZVI, decreasing the amount of electrons available for the reduction of targeted species (Figure 1.7).⁷⁶ Consequently, these species will increase the rate of oxidation of nZVI. This reduces

the particles life-times as electrons are depleted from the core.^{82,83} Thus, nZVI in aqueous systems is limited by short lifetimes and low stability.⁸³ For *in situ* remediation, mZVI is typically used rather than nZVI as it is less susceptible to oxidation by water. Although mZVI is less reactive towards contaminants, it is also less reactive towards water or oxygen.⁷⁶

FIGURE 1.7: Electron demand decreases due to competitive reactions between reducible species for reduction by nZVI

A lot of nZVI research has been focused on improving the reactivity of nZVI, with less attention given to improving particle stability in aqueous systems.⁷⁶ Therefore, instead of increasing reactivity of nZVI, improving and increasing the stability of nZVI in solution should be the focus for future research.

1.7 Sulfidation of nZVI

1.7.1 Improvements in reactivity with S-nZVI

The replacement of the iron oxide (FeO) surface on nZVI, with iron sulfide (FeS) has recently been applied to reduce oxidation of nZVI in the presence of water and oxygen.^{84–90} The use of sulfide coated nZVI (S-nZVI) has been frequently used in the reduction of organohalides such as trichloroethylene

(TCE) and 1,2-dichloroethene (DCE).^{90–93} However, S-nZVI has been applied to other contaminants such as Cr(VI),^{87,94} and Cd(II).^{84,95}

The reduction of organohalides, such as TCE and DCE, by nZVI, is slow or ineffective. However, when S-nZVI was used for remediation of TCE, the reduction of TCE was faster and more efficient.⁷⁶ DCE reduction was also faster and more effective with S-nZVI than bimetallic palladium-doped nZVI. Thus, in the reduction of these halogenated species, S-nZVI is an effective tool.⁹⁶ Analysis by Rajajayavel and Ghoshal,⁹⁰ found that the ratio of sulfur to iron can affect the reduction of TCE with the optimal mole ratio of sulfur to iron (S/Fe) found to be 30%.⁸⁶ When sulfide loading was too high, the reactivity of S-nZVI decreased, with the observed rate constant (k_{obs}), decreasing. This was attributed to the formation of pyrite (FeS_2). For low sulfide loading's, the rate constant, k_{obs} , was low as the FeS layer was discontinuous, forming a thin layer at the surface of the nanoparticle. Therefore, there was more competition between target contaminants and water than for S-nZVI with higher S/Fe loadings.⁸⁶

Sulfide-modified nZVI also showed to improve the reduction of Cr(VI) compared to unmodified nZVI.⁹⁴ When supported by biochar, S-nZVI showed higher capacity for Cr(VI) removal and faster reaction times, compared to nZVI supported by biochar.⁸⁷ The presence of FeS therefore enhanced the reactivity of nZVI, by acting as an electron transfer mediator.⁹⁴ However, amorphous FeS will reduce Cr(VI) to Cr(III), itself.⁹⁷ Thus, the reduction of Cr(VI) by FeS coated nZVI is improved due to the mediation of electron transfer as well as reduction by FeS. Cr(VI) removal increased as S/Fe ratios were increased with, XPS identifying Cr(III) at the surface of the nZVI particle.⁹⁸ This confirms that Cr(VI) is reduced to Cr(III), then immobilised with Fe(III) as insoluble hydroxides, similar to pristine nZVI.

The removal of Cd(II) from solution by S-nZVI has been shown to be significantly faster than nZVI.^{84,95,99} Changes in pH, ionic strength and the presence of humic acids, had little effect on the amount of Cd(II) removed by S-nZVI.⁸⁴ Increasing S/Fe ratios were found to increase reactivity, however, this is expected as CdS is very insoluble. Thus, at low S/Fe ratios, absorption to the surface is the dominant mechanism, However, as the S/Fe ratio increases, the removal of Cd(II) is due to the displacement of Fe in FeS.⁹⁵

Stability is a significant issue with nZVI in solution as it will rapidly oxidise to form a thick iron oxide outer layer, decreasing reactivity of nZVI. However, sulfidation has been shown to improve the stability of S-nZVI in solution, compared to pure nZVI. In aqueous conditions, nZVI became fully degraded within 1 week. However, S-nZVI was stable in aqueous systems for up to 3 weeks.⁷⁶

1.7.2 Synthesis of S-nZVI

The synthesis of S-nZVI can be performed *via* two different methods. The first method is the 'one-pot' method. This involves the addition of the sulfidation reagent alongside the reducing agent. For example, Kim, *et al.*,¹⁰⁰ added a solution of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and sodium borohydride (NaBH_4) to FeCl_3 to synthesize S-nZVI. However, transmission electron microscopy (TEM) images show that the surface morphology of S-nZVI is 'flake-like' and the particles are inconsistent in size and shape.⁹¹ The second method is referred to as the post-synthesis method. This method involves the synthesis of nZVI, usually by chemical reduction of Fe(II) salt, prior to the addition of the sulfidation reagent.^{76,91} The resulting mixture is left to equilibrate for a period of time. TEM images of S-nZVI produced in the post-synthesis method had a uniform surface similar to unmodified nZVI.⁹¹

a) One-pot method

b) Post-synthesis method

FIGURE 1.8: Synthesis of S-nZVI by either (a) the pre-synthesis (one-pot) method, or, (b) the post-synthesis method

The most common reagents used for the synthesis of S-nZVI are sodium dithionite (Na₂S₂O₄), sodium thiosulfate (Na₂S₂O₃), and sodium sulfide (Na₂S).⁹¹ A comparison between the use of sodium dithionite and sodium sulfide showed that sodium sulfide produced more reactive nanoparticles as it only coated the outer layer, whereas, sodium dithionite converted more iron to iron sulfide resulting in a thick FeS outer layer and smaller Fe(0) core. The resultant S-nZVI (with sodium dithionite), had a slower rate of TCE reduction than S-nZVI produced using sodium sulfide.^{76,91} However, sodium sulfide is toxic, flammable, and corrosive, liberating toxic H₂S gas in aqueous solution.⁹¹ Thus, it is an unfavourable reagent for the synthesis of S-nZVI for environmental remediation. On the other hand, while sodium dithionite is not toxic, it will decompose to many different products, such as sulfate, sulfite, thiosulfate and sulfide, depending on the pH.¹⁰¹ Thus, the sulfidation process is not efficient or effective. Unlike sodium sulfide, sodium thiosulfate is non-toxic and will not rapidly decompose to form H₂S in solution. sodium thiosulfate is preferential over sodium dithionite as well because the reduction of sodium thiosulfate to form

HS^- by $\text{Fe}(0)$ is known. Reduction only occurs on the bare metal, not the oxide layer. Therefore, using sodium thiosulfate as a reagent is an effective method to form a FeS outer layer. Experimental results comparing the reduction of TCE by S-nZVI produced using sodium dithionite and sodium thiosulfate, found that S-nZVI synthesised with sodium thiosulfate was more effective than S-nZVI from sodium dithionite sulfidation.⁹¹

1.8 Overview of research

This research investigated the synthesis of sulfide-modified misi-supported nZVI (S-nZVI@misi), and the effect this modification had on the reactivity towards different contaminants. Sodium thiosulfate was chosen as the sulfidation agent for the reasons cited in Section 1.7.2. Adjustments to the percentage of sulfur-to-iron (S/Fe) were made by increasing the sulfidation time and reagent concentration. Initial analysis focused on the reactivity of S-nZVI@misi towards nitrate and nitrophenol. However, S-nZVI@misi was found to be most promising for the remediation of metal contaminants cadmium ($\text{Cd}(\text{II})$) and hexavalent chromium ($\text{Cr}(\text{VI})$). Awareness for the effect the FeOOH -coating on the microsilica support had on the reduction of nitrate was also of interest to the Fulton group. Therefore, the removal of heavy metals from solution by S-nZVI and nZVI supported by FeOOH -coated and un-coated microsilica was investigated.

The structure of this thesis is as follows;

Chapter 2 discusses the methods used in this thesis. This includes the preparation of microsilica support, and the synthesis of S-nZVI@misi. It discusses the methods and analytical techniques used to determine the concentrations

of nitrate, 4-nitrophenol, cadmium (Cd(II)), chromium (Cr(VI)) and iron (total and Fe(II)) using flame atomic absorption spectroscopy (FAAS), ion chromatography (IC) and spectrophotometry. Characterisation techniques are also explained, such as scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), scanning transmission electron microscopy (STEM) and X-ray powder diffraction (XRD).

Chapter 3 discusses the characterisation of S-nZVI@misi using SEM-EDS to determine S/Fe percentages and the impact of increasing the concentration of reagent and sulfidation time. It also details results from the digestion of S-nZVI@misi, STEM-EDS maps of S-nZVI, XRD spectra of materials and results from the leaching of iron from S-nZVI@misi in deionised and deoxygenated water over 30 minutes.

Chapter 4 presents the experimental findings of S-nZVI@misi when reacted with nitrate, 4-nitrophenol, cadmium and chromium. This chapter details the impact of increasing the concentration and duration of sulfidation on the removal of these contaminants. It also presents results on the effect the FeOOH-coated misi has on the removal of Cd(II) and Cr(VI) by sulfide modified nZVI.

Chapter 5 summarises the findings in this thesis and suggests future directions that could be investigated.

Chapter 2

Methodology

2.1 Microsilica Preparation

FeOOH-coated misi (misi)

Microsilica600 was donated by Golden Bay Cement and stored in airtight bags. The method for the preparation of misi was determined by H. Putri Fraser..⁴³ Microsilica was placed in ceramic crucibles for 6 hours at 600 °C, in air. After calcination, the crucible was allowed to cool to room temperature overnight in the oven. Misi (~4 g) was then transferred into an Erlenmeyer flask with 100 mL deionised water (DI) and boiled for 2 hours with stirring in air to activate silanol groups on the silicate. To this suspension, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (~2 g) was added to the resultant mixture and left to stir for a further 30 minutes at 100 °C. After filtration, the material was washed twice with DI water and ethanol. The washing process, consisted of placing the microsilica in centrifuge tubes with DI water or ethanol before the material was sonicated for 15 minutes. The samples were then centrifuged to separate the solid material from the wash solution, which was decanted. After the wash solution was decanted, the solid material left in the centrifuge tubes was placed in a 60 °C oven overnight to dry and then placed in a 120 °C oven for an hour to ensure material is completely

dry. This FeOOH-coated microsilica is denoted as 'misi' throughout the rest of this thesis.

Un-coated microsilica (misiUC)

Microsilica without FeOOH coating was prepared similar to the above method. Microsilica600 was calcined for 6 hours at 600 °C before activation of silanol groups by boiling in DI water. However, after activation, FeSO₄·7H₂O (2 g) was not added. Instead the activated misi was washed and dried in the same method as above. This un-coated microsilica is denoted as misiUC throughout the rest of this thesis.

