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Chemical Stabilization of Zinc from Contaminated Soil Using Nano Zero-Valent Iron
and Iron Oxides

Master's Diploma Thesis

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DIPLOMA THESIS ASSIGNMENT

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Thesis title

Chemical stabilization of zinc from contaminated soil using nano zero-valent iron

Objectives of thesis

Aim of this study is to optimize a dose of applied $n\text{Fe}(0)$ using batch experiment and to compare the application of $n\text{Fe}(0)$ as a thin layer against the well-mixing with the soil. Additional aim is to provide geochemical modelling of zinc speciation and its potential precipitation in the leachate.

Methodology

First, review of the $n\text{Fe}(0)$ presence to metal(loid)s behaviour in the soil will be provided.

Next, a batch experiment will then be realized in order to test optimal dose of tested nano zero-valent iron. Nano $\text{Fe}(0)$ at optimized dose will then be used for column leaching test in order to compare the application separately (as a thin layer) against the mixing together with soil. Continuously, pore water and leachate will be analysed for Zn and other elements concentration, pH, Eh and EC. Finally, all obtained data will then be used for geochemical modelling using Visual Minteq software package.

The proposed extent of the thesis

50-60

Keywords

chemical stabilization, column leaching, nano iron, modelling

Recommended information sources

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DT author's declaration:

I hereby declare that I wrote this diploma thesis independently, under the direction of Lukáš Trakal. I have listed all literature and publications from which I have acquired information.

Abstract:

The anthropogenic increase of zinc in Příbram, Czech Republic, caused by a nearby smelting plant has caused vast contamination to the nearby soils and Litavka River. The use of nano zero-valent iron (nZVI) for adsorption and stabilization of zinc offers an interesting remediation technique due to its large surface area and therefore, heightened reactivity. Since it is an in-situ method, it is less invasive, produces less waste, is more cost effective, timely, and can cover a wide range of contaminant categories. To determine the efficacy of nZVI, soil was taken from Příbram and used in a soil column leaching experiment. Specifically, the column experiment was used to determine which application method of nZVI was most efficient; either distributed evenly throughout the contaminated soil, or in a single layer below the contaminated soil. A batch experiment was conducted first to determine the sorption efficiency of nZVI, followed by a leaching experiment to determine optimal dosage of nZVI, and finally a column leaching experiment to determine which application method was most efficient at stabilizing zinc in the soil. The results showed the optimal dose of nZVI was 2% and having nZVI significantly reduced the amount of zinc in the leachate and pore water. However, the applications only showed significant results when compared to the control. When the two application methods were compared to each other, there was no statistical significance. This means having nZVI in the soil, no matter what the application, will significantly stabilize zinc, making it safe from further soil, crop, or water contamination.

Antropogenní nárůst koncentrace zinku v oblasti Příbramska (způsobený přítomností nedalekých kovohutí) zapříčinil obrovskou kontaminaci okolních půd a říčky Litavky. Použití elementárního nanoželeza (nZVI) pro sorpci a stabilizaci zinku se jeví jako zajímavý sanační technika vzhledem ke svému velkému povrchu, a tudíž i zvýšené reaktivitě. Jedná se o in-situ metodu, to je méně invazivní, produkující méně odpadu, nákladově efektivní, včasnou která může zahrnovat širokou škálu kontaminantů. Pro stanovení účinnosti nZVI byla použita právě půda z oblasti Příbramska s použitím loužičího experimentu. Pro tyto účely byl použit kolonový experiment, kdy byla testována aplikace nZVI ve vrstvě resp. homogenní zapravení do testovaného profilu. Nejprve však byly realizovány vsádkový respektive loužicí experiment ke zjištění optimální dávky zkoumaného sorbentu, následovaný právě kolonovým experimentem ke zjištění způsobu aplikace. Výsledky ukazují, že optimální dávka nZVI byla 2 %, kdy koncentrace Zn v půdní vodě byla významně snížena. Oba způsoby aplikace sice ukazují signifikantní snížení oproti kontrole, ale samotný způsob aplikace nevykazuje statisticky významný rozdíl. Což poukazuje na skutečnost, že není podstatné jakým způsobem je nZVI aplikováno do půdy na každý pád však dojde ke značnému snížení biodostupné koncentrace zinku.

Keywords: zinc, nanoparticles, sorption, remediation, metal oxides

Keywords: zinek, nanočástice, sorpce, sanace, oxidy kovů

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1. Introduction

Contamination of soil and water by inorganic metals and/or metalloids is known to be a serious environmental issue since they degrade vital natural resources and can cause toxicity to the environment and organisms even in trace amounts. Specifically, zinc has been shown to reduce crop yield and its quality, deteriorate flora, harm fauna, and degrade microbial activity (Adriano, 2001). Common remediation techniques are extremely costly, lengthy, and often ineffective. On the contrary, nanoparticles, specifically nano zero-valent iron (nZVI), have large surface areas which result in an increased reactivity, offering an efficient and versatile remediation technique that is also cost effective and environmentally friendly (Li et al., 2016). In the United States alone, there are over 1,200 sites listed on the National Priority List, 64% of which are contaminated by heavy metals (Mulligan et al., 2001). In the European Union, 53% of all sampled land demonstrated levels of heavy metal contamination that were above the threshold value (Toth et al., 2016). This illustrates the vast problem of metal pollution and indicates the importance of adopting feasible remediation techniques such as nanoparticles.

Although zinc is the 24th most abundant element naturally occurring on earth, its concentrations have been on the rise due to anthropogenic activity, specifically mining, steel production, and coal and waste combustion (ASTDR, 2005). Zinc has been mined since around 20 BCE-14 CE when the Romans were using it for brass. Although the peak production and mining of zinc was in the 1900s, there is still production occurring today (Gutiérrez et al., 2016), increasing the amount of zinc in the environment. Another serious problem is the waste left behind after a mining company closes down since it offers an easy way for the contaminants to continually be released into the environment. Many of these waste sites have been around for 50-100 years, and since the tailings are in such small pieces and are exposed to rain and other environmental factors, they are easily weathered and distributed into the surrounding environment. This is why uncontained tailings are considered among the worst environmental issues (Gutiérrez et al., 2016).

Zinc substances are especially prevalent in, but not limited to, the production of pennies, rubber, white paints, deodorant, sunblock, galvanization of steel, and production of brass and bronze when mixed with other metals (ASTDR, 2005). Too

much zinc in the environment negatively impacts water resources, soils, crops, and even humans and other fauna in larger amounts. Trace metals such as zinc are especially dangerous because they can lead to biomagnification. Biomagnification occurs when the concentrations of the particular metal increase as it travels up the food chain. With humans being at the end of the food chain, we are at risk for the highest concentrations of contamination.

Organic contaminants are oxidized to carbon (IV) oxide by microbial activity. However, inorganic contaminants such as zinc do not undergo such actions, and therefore persist in the environment long after they are introduced (Wuana and Okieimen, 2011). If these metals are immobilized or stabilized in the soil by redox or adsorption reactions, they are not a threat to the environment or organisms because they are considered inert. However, if they are not stabilized, the fate of these metals include them becoming mobile, bioavailable, and leachable. If they are mobile in the soil environment, they are harder to control because they can leach into the groundwater, runoff into rivers or lakes, or be uptaken by plants which are then eaten by larger organisms such as ourselves (Mulligan et al., 2001). Overall, metals such as zinc are excessively put into the environment by humans, and so, humans too must also take it out of the environment since it does not break down over time by itself.

2. Aims of the thesis

The aims of this thesis are to provide a clear understanding of how nano zero-valent iron can be used as a remediation agent for soils contaminated with zinc. Specifically, the aim is to determine the best dosage and application of zero-valent iron nanoparticles in the soil. The different approaches compared whether having the nZVI in a layer or having it evenly distributed within the soil would be better for stabilization of zinc.

3. Literature Review

3.1 Zinc in the Environment

Metals can be classified into two groups; essential and nonessential in regards to life. Zinc is an essential metal since it is needed in living organisms for growth, development, and for our bodies to function normally. Other metals that can be grouped into this category are iron, calcium, magnesium, copper, sodium, and potassium. Although these metals are necessary, when their concentrations are elevated, they become toxic (Rzymiski et al., 2013). When zinc reaches toxic levels in the human body, symptoms may vary, but the most common ones include: inhibition of the uptake of copper and iron, vomiting, fever, nausea, headache, tiredness, and abdominal pain (Irwin et al., 1997).

Zinc found in soil, particularly the soil solution, is dangerous because it is through the soil solution which plants uptake nutrients and which can then lead to phytotoxicity. Phytotoxicity is of concern because it results in crop yield and quality reduction and is hard to control (Adriano, 2001). Although the most quoted range for total zinc in normal soils is 10 to 300 ppm, with the most recent mean content found to be 40 ppm for world soils (Adriano, 2001), the impacts vary depending on the type of crop and the levels of concentration.

In a survey conducted by the LUCAS Programme in 2009 and 2012, 22,000 sample were systematically collected from 27 EU Member States. They were testing for numerous heavy metals, with zinc included. From their results, they found that out of all lands surveyed, the ones with the most heavy metal contamination were agricultural lands. Furthermore, out of all lands surveyed, 53% of them were above the threshold values. For zinc, this value was 200 mg/kg.

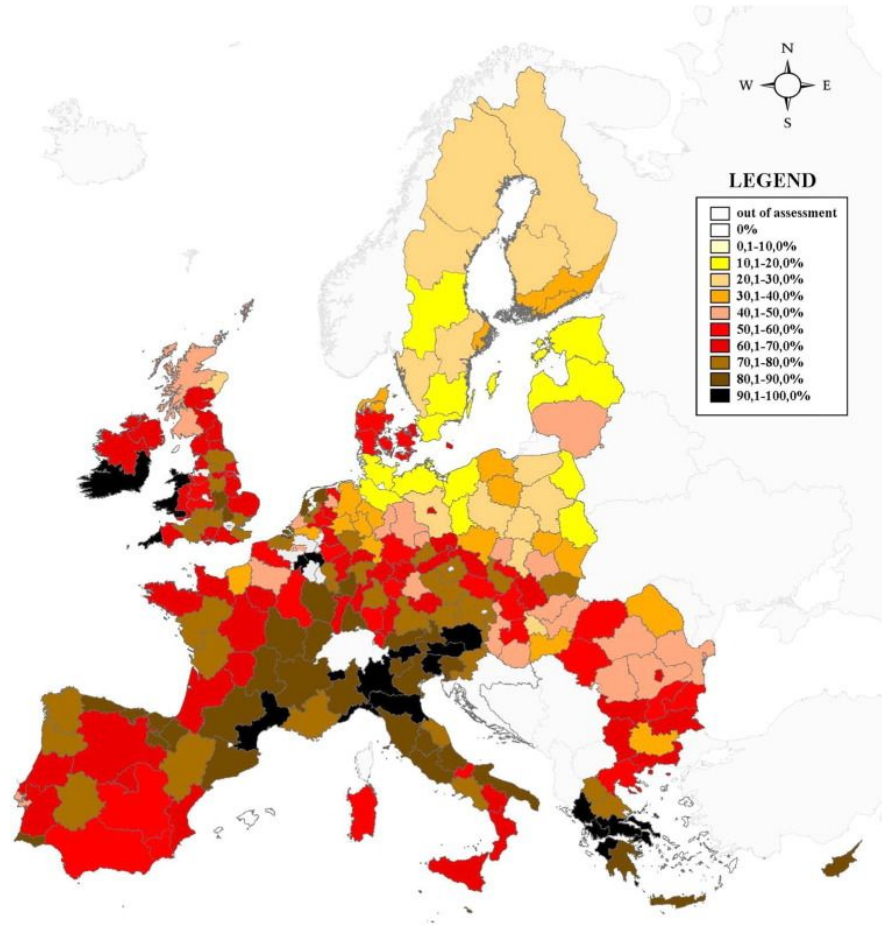


Figure 1: Illustration of the percentage of soil samples that were above the threshold value in all LUCAS samples, with the darker colors indicating higher values of contamination (Toth et al., 2016).

The LUCAS Programme found zinc above threshold values in 20% of all agricultural lands surveyed, but less than half of 1% of all accounted land (Toth et al, 2016). It is hard to determine an exact amount at which zinc becomes toxic, as it differs depending on the person and species. For example, when zinc was found in concentrations of 200 ppm in apple seedlings, there was no top growth. There was a 10% decrease of crop yield in rice paddies with concentrations of 460 ppm in soils in Japan, and concentrations as little as 50 ppm found in pea tissue were found to be toxic, resulting in reduced growth (Adriano, 2001).

In one specific case in a forest near a zinc smelting plant in Palmerton, Pennsylvania, there has been well-documented severe environmental degradation to

the forest including its streams, soil, flora and fauna. The smelting plant had been in operation for years, emitting zinc at levels of 50-100 kg/l, with an estimate of 260,000 tons having been emitted in total. On average, the most contaminated soils occur within six kilometers of the smelting plant. The forest showed effects of the zinc contamination from its thinning canopy, discolored and curled leaves, and its inhibition to promote root seedling elongation. This means the forest lost its ability to regenerate, and this caused eventual erosion as well since there weren't any plants to keep the soil in place. On the floor of the forest, microorganism diversity was dwindling, resulting in the halt of nutrient cycling since dead organisms were no longer being decomposed. In nearby farms, farmers noticed reduced crop yield, chlorosis of leaves, and horses were ill with zinc-induced copper deficiencies (Adriano, 2001).

Zinc is also shown to acidify waters and enter the bodies of fish, which biomagnify up the food chain (Wuana and Okieimen, 2011). It was found that elevated concentrations of zinc in aquatic environments are especially toxic to biota that live there such as phytoplankton, crustaceans, molluscs, odonates, salmonids, etc. These organisms are the most sensitive to zinc as it negatively affects their growth rates and reproduction, which then affects biodiversity (Neff, 2002). As it's known, these organisms which are most sensitive to zinc are what supply other wildlife with nutrition, so as stated earlier, there is potential for biomagnification of zinc as it moves up the food chain (Beyer et al., 2004), with higher concentrations found in meat products than in fruits or vegetables (Toth et al., 2016). Some are even keystone species, making them very important for an ecosystem since if they were to die out, the entire ecosystem could fail. These are just a few examples of the harmful effects zinc smelting has on the environment.

3.2 Effects of Pollution on the Economy

Soil and water are the foundations on which life can exist, and contaminating these resources correlates to degrading not only the environment and life itself, but also the economy. Although agriculture only contributes to four percent of the world's GDP, the contribution is actually substantially higher when factoring in other sectors

such as forestry, fishing, food and beverage, textiles, tobacco, and leather products, all of which stem from agriculture (The World Bank, 2014). Since agriculture is dependent on the quality of soils and water, it is necessary to find viable methods to remove and/or stabilize metals such as zinc from the environment before it enters the food chain, water resources, or destroys crops and vegetation. It is for these reasons, among others, that zinc is listed as one of the 129 priority pollutants (EPA, 2014) and why it is necessary to find viable remediation methods for our soil and water which may be contaminated with such substances. The cost to remediate all of the contaminated sites in the European Union alone would be about 17.3 billion Euros annually (Toth et al, 2016). This goes to show how big the problem is not just in select countries, but all over the world.

3.3 Zinc Behavior in Soils and Water

Metals such as zinc cause great harm to the environment and organisms due to its solubility and mobility (Mulligan et al., 2001). The physicochemical properties of zinc and the soil are very important details to take into account when dealing with zinc contamination since these factors determine its solubility and mobility. Also, different species of zinc are absorbed at different rates, which can also be estimated depending on the soil properties (Toth et al., 2016). This means the toxicity levels vary depending on local environmental conditions. Often times, when scientists look at contamination sites, before even thinking of a remediation technique they first ask “how much” and “in what form”. Different factors can influence the “form” of a contaminant, and therefore predict its movement and availability. In soils these factors include the pH, redox potential (Eh), electrical conductivity (EC), chemical speciation, particle size, particle morphology, soil organic matter (SOM), clay content, time, among others.

When determining metal concentrations in soils, it is also crucial to focus on the soil solution instead of the total concentration, since it is when it's in the soil solution that is how metals become bioavailable and mobile. Once a metal is bioavailable, it means it can be uptaken by plants and can negatively impact the plant or be introduced into the food chain. When a metal becomes mobile, it is able to circulate throughout

the soil, aquatic systems, and organisms, making it even harder to control (Violante et al., 2010). This is why determining a metals total concentration is not an effective method for determining contamination risk, since it does not take into account bioavailability and mobility. Determination of metal concentration is done by extracting the contaminant with acids such as nitric or perchloric acid. These are the ions that are strongly bound within the solid phase of the soil. Therefore, these metal concentrations are not available for plant uptake and are not as mobile (Rieuwerts et al., 1998). Accordingly, it is crucial to analyze the soil solution to truly determine the toxicity of zinc.

Measuring the redox potential (Eh) and the acidity or alkalinity of the soil (pH) are extremely important to take into account when analyzing a contaminants' mobility. The redox potential measures the transfer of electrons. If conditions are reducing, it means it is gaining electrons with the addition of gaining protons and losing oxygen. This is typical of soils that are waterlogged, in which case the Eh is lower. On the other hand, oxidizing conditions are well-aerated soils. They are losing electrons with the addition of possibly losing protons and gaining oxygen. Conditions such as these have a higher Eh value. The pH measures the transfer of protons. In conditions with a low pH, there are more protons in the environment, making it acidic. When conditions are more alkaline, there are less protons in the environment. The pH and redox reactions occurring in the soil determine how a contaminant will change forms, hence becoming more mobile or stable, depending on the conditions.

After doing much research, it is apparent that there are many contrasting responses when talking about how zinc reacts to differing Eh levels, which leads to inconclusive results. For example, some scientists say that large amounts of zinc can be released into soil solution if the sediment become oxidized, and that substantial amounts of soluble zinc are present in well-oxidized environments (John and Leventhal, 1995). The reasoning for that being that in anoxic soils, many metals such as zinc are reduced to a relatively insoluble metal sulfide (ZnS). These sulfides are only mobile when oxidized to a sulfate when Eh levels are high. For this reason, some scientists have concluded that water soluble zinc decreases with decreasing Eh, or reducing conditions (Rieuwerts et al., 1998).

On the other hand, a lot of scientists and researchers have concluded the opposite. Adriano (2001) stated that higher amounts of zinc were found either in the exchangeable or organic form at low Eh (reducing conditions) than compared to oxidizing conditions. Ashraf et al., (2012) stated the same conclusion by saying under reducing conditions zinc will be easily mobilized to the environment. And finally, another author concluded zinc availability increased with soils that were poorly drained and waterlogged, which is typical of explaining reducing conditions. They went on to say that laboratory experiments confirmed that with anaerobic, flooded soils, zinc was effectively mobilized and solubility increased (Rieuwerts et al., 1998). To make sense of these clashing results, it can be said that generally, zinc becomes more mobile and soluble under reducing conditions (low Eh), however, if zinc is in its sulfide form of ZnS, in which case it is insoluble, and the environment becomes suddenly oxidized, zinc has the potential to oxidize to a sulfate and once again become mobile.

The level of pH may be viewed as the biggest determining factor of how a contaminant will react in an environment. Unlike the debate on how Eh levels determine the mobility of zinc, It is well known that several trace metals such as zinc, are easily mobile and available to plants in acidic conditions (low pH). Likewise, the level of dissolved zinc increases as the pH of the water decreases, enhancing its mobility (Kabata-Pendias, 2004). Specifically, it was shown that the solubility increases 100-fold for each unit of decrease in pH, meaning it becomes substantially more soluble as conditions become more acidic (Rieuwerts et al., 1998). Continuing with that thought, when the pH was decreased from 7- 4.55, the levels of exchangeable zinc increased, which is the most mobile fraction of zinc (Rieuwerts et al., 1998). Particularly when the pH was <5.6, zinc was found in the exchangeable fraction ten times as much (Adriano, 2001). Below is a picture to demonstrate how zinc changes speciation depending on the pH, indicating how important pH is.

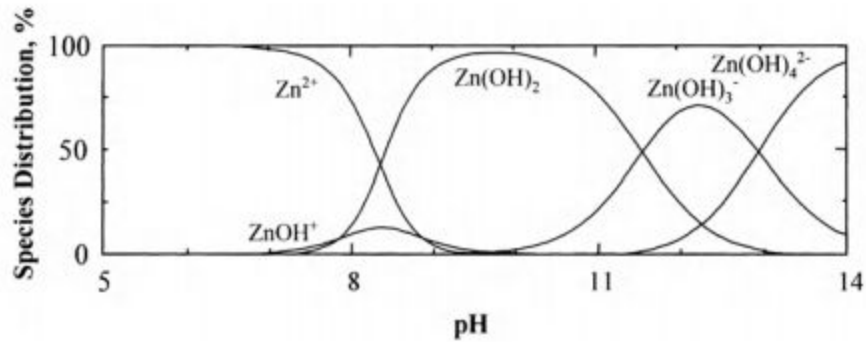


Figure 2: Graph illustrating how species of zinc vary depending on whether the pH is acidic or alkaline (Adriano, 2001).

As demonstrated by Figure 2, zinc is in its cationic form of Zn²⁺ even when the pH is 7. This is perhaps a little surprising, because the soil conditions don't even have to be acidic in order for zinc to be mobile, but rather just neutral. This is the form zinc is most commonly found in, since most soils have a more slightly acidic-neutral pH. As conditions become more alkaline, it changes form to become zinc hydroxide. This is insoluble in water, and hence, more stable in the environment. Zinc hydroxide is amphoteric, meaning it reacts with both acids and bases, ready to either donate or accept protons as soon as conditions favor such a reaction. In especially alkaline conditions however, it becomes zincate and is soluble in water again. This explains how zinc can be mobile and bioavailable in both slightly acidic and extreme alkaline conditions.