2.2 Synthesis of Materials

nZVI@misi

Microsilica supported nZVI (nZVI@misi and nZVI@misiUC) was synthesised under N₂ atmosphere using standard Schlenk techniques. In the standard procedure for the synthesis of supported nZVI, 2.0 g of microsilica (either misi or misiUC) was mixed with 1.0 g of FeSO₄·7H₂O in 30 mL of deionised, de-oxygenated (DI/DO) water that had been purged with N₂ gas for 20 minutes). This was left for 10 minutes to ensure that all FeSO₄·7H₂O had been dissolved, after which a solution of 0.50 M NaBH₄ (30 mL) in DI/DO water was added drop-wise to the reaction vessel using a syringe pump (NE-1000, New Era Pump System) at a rate of 0.2 mL/minute (Stir-rate: 750 rpm). Bubbling and the formation of a black precipitate was observed upon the addition of NaBH₄. Once all of the NaBH₄ was added, the reaction was left to stir until all bubbling had ceased. The black particles were magnetic and were separated from the solution using a strong magnet. The solution was removed

using a cannula before being washed twice with DI/DO water and twice with DO ethanol. The particles were then dried under vacuum overnight.⁴³

Unsupported nZVI was synthesised in a similar method, however, no microsilica was added to the reaction mixture prior to the addition of the reduction agent.

S-nZVI@misi

Sulfide-modified microsilica-supported nZVI (S-nZVI@misi and S-nZVI@misi-UC) were synthesised under N₂ using standard Schlenk techniques. Fresh microsilica supported nZVI was synthesised using the method outlined previously and washed 3 times with DI/DO water. To washed supported nZVI, a 30 mL solution of sodium thiosulfate dissolved in DI/DO water was added. The concentration of the thiosulfate solution depended on the desired molar ratio of sulfur to iron. These molar quantities of the reagent are outlined in Table 2.1. After the addition of sodium thiosulfate, the resultant mixture was stirred for 30 minutes, 3 hours or 24 hours, depending on the desired degree of sulfidation, under N₂ atmosphere. After the desired sulfidation time had passed, the particles were separated with a strong magnet and the solution removed *via* cannula. The microsilica-supported S-nZVI was washed twice with DI/DO water and twice with DO ethanol. The material was then dried under vacuum overnight.

Unsupported S-nZVI was synthesised in a similar method, using unsupported nZVI.

30S-nZVI@misi-1pot

S-nZVI@misi in a '1-pot' synthesis was prepared following the method described by Kim *et al.*,¹⁰⁰ This material was synthesised under N₂ atmosphere using Schlenk techniques. To a Schlenk flask, 2.0 g of FeOOH-coated microsilica and 1.0 g of FeSO₄·7H₂O was mixed with ~ 30 mL of DI/DO water.

Once all $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ had dissolved, a 30 mL solution of NaBH_4 (0.50 M) and $\text{Na}_2\text{S}_2\text{O}_3$ (0.036 M) was added drop-wise to the reaction vessel using a syringe pump (NE-1000, New Era Pump System) at a rate of 0.2 mL/minute. After all the solution had been added, the mixture was left to stir for a further 20 minutes until bubbling had ceased. Particles were then separated from solution using a magnet and the solution removed *via* cannula. The material was then washed twice with DI/DO water and twice with DO ethanol before being dried under vacuum.

Bimetallic S-nZVI@misi

Bimetallic microsilica-supported S-nZVI was synthesised *via* three methods. All materials were synthesised under a N_2 atmosphere using Schlenk techniques.

Method A: 5%Ni-nZVI@misi was prepared using the co-reduction method. In a Schlenk flask, 2.0 g FeOOH-coated microsilica, 1.0 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.0233 g of anhydrous NiCl_2 was mixed with 30 mL of DI/DO water. Once all the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and anhydrous NiCl_2 had dissolved, a solution of 0.50 M NaBH_4 (30 mL) in DI/DO water was added drop-wise to the reaction vessel using a syringe pump (NE-1000, New Era Pump System) at a rate of 0.2 mL/minute. A black precipitate began to form immediately. Once the addition of NaBH_4 was complete, the solid particles were separated using a strong magnet and the solution was drained *via* cannula. The material was then washed 3 times with DI/DO water before 30 mL of $\text{Na}_2\text{S}_2\text{O}_3$ (0.036 M) was added and the mixture was left to stir for 3 hours. The resultant material was then separated from solution using a magnet and the solution removed *via* cannula. The material was then washed twice with DI/DO water and twice with DO ethanol before being dried under vacuum.

Method B: Freshly prepared nZVI supported by FeOOH-coated microsilica was washed 3 times with DI/DO water. Once the wash solution had been

removed *via* cannula, a 20 mL solution of NiCl_2 (0.0233 g/ 9 mM) was added. The mixture was left to stir for 30 minutes before the reaction mixture was separated using a magnet and the solution was removed *via* cannula. The material was then washed 3 times with DI/DO water before 30 mL of $\text{Na}_2\text{S}_2\text{O}_3$ (0.036 M) was added and the mixture was left to stir for 3 hours. The resultant material was then separated from solution using a magnet and the solution removed *via* cannula. The material was then washed twice with DI/DO water and twice with DO ethanol before being dried under vacuum.

Method C: Unlike the previous methods where nickel was added to the material prior to sulfidation, in method C, the addition of nickel came after sulfidation. To freshly prepared S-nZVI supported by FeOOH-coated microsilica (sulfidation time, 3 hours; reagent, 0.036 M/30 mL) which had been washed 3 times in DI/DO water, a 20 mL solution of NiCl_2 (0.0233 g/ 9 mM) was added. The mixture was left to stir for 30 minutes before the reaction mixture was separated using a magnet and the solution was removed *via* cannula. The resultant material was then separated from solution using a magnet and the solution removed. The material was then washed twice with DI/DO water and twice with DO ethanol before being dried under vacuum.

Molar % of S to Fe	Thiosulfate (mol)	Thiosulfate conc.(M)
0%	0	0
10%	3.60×10^{-4}	1.20×10^{-2}
30%	1.08×10^{-3}	3.60×10^{-2}
50%	1.80×10^{-3}	6.00×10^{-2}
70%	2.52×10^{-3}	8.39×10^{-2}
75%	2.70×10^{-3}	8.99×10^{-2}
100%	3.60×10^{-3}	1.20×10^{-2}
150%	5.40×10^{-3}	1.80×10^{-2}
200%	7.19×10^{-3}	2.40×10^{-2}
300%	1.08×10^{-3}	3.60×10^{-2}

TABLE 2.1: The molar % of S/Fe and the concentrations of sodium thiosulfate used in the sulfidation of S-nZVI@msi. The molar amount of Fe in each experiment was 3.60×10^{-3} mol

2.3 Characterisation

2.3.1 Determination of S/Fe ratio and total iron

S-nZVI@msi digestion

S-nZVI@msi (0.05 g) was quantitatively transferred to a flask, after which 2 mL of 15% HNO_3 was added. The mixture was left to digest overnight before being transferred to a 20.00 mL volumetric flask and DI water was added to the line. Solutions were stored at 4 °C prior to analysis by flame atomic absorption spectroscopy (FAAS) (ThermoFisher iCE 3500 with SOLAAR software). Each solution was diluted 100-fold prior to analysis of iron concentration by FAAS to fit a range of 0.25 to 5 ppm. The fuel used for analysis was air/acetylene with a flow rate of 0.9 mL/minute. and deuterium lamp background correction was used. Principles behind FAAS are explained in Section 2.5.1.

SEM-EDS determination of S/Fe

The percentage of S/Fe was analysed using Scanning electron microscope - electron dispersive spectroscopy (SEM-EDS). Specimen stubs with a diameter of 1 cm, were prepared by depositing a small amount of powdered material on a small square of carbon tape. The samples were then coated 2-4 times by carbon to ensure good coverage, before being desiccated overnight. Each scan was taken at a magnification of 10,000x and focused on an area of high particle concentration. Areas for analysis were randomly chosen with 6 EDS spectra per sample. Principles behind SEM-EDS are explained in Section 2.5.2.

2.3.2 Size distribution analysis

Using images taken from SEM, at 10,000x magnification, the particle size was measured using ImageJ, a freeware provided by nih.gov. Due to the presence of microsilica in the background, contrast and brightness has to be adjusted prior to adjusting threshold. Chains of particles and other background noise were eliminated prior to size analysis. Principles behind SEM are explained in Section 2.5.2. See Appendix E for a step-by-step procedure.

2.3.3 TEM/STEM-EDS analysis

Samples were loaded onto heavy carbon-coated TEM grids. This was done by grinding a small amount of material in ethanol before depositing a single drop of the dispersed sample onto the grid. The grid was then placed under a lamp to evaporate the ethanol. Prior to loading the sample into the TEM, the sample was plasma cleaned for 15 minutes. STEM-EDS was run on a Jeol 2100F TEM with a working voltage of 200 kV and the emission current of 120 μ A. Principles behind TEM and STEM-EDS is explained in Section 2.5.2.

2.3.4 X-ray Diffraction

A PANalytical X'Pert PRO diffractometer was used to analyse powdered samples using a spinner stage. Samples (1 g) were loaded into stainless steel holders and compacted to make a smooth surface. A Cu K α tube was used as the X-Ray source, operating at 45 kV and 40 mA current. A PIXcel detector was used to measure scans and which ranged from 5-90° with step sizes of 0.013°. HighScore, the software provided by PANalytical, was used to analyse the materials. However, RRUFF.info was also used to identify any mineral forms. RRUFF.info ID for minerals identified are given for all spectra provided. Principles behind XRD are explained in Section 2.5.2.

2.4 Experimental analysis

2.4.1 Nitrate

In a typical experiment, under a N₂ atmosphere, 50 mL of 10 ppm NO₃⁻ (as nitrogen) was deoxygenated by bubbling N₂ gas through the solution. To this, S-nZVI@misi (0.25 g) was added. Aliquots of 5 mL were taken at 5 minutes, 15 minutes and 30 minutes. These aliquots were filtered using a 0.20 μ m syringe filter before nitrate concentration was determined using ion chromatography (IC). The eluent used was Dionex AS23 eluent concentrate, diluted to 3.5 mM Na₂CO₃/1 mM NaHCO₃. The method used was determined by previous members of the Fulton Group.⁴³ A Thermofisher IC 1100 was used with Dionex IonPac AS14 column, Dionex IonPac AG 14 column guard, Dionex AERS 500 suppressor and an injection volume of 25 μ L was used for this research. Principles of IC are explained in Section 2.5.1.