To display the degree of mobility of metals when in the exchangeable phase, the hierarchy of mobility is as follows: exchangeable > bound to carbonates > bound to oxides > bound to organics > residual (Ashraf et al., 2012). Mobility in the exchangeable fraction is highest, with release of the metal due to ion exchange. Mobility when bound to carbonates is second most mobile due to ease of dissolution. Mobility when bound to oxides is third most mobile because changing redox reactions can greatly influence whether the metal is released back into the environment or not. When metals are bound to organics, they are more stable, but still can become mobile if major oxidation or decomposition occurs to the organic matter it is bound to. When zinc is in sulfide form as ZnS in anoxic conditions, it is even more stable, yet can still be released if it

experiences severe oxidative reactions, as explained before. The most stable form of any metal is when it is in its crystalline fraction, in which case it can only become mobile after much weathering and time (John and Leventhal, 1995).

The potential mobility of a contaminant can be determined by adding up the % fraction that is exchangeable +% fraction bound to carbonate +% fraction bound to oxides +% fraction bound to organics (you would exclude the residual fraction because that is not mobile at all). In zinc's case, it's potential mobility is 65.94%, according to Ashraf et al. (2012). In another study by Vaněk et al., (2005), they also concluded zinc's mobility factor was between 19-62% from the soil they tested in Přebor - the same location where the contaminated soil tested for this experiment was from. The mobility factor is different from the potential mobility in the sense that it only accounts for the fraction of zinc found in the exchangeable form and carbonate-bound form. This explains why the mobility factor is less than the potential mobility, since it only takes into account two fractions compared to four.

Furthermore, zinc's residual fraction was the lowest out of five other trace elements studied (including Pb, Cr, Cu, As, Sn), meaning zinc has the greatest potential for toxicity in the environment since it is the most available (Ashraf et al., 2012). One can determine a site's degree of pollution by assessing what percent of the metal's fraction is in residual form. If it has a higher percentage in residual form, then the pollution rate is lower since it is stable in that form and cannot be released to the environment. The picture below illustrates zinc and other metals' fractionation percentages.

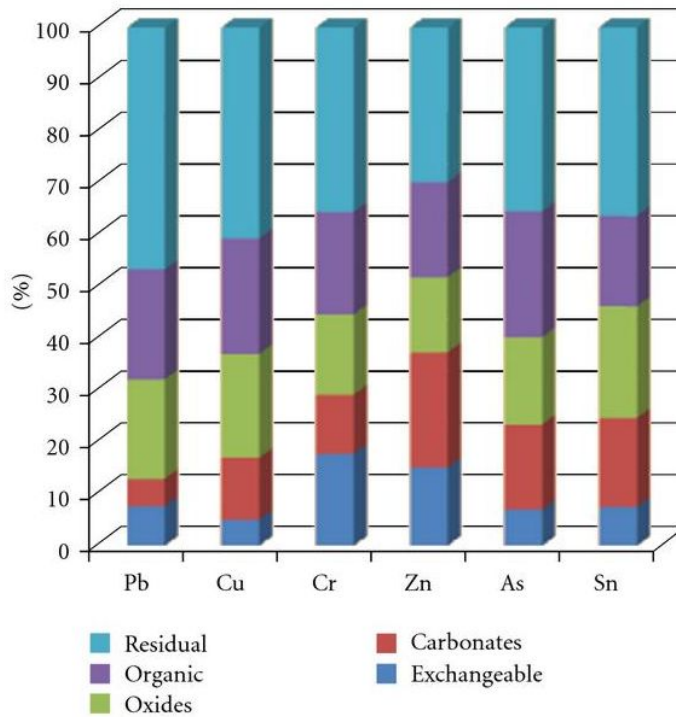


Figure 3: Common trace metals and their percentage in various fractions. For zinc, it is mostly bound to carbonates and the least percent found in residuals (Ashraf et al., 2012).

When zinc is in the exchangeable fraction, it can be adsorbed as a cation to negatively charged sites on mineral and organic colloids through electrostatic attraction. If zinc is fixed within the clay crystal structure, it can only become available after it has been weathered (Adriano, 2001). As talked about before, at a very high pH, zinc is bioavailable, making it available for plant uptake (Mulligan et al., 2001). This is due to the solubility of its organic and mineral colloids which it is bound to. When most metals such as zinc are bound to organics, they become stable, but can become mobilized under highly oxidizing conditions due to the degradation of the organic matter which they are bound to (Ashraf et al., 2012). This makes sense by realizing in basic environments, there are less H^+ protons, therefore the uptake competition is less, meaning zinc can more easily be taken up when it doesn't have to compete with H^+ for adsorption sites. This also explains why sorption onto Fe-oxides is better in alkaline environments - due to the lack of competition for adsorption sites.

However, when bound to oxides, zinc becomes more mobile in acidic and

reducing conditions (Ashraf et al., 2012). It is important to note that organic content also plays an important role in mobilization of zinc. Since organic content normally has a lower pH, zinc can be more mobile in these areas. There was a positive correlation found between zinc from an exchangeable form and the amount of organic content and clay content (Ashraf et al., 2012). Meaning, the more clay and carbon there was in the soil, the more zinc was found in its most mobile fraction.

Not only is zinc mobility dependent on pH and Eh, but also the presence of secondary minerals, meaning that a significant part of the metal is found in the reducible (Fe-, Mn-oxide) phase. In anoxic conditions, ZnS can form under precipitation, while the unprecipitated forms of zinc include $ZnOH^+$, $ZnCl^+$, and $ZnCO_3$ (Mulligan et al., 2001). It was also found that particle size contributed to mobility as well, with a finer, more weathered particle correlating to enhanced mobility (Byrne et al., 2010).

In regards to electrical conductivity, or EC, a study concluded that plant uptake of zinc decreased as the EC increased, meaning the more salinity that was in the soil, the lower the concentrations of zinc in the plants' shoots. It was also shown that with an increased EC was an increase of zinc mobility in the soil (Salimi et al., 2012).

A study by Violante et al., (2010) showed irreversible adsorption of zinc to ferrihydrite (a type of Fe-oxide) in the presence of copper with regards to residence time. The study showed as time went on (with a total of 336 hours), the sorption of zinc continued to increase. This could be explained by the zinc slowly forming precipitates over time along with the combination of the zinc penetrating into the Fe-oxides' micropores, rendering the adsorption as irreversible (Violante et al., 2010).

These properties tell us the solubility, mobility, and bioavailability of zinc, and hence, how risky it is in the environment. Furthermore, analyzing these characteristics determine which remediation technique is best suited for the job. For a basic summary of how different factors affect the properties of zinc, refer to the table below.

Influencing Factor	Effect on Zn
Particle size	Smaller=more mobile
Particle morphology	More weathered=more mobile
pH	Low pH= (in general) more mobile, more soluble (dissolves easily), increased exchangeable levels Very high pH=can become mobile again
Eh	Low Eh= (generally) more mobility, solubility
EC	High EC=decreased uptake in plants but increased mobility in soil
Chemical speciation	Mostly bound to carbonates
Time	More time= irreversible adsorption to Fe-oxides
Organic carbon content	More OC=increased activity of zinc
Clay content	More clay=increased activity of zinc

Table 1: Parameters which affect various properties of zinc such as solubility, mobility, leachability, and bioavailability.

3.4 Remediation Techniques for Zinc

Remediation methods can be characterized as being chemical, biological, or physical, and are either *ex situ* or *in situ*. When choosing a remediation technique, one must consider the cost, the efficacy, and the lasting effects on the treated area. More specifically, the type of pollutant, concentration, soil characteristics at the site, and what the area will be used for after the treatment must be acknowledged (Mulligan et al., 2001). Classic methods of remediating soil included *ex situ* methods which involves excavating the soil and transferring it to another location to be remediated of the contaminants. Not only is this method expensive, it also is intrusive and destroys the entire habitat.

3.4.1 Excavation and Burial

The current and most common technology for the cleanup of toxic metal-contaminated soils is the excavation and burial of the soil at a hazardous waste site with the average cost of \$1,000,000 per acre. “In the U.S. alone, the cost of cleaning up sites contaminated with toxic and radioactive metals is estimated to be \$300 billion.” (Raskin et al, 1997). Furthermore, it is estimated the average cost for cleaning up a Superfund site in the U.S. is more than 25 million dollars (Zhang, 2003). On the other hand, the average total cost to clean up a site using nanoparticles is about 300,000 dollars (EPA, 2007). Another source says remediation with nZVI could cost between 120-200 euros per cubic meter of contaminated area (Mueller & Nowack, 2010). Again, this is because using nanoparticles is *in situ*, meaning the particles are injected straight into the soil where the contamination occurs. Therefore, big machinery is not needed to dig up the soil or transfer it anywhere, not only saving a lot of money, but also sparing the environment from more CO₂ emissions since there is no need for big diesel vehicles or machinery.

Category	Remediation technologies
Isolation	(i) Capping (ii) subsurface barriers.
Immobilization	(i) Solidification/stabilization (ii) vitrification (iii) chemical treatment.
Toxicity and/or mobility reduction	(i) Chemical treatment (ii) permeable treatment walls (iii) biological treatment bioaccumulation, phytoremediation (phytoextraction, phytostabilization, and rhizofiltration), bioleaching, biochemical processes.
Physical separation extraction	(i) Soil washing, pyrometallurgical extraction, <i>in situ</i> soil flushing, and electrokinetic treatment.

Table 2: Various categories of remediation techniques and examples of each (Wuana and Okieimen, 2011).

3.4.2 Phytoremediation

Another common remediation technique, that is just as well environmentally friendly, is phytoremediation. Phytoremediation is the use of plants to either stabilize, filtrate, or extract the contaminant from the soil (Wuana and Okieimen, 2011). Phytoremediation is especially useful for contamination of zinc because it is an essential metal, therefore making it easy or the plant to uptake and accumulate.

Phytoextraction uses plants that are considered metal hyperaccumulators because they uptake the metals in their roots 100-fold more than normals plants and translocate them to other areas in the plants above the soil. Due to their vast rates of accumulating metals, a typical hyperaccumulator will concentrate as much as 10,000 ppm of zinc. Examples of such hyperaccumulators with respect to zinc are: *Brassica junica*, which can accumulate 2,600 ppm zinc, *Cystus ladanifer*, with 7,695 ppm zinc,

and *Thlaspi caerulescens*, which can accumulate an astonishing 10,000-15,000 ppm zinc (Wuana and Okieimen, 2011). These plants ideally have long roots which can reach deep into the soil, they grow fast, have a high biomass, and have a high tolerance for metal contamination.

These types of plants are perfect for metal contamination remediation because they have evolved to adapt to thrive off of land that is polluted and instead of the metal being stabilized in the soil, it is actually taken out of the soil entirely. Once the metal has been uptaken by the plant and stored in other tissues above ground, the plants can be harvested and the metals can even be extracted from the plant to be used again by ashing, although technologies for this aren't quite developed yet. Naturally, the disposal of hyperaccumulator plants that have been used for remediation has to be done carefully, otherwise the risk of the contamination being released back into the environment is an issue again. Disposal of such plants can include controlled combustion, in which the end product is gas which can be used for thermal or electrical energy. Otherwise, other disposal methods include composting and compaction (Wuana and Okieimen, 2011).

Phytostabilization is different from phytoextraction because the contaminants aren't uptaken by the plant, but rather accumulated or adsorbed onto the plants' roots or precipitated into the rhizosphere, thus reducing the mobility of the contaminant (Wuana and Okieimen, 2011). The ideal plants for phytostabilization should be able to retain the water in the soil, thus preventing contaminated leachate from percolating into the groundwater. They should also act as a barrier to protect other organisms from direct contact with the contamination and be able to hold the soil well to prevent erosion, since erosion could also aid in the distribution of the contaminant to other areas (Wuana and Okieimen, 2011).

Finally, the last sector of phytoremediation is phytofiltration. This category is similar to phytostabilization in the sense that it uses the plants' roots or seedlings to adsorb/absorb the contaminant. The difference is that phytofiltration removes contaminants from the water and phytoextraction removes contaminants from the soil. Ideal plants for phytofiltration should have large root masses. The plants are first grown in hydroponic pools with clean water and are slowly introduced to a certain

contaminant, gradually increasing its tolerance for it so it acts as a good ad/absorbent. This is a practical application that has even been used to filter radioactively contaminated pools in Chernobyl with the use of sunflowers (Wuana and Okieimen, 2011).

Overall, phytoremediation offers a remediation technique that is energy efficient, low maintenance, and aesthetically pleasing as a bonus. For optimal efficiency, it can also be applied with other techniques such as nanoparticles or biochar.

3.4.3 Soil Washing

The use of soil washing is also viewed as an efficient remediation method. It can be *in situ*, but is most commonly an *ex situ* method. So, the soil must be excavated and is either washed physically, chemically, or a combination of both. Physically washing the soil includes separating the soil from the particles which contain the contaminant, while chemical washing involves adding aqueous chemicals to extract the contaminant from the soil (Wuana and Okieimen, 2011). The contaminants which are separated from the soil then go to a hazardous landfill for disposal. This is a nice remediation option because it completely removes the contaminant from the soil and the results are maintained long-term (Wuana and Okieimen, 2011). Yet, it still has its drawback as mentioned before with *ex situ* methods due to the labor, expense, invasiveness, need for big machinery, and destruction of habitat.

3.4.4 Immobilization

Other methods of remediation include immobilization. These techniques don't necessarily take the contaminant out of the soil itself, but rather stabilize it in a way so it becomes immobile or inert and no longer poses a threat to the surrounding environment. Immobilization includes vitrification, which makes contaminants (such as radioactive substances) into glass by heating it up at such a high temperature that it turns into a liquid phase, then rapidly cools into glass. Immobilization also includes

stabilization techniques such as the use of clay, cement, fly ash, calcium carbonate, and charcoal (such as biochar) (Wuana and Okieimen, 2011). Regarding the use of clay, one study showed the use of magnesium aluminum silicate clays, which were shown to be very effective amendments as they removed readily extractable zinc from polluted mining soils by 79-99%. Likewise, alkaline materials such as coal fly ash and red mud also reduced the leaching of zinc by 99%. On the other hand, amendments such as iron sulfate and lime were reported to increase the mobility of zinc by five times. (Kumpiene et al, 2008). All of these remediation techniques show promising results for stabilizing zinc in the soil which are environmentally friendly in other aspects at the same time.

3.4.5 Biochar

Biochar is the product of charred organic matter from pyrolysis and is also classified as an immobilization technique. Biochar can be used not only for remediation, but also for carbon sequestration, erosion control, and as a soil amendment, since it provides plants with nutrients, has good water holding capacity, and increases microbial activity in the soil, thus increasing crop yield (Mohan et al., 2014). Biochar can either be produced from fast or slow pyrolysis, and can be made out of numerous different plant matter. Like nZVI, biochar offers a nice adsorbent option due to its high surface area:volume ratio, making it very reactive.

In fact, there have been several studies conducted in a field experiment using between 0.5-2% biochar to remediate zinc from the soil. One study concluded that biochar application reduced the extractable fraction of zinc in the soil as well as other harmful contaminants as rapidly as just one week after the application (Rees et al., 2014). Other studies concluded similar results, specifically when using biochar made from cottonseed hull and *Miscanthus* straw (Houben et al., 2013). Finally, a study lasting over a span of three years showed promising results that biochar can be considered a good solution for long-term stabilization of zinc. This particular study was carried out in post WWII industrial sites in the United Kingdom and the study showed the exchangeable fraction of zinc was reduced by 83%-97%, the leachable fraction of

zinc was reduced from 0.12%-0.01%, and the residue fraction of zinc actually increased from 7%-27-35% (Shen et al., 2016). This is all promising news, especially since biochar can not only be used for soil remediation, but also as a soil amendment, carbon sequestration, among other beneficial applications.

3.4.6 nZVI

The remediation technique that was used for this research, nZVI, in regards to zinc contaminated soil, is classified as immobilization since it stabilizes the zinc and reduces the toxicity by sorbing the zinc onto the surface of the nanoparticle through physical-chemical forces via inner sphere complexes. This can also be done with naturally occurring oxides such as Mn or Fe-oxides since they also have structures in the nanometer scale and therefore have a high volume: surface area ratio and are effective adsorbents. Since the reaction between the nanoparticle and the contaminant uses physical-chemical forces, the zinc is definitively immobile and can no longer pose a threat since it stuck on the nanoparticle and cannot be uptaken by plants or leached into the groundwater. Not only can nZVI particles be used for soil remediation, but also for groundwater remediation. For example, nZVI has been used as a permeable reactive barrier to sorb contaminants in the water as they flow through (Mueller and Nowack, 2010). This method is much less expensive and faster than the conventional method of pumping and treating *ex situ*.

The nZVI particles are applied to a contaminated site by injection into the ground via infiltration wells. Injection can be done several ways, such as using a direct push rig, which is a stationary injection site, or pneumatic fracturing, which pushes air in the soil to create a network of cracks and making it easier for nZVI to flow through. Other methods include pressure pulse technology, which uses pulses of pressure to inject nZVI, and finally, liquid atomization injection, which joins the nZVI in slurry form with a carrier gas to create an aerosol and easily injects into the soil surface (Mueller & Nowack, 2010). The injection pressure in all cases less than 1-2 bar.

In order to get the nanoparticle and the zinc, which is stuck on the surface of the nanoparticle, out of the environment, common methods include using a magnet

(Boparai et al., 2011), since iron is magnetic. This technique of using the combination of iron nanoparticles and magnets offers an easy and affordable way to not only immobilize/stabilize the zinc contamination, but also effectively completely remove it. If a magnet can't be used, having nZVI in the soil causes no harm to the surrounding environment anyways since it rapidly oxidizes to Fe-oxides which are naturally found in soils. Also, since this method is *in situ*, it means the soil fertility and nutrient cycling can be restored, it is less invasive, less expensive, less labor, simple and rapid, minimal waste, and can cover a broad range of pollutant categories.

3.4.7 Drawbacks to nZVI

The drawbacks to *in situ* treatments is that the contaminant is strictly immobilized, and therefore, not entirely removed from the environment, so permanent monitoring is needed (Wuana and Okieimen, 2011). Monitoring includes measuring oxidation-reduction potential levels in order to see if any conditions in the soil have changed. If so, re-application may be needed. Yet, if used in combination with phytoremediation, or removing nZVI with a magnet, then it could in fact be removed from the environment and prove to be a long-term solution. Other issues with using nZVI particles are namely due to the limited mobility and lifetime of nZVI particles. This means the adsorption processes cannot continually occur over a long period of time (Mueller and Nowack, 2010). On the other hand, this means the adsorption process occurs very fast, which could also be looked at as a plus with this technology, since this would mean the remediation process would be very fast, saving everyone time and money.

Yet, since this is a relatively new technology, the site owners, consultants, and government agencies may have some hesitance with proceeding forward with large-scale practical application at remediation sites simply because they are unfamiliar with it (Mueller and Nowack, 2010). Czech Republic has completed several remediation projects using nZVI already and tend to be open-minded about its use. The same can be said about Germany, who carried out at least one full-scale remediation project using nZVI. However, countries like Finland and the UK are still

waiting to hear more about the technology and have not implemented any field tests yet (Mueller & Nowack, 2010).

3.5 Fe-oxides and nano-Fe as Sorbents

In recent years, nanoparticles have gained interest in the scientific community since they are highly selective, have large surface areas, which corresponds with higher reactivity, are versatile, and affordable. Nanoparticles are particles which are 1-100 nanometers and can be more accurately described as, “the creation and use of structures, devices and systems that have novel properties and functions because of their small size” (EPA, 2007). The fact that these particles are extremely small is what makes them so unique. For example, aluminum used in cans is harmless, yet nano-sized aluminum is highly explosive and is used in rocket fuel. Titanium dioxide is often used to color paints white, yet at the nanoscale it is transparent. Also, at the nanoscale, gold can act as a catalyst, and zero valent iron ignites spontaneously when it comes in contact with air (Mueller & Nowack, 2010). These are just a few examples of how different elements can behave at the nano-scale, especially in regard to reactivity.

Nano zero-valent iron (nZVI) has become one of the most widely applied nanoparticles in remediation practices due to its low cost and safety in terms of environmental and health risks (Li et al., 2016). When comparing millimeter-sized particles to nanoparticles, nanoparticles are also more useful for application purposes in remediation since they are easier to inject and more efficiently dispersed into the pollution sites due to their small size.

Once injected into the soil, the zero valent iron, Fe(0), oxidizes quickly to form crystalline Fe oxides (Kumpiene et al., 2008), and as it is known, the crystalline form of any mineral is the most stable, therefore, once zinc is adsorbed onto the crystalline Fe-oxide, it is immobile and stabilized. Also, since nZVI sticks to the surface of the soil, it is best suited for remediation where the contamination is mainly on the surface; as opposed to contamination that is deep in groundwater (Mueller & Nowack, 2010). The mobility of nZVI mainly depends on the aggregation potential of the particles, nZVI-soil

particle interactions, geochemistry, the application method, permeability of the soil, and the particle size of the nZVI (Citychlor, 2013). The nZVI particles tend to slightly increase the pH and decrease the Eh, since it is consuming the oxygen and creating reducing conditions (Mueller & Nowack, 2010). This may not be a negative effect, however, since many trace metals such as zinc become immobile when pH raises.