2.4.2 4-Nitrophenol

In a typical experiment, under N₂ atmosphere, to a 25 mL deoxygenated solution of 40 ppm 4-nitrophenol (4-NP), 0.0500 g of S-nZVI@misi was added. Aliquots (1 mL) were taken at 5 minutes, 15 minutes and 30 minutes for S-nZVI@misi and at 1, 2, 3, 4 and 5 minutes for nZVI@misi, before being filtered using a 0.20 μ m syringe filter. To the samples, 1 mL of 0.1 M NaOH was added and diluted 4 times. NaOH was needed to convert 4-NP to the 4-nitrophenolate (4-NP*) ion. This could then be used to determine the concentration of 4-NP *via* UV/Vis (Cary Bio-50 spectrophotometer) with λ_{max} at 400.5 nm. The Cary Bio-50 spectrophotometer uses a Xenon flash lamp which allows for fast data collection of 80 points per second and maximum scan rates of 24,000 nm/minute. To determine reproducibility of results, each material was tested in triplicate. The method was developed within the Fulton group.

2.4.3 Cadmium

In a typical experiment, a sample of 0.10 g of S-nZVI@misi was added to a 25 mL deoxygenated solution of 20 ppm Cd(II), under an N₂ atmosphere. Aliquots of 7 mL were taken at 5 minutes, 15 minutes and 30 minutes. These aliquots were filtered using a 0.20 μ m syringe filter and analysed *via* FAAS using parameters previously determined within the research group. Samples were diluted to fit a calibration curve of 0.1 ppm to 5 ppm and the fuel was air/acetylene with a flow rate of 1.1 mL/minute. A deuterium lamp was used for background correction. To determine reproducibility of results, each material was tested in triplicate. The method was developed within the Fulton group.

2.4.4 Chromium

A sample of 0.10 g of S-nZVI@misi was added to 25 mL deoxygenated solution of 20 ppm Cr(VI) sourced from $\text{K}_2\text{Cr}_2\text{O}_{4(s)}$, under an N_2 atmosphere. Aliquots of 7 mL were taken at 5 minutes, 15 minutes and 30 minutes. These aliquots were filtered using a $0.20\ \mu\text{m}$ syringe filter and Cr(VI) concentration determined spectrophotometrically as described in Standard Methods for Examination of Water and Wastewater.¹⁰² Briefly, 1 mL of sample was acidified until the pH was 1. 1,5-diphenylcarbazide (DPC) in acetone ($100\ \mu\text{L}$) was then added to the acidified solution. Samples were made up to 10.00 mL, placed in quartz cuvettes and run on UV/Vis with λ_{max} of 560 nm. To determine reproducibility of results, each material was tested in triplicate.

2.4.5 Iron(II) concentration

In a typical experiment, iron(II) concentrations were determined for samples post-cadmium reduction in a method developed within the Fulton group. A 2 mL aliquot was placed into a 10.00 mL volumetric flask. To this, 0.1 mL Conc. HCl, 1 mL acetate buffer, and 2 mL of o-phenanthroline solution was added. The sample was then made up to 10 mL and left for 30 minutes to form the $[\text{Fe}(\text{phen})_3]^{2+}$ complex. After 30 minutes, the concentration of Fe(II) was determined spectrophotometrically with a λ_{max} of 510 nm.

2.4.6 Total iron

In a typical reaction, total iron concentration was determined for samples post removal of cadmium and chromium. Concentration of iron was determined using FAAS. Samples were diluted to fit a range of 0.25 to 5 ppm. The fuel was air/acetylene with a flow rate of 0.9 mL/minute. A deuterium lamp was

used for background correction. This method was developed within the Fulton group.

2.4.7 Iron leaching experiments

A sample of 0.10 g of S-nZVI@misi was added to 25 mL of DI/DO water. Aliquots of 7 mL were taken at 5 minutes, 15 minutes and 30 minutes. These aliquots were filtered using a 0.20 μm syringe filter and analysed using FAAS. Parameters for iron determination were the same as those used to determine total iron.

2.5 Principles behind instruments used

2.5.1 Reaction monitoring

Flame Atomic Absorption Spectroscopy (FAAS)

Flame atomic absorption spectroscopy (FAAS) was used to analyse the change in concentration of Cd(II) and total Fe in solution. FAAS measures the absorption of light of a sample vaporised by either an air/acetylene flame or nitrous oxide/acetylene flame, using a hollow cathode lamp. The hollow cathode lamp is specific to the element being analysed (*e.g.* Cd lamp for Cd) (Figure 2.1).

Concentrations were determined by comparing absorption of samples to a calibration curve. A deuterium lamp was used for background correction for samples whose absorption maxima were below 350 nm. This is because interference of external signals in the ultraviolet region need to be subtracted from the sample signal to obtain the net signal. Deuterium lamp background

FIGURE 2.1: Schematic diagram of FAAS

correction uses the continuous radiation of a deuterium lamp to measure the average background absorption over the wavelength monitored.

Suppressed-ion anion chromatography

Ion Chromatography was used to analyse the change in concentration of nitrate. The principle behind suppressed-ion anion chromatography involves the separation of anions using an ion exchange stationary phase. The retention time on the column depends on the ionic charge/mass ratio. Conductivity is used to measure ion concentration with the resulting chromatogram showing the retention time of the different ions. Concentration was determined by comparing sample conductivity to a standard curve. The mobile phase for anion analysis was a 3.5 mM Na_2CO_3 /1 mM NaHCO_3 buffer solution. This buffer is highly conductive, therefore, the solution passes through a suppressor column prior to passing through the conductivity detector. The ion suppressor has a cation exchange membrane that allows for H^+ to pass into the mobile phase in exchange for Na^+ . This results in the effective neutralisation of CO_3^{2-} and

HCO_3^- to H_2CO_3 and the ionic species of the eluent are suppressed (Figure 2.2).

2.5.2 Characterisation Instrumentation

X-ray Diffraction

Powder X-ray diffraction (XRD) is used to identify crystalline materials by measuring the interaction of incident rays and diffracted rays when encountering a sample in accordance with Bragg's law ($n\lambda = 2d \sin \theta$). Bragg's law relates the wavelength ($n\lambda$) and diffraction angle to the lattice spacing within a unit cell. In powder XRD, it is important that the powder is fine to ensure randomness in the orientation of lattice structures. Therefore, a selection of diffraction angles are measured over a range of 2θ values.¹⁰³ The PanAlytical X'Pert Pro with $\text{Cu K}\alpha$ radiation will be used for powder X-ray diffraction on each of the samples. The X-rays are produced by bombardment of a target material such as copper by electrons. X-rays are filtered so that only monochromatic $\text{K}\alpha$ x-rays are used.

FIGURE 2.2: Schematic of ion chromatography

Scanning electron Microscope

The JEOL 6600LV is a scanning electron microscope (SEM) that can analysis of the surface distribution of nanoparticles on misi. SEM uses an electron gun to focus a fine beam of electrons onto the sample, scanning the surface in a raster scan pattern. This gives information of the topology and composition of the surface with secondary electron image (SEI) and backscatter/compositional images (COMPO). SEM is capable of electron dispersive spectroscopy (EDS). EDS is useful as it allows for elemental mapping of nanoparticles, *i.e.*, the elemental composition of the surface of S-nZVI@misi. It works by bombarding the sample with electrons. This causes x-rays to be emitted at a specific wavelength dependant on that element. This data is then used to identify the ratio of elemental composition. SEM uses a voltage of 20 kV and probe current of 15 mA.

(Scanning) Transmission Electron Microscope

Transmission Electron Microscopy (TEM) can be used to analyse the morphology of nanomaterials. TEM uses an electron beam focused (in a vacuum) onto a thin sample in which electrons are transmitted, collected and projected onto a camera (Gatan Peltier cooled CCD) at the bottom of the column. The JEOL 2010 is a high resolution TEM equipped with STEM and EDS. STEM works in the same way as SEM to collect EDS data, however, it has higher resolution. Thus, we can use STEM-EDS to determine the elemental composition at the surface of S-nZVI@misi.

Chapter 3

Characterisation

3.1 S-nZVI@misi sample names

The names for the samples used for S-nZVI@misi were based on the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ used and duration of sulfidation. For example, 100S-nZVI@misi-3 denotes that the concentration of sulfidation reagent was 100% of the molar concentration of iron in nZVI used (a 1:1 mol ratio), with a duration of sulfidation of 3 hours. Similarly, 100S-nZVI@misi-24 signifies that the concentration of sulfidation reagent was also 100% of the molar concentration of iron used but sulfidation duration was 24 hours. On the other hand, 50S-nZVI@misi-24 had a sulfidation time of 24 hours but only 50% of the molar concentration of iron in the nZVI in the sample.

Bimetallic, sulfidated, misi-supported nZVI is denoted differently. Firstly, 30S-5Ni-nZVI-misi-3a indicates that nZVI@misi was first doped with 5% nickel before sulfidation. It is labelled '3a' to denote that the method of nickel doping was by co-reduction of NiCl_2 with Fe(II) salt to form Ni-doped nZVI. This is unlike 30S-5Ni-nZVI-misi-3b, where nickel was added to freshly synthesised nZVI. The final bimetallic S-nZVI@misi, 5Ni-30S-nZVI-misi-3c, was generated by sulfidation of nZVI@misi prior to nickel doping. A 'one-pot' method, was also used and is denoted as 30S-nZVI@misi-1pot.

The supporting microsilica was prepared following the methodology established by the Fulton group, with a FeOOH coating. FeOOH has been shown to increase the reactivity of nZVI towards nitrate.⁴³ To analyse the effect the FeOOH coating has with S-nZVI, microsilica without the FeOOH coating was prepared. To differentiate between microsilica with FeOOH coating and microsilica without FeOOH coating, these materials have been defined differently. FeOOH coated microsilica is defined as misi, whereas, microsilica without the FeOOH coating, this is defined as misiUC (C indicating calcined only). For example, nZVI supported by FeOOH coated microsilica is denoted as nZVI@misi whereas, nZVI supported by uncoated microsilica is denoted as nZVI@misiUC.

3.2 Determination of S/Fe with SEM and AAS

3.2.1 Limitations with SEM-EDS

The percentage of S/Fe in the materials was examined using SEM-EDS in order to determine the effect of differing sulfidation reagent concentrations and durations. SEM-EDS is not a fully quantitative method as it uses remote standards. Remote standards are measured intensities of pure elements and compounds that were determined at multiple beam energies. These standards form a database that can be used to identify the elements.¹⁰⁴

Standard intensities are adjusted in accordance with the photon energy efficiency of the different EDS detectors. These intensities are then normalised so that elemental composition is represented as a fraction of a whole (100%). Errors arise as the different conditions used in our EDS measurements may differ to that of the standards, thus, limiting the accuracy of final results. Therefore, remote standard intensities only give an estimated composition of materials,

rather than an accurate measurement, with the final results prone to large error distributions.¹⁰⁵ Fully quantitative analysis can be performed. However, this involves analysing standards on the same SEM-EDS equipment and in the same conditions as samples, and thus, is time-consuming.