Nano zero-valent iron is relatively unstable. As mentioned before, when in contact with air, it will spontaneously ignite, which is why nZVI is mainly transported in a slurry or in an inert atmosphere, such as nitrogen (Mueller & Nowack, 2010). Yet, when in suspended form, it oxidizes extremely fast, starting with Fe(0) and ending with FeOOH, the most stable crystalline Fe-oxide. When comparing nZVI to iron salts, the main advantage of nZVI is that it has three times as much iron per unit of weight, once again explaining why its reactivity is so well recognized (Kumpiene et al., 2008). Also, when comparing nZVI to granular iron, the reaction rates are 10-1,000 times faster and the sorption capacity is dramatically higher all because the surface area of nZVI is 30 times greater than granular iron (Mueller & Nowack, 2010). This goes to show how important surface area is when speaking of reactivity and sorption capacity.

Since nano zero-valent iron doesn't occur naturally, it must be made in a lab. There are several methods to do this, either by reacting ferric chloride in water with sodium borohydride, heating iron pentacarbonyl to 200-250°C, or reacting iron oxides with hydrogen, among others (Mueller & Nowack, 2010). All of these methods make a slightly different nZVI due to difference in size, also affecting their surface area and therefore, reactivity. For example, the second method mentioned will result in nZVI particles that are about 5 nm, while the last method mentioned will result in nZVI particles ranging from 200-300 nm (Mueller & Nowack, 2010). The size also has an effect on how the particle will move throughout the soil, and a study conducted by Lehigh University concluded nanoparticles the size of 20-50 nm have the highest mobility and also reduced their tendency to aggregate together; making dispersal of nZVI more efficient (Mueller & Nowack, 2010). Mobility and stability of nZVI particles can also be enhanced by coating them with surfactants, polyelectrolytes, or combining with other metals (Mueller & Nowack, 2010). Overall, the realistic radius of influence for uncoated nZVI particles is limited to a few meters (Mueller & Nowack, 2010).

It was also shown that the lifetime of the nZVI particles depends on the pH of the suspension and the type of nZVI particle. Since it is known different nZVI particles are created by different laboratory procedures, it can also be expected to see different results with how they react to varying environmental parameters such as pH levels. For example, nZVI particles that were created by reacting ferric chloride in water with sodium borohydride to form a nanoparticle which is 10-100 nm (also known as Fe(B)), took two weeks to completely oxidize at pH 8-9, while reactive nano-scale iron particles (RNIP) materials, made by the reduction of FeOOH to form a crystalline nano iron, took almost a year to oxidize at that same pH. Yet, when the pH was reduced to 6.5, it took RNIP the same amount of time as Fe(B) to oxidize (Mueller & Nowack, 2010).

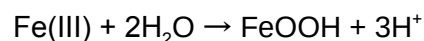
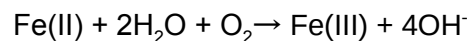
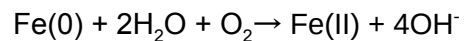
This is an incredible drop in oxidation time, all due to a decrease of pH by 1.5 units. Once the nanoparticles become completely oxidized, they are no longer in their reactive form, so their lifetime as a remediation agent is over. This supports the notion that pH and redox reactions are extremely important in remediation sciences. Another source agreed on the short lifetime of nZVI, estimating it to be about 0.8 years, with a decreasing reactivity as its ages (Citychlor, 2013). Also, since nZVI has a short lifetime, the remediation injections must be done more than once at each site in order to get better results. Below is a table to help understand how different variables affect the mobility and effectiveness of nZVI.

Influencing Factor	Effect on nZVI
Size	Best for mobility = 20-50 nm
Concentration	Mobility decreases with increasing concentration (due to aggregation)
pH	High pH= better sorption
Lifetime	Varies, but around 0.8 years
Radius of influence	Few meters
Most effective location in soil	Soil surface
Eh	Closer Eh values= better sorption

Table 3: Variables which can affect the mobility, adsorption, and overall effectiveness of nZVI.

By using the standard redox potential between the nano iron and the contaminant, the zinc is definitively sorbed onto the surface of the nanoparticle through physical-chemical forces and rendered effectively immobile (Boparai et al., 2011). The redox potential is a substance's affinity for electrons and the closer the two redox potentials between contaminant and nanoparticle are, the more efficiently it will sorb. Using the laws of thermodynamics, the rate of sorption can be determined by measuring the temperature. Since adsorption is an endothermic process, heat is given off during the reaction. Boparai et al. (2011) concluded in their studies with adsorption of cadmium and zero-valent nano iron that as the temperature of the reaction increased, the rate of adsorption also increased, with temperatures reaching 307-333 K within 12 hours of the reaction, and consistently dropping after that, since reactivity decreases over time (Boparai et al., 2011).

Nano zero-valent iron, Fe(0), is essentially added to soils as a precursor for iron oxides, since once injected into the soil, that is what it turns into. As time passes and nZVI oxidizes, it gradually becomes more stable, with the final result being the most stable iron oxide, goethite (Komárek et al., 2013). When zinc binds to goethite, it forms shorter, and therefore stronger, Zn-Fe bonds which correlate to bidentate (bond length of 3.26 Å) and tridentate (bond length of 3.07 Å) face-sharing complexes (Chesne and Kim, 2014). The oxidation of nZVI can be illustrated as below:



At first, the redox reaction produces a poorly crystalline iron oxide, but with time, it gains stability and structure. Found naturally in the soil, iron oxides, or Fe-oxides, are secondary minerals which are the product of weathered primary minerals. Iron itself is the fifth most common element found in soil and mineral particles such as Fe-oxides make up about 45% of soil. This is why leaving the remediation agent, nZVI, in the soil is considered safe. Other constituents of soil

include soil organic matter, water, and gases. Examples of other secondary minerals include clay minerals, carbonate and sulfate minerals, and finally Fe, Al, Mn-oxides (Komárek, 2017). The reason why Fe-oxides make good adsorbents is because just like nZVI, they are small (from tens nm to thousands μm), so they have a large specific surface area, creating a large amounts of reactivity. They also have low solubility in most soil pH ranges (Komárek et al., 2013). The specific surface area of Fe-oxides is 70-250 m^2/g and Mn-oxides are 5-360 m^2/g (Komárek, 2017). This shows Mn-oxides can actually be more reactive than Fe-oxides and are more stable, however they are not as abundant as Fe-oxides are in the soil. Another reason Fe-oxides are good adsorbents is because their crystalline structure and charge sorb specific trace elements in cationic form such as zinc (Violante et al., 2010).

Fe-oxides and nZVI particles both work as remediation technologies by adsorbing the contaminant to the surface via inner sphere complexes which are chemically coordinated, thus rendering it immobile and stable, accompanied by redox reactions, which reduce the contaminant to a less toxic form. Adsorption can also be looked at as a precursor for surface precipitation, since if a high enough concentration of the metal has been adsorbed, it can precipitate out, with zinc precipitating out as $\text{Zn}(\text{OH})_2$ (s).

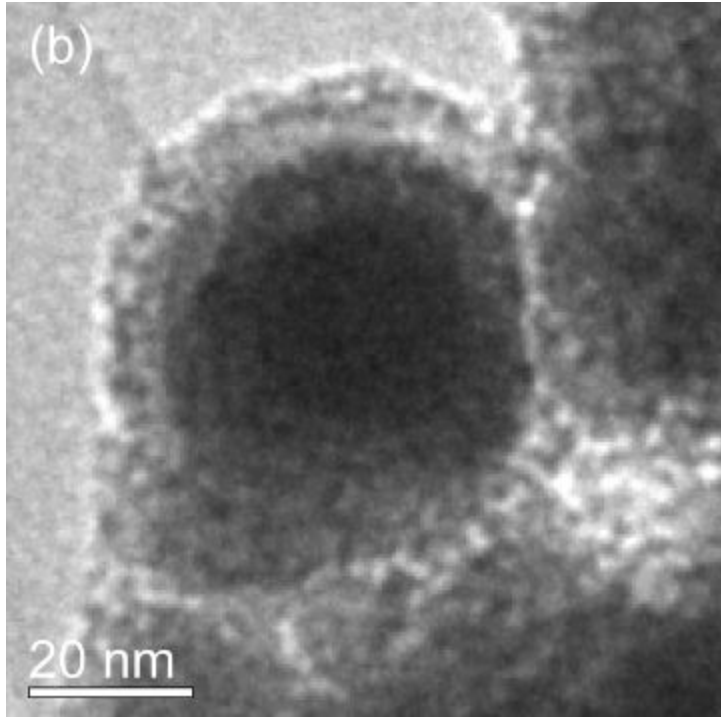


Figure 4: TEM image of a nZVI particle with Zn²⁺ adsorbed to the surface (Liang et al., 2014).

The adsorption efficiency and reactivity of both Fe-oxides and nZVI strongly depends on the makeup of the soil; the pH, Eh, if there is a lot of organic material, clay minerals, or other oxides. The reason why trace metals become degraded when sorbed onto Fe-oxides is because the iron donates electrons to the contaminant, reducing it to a less toxic form (Mueller & Nowack, 2010), showing the importance of redox reactions. Also, the sorption efficiency of metal cations increases with an increasing pH and decreases with a lower pH (Violante et al., 2010).

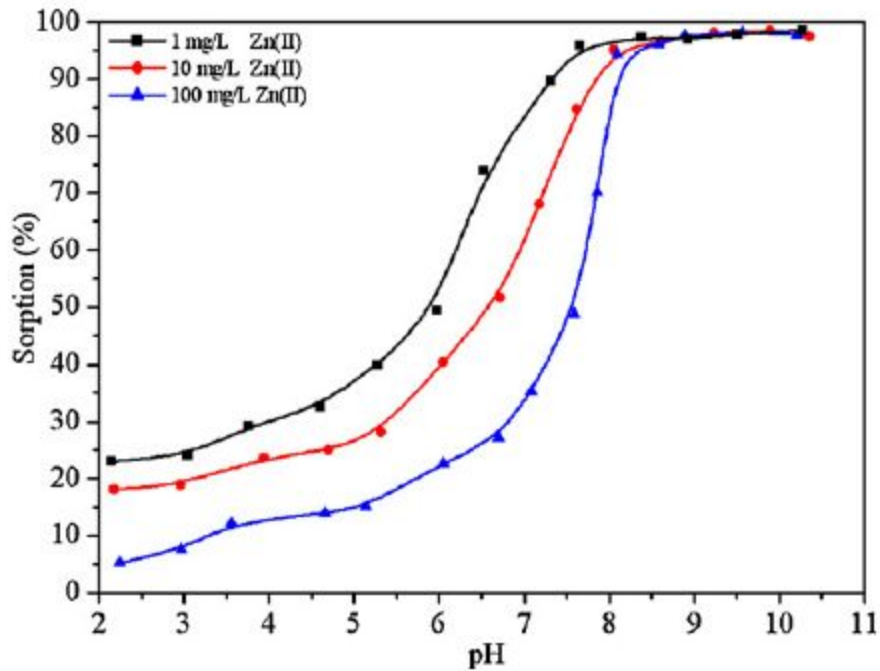


Figure 5: Percentage of zinc adsorbed onto iron oxide as a function of pH and varying concentrations of zinc (Yang et al., 2012).