To minimise errors, multiple scans of samples were performed to identify a standard error. However, this data should be treated as semi-quantitative. Its main purpose is to identify the effect sulfidation duration and reagent concentration has in relation to the percentage of sulfur-to-iron.

3.2.2 SEM-EDS detection of S/Fe

Before analysis of S/Fe percentages by SEM-EDS, determination of the mass of iron per gram of material was determined. The mass of iron per gram of material was determined by digesting materials in concentrated nitric acid and analysing the concentration of iron by flame atomic absorption spectroscopy (FAAS). The mass of iron, per gram of material, varied from 71 mg/g for 100S-nZVI@misi-3 to 125 mg/g for 30S-nZVI@misi-1pot (Figure 3.1) giving an iron/misi loading between 7.1 - 12.5 %. This is close to the theoretical iron to misi loading of 10% (0.1 g Fe/1 g misi). Higher values may be due to small

FIGURE 3.1: Increasing S/Fe ratio as the concentration of sulfidation reagent concentration and time increases, and iron mass per total mass of material (mg/g)

amounts of iron in the FeOOH-coated misi support. There was no noticeable trend that can be identified for different sample preparation methods.

Controls were run to determine the percentage of sulfur to iron (S/Fe) that is present in just misi as well as nZVI@misi. The misi support was found to have an S/Fe percentage of $140 \pm 13\%$. However, in the context of the amount of iron present per gram of material, the actual total amount of sulfur present is negligible. Any sulfur that is present is presumably due to the use of iron sulfate during the preparation of FeOOH-coated misi. The S/Fe percentage for nZVI@misi was $5 \pm 2\%$ indicating that sulfur is present after washing freshly synthesised nZVI@misi. However, the actual amount of sulfur is small compared to the amount of iron present.

An increase in the relative S/Fe percentage was observed as the concentration of sulfidation reagent increased (Figure 3.1). However, a greater change in S/Fe was observed as sulfidation time was increased. For example, when the concentration of $\text{Na}_2\text{S}_2\text{O}_4$ was held at 50% molar ratio after three hours (50S-nZVI@misi-3) the S/Fe percentage was $12 \pm 2\%$, however, after increasing sulfidation time to 24 hours (50S-nZVI@misi-24) the S/Fe percentage was $25 \pm 1\%$. These results were also observed for the other concentrations of $\text{Na}_2\text{S}_2\text{O}_3$; that is, with the longer soaking time, the S/Fe percentage was almost double of the corresponding 3-hour materials.

For bimetallic S-Ni-nZVI@misi, it was found that S/Fe percentage was dependent upon the order of addition of nickel and sulfur. The addition of nickel after sulfidation (5Ni-30S-nZVI@misi-3c) had the lowest S/Fe percentage of all bimetallic S-Ni-nZVI@misi. This is potentially due to nickel reacting with and then removing sulfur. However, this was not further analysed. Both bimetallic materials prepared with nickel added before sulfidation method A or B (30S-5Ni-nZVI@misi-3a/3b) had higher S/Fe percentages than bimetallic materials prepared when nickel was added after sulfidation (5Ni-30S-nZVI@misi-3c)

indicating enhanced uptake of sulfur to the nickel-doped nZVI@misi (Figure 3.1).

A comparison of different synthesis methods with the same sulfidation reagent concentration of 30% molar ratios (30S-nZVI@misi-3, 30S-nZVI@misi-24 and 30S-nZVI@misi-1pot), found that the 'one-pot' method had a larger S/Fe percentage, potentially due to some $\text{Na}_2\text{S}_2\text{O}_3$ being directly reduced by NaBH_4 .

3.3 STEM-EDS of S-nZVI

Although SEM-EDS was used to determine the S/Fe percentage, it was unable to identify the actual distribution of sulfur on nZVI due its limited resolution. Thus, STEM-EDS was used to examine the samples in greater detail. Initial analysis of S-nZVI@misi using STEM-EDS was difficult. This is because particles were prone to changes in morphology under the electron beam, indicating instability of the material, with the outer layer become thicker after scanning 30 minutes (Figure 3.2). Adjustments to the condenser aperture allowed for a decrease in the intensity of the electron beam impacting the sample. The downside was that scans required 1 - 2 hours in order to obtain useful STEM-EDS maps. Nevertheless, STEM analysis allowed for the identification of sulfur in the samples after sulfidation.

For the S-nZVI@misi samples that underwent a 3-hour sulfidation, STEM-EDS detected sulfur at the surface of the particles (Figure 3.3)(See Appendix B). The concentration of sulfidation reagent had little effect on the morphology of S-nZVI@misi with 3-hour sulfidation with all particles resembling small 'balls' immobilized on misi. Oxygen was present at the surface of all of these materials, indicative of a mix of iron oxide and iron sulfide at the particle surface. STEM-EDS did not allow for the determination of the thickness of the outer

FIGURE 3.2: STEM-bright field images of 10S-nZVI@msi-3 before scan began and after scan finished with 1 condenser aperture used

iron oxide/sulfide layer, the oxidation state of sulfur materials or the crystal structure of the iron oxide or iron sulfide compounds.

In contrast to S-nZVI@msi with 3-hour sulfidation, when sulfidation time was increased to 24-hours, voiding at the core of the particle was observed. The S-nZVI@msi with 24-hour sulfidation resembled hollow 'donuts,' rather than 'balls' (Figure 3.3). As the concentration of the sulfidation reagent increased, the void observed became more prominent, with sulfur and oxygen detected in the core of S-nZVI. This is presumably due to the diffusion of sulfur and oxygen into the core, as Fe(II) ions diffused towards the surface (See Section 1.6).

FIGURE 3.3: STEM-EDS of nZVI@misi after 3 hours and 24 hours sulfidation with increasing sulfidation reagent.

3.3.1 Void formation in S-nZVI@msi

Cross-sections of the 24-hour sulfidation S-nZVI@msi (Figure 3.4), demonstrate that as the concentration of sulfidation reagent was increased, the size of the void increased. Cross-sections indicated that there was a general increase in the size of particles as sulfidation reagent concentration increased. This would be expected if nZVI is oxidising from the core-outwards as Fe(0) in the core is oxidised to Fe(II), before diffusing to the outer surface of nZVI (Section 1.6). This results in a net increase in the size of the particle.⁷⁷

Size distribution analysis did not conclusively determine if average size differed due to sulfidation time. From 3 SEM back-scatter images, 300 particles were counted and analysed to determine the mean size of particles after sulfidation in different molar concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ for 3 and 24 hours (Figure 3.5). These results indicate that there is an increase in the median size of particles when the sulfidation concentration was increased to 100% molar concentration of iron and higher (*e.g.* 150 and 300%). The difference in sulfidation time between materials with the same concentration of sulfidation reagent did not show any variance in particle size. For example, S-nZVI with 100% molar concentration of reagent showed no difference in median particle size when

FIGURE 3.4: Cross-sections of S-nZVI@msi-24 with increasing sulfidation reagent concentrations

FIGURE 3.5: Size distribution of nZVI@msi and S-nZVI@msi with different sulfidation reagent concentrations and 3 and 24 hour sulfidation

sulfidation was increased from 3 hours (100S-nZVI@msi-3) to 24 hours (100S-nZVI@msi-24). Similar results can be observed for materials with 50% molar concentration where the median particle size after 3 hours sulfidation was similar to that after 24 hours sulfidation. Therefore, increased sulfidation time has little effect on increasing particle size.

Voiding was also observed in aged nZVI@msi. Figure 3.6 shows an image of freshly prepared nZVI@msi. In this, the iron-oxide surface is observed as a shell with a lighter contrast on the surface of the nanoparticle. After stirring in DI/DO water for 24 h, the interior of the nanoparticle appears to have voided. STEM-EDS shows a higher intensity of oxygen versus iron at the core of the particle thus, confirming voiding has occurred in the aged nZVI@msi particle. These results indicate that some depletion in the core is due to ageing in water. However, sulfidation appears to enhance void formation.

3.4 XRD of supported and unsupported materials

X-ray diffraction (XRD) studies are commonly used to determine the composition of materials. In our samples, XRD analysis identified the presence of α -Fe

FIGURE 3.6: Fresh nZVI@misi *vs.* nZVI@misi after 24-hours in DI/DO water

on nZVI@misi and quartz and cristabolite from the microsilica support (Figure 3.7). However, XRD did not identify any peaks other than cristabolite or quartz in S-nZVI samples (See Appendix D). Therefore, XRD is not a useful method to identify species on the S-nZVI@misi surface. Unsupported nZVI and S-nZVI (nZVI@misi, 50S-nZVI@US-3 and 50S-nZVI@US-24) was synthesised to identify mineralogy at the surface of S-nZVI. Unfortunately, other than the presence of pyrrhotite (Fe_7S_8 , RRUFF ID R060440) in 50S-nZVI@UC-3 (Figure 3.8)

FIGURE 3.7: X-ray diffraction patterns of misi and nZVI@misi. Green * indicates Quartz, red cristabolite and blue α -Fe

FIGURE 3.8: XRD patterns of unsupported S-nZVI

no other minerals could be detected. Instead, significant peak broadening was observed, indicative of the presence of amorphous FeS and Fe(O) structures.

Other researchers have postulated that the initial formation of FeS is a mix of amorphous and nanocrystalline mackinawite.^{24,95,106} However, Han and Yan,⁹¹ found that S-nZVI synthesized using sodium thiosulfate formed magnetite (Fe₃O₄) and did not observe any crystalline iron sulfides. Using XPS, Han and Yan⁹¹ did conclude amorphous iron sulfide formed on unsupported S-nZVI. In our samples, XPS is not sensitive enough to differentiate between the surface of S-nZVI and misi in the supported materials.

3.5 Iron evolution in DI/DO water

The stability of the materials was examined by measuring the iron evolution by S-nZVI@misi. In these experiments, the materials were stirred in DI/DO water and the amount of iron released into solution was measured over 30 minutes. The pure nZVI@misi released the lowest amount of iron into solution, whereas 100S-nZVI@misi-3 released the most after 5 minutes. All 3-hour

sulfidation materials released more iron than the 24-hour sulfidation materials (Figure 3.9). Thus, S-nZVI@misi was less stable in solution compared to nZVI@misi. This may be due to the diversity of iron-sulfur structures on the surface of the nanomaterial as pure iron sulfide is insoluble at neutral pH.¹⁰⁷ In all cases, a higher concentration of iron was found after 5 minutes, after which the iron concentration decreased. This potentially is due to the formation of iron(III) oxides. The measured pH of the DI/DO water used was ~ 8 , therefore it could be possible that Fe(III) oxides will precipitate from solution. This would then have been filtered from solution before FAAS analysis, and therefore, not analysed.

From these results, we can conclude that S-nZVI@misi is not more stable than nZVI@misi due to the consistently higher concentrations of iron that were determined. However, why these materials have higher iron concentrations and the decrease of iron over the course of the experiments needs to be analysed in further studies.