In the image above, it shows the sorption of zinc onto iron oxide reaches equilibrium after about pH of 8, with sorption increasing with pH. It also shows that zinc particles that are in a lower concentration are more easily adsorbed onto Fe-oxide. This could be explained by competition for adsorption sites with the cationic metals and hydrogen ions in the soil, making adsorption less effective. Also, adsorption gets worse with a decreasing pH because the additional H^+ inhibit the formation of iron oxide (Liang et al., 2014). The critical sorption value for Fe-oxide in association with zinc is about 5-6.5 (Rieuwertts et al., 1998). Factors such as these and others make a huge difference on how the remediation agent will work because they all interplay with each other and react with each other.

A study done by Lee et al, (2011) showed how nZVI at a concentration of 2% affected soils contaminated with zinc in concentrations of 260 ppm. The major results included the reduction of bioavailable zinc and reduced exchangeable fractions, meaning it was less mobile. Specifically, after testing lettuce that was growing in the

zinc contaminated soil, they found there was reduced uptake of zinc by the lettuce and the biomass yields of the lettuce were very similar when compared to lettuce that was grown without any contamination. Similarly, when zinc contaminated soils were treated with nZVI 1%, it showed long-term stability of the contaminant (Komarek et al., 2013). Both of these studies show promising results of how nZVI 2% can positively affect the soil and agriculture. Another study showed when nZVI was in 1g/L, more than 85% of zinc was removed in an aqueous environment within two hours (Liang et al., 2014). These results show a high stabilization efficiency of zinc with nZVI.

4. Materials and methods

4.1 Description of Sample Site

In this research, the goal was to determine the sorption efficacy of nano zero-valent iron with soils that have been contaminated with zinc. In this case, the soil used in this experiment was located near the Litavka River in Příbram, Czech Republic and it had been contaminated with zinc, lead, and other metals as a result of smelting activities. The location was chosen because there was a combination of contamination coming from atmospheric deposition and from the river, making it a probable site for most contamination in that area. The soil was collected by digging and removing the first 10 cm of the topsoil. The maximum depth was 25 cm, so the soil used was found in the 10-25 cm range. To remove the water, the soil was dried in the greenhouse until it maintained a constant weight and homogenized by sieving it through a 2mm sieve.

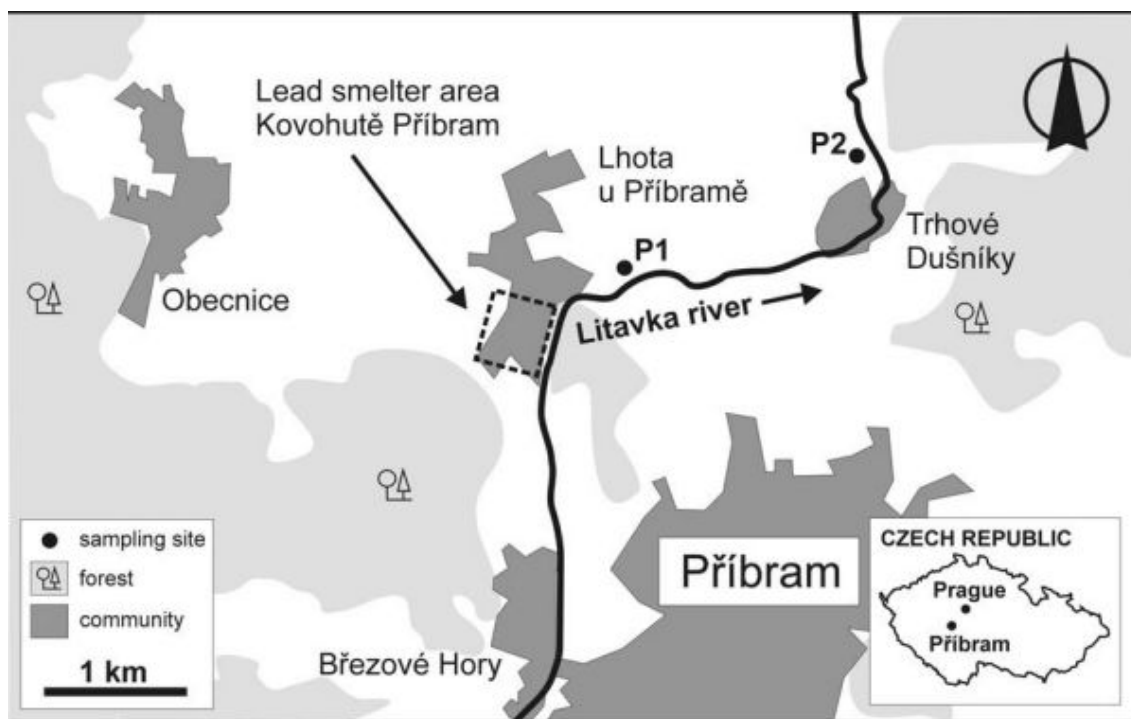


Figure 6: Map of the area where the soil samples were taken in Příbram, Czech Republic (Vaněk et al., 2005). The sample point was located at P2.

Příbram is considered to be one of the most contaminated areas in the country due to this smelting plant, which was first established in 1311. The geology of Příbram is what dooms this city with such a history of mining and smelting. The city site is a result of pre-platform development and consists of greywacke and sandstone from the Cambrian period. It lies on the Clay Fault, and there are four main shafts, or veins in the area. Of these veins, the Jánská vein is the most productive, and is also the main source of mineralization and ores such as silver, lead, and zinc (Škácha, P. et al., 2009). Specifically, the main ore that zinc is found in is called sphalerite, which is cubic ZnS. This geology explains why mining and smelting has been so popular in this area for so long.

4.2 Batch Experiment/ Kinetics Test

In order to measure the sorption efficiency, kinetics, and equilibrium of nZVI with zinc sampled in time, a batch experiment was conducted. Here, 1g of nZVI was

mixed with a solution of 1mM of zinc while maintaining a constant pH of 5.0 by adding 0.01 M HNO₃ when needed. The entire experiment took two hours and the remaining concentration of zinc was analyzed to determine the sorption efficiency. The samples were filtered through a 0.45 µm filter and diluted 10-times to be analyzed by ICP-OES. The formula for sorption efficiency looks as follows:

$$sZn = \frac{(C_i - C_r)}{C_i} [100\%]$$

Where C_i is Initial concentration of zinc; C_r is Remaining concentration of zinc after trial; and sZn is calculated sorbed amount of Zn.

4.3 Column Experiment for Dosage Optimization

Optimization of different doses of nZVI was completed to see which had most efficient sorption capacity in the soil. This was done by testing concentrations of 1%, 2%, and 5% w/w nZVI. To make these initial concentrations, 100g of soil was mixed with 1g nZVI to create a 1% concentration, 100g soil with 2g nZVI to create a 2% concentration, and finally 100g soil with 5g nZVI to create a 5% concentration. The contaminated soil and nZVI were mixed together for 10 minutes and a 60% water holding capacity was achieved to activate the nZVI.

To fill the columns, two filters were placed at the bottom of each column, filled with the mixture of dried contaminated soil and nZVI, and tapped to get rid of any holes or air pockets which could influence how the water ran through it. The columns were filled to the top, which ended up being 50g of the mixed contaminated soil and nZVI in each column. Finally, one more filter was placed at the top and the cap was secured. Then, the differing concentrations of nZVI + contaminated soil from Litavka were run through an automatic sampling machine which was 12cm x 2.5cm, and a control was used containing the contaminated soil and deionized water.

The automatic sampling machine continually percolated water throughout the columns at a speed of 0.6 mL/minute so the water ran evenly down the mixture of contaminated soil and nZVI and the excess water filled up a beaker at the bottom of the column. Before the machine run was turned on, though, the columns had to be fully saturate. This was done by blocking the end of the columns and running the machine

until the columns looked to be fully saturated. This also got rid of any air pockets or holes that were missed while packing the soil into the columns and also prevented the water from running through the column too fast, resulting in inaccurate results. The samples for optimization of dose were filtered through a 0.45 μm filter and diluted 5-times before being sent for analysis by ICP-OES. The entire experiment would take six hours, with the following time steps (Table 4):

Hour #	Frequency of Sampling	Number of Samples
1	Every 15 minutes	4 samples
2-3	Every 30 minutes	4 samples
4-6	Every hour	2 samples
Total	6 hours	10 samples

Table 4: Schedule for the column experiment for nZVI concentration optimization was automatically sampled by every hour and the number of samples received throughout the experiment.

4.4 Column Leaching Experiment

4.4.1 Preparation of Columns

The experiment was completed using a column leaching test within a controlled laboratory setting. Column tests are very practical because they can resemble a real-scale situation, are inexpensive, and comprehensive. The only materials needed for a column experiment such as this include plastic columns with a hole at the top and bottom for an inflow and outflow of water and three holes at equal distances from each other on the sides where the rhizons will be placed to test the soil pore water. The columns used for this experiment were 6 cm diameter x 15 cm length plexiglass. A peristaltic pump to percolate water at a constant rate was used, deionized water which acted as the leaching solution, a jug to hold the water, rhizons, beakers at base of columns to collect the outflow, the contaminated soil, filters in the columns, and the remediation sorbent (nZVI).

After the optimization of nZVI dosage, the columns were set up to ultimately determine the aim of the research; did the nZVI work best when it was evenly distributed throughout the contaminated soil or when it was distributed in a single layer between the two filters that separated the synthetic soil and the contaminated soil? The columns were set up as shown below:

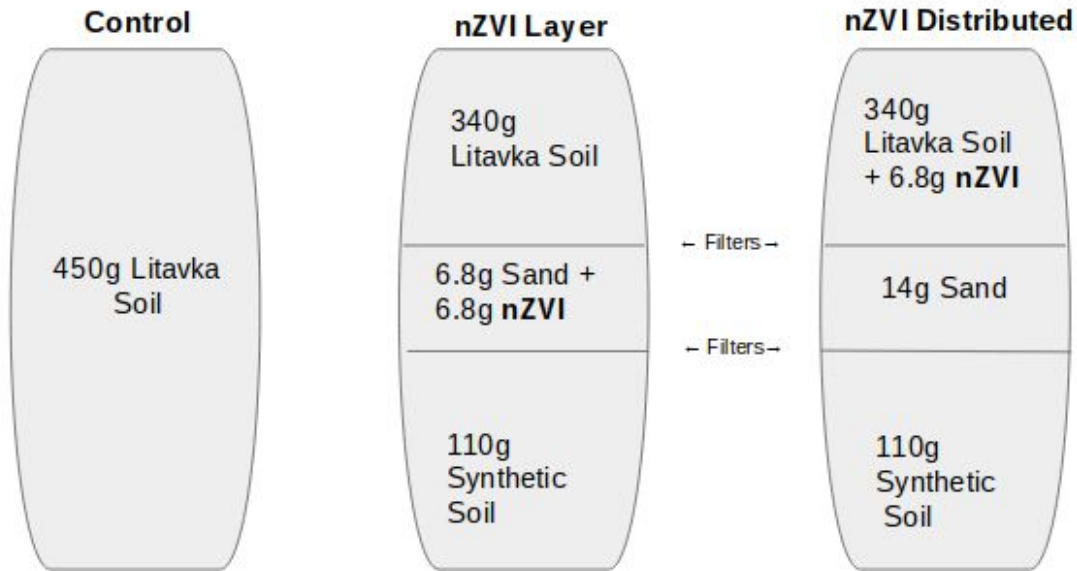


Figure 7: Column setup for the column leaching experiment

The results from the control column were important because they showed what the contamination of the soil pore water and leachate would be like without nZVI. The rhizons were inserted in each of the three different layers. The reason there was sand in the middle of the columns was to improve hydraulic conductivity and because sand is simply silica oxide, therefore, it is inert and will not react with the remediation sorbent. The synthetic soil was prepared in the lab and was also used to increase hydraulic conductivity, or the flow of the water, and to let the water run through a soil of a known composition which was created to mimic the composition of the soil from Litavka. Mainly, the synthetic soil contained certain oxides that real soil would, which can influence the remediation sorbent, but it didn't contain any contamination.

The movement of the contaminant can be seen throughout the soil profile by

testing the concentrations of zinc in both the outflow leachate and soil pore water. This is also what determines how effective the nZVI remediation technology is. If there are high amounts of zinc in the outflow or any rhizon that is below the layer where the nZVI is located, that means the nZVI did not do an efficient job of stabilizing the zinc.

The columns were set up in the lab at Czech University of Life Sciences Prague and there was a set schedule for testing the leachate and rhizon solutions. The columns had a shower system in the top to well distribute the water. The water was held in a jug which was hung above the columns and was controlled by a peristaltic pump which continually supplied water at a constant speed of 0.6 mL/minute. Before the experiment could begin, just as was done with the optimization of concentrations, the columns has to be fully saturated. This was done by plugging the outflows of the columns and running the machine for 3-4 hours. Once the columns were saturated, the outflows were allowed open and the machine continued to let water run through the columns.

4.4.2 Pore Water

Rhizons are the tools which collected the soil pore water. So, in each column there were three holes on the sides where the rhizons were inserted, which allowed for the soil water to be collected at each level (top, middle, and bottom of the column). Therefore, the top rhizon was situated right in the layer containing the contaminated soil (either with or without the nZVI, depending on the column), the middle rhizon was situated in the sand layer (again, either with or without the nZVI, depending on the column), and the bottom rhizon was situated in the synthetic soil layer. The rhizons were vacuums, making the first available water ready to be sucked up, and only allowed solution through, not particles. During each sampling event, each of the three rhizons were removed from the columns, labeled, and placed in the refrigerator. At the end of the experiment, 2 mL were removed and diluted by 5-times with demineralized water which would be used for ICP-OES analysis. Some samples had to be diluted 9-times if there was only 1 mL available so the total volume for ICP-OES testing would be at least 10 mL. The remaining would be tested for pH and also discarded.

4.4.3 Leachate

The outflow, or leachate, from the columns mimic groundwater in a field experiment. Therefore, the columns also had holes at the bottom which allowed the excess water to leach out and was collected in beakers.

During each sampling, we first tested the pH directly from the beaker. Then, 4 mL of solution was extracted from the beaker containing the leachate and 1-2 drops nitric acid (HNO_3) was added. It was then diluted by 5-times with demineralized water and put in the fridge. These would be the samples used for ICP analysis later. Finally, the volume of the leachate was recorded after having removed the 4 mL from it. This remaining volume would simply be discarded. The testing schedule looked as described below:

Step	Date	Hour Tested	# of hours later	# of hours since beginning
1	March 21, 2016	12:00	0	0
2	March 21, 2016	21:00	9	9
3	March 22, 2016	9:30	11.5	20.5
4	March 22, 2016	13:30	4	24.5
5	March 23, 2016	12:30	23	47.5
6	March 24, 2016	12:00	23.5	71

Table 5: Schedule that was kept during the whole of the experiment to ensure controlled and reliable testing.

4.5 Analysis of Results

The results from the rhizons and the outflow leachate which were all filtered through 0.45 µm filters and diluted 5-times. All samples from the entire experiment were analyzed via inductively coupled plasma optical emission spectrometry, also known as, ICP-OES. ICP-OES is a common analytical technique used to detect trace metals and is done by using inductively coupled plasma to excite ions and atoms in order to emit electromagnetic radiation at wavelengths which each element can be characterized by. The concentration of a certain element in the sample can be measured by the intensity of the emission. The solution from the leachate and rhizons were also analyzed with a pH probe, and a graduated cylinder was used to collect the volumes of the leachate.

4.6 Statistical Tests

After obtaining the results, a normality test was performed to determine if the data was normally distributed. Then, a one-way ANOVA was run to test the statistical significance, followed by a Tukey-Kramer test to identify where the significance laid. The statistical tests were run to see if the zinc concentration found in the leachate and pore water was significantly different between treatments.

5. Results

5.1 Soil and nZVI Characteristics

The characteristics for the soil sampled at Příbram can be found in Table 6.

Characteristic	Value
Concentration of zinc	4,000 ppm
Particle size	75% sand 20% silt 5% clay
pH	5.95 ± 0.01
CEC	9.08 ± 0.52 mmol/100g
Total Carbon %	2.15 ± 0.05
Inorganic Carbon %	0
Organic Carbon %	2.15 ± 0.05

Table 6: Certain characteristics for the soil collected at site P2 in Příbram.

The soil sample used contained about 4,000 ppm zinc. With the Czech regulation limits of zinc in soils being 200 ppm (Vaněk et al., 2005), the concentrations were 20 times above the regulation limit value. The soil samples taken by Vaněk et al., (2005) in Příbram contained 333 ppm-8,728 ppm, so the value obtained for the use of this experiment was about in the middle of what they concluded. The soil was considered sandy-loam, with 75% categorized as sand, 20% categorized as silt, and 5% categorized as clay. The average pH of the soil was 5.95, which is relatively neutral, but leaning towards the acidic end of the spectrum. The totals for organic carbon and total carbon were 2.15% and the CEC of the soil was 9.08 mmol/100g.

Characteristic	Value
Particle size	50 nm
pH	11-12
Specific surface area	>25 m ² /g
Substance	Ferrous powder with non-valent chain
Core	Zero-valent iron
Specific charge	0
Molecular weight	55.85 g/mol
Color	Black

Table 7: Specific characteristics of the nZVI used in the experiment.

The nano zero-valent iron particles used in the column leaching experiment are commercially sold, and therefore, well studied. The product used is called Nanofer Star, with “STAR” standing for surface stabilized, transportable, air-stable, and reactive. The surface is stabilized with a thin inorganic layer to prevent it from rapidly oxidizing when in contact in air. If the nZVI wasn’t coated with this thin layer, it could combust when it came in contact with air. This is why the nZVI particles are sold either with a stabilized coating like this one, or in a slurry (NANO IRON, s.r.o., 2016). The particle size is around 50nm, which according to previous research, is in the range for the best mobility of the particle. Also, its pH is 11-12, which means it can be expected to make the soil environment more alkaline when introduced. This can be beneficial, since when the pH is higher, contaminants such as zinc become less mobile and the sorption efficiency of nZVI for zinc increases.

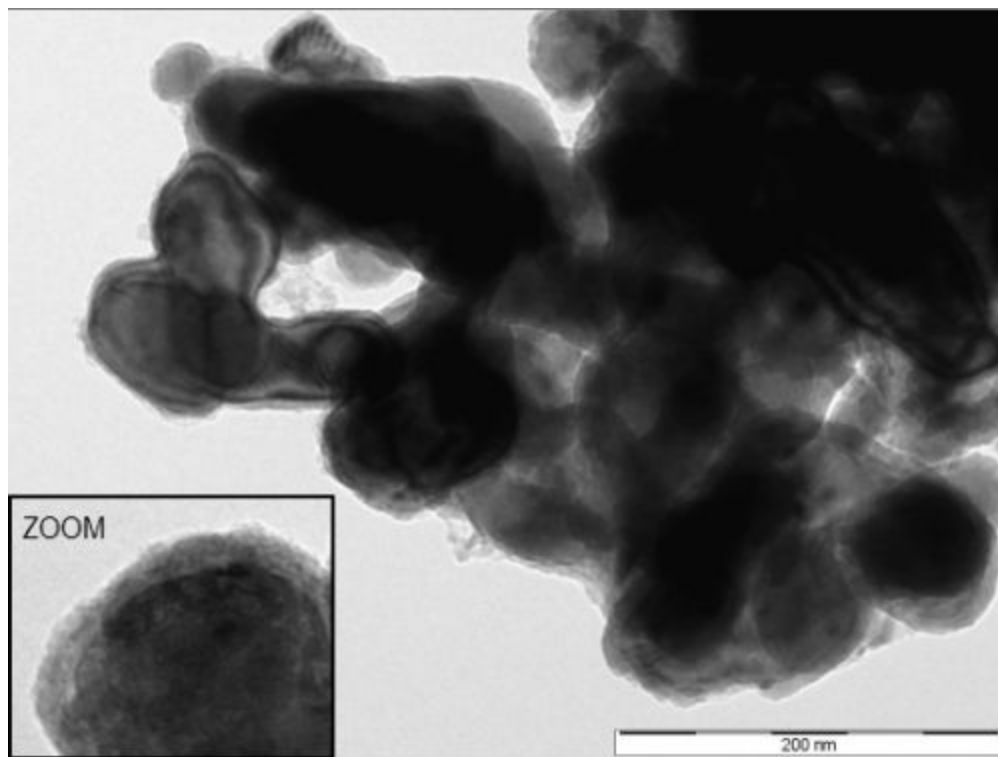
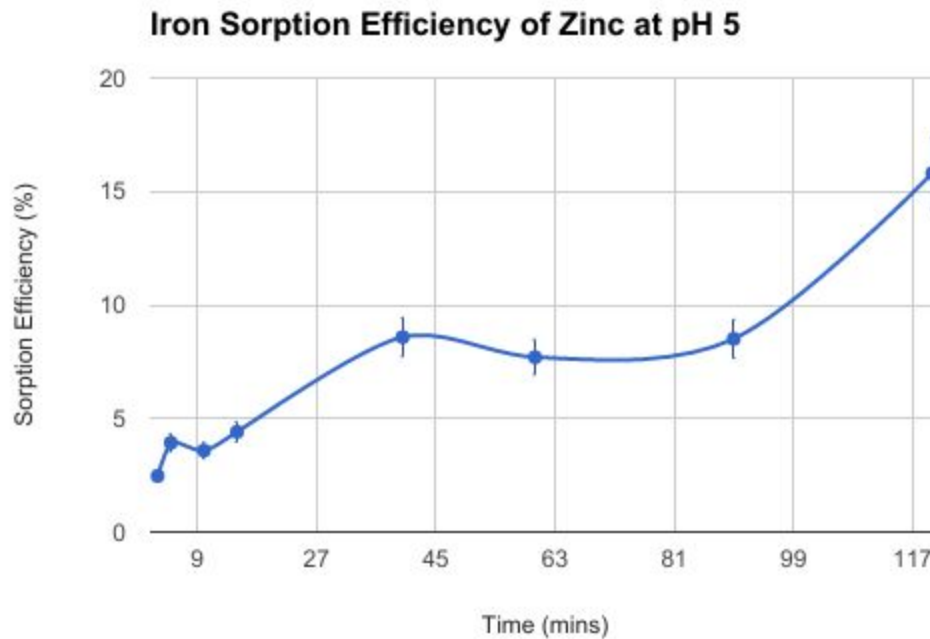


Figure 8: Picture taken with Transmission Electron Microscopy (TEM) of the iron nanoparticle with stabilizing shell (NANO IRON, s.r.o., 2016).