FIGURE 3.9: Iron concentrations after soaking in DI/DO water

Chapter 4

Contaminant removal by S-nZVI@misi

4.1 Nitrate

Nitrate (NO_3^-) in waterways, is a contaminant that can lead to eutrophication of fresh water and the growth of toxic cyanobacteria (See Section 1.2). However, nZVI can be used to reduce nitrate to nitrite (NO_2^-) and then to ammonium (NH_4^+).^{108,109} However, nitrate has also been identified as a species that will compete with the reduction of target contaminants by nZVI, such as trichloroethylene (TCE), therefore, decreasing the reactivity of nZVI.^{110,111} Thus, sulfidation of nZVI has been proposed to reduce the loss of reactivity of nZVI due to side reactions reducible species such as nitrate. The reasons for the decreased reactivity of sulfidated nZVI is unclear as FeS in sediment will naturally reduce nitrate in groundwater. However, the reduction is slow, taking days to reach completion.^{112,113} Therefore, we attempted to reduce nitrate with S-nZVI@misi to determine if sulfidation of nZVI had any effect on reactivity.

The effect of sulfidation of nZVI@misi was examined. For these experiments,

we used a wide range of sulfidated nZVI@misi, including bimetallic S-Ni-nZVI@misi and by increasing the sulfidation time from 30 minutes to 3 hours and 24 hours. The initial concentration of nitrate was 10 ppm and changes in concentration over 30 minutes were analysed using suppressed-ion anion chromatography. However, by 30 minutes, it was evident that no decrease in the concentration of nitrate occurred in any of the sulfidated samples (Figure 4.1). No intermediate product (nitrite), was detected either. Therefore, we can conclude the S-nZVI does not remove nitrate from the solution.

The impact in environmental conditions was investigated. This included performing the reaction in air, in acidic environments and in the presence of Fe(II), using S-nZVI@misi prepared with 30% molar concentration of $\text{Na}_2\text{S}_2\text{O}_3$ and 3 hours sulfidation. However, there was no decrease in the concentration of nitrate and nitrite observed due to these changes (Figure 4.1(a)).

The reason for this dramatically diminished reactivity is presumably due to the decreased level of hydrogen bonding on the iron-sulfur surface. The presence of FeS species on the surface thus prevents nitrate from binding to the surface of S-nZVI. FeS minerals and S-nZVI is known to improve the selectivity of nZVI towards hydrophobic, 'target contaminants' such as organohalides.^{111,114} In contrast, hydrophilic species such as nitrate, will be less attracted to the surface of S-nZVI and will not undergo reduction.

To analyse if the presence of FeS on the surface decreased the reductive capability of nZVI, a nitroaromatic compound, 4-nitrophenol (4-NP), was used as a potential model for nitrate.

FIGURE 4.1: (a) Reduction of 10 ppm nitrate (as nitrogen) by S-nZVI@misi, S-Ni-nZVI@misi and nZVI@misi and (b) by S-nZVI@misi in air, acidic conditions and Fe(II) (1mM)

4.2 4-Nitrophenol

The removal of nitroaromatic compounds by nZVI have been investigated at length. Nitroaromatic compounds have become contaminants due to their prevalence in pesticides and explosives.²⁶ The analysis of nZVI in the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) occurs in a step-wise mechanism *via* intermediates, 4-nitrosobenzene (4-NSP) and 4-(hydroxyamino)-phenol (4-HAP) (Figure 4.2).²⁹ The change in concentration of 4-NP (40 ppm) was monitored using spectrophotometric analysis. However, 4-NP has a λ_{max}

of 325 nm while its reduction product, 4-aminophenol (4-AP), has a λ_{max} of 254 nm (Figure 4.3). The closeness of these absorption peaks meant that accurate concentration analysis of the reaction mixture by UV/Vis is difficult. This was overcome by the addition of base to the reaction aliquots, resulting in the deprotonation of 4-NP to 4-nitrophenolate (4-NP*), which has a λ_{max} of 405 nm. It would be expected that protonation of 4-AP would occur in basic conditions, but there was no observed difference in the intensity of the peaks detected.

The concentration of 4-AP was not quantifiable using UV/Vis due to oxidation in air.¹¹⁵ Also, the intermediate products were non-detectable using UV/Vis. Due to time constraints, we were not able to analyse the data using gas chromatography mass spectroscopy (GC-MS).

Tang *et al.*,¹¹⁶ observed an increase in reactivity of S-nZVI towards 4-NP compared to nZVI. However, our results indicate that S-nZVI@misi was slower than nZVI@misi at reducing 4-NP (Figure 4.4). The reaction profiles were similar for S-nZVI@misi prepared with different sulfidation reagent concentrations and 3 hour sulfidation (Figure 4.4(a)). Although the S/Fe percentages of these materials increased from 8% (10S-nZVI@misi-3) to 15% (100S-nZVI@misi-3) no correlation between S/Fe percentage was observed as all results were within

FIGURE 4.2: Reaction scheme for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP)

FIGURE 4.3: UV/Vis spectrum of 4-nitrophenol (4-NP), 4-nitrophenolate (4-NP*), 4-aminophenol (4-AP)

the margin of error.

The effect of nickel-doped sulfidated iron nanoparticles was also examined. The addition of 5% Ni to 30S-nZVI@misi-3 had a greater effect on the reduction of 4-NP than undoped 30S-nZVI@misi-3, with lower concentrations of 4-NP detected at 5 and 15 minutes than un-doped 30S-nZVI@misi-3. Nevertheless, the concentration of 4-NP at 30 minutes after reduction by Ni-doped S-nZVI@misi was similar to that of 4-NP at 30 minutes after reduction by 30S-nZVI@misi-3. Therefore, the presence of nickel initially showed a small improvement in reactivity over un-doped 30S-nZVI@misi-3, but overall did not improve removal efficiency of S-nZVI@misi (Figure 4.4(b)). Different synthetic methods of S-nZVI@misi indicated that "one-pot" 30SnZVI@misi-1pot was as efficient as 30S-nZVI@misi-3 in reducing nitrate. Thus, it can be concluded that different synthetic methods had little effect on the reduction of 4-NP by S-nZVI@misi.

Mixed results were observed when the effect of sulfidation time in the preparation of S-nZVI@misi on 4-NP reduction was examined (Figure 4.4(c)). For instance, when the sulfidation time was either short (30 minutes, 30SnZVI@misi-0.5) or long (24 hours, 30S-nZVI@misi-24), the reduction of 4-NP was faster

than with material that had been prepared with a 3 hour sulfidation time (30S-nZVI@misi3), indicating that there may be a significant difference in the composition of the outer layer of S-nZVI@misi (Figure 4.4(c)). According to Fan *et al.*,¹¹⁷ low sulfidation/short sulfidation duration's have a sporadic FeS coating, with iron oxides still present on the outer layer. The presence of iron oxide potentially enhances the reduction of 4-NP, whereas, FeS inhibits reduction, however, this is inconclusive and more experimental analysis is needed. As 30S-nZVI@misi-24 was the only S-nZVI@misi that was analysed, it cannot be concluded that the difference in sulfidation time led to this materials increased removal efficiency compared to other 30S-nZVI@misi-3.

These results do not confirm why there is such a significant decrease in reactivity for S-nZVI@misi compared to nZVI@misi in the reduction of 4-NP. More experimental analysis is needed to examine if the FeS-coating on nZVI either slows electron transfer or prevents binding at the surface by hydrophilic species. This could be done by using S-nZVI in the reduction of hydrophobic nitroaromatic species such as 4-nitrotoluene or 4-nitrobenzene.

FIGURE 4.4: 4-Nitrophenol reduction by S-nZVI@misi with (a) increasing sulfidation reagent concentrations (b) Ni-doping and 1-pot synthesis and, (c) increasing the duration of sulfidation.

4.3 Cd(II) removal

4.3.1 Overview

Unlike nitrate and 4-NP, the accepted mechanism for cadmium removal by nZVI is adsorption.^{55,56} This is because the reduction potentials for Fe(0)/Fe(II) and Cd(0)/Cd(II) are too close for direct reduction (Table 4.1). XPS was used by Zhang *et al.*,⁵⁶ and confirmed that adsorption was the probable mechanism, as Cd(II) and not Cd(0) was identified on the surface of nZVI (See Section 1.5.2).

Fe(0)/Fe(II)	-0.44 V
Cd(0)/Cd(II)	-0.40 V

TABLE 4.1: Reduction potentials of Fe(0)/Fe(II) and Cd(0)/Cd(II)

4.3.2 FeS, misi and elemental sulfur for Cd(II) removal

Initial control experiments analysed the effect of FeS, nZVI@misi and elemental sulfur in the removal of Cd(II) (Figure 4.5). There was little difference in the change in Cd(II) concentration by either misi or sulfur, providing evidence

FIGURE 4.5: Cd(II) removal by nZVI@misi, FeS, misi, sulfur and Fe(II)

that there is no adsorption in the presence of these species. FeS powder (<250 μm) removed 40% of Cd(II) from solution after 30 minutes. However, after 30 minutes, the concentration of Cd(II) was less than 5 ppm for nZVI@misi. Thus, FeS is less effective than nZVI@misi at removing Cd(II).

To determine the fate of Cd(II), the reaction mixture was analysed for Fe(II) after nZVI@misi was used to remove Cd(II). For this, the soluble Fe(II) concentration was determined by using *o*-phenanthroline to form $[\text{Fe}(\text{phen})_3]^{2+}$ which was then be analysed spectrophotometrically. Total Fe concentration was determined using FAAS. If Cd(II) removal was undergoing direct substitution with Fe(II) on the surface of nZVI, then the molar equivalent of Fe should be observed, *i.e.*, if 20 ppm Cd(II) (112 g/mol) is removed then 10 ppm of Fe(II) (56 g/mol) should be detected. For nZVI@misi, the total amount of Fe was approximately 60% less than the theoretical amount. Of the total iron detected at 5, 15 and 30 minutes, only approximately 50 - 60% of this was Fe(II) (Figure 4.6).

To discern if iron in solution as Fe(II) will remove Cd(II), 5 ppm of Fe(II) was added to a 20 ppm solution of Cd(II). There was a small decrease in Cd(II) concentration (~ 3 ppm), however this was negligible (Figure 4.5). Thus, Fe(II) does not remove Cd(II) from solution.

FIGURE 4.6: Concentration of Fe(II) and total iron after Cd(II) with nZVI@misi

4.3.3 Cd(II) removal by S-nZVI@misi

Sulfide-modified nZVI (S-nZVI@misi) showed an improved ability for the removal of Cd(II) in comparison to nZVI@misi (Figure 4.7(a)). A linear correlation was observed between the concentration of Cd(II) at $t = 30$ minutes and S/Fe ratios of S-nZVI@misi where sulfidation time was 3 hours (Figure 4.7(b)). This indicated that increasing S/Fe ratios increased the removal efficiency for nZVI in Cd(II) remediation. Interestingly, at $t = 5$ min (Figure 4.7(a)), the concentration of Cd(II) was higher for all S-nZVI@misi-3 materials than standard nZVI@misi. This signifies that differing kinetic profiles may exist for the removal of Cd(II) with S-nZVI@misi-3 than nZVI@misi.

Kinetic analysis demonstrated that S-nZVI@misi, that had a 50% molar concentration of reagent and 3 hour sulfidation (50S-nZVI@misi-3), fitted pseudo-first order with a k_{obs} of 0.070 (Figure 4.8(b)). Conversely, nZVI@misi presented a problem as it initially fitted pseudo-second order kinetics, from 0 - 4 minutes, with k_{obs} equaling 0.027. From $t = 5$ minutes to 45 minutes, the data points also

FIGURE 4.7: (a) S-nZVI@misi-3 vs time with 20ppm Cd(II) solution and (b) the relationship between the concentration of Cd(II) remaining in solution at 30 minutes versus S/Fe ratios

FIGURE 4.8: Kinetic analysis of (a) nZVI@misi (second order) and (b) 50S-nZVI@misi-3 (first order).

fitted pseudo-second order kinetics, with k_{obs} of 0.0018 (Figure 4.8(a)). However, these results indicate that the initial adsorption of Cd(II) to the surface of nZVI@misi slows the further removal of Cd(II) after 5 minutes. As this change in k_{obs} is not observed for 50S-nZVI@misi-3, we can assume that different processes are occurring at the surface of S-nZVI compared to the surface of nZVI.

4.3.4 STEM-EDS post Cd(II) removal

STEM-EDS of nZVI supported by FeOOH-coated misi (nZVI@misi) (Figure 4.10(a)) post Cd(II) removal (100 ppm Cd, $t = 30$ minutes), revealed that Cd was absorbed to the surface of nZVI@misi forming a 'flake-like' structure. Closer examination of these areas shows significant levels of Cd, Fe and O in the EDS spectra (Figure 4.9). Potentially, this is due to the formation of fibrous cadmium ferrite (CdFe_2O_3).⁵⁸ This build-up of CdFe_2O_3 prevents that further adsorption of Cd(II) to the surface of nZVI. This suggests that the reduction of reactivity after 5 minutes observed in the kinetic analysis of Cd(II) removal by nZVI@misi could, therefore, be attributed to the formation of CdFe_2O_3 at the surface.

FIGURE 4.10: 50S-nZVI@misi-3 post Cd(II) removal (Cd(II) concentration = 100 ppm, t = 30 minutes)

4.3.5 Effect of increasing S/Fe percentage

Increasing sulfidation time for S-nZVI@misi from 3 hours to 24 hours had a significant impact on these materials efficiency in removing Cd(II) from solution. Characterisation of these materials indicated that the S/Fe percentage increased dramatically for materials with the longer sulfidation time.

All S-nZVI@misi with 24 hour sulfidation times and molar concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ greater than 30%, were effective at removing Cd(II) with the concentration of Cd(II) almost below or below detection limits by 5 minutes. 30S-nZVI@misi-24, had a lower S/Fe percentage found by SEM-EDS compared to other S-nZVI@misi-24, of $13 \pm 1\%$. This is similar to materials with high sulfidation reagent concentrations and 3 hour sulfidation, 100S-nZVI@misi-3 and 70S-nZVI@misi-3 ($15 \pm 1\%$ and $14\% \pm 2\%$ respectively). Thus, we observe that 30S-nZVI@misi-24 showed similar removal efficiency as 100S-nZVI@misi-3 and 70S-nZVI@misi-3 due to similarities in surface composition (see Figure 4.11).

FIGURE 4.11: Cd(II) removal by 30S-nZVI@msi-24 compared to 100S-nZVI@msi-3 and 70S-nZVI@msi-3

FIGURE 4.12: Cd(II) concentrations at 5 minutes for S-nZVI@msi-24.

The S/Fe percentages of the S-nZVI@msi-24, other than 30S-nZVI@msi-24, were greater than 25%, therefore had a greater amount of sulfide present to remove Cd(II). Observations at $t = 5$ minutes (compared to $t=30$ in Figure 4.7b), found that the materials with S/Fe percentages between 30-35%, *i.e.*, the materials with 70 and 100% molar concentration of sulfidation reagents and 24 hour sulfidation (*i.e.* 70S-nZVI@msi-24 and 100S-nZVI@msi-24), consistently outperformed other materials with higher and lower values of sulfidation (Figure 4.12). This was not expected, as previously stated the presence of higher S/Fe

ratios should lead to increased efficiencies in the removal of cadmium. However, similar results were attained by Lv *et al.*,⁸⁴ in the removal of Cd(II) from solution with unsupported S-nZVI. S-nZVI with an S/Fe percentage of 30% was faster at removing Cd(II) from solution compared to S-nZVI with higher and lower S/Fe percentages. Results reported by Rajajayavel *et al.*,⁹⁰ stated that S-nZVI with S/Fe percentages higher than 30% indicated decreased reactivity towards trichloroethylene (TCE). This was reportedly due to the formation of pyrite (FeS_2) on the surface of S-nZVI, whereas, S/Fe percentages of 30% consisted of amorphous FeS or monosulfide minerals like mackinawite.⁹⁰ Decreased reactivity due to the presence of pyrite is supported by Ozverdi and Erdem,¹¹⁸ where Cd(II) removal by pyrite was lower than that of synthetic FeS, composed of the mono-sulfide mineral troilite and metallic iron. XRD analysis of S-nZVI@misi did not provide enough data to identify the mineral structure of the materials used (Section 3.4). This is due to the presence of amorphous silicates which obscure mineral patterns.

4.3.6 Iron concentrations post Cd(II) removal

Iron concentrations detected during the removal of Cd(II) by S-nZVI@misi was higher for all sulfidated materials compared to nZVI@misi (Figure 4.13). Detected iron concentrations ranged from 12 - 20 ppm at $t = 30$ minutes. The spectrophotometric determination of Fe(II) showed that most of the detected total iron was in the +2 oxidation state at $t = 30$ minutes for almost all S-nZVI@misi materials, unlike nZVI@misi where the percentage of Fe(II) of total iron is $\sim 50\%$ (Figure 4.13(a)). This was significantly higher than iron detected with nZVI@misi and that of iron detected after soaking in DI/DO water (~ 2 ppm). The increase in iron concentration post-Cd(II) removal, and the difference in kinetic profiles indicated that the Cd(II) removal mechanism is very different

FIGURE 4.13: (a) Fe(II) and total Fe at 30 minutes after Cd(II) removal by S-nZVI@misi and total iron concentrations during the removal of Cd(II) by S-nZVI@misi with (b) 3 hour and (c) 24 hour sulfidation

between S-nZVI@misi and nZVI@misi. The accepted mechanism for Cd(II) removal by nZVI@misi was adsorption.⁸⁴ However, the high concentration of Fe(II) emitted for sulfidated nZVI@misi, suggests that Fe(II) has been substituted for Cd(II) to form insoluble CdS on the surface of S-nZVI. CdS has a solubility constant (K_{sp}) of 1×10^{-27} at 25°C which is significantly lower than that of FeS ($K_{sp} = 8 \times 10^{-19}$). This indicates a higher preference of sulfur towards cadmium than iron.¹¹⁹ Lv *et al.*,⁸⁴ confirmed that the increased rate of Cd(II) removal is due to the formation of CdS. In our system, the composition of the cadmium mineral formed would be difficult to prove due to the difficulties in analysing the misi-supported materials using XPS and XRD. The presence of misi in materials overwhelms any signal from FeS in XRD due to the large amount of silicate present in our materials (Section 3.4).

4.3.7 Effect of synthetic methods and Ni-doping on cadmium removal

The S-nZVI@misi synthesised in the 'one-pot' method with 30% molar concentration of sulfidation reagent (30S-nZVI@misi-1pot), was shown to be more efficient in the removal of Cd(II), compared to either S-nZVI@misi with the same molar concentration of reagent but synthesised in the post-synthesis method with 3 hour and 24 hour sulfidation (30S-nZVI@misi-3 and 30S-nZVI@misi-24) (Figure 4.15). This could be due to the percentage of S/Fe being higher

FIGURE 4.14: TEM images of (a) 30S-nZVI@misi-3, (b) 30S-nZVI@misi-24 and (c) 30SnZVI@misi-1pot. TEM images were taken using a JOEL 2100f HRTEM

($22 \pm 3\%$), therefore, more sulfide is available to react with Cd(II). However, the morphology of particles of the '1-pot' method is different to S-nZVI@misi synthesised by the post-synthesis method, as particles have an irregular fibrous surface (Figure 4.14). The fibrous surface is believed to increase the surface area of S-nZVI@misi particles, thus, increasing adsorption sites for Cd(II).⁹¹ Attempts were made to analyse this material using STEM-EDS. However, 30S-nZVI@misi-1pot was prone to changes in morphology under the electron beam.

Ni-doping of nZVI@misi has been shown to catalyse the removal of cadmium, increasing the efficiency of nZVI.⁴⁶ Therefore, it would be expected that nickel-doped S-nZVI@misi would also show an increase in the efficiency of cadmium removal compared to un-doped S-nZVI@misi. All Ni-doped S-nZVI@misi that were used in this experiment had the same concentration of sodium thiosulfate (30% molar concentration) and sulfidation time (3 hours) but the addition

FIGURE 4.15: Effect of synthesis methods and Ni-doping on S-nZVI@misi removal of Cd(II). For all materials, the molar concentration of the sulfidation reagent was 30% of the Fe present

of Ni was performed in different ways. However, of the three Ni-doped S-nZVI@misi synthesised, only two removed almost all Cd(II) within 30 minutes.

Materials that were doped with nickel before sulfidation (30S-5Ni-nZVI@misi-3a and 30S-5Ni-nZVI@misi-3b) were significantly more efficient at removing Cd(II) than the material in which nickel was added after sulfidation (5Ni-30S-nZVI@misi-3c). For 5Ni-30S-nZVI@misi-3c, the change in concentration over time was similar to that of the un-doped 30S-nZVI@misi-3. This is because 5Ni-30S-nZVI@misi-3c had a low percentage of S/Fe of $8 \pm 2\%$ which was similar to that of 30S-nZVI@misi-3 which was $9 \pm 1\%$. Therefore, for 5Ni-30S-nZVI@misi-3c the presence of nickel did not catalyse the removal of Cd(II) from solution.

30S-5Ni-nZVI@misi-3a was prepared using the co-precipitation method; nickel salt is reduced in the same step the nZVI particles are synthesised by NaBH_4 . 30S-5Ni-nZVI@misi-3b was synthesised using the 2-step method, where nickel is added to freshly synthesised nZVI@misi particles. Both materials have a higher S/Fe percentage compared to 5Ni-30S-nZVI@misi-3c, of $11 \pm 3\%$ for 30S-5Ni-nZVI@misi-3a and $15 \pm 3\%$ for 30S-5Ni-nZVI@misi-3b. While both materials that were sulfide-modified after Ni-doping showed an increase in the removal of Cd(II) before 5 minutes compared to materials with similar S/Fe percentages, such as 30S-nZVI@misi-24 (S/Fe = $13 \pm 1\%$), the final concentration of Cd(II) at 30 minutes was not different. Therefore, it cannot be concluded that nickel-doping increases the efficiency of Cd(II) removal by S-nZVI@misi. It could be stated instead that increasing the percentage of sulfide to iron is of higher significance.

4.4 Cr(VI) removal

4.4.1 Overview

Chromium reduction by nZVI, Fe(II) and FeS has been well documented (see Section 1.5.3). Analysis of Cr(VI) reduction by S-nZVI supported by biochar (S-nZVI@BC)⁸⁷ and unsupported S-nZVI (S-nZVI@US)⁹⁸ had previously been published. It was expected that our S-nZVI@misi would work similarly to S-nZVI in literature, where increasing S/Fe percentages would improve reduction of Cr(VI). Cr(VI) concentrations were determined spectrophotometrically using the acidified 1,5-diphenylcarbazide method.¹⁰²

4.4.2 FeS, misi and elemental sulfur for Cr(VI) removal

Initial control experiments were undertaken to determine the effect misi, elemental sulfur, FeS and nZVI@misi would have of a solution of Cr(VI). Analysis shows that with misi and elemental sulfur no significant change occurred, indicating that Cr(VI) will not absorb to the surface of misi, or be reduced by elemental sulfur (Figure 4.16). Amorphous FeS has been shown to reduce Cr(VI) in solution.⁹⁷ In our research, FeS (250 μm), did not initially prove to be faster at removing Cr(VI) from solution compared to nZVI@misi. However, for FeS, the final concentration of Cr(VI) after 30 minutes was 15 ± 1 ppm, similar to the final concentration of Cr(VI) after reduction by nZVI@misi which was 15.1 ± 0.2 ppm (Figure 4.16). With regards to Cr(VI) removal by nZVI@misi, most removal was observed in the first 15 minutes. In contrast, the removal rate of Cr(VI) by FeS was constant. This loss of reactivity by nZVI@misi towards Cr(VI) removal could be potentially due to the formation of $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(s)}$ ⁶⁵ on the surface of nZVI, thus, hindering electron transfer.

FIGURE 4.16: Reduction of Cr(VI) by nZVI@misi, FeS and Fe(II) compared to adsorption by misi

4.4.3 Removal of Cr(VI) by S-nZVI@misi

In the reduction of Cr(VI) by S-nZVI@misi, as S/Fe percentages increased, the removal of Cr(VI) became faster (Figure 4.17(a)). S-nZVI@misi synthesised with 50% molar reagent concentration of iron but with 3 hours sulfidation (50S-nZVI@misi-3), was only slightly faster at removing Cr(VI) from solution than nZVI@misi. However, when sulfidation reagent concentration was increased to 100% molar concentration of iron, (100S-nZVI@misi-3), this material was significantly faster, removing over three-quarters of Cr(VI) from solution within 30 minutes.

Cr(VI) removal was faster for all S-nZVI@misi, with 24 hour sulfidation, compared to S-nZVI@misi with 3 hour sulfidation (Figure 4.17(b)). However, S-nZVI@misi with 200% molar concentration of sulfidation reagent (200S-nZVI@misi-24) is observed to be slower than other 24 hour materials. The reason for

this is unknown as it had higher a S/Fe ratio. We can assume that other processes are occurring at the surface to hinder reactivity. In general, the increasing percentage of sulfur-to-iron has a significant effect on the Cr(VI) concentration at $t = 5, 15$, and 30 minutes. The material with the highest molar concentration of sulfidation reagent, 300S-nZVI@misi-24, removed all detectable Cr(VI) solution within 5 minutes. Materials with lower concentrations of sulfidation reagent, 100S-nZVI@misi-24 and 50S-nZVI@misi-24, were proven to be slower at reducing Cr(VI), with the concentration of Cr(VI) undetectable by 15

FIGURE 4.17: Cr(VI) reduction by (a) S-nZVI@misi-3 vs nZVI@misi and (b) S-nZVI@misi-24

FIGURE 4.18: Comparison of decreasing Cr(VI) concentration at $t = 5, 15$, and 30 minutes versus increasing S/Fe percentages

minutes and 30 minutes, respectively.

As shown in Figure 4.18, a relationship between the concentration of Cr(VI), at 5, 15 and 30 minutes, and percentage of S/Fe is observed. At each time point, the concentration of Cr(VI) decreased as S/Fe increased. Thus, we can conclude that increasing S/Fe increased the rate and efficiency of the reduction of Cr(VI) by S-nZVI@misi. This is consistent with what has been observed by other research groups (Section 1.7.1).

4.4.4 Iron evolution post-Cr(VI) removal

The concentration of iron after reduction of Cr(VI) is significantly lower than the iron detected for the same materials after the removal of cadmium and after leaching in DI/DO water (Section 3.5). The iron concentrations are presented in Table 4.2. Interestingly, when the concentration of iron was greater than 1 ppm (indicated in bold), the concentration of Cr(VI) was mostly undetected. Fe(II) has been reported to reduce aqueous Cr(VI) to form a brown precipitate composed of $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(s)}$ (Section 1.5.3).^{65,67} To investigate the rate of this reaction, Fe(II) was added to a solution of Cr(VI) after which a brown precipitate immediately formed and the yellow $\text{K}_2\text{Cr}_2\text{O}_7$ solution became colourless,

Sample	5 minutes	15 minutes	30 minutes
300S-nZVI@misi-24	0.10 ± 0.02 ppm	2.0 ± 0.7 ppm	1.1 ± 0.2 ppm
100S-nZVI@misi-24	0.08 ± 0.05 ppm	1.1 ± 0.9 ppm	4.9 ± 0.8 ppm
50S-nZVI@misi-24	0.13 ± 0.02 ppm	0.15 ± 0.02 ppm	6 ± 2 ppm
100S-nZVI@misi-3	0.17 ± 0.05 ppm	0.10 ± 0.03 ppm	0.10 ± 0.02 ppm
50S-nZVI@misi-3	0 ppm	0 ppm	0 ppm
nZVI@misi	1.1 ± 0.6 ppm	0.11 ± 0.04 ppm	0.10 ± 0.03 ppm
FeS (0.1 g)	0 ppm	0 ppm	0 ppm
misi (0.1 g)	0.19 ± 0.05 ppm	0.16 ± 0.02 ppm	0.15 ± 0.01 ppm

TABLE 4.2: Iron concentrations post-Cr(VI) reduction in ppm.
The concentrations greater than 1 ppm have been **bolded**

consistent with previous observations.^{63,65,66} Therefore, it could be speculated that the low concentration of iron detected after the reduction of Cr(VI) was because Fe(II) in solution reduced Cr(VI) to Cr(III). However, we were unable to analyse S-nZVI@misi after the reduction of Cr(VI) because of contamination of chromium on the column of the TEM. This contamination means that any STEM-EDS results we would get would not be quantifiable.

4.5 Role of FeOOH-coating of misi on contaminant removal by S-nZVI@misi

4.5.1 Overview

The misi support used in the previously reported experiments was coated with FeOOH. While this coating does not improve adsorption of nZVI onto misi, it has been shown to improve the reactivity of nZVI in the reduction of nitrate.⁴³ For nitrate remediation, it is theorised that the FeOOH layer acts as a catalyst to decrease the standard reduction potential of Fe(II) increasing the rate of nitrate reduction. The oxidation of Fe(II) and Fe(0) also forms Fe₃O₄ which assists in the transfer of electrons as it is conductive and lowers electrical resistance.^{43,120,121}

In order to analyse if the FeOOH coating on the misi support affected the removal by S-nZVI of Cd(II) or Cr(VI) from solution, three materials were synthesised and subsequently tested. These materials were nZVI@misiUC, and S-nZVI@misi synthesised using 50% molar concentration of sulfidation reagent with 3 hour (50S-nZVI@misiUC-3) and 24 hour sulfidation (50S-nZVI@misiUC-24). The 50% samples were chosen due to their differences in analysis. Tests were performed in the same conditions as the previous experiments by S-nZVI@misi with Cd(II) concentration determined using FAAS and Cr(VI) determined spectrophotometrically.

4.5.2 Cd(II) removal by S-nZVI@misiUC

In the removal of Cd(II) from solution, the nZVI and S-nZVI supported by un-coated misi (nZVI@misiUC, 50S-nZVI@misiUC-3 and 50S-nZVI@misiUC-24), removed Cd(II) slower and less efficiently than their counterpart materials

absorbed onto FeOOH-coated misi, (nZVI@misi, 50S-nZVI@misi-3, and 50S-nZVI@misi-24) (Figure 4.19). Therefore, the removal of Cd(II) by nZVI@misi and both S-nZVI@misi materials was significantly enhanced in the presence of FeOOH on misi. The higher S/Fe ratio still showed faster initial removal of Cd(II).

Interestingly, Fe concentrations, after 30 minutes in Cd(II), were significantly lower for materials supported by un-coated misi compared to materials supported by FeOOH-coated misi (Table 4.3). The increase in iron detected for

FIGURE 4.19: Reduction of Cd(II) with nZVI@misi, and S-nZVI supported by (a) FeOOH-coated misi and (b) un-coated misi.

S-nZVI supported by FeOOH-coated misi can be attributed to enhanced substitution of Fe by Cd. Because the rate of Cd(II) removal was so much greater for S-nZVI supported by FeOOH-coated misi, it would be expected that there would be a larger quantity of iron detected at 30 minutes. This difference indicates that the FeOOH coating on misi increases the rate of Cd and Fe substitution by S-nZVI. However, detected iron concentrations was similar for nZVI on un-coated misi and nZVI supported by FeOOH-coated misi. Since adsorption is the accepted mechanism for pure-nZVI, a major difference in iron concentration would not be expected. These results suggest that the detected iron concentrations in solution is due to leaching by nZVI@misi. Therefore, we can conclude from this that there is an increase in the rate of Cd(II) removal due to the FeOOH coating on misi. These results also confirm that the mechanisms for Cd(II) removal are different between pure nZVI@misi and S-nZVI@misi.

Sample	Fe concentration at 30 minutes
nZVI@misi	4.9 ± 0.5 ppm
nZVI@misiUC	5.9 ± 0.9 ppm
50S-nZVI@misi-3	19.0 ± 0.3 ppm
50S-nZVI@misiUC-3	6.7 ± 0.9 ppm
50S-nZVI@misi-24	14.0 ± 2 ppm
50S-nZVI-misiUC-24	4.4 ± 3 ppm

TABLE 4.3: Iron concentrations at 30 minutes for nZVI/S-nZVI on FeOOH-coated- and uncoated-misi

4.5.3 Cr(VI) removal by S-nZVI@misiUC

Un-coated misi as a support for nZVI and S-nZVI was used in the reduction of Cr(VI) and compared to results from analysis of nZVI and S-nZVI supported by FeOOH-coated misi (Figure 4.20). In the reduction of Cr(VI) by nZVI supported on un-coated misi, there was no significant change in initial

concentration observed. This is also shown in the reduction of Cr(VI) by 50S-nZVI@misiUC-3, which shows a decrease in reactivity towards Cr(VI) compared to the same material supported by FeOOH-coated misi. Therefore, the presence of FeOOH enhances the reduction of Cr(VI) for nZVI@misi and 50S-nZVI@misi-3. However, at $t = 5$ minutes, after reduction by 50S-nZVI@misi-24 compared to 50S-nZVI@misiUC-24, this difference in reactivity is minimal. The concentration of Cr(VI) at 15 minutes was similar after reduction with these materials and no Cr(VI) was detected at 30 minutes. Thus higher sulfidation of materials is more important in the reduction of Cr(VI) than the coating of the supporting materials.

4.5.4 Implications of FeOOH coating on misi

The significance of these results indicates that FeOOH is acting as a catalyst in the removal of Cd(II) and Cr(VI). However, the effect FeOOH has is very different for each species. Cd(II) removal is significantly enhanced by the FeOOH-coated misi support compared to the un-coated misi support. An initial analysis determined that FeOOH-coated misi did not remove Cd(II) from solution (Section 4.3.2). Therefore, the improvement in Cd(II) removal is not due to adsorption to the surface of the misi support, but in the properties of FeOOH as a catalyst. The presence of FeOOH on the outside of nZVI has previously been noted to enhance the adsorption of Cd(II).⁵⁸ In oxygen-rich conditions, FeOOH forms on the surface of nZVI. This is thought to then catalyse the formation of cadmium ferrite on the surface of nZVI.⁵⁸ FeOOH on the surface also enhanced the adsorption of Zn(II) onto the surface of nZVI, however, the reason why is not stated.¹²² Therefore, we can speculate that the faster adsorption of Cd(II) by nZVI@misi (compared to nZVI@misiUC) is due to catalysis by FeOOH. It is also probable that the substitution of Fe(II) for Cd(II) at the surface of S-nZVI supported by FeOOH-coated misi is catalysed by FeOOH.

FIGURE 4.20: Reduction of Cr(VI) by nZVI and S-nZVI supported by (a) FeOOH-coated nZVI and (b) un-coated nZVI

Cr(VI) reduction is less influenced by FeOOH. There is an increase in Cr(VI) reduced by nZVI@misi and 50S-nZVI@misi-3 with FeOOH-coated misi compared to these same materials supported by un-coated misi. However, by increasing sulfidation time in the synthesis of 50S-nZVI@misi-24, the difference between samples supported by FeOOH-coated misi and un-coated misi is insignificant. Analysis has shown that FeOOH-coated misi does not adsorb Cr(VI). Therefore, this is not the reason for the increase in reactivity of nZVI and S-nZVI supported by FeOOH-coated misi (Section 4.4.2). This increased

rate suggests that FeOOH does act as a catalyst in the reduction of Cr(VI) by materials supported by FeOOH-coated misi. However, increasing sulfidation duration of S-nZVI appears to have more of an effect on the rate of removal of Cr(VI) than catalytic effects of FeOOH. Therefore, any catalytic effect FeOOH has is minimal compared to high S/Fe percentages. It would be expected that if materials, supported by un-coated misi, with higher S/Fe percentages were tested, the difference in reactivity would be insignificant.

Chapter 5

Conclusions and Future directions

5.1 Conclusions

In conclusion, sulfidation of nZVI using sodium thiosulfate as a reagent produces very reactive nZVI particles that effectively remove cadmium and chromium from solution. By increasing the sulfidation reagents concentration and the duration of time in which sulfidation occurs, we can increase the S/Fe ratio. However, with increasing time from 3 hours of sulfidation to 24 hours, voiding at the core of the material occurs. The formation of voids do not have any effect on the removal of Cd(II) or Cr(VI). Rather, the significant increase in the percentage of S/Fe in S-nZVI@misi after 24 hours sulfidation meant that these materials were faster at removing these contaminants.

Unlike the removal of cadmium and chromium, sulfidation of nZVI@misi resulted in no nitrate being reduced. Changing environmental conditions had no impact on the reduction of nitrate by S-nZVI@misi, and thus, we can conclude that S-nZVI@misi will not reduce nitrate. The reduction of 4-nitrophenol (4-NP) by S-nZVI@misi was observed to be significantly slower than nZVI@misi. Increasing sulfidation of S-nZVI@misi had mixed results but overall all S-nZVI@misi including materials with 3 and 24 hour sulfidation, increasing reagent

concentration and nickel-doping were not effective at reducing 4-NP. The reason for the decreased reduction of nitrate and 4-NP, presumably could be due to the hydrophobicity of surface iron sulfides compared to iron oxides. The hydrophobic surface decreases the attraction for hydrophilic compounds like nitrate. Therefore, it could be assumed that FeS coated nZVI has increased targetability towards less hydrophilic species.

The mechanism for Cd(II) removal by nZVI@misi is adsorption. However, kinetic and STEM-EDS results conclude that different mechanisms occur for S-nZVI@misi. Kinetic analysis shows that Cd(II) removal by nZVI@misi is second-order with the rate decreasing significantly after 4 minutes. However, for S-nZVI@misi, it Cd(II) removal is a first-order reaction. STEM-EDS maps show the formation of different structures at the surface of S-nZVI@misi compared to nZVI@misi, presumably due to substitution of Cd(II) for Fe(II) at the surface of S-nZVI@misi. The substitution mechanism theory is backed by the presence of significant quantities of Fe(II) detected at 30 minutes after Cd(II) removal. Results indicate that increasing S/Fe ratios indicate more sulfide present at the surface of S-nZVI, therefore, the removal of Cd(II) is faster. S-nZVI@misi also is resistant to the decrease in reactivity that occurs with nZVI@misi. This decrease could be presumed to be because as Cd(II) adsorbs to the surface of nZVI, this forms cadmium ferrite, which prevents further adsorption to the surface for Cd(II). This does not occur for S-nZVI, and as long as sulfide is present it would be assumed that it would be able to maintain reactivity for a longer period of time.

In comparison, increasing S/Fe increases the reactivity for Cr(VI) reduction. Unlike the removal of Cd(II) which had high levels of Fe detected at 30 minutes, iron concentrations after Cr(VI) reduction were low. This decrease in iron was presumably due to Fe(II) in solution also reducing Cr(VI) in conjunction with S-nZVI@misi. Similar to the removal of Cd(II), nZVI@misi was found

to be slower at removing Cr(VI) compared to sulfide-modified nZVI@misi. In comparison, sulfide modified nZVI@misi with 24 hours sulfidation were found to be the most efficient in the reduction of Cr(VI) compared to materials with 3 hours sulfidation.

The presence of FeOOH-coating on the microsilica support, has significant effects on the reactivity towards Cd(II) and Cr(VI). In the removal of Cd(II) by nZVI@misi, 50S-nZVI@misi-3 and 50S-nZVI@misi-24, the FeOOH-coating on the microsilica enhanced and quickened the removal of Cd(II). While this was also true for the removal of Cr(VI) by these same materials, the difference in Cr(VI) concentration at 30 minutes between the FeOOH-coated and uncoated microsilica was not as great compared to the Cd(II) removal. Interestingly, the reduction of Cr(VI) by 50S-nZVI@misi with 24 hour sulfidation (50S-nZVI@misi-24 and 50S-nZVI@misiUC-24), showed that the increased S/Fe ratio had a greater effect as the difference in rate of Cr(VI) removal between the material supported by the FeOOH-coated microsilica and the uncoated microsilica was minimal. Thus, FeOOH-coating on the microsilica support acts as a catalyst in the removal of Cd(II) and Cr(VI). However, increasing the sulfidation of S-nZVI@misi had the greatest impact on the removal of cadmium and chromium.

5.2 Future directions

Future analysis of S-nZVI@misi is necessary to identify the reasons for decreased reactivity towards nitrate and nitrophenol. This includes;

1. Identify the surface composition of S-nZVI using more sensitive methods. This includes using techniques such as X-ray photoelectron spectroscopy (XPS) or Ramen spectroscopy.

2. Analyse hydrophobicity of FeS to determine if this is the reason for decreased reactivity towards nitrate and 4-nitrophenol. This could be done by comparing reactivity in more hydrophobic nitroaromatic compounds (*e.g.* nitrobenzene, nitrotoluene)
3. Determine reactivity of S-nZVI in respect to other heavy metal contaminants such as arsenic, lead, and mercury as well as organic contaminants such as trichloroethylene (TCE).
4. Determine reactivity towards tetracycline antibiotics and the mechanism of degradation. Initial studies show that S-nZVI@misi was faster at removing tetracycline from solution, however due to time constraints this was not analysed further.
5. Apply S-nZVI@misi in real water environments to determine the effect of natural organic matter and other compounds in the removal of heavy metals and organic contaminants.

Appendix A

SEM-EDS Spectra

FeOOH-coated microsilica

nZVI@msi

10S-nZVI@msi-3

30S-nZVI@msi-3

50S-nZVI@msi-3

70S-nZVI@msi-3

100S-nZVI@msi-3

30S-nZVI@msi-24

50S-nZVI@msi-24

75S-nZVI@msi-24

100S-nZVI@msi-24

150S-nZVI@msi-24

200S-nZVI@msi-24

300S-nZVI@msi-24

30S-nZVI@msi-1pot

30S-5Ni-nZVI@msi-3a

30S-5Ni-nZVI@msi-3b

5Ni-30S-nZVI@msi-3c

Appendix B

STEM-EDS of S-nZVI@misi

30S-nZVI@misi-24

50S-nZVI@misi-24

75S-nZVI@misi-24

100S-nZVI@misi-24

Appendix C

STEM-EDS maps

Red = Fe, Green = S and Blue = oxygen

Appendix D

XRD of samples

Appendix E

Size Distribution analysis using ImageJ

1. Open image in ImageJ
2. Set scale by drawing line over scale. Select analyse, then set scale.

3. Delete label box by drawing box over it and selecting edit, clear.
4. Select process, band filter and select ok.

5. Select image, adjust threshold. Adjust threshold until 'red' covers white dots.

6. Select drawing tools, eraser, and erase any red areas you do not want to analyse (chains etc.)
7. Select analyse, analyse particles. Select 0.0009 as minima to avoid any noise.

Copy and paste the final data into an excel spread sheet. Units are in μm^2 .

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