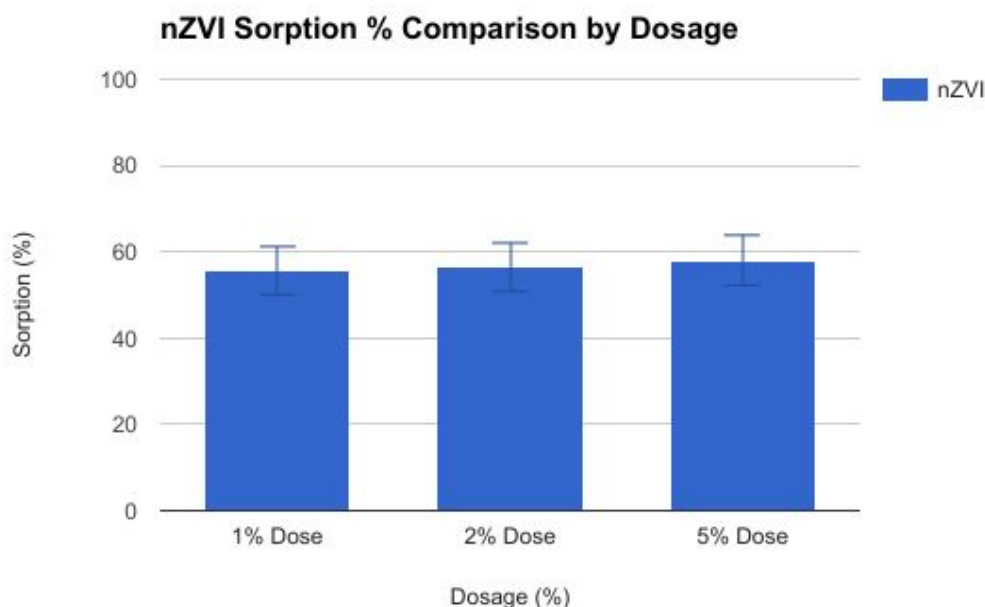
5.2 Batch Experiment



Graph 1: Isotherm graph from batch experiment showing the sorption efficiency of iron to zinc at pH 5.

From Graph 1, sorption efficiency of iron to zinc at pH 5 increases with time, with the efficiency starting with about 2% and rising to over 15%. Perhaps if the experiment lasted longer there would be an equilibrium stage where the sorption rate flattens out, yet this experiment was only 120 minutes, so the results simply show the sorption increases with increasing time.

5.3 Column Experiment for Dosage Optimization



Graph 2: Dosage optimization of nZVI with zinc testing 1, 2, and 5% dosages.

After analyzing the results from the optimization experiment to determine which concentration of nZVI would be most efficient, the 2% was determined as the best dose. This was determined by analyzing the concentrations of zinc found in the leachate. As the dose increased, the sorption efficiency also increased, with the 5% dose stabilizing the most zinc and the 1% dose stabilizing the least amount of zinc. However, when comparing the 2% dose with the 5% dose, the difference wasn't significant. It is also more economical in the sense that less of the product is being used, and therefore saving money. So, since the difference between 2% and 5% wasn't significant, it's more economically friendly and more similar to natural conditions, the decision was made that the 2% dose was best.

5.4 Column Leaching Experiment

5.4.1 Pore Water Sampling

The following results were obtained using a pH probe to collect pH values, a graduated cylinder to obtain the volume of leachate, or through ICP-OES analysis in order to obtain the concentration of zinc found in the rhizons or leachate. In the results from the pore water samples, it is important to note that there were three rhizons inserted into the columns, one at the top, middle, and bottom, as explained in Chapter 4.

The pH values for the pore water sampling had no significant changes, as all samples were relatively neutral and had similar values. The graphs for these values can be found in Chapter 9 in the appendices along with the leachate volumes.

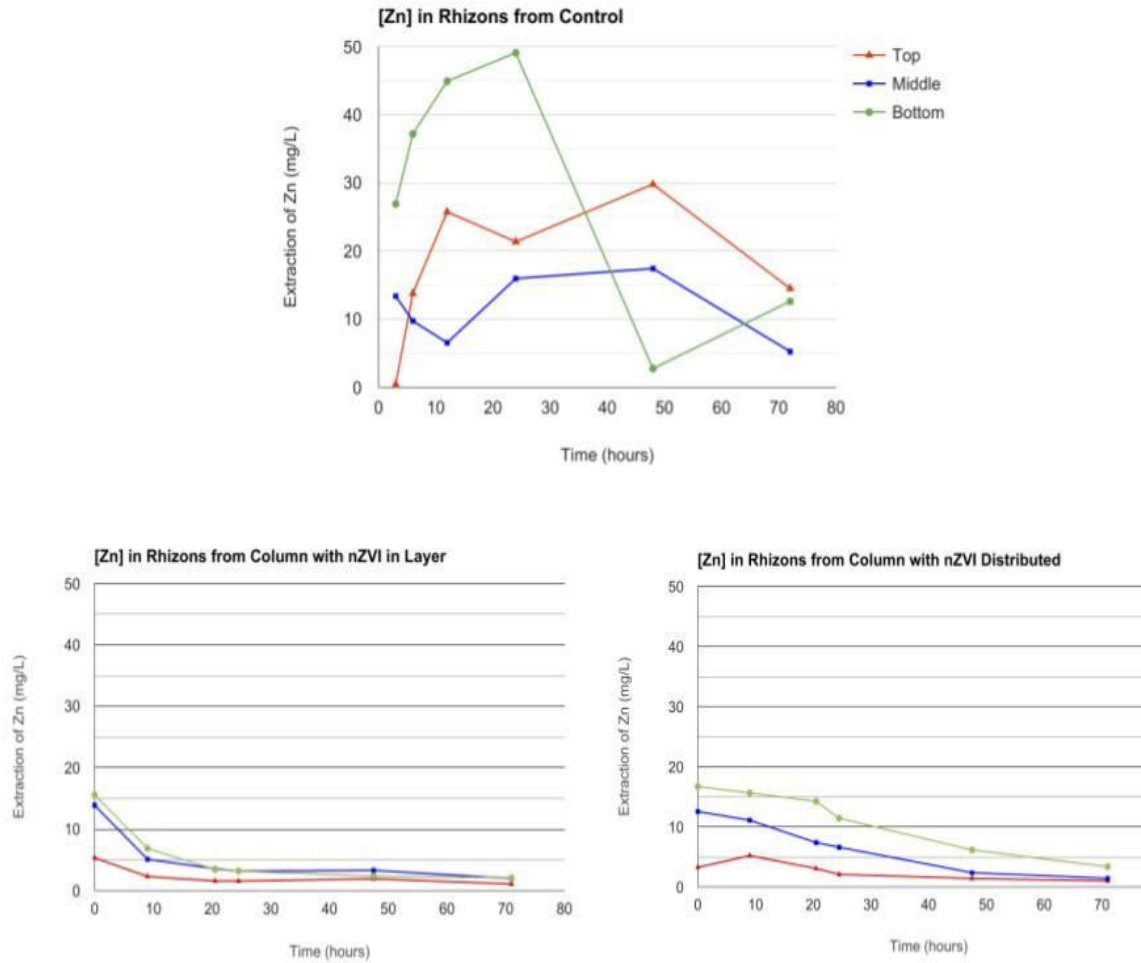


Figure 9: Zinc concentration found in the pore water samples collected from rhizons from both application methods including the control.

Figure 9 shows the concentrations of zinc in the rhizons followed the same trend regardless of the nZVI application method, as both started and ended with about the same amount of zinc in the pore water samples. Also, when comparing having nZVI in the soil to the control, it's obvious the control did not follow a trend as much as having nZVI in the soil does, and the control also ended up with more zinc in the pore water at the end of the experiment. The average zinc concentration at the end of the experiment for the application where nZVI was layered was 1.699 mg/L and when nZVI

was distributed, the zinc concentration was 1.918 mg/L. Compared to the control, which had an end average of 10.780 mg/L, it's clear the nZVI had a positive effect in stabilizing the zinc in the soil, as proven by the lower concentrations of zinc found in the pore water in the columns where nZVI was present. Furthermore, the highest concentrations of zinc in the pore water with nVI was about 16 mg/L, while the highest concentration for the control pore water was about 50 mg/L, which is about 6.3 times higher than with the nZVI. Unlike the leachate, which gradually increased with zinc concentrations over time (because it was the cumulative amount of zinc), the rhizons decreased in zinc, both starting at about 16 mg/L and ending with about 2 mg/L.

After running a one-way ANOVA for each of the rhizons (A, B, and C) and comparing them between the different applications, it showed that rhizons A and C were statistically significant, with $P= 0.0007$ for rhizon A and $P= 0.007$ for rhizon C, but rhizon B showed $P= 0.087$. Also, the significance for A and C laid only when comparing the values to the control. $P= 0.001$ when rhizon A compared the layered method to the control and $P= 0.002$ when rhizon A compared the distributed method to the control. Also, $P= 0.008$ for rhizon C when comparing layered to control and $P= 0.043$ for rhizon C when comparing distributed to the control. In both cases, the significance was higher for the layered method, although both methods were significant. However, when the values were compared between distributed and layered, there was no significance. This means that having nZVI in the soil at all, no matter what the application method is, will significantly stabilize the zinc in the soil.

1-Way ANOVA	Rhizon A	Rhizon B	Rhizon C
P Value	0.0007 ($P<0.01$)	0.087	0.007 ($P<0.01$)

Table 8: Summary of the statistical results after running a one-way ANOVA comparing the zinc concentration between different application methods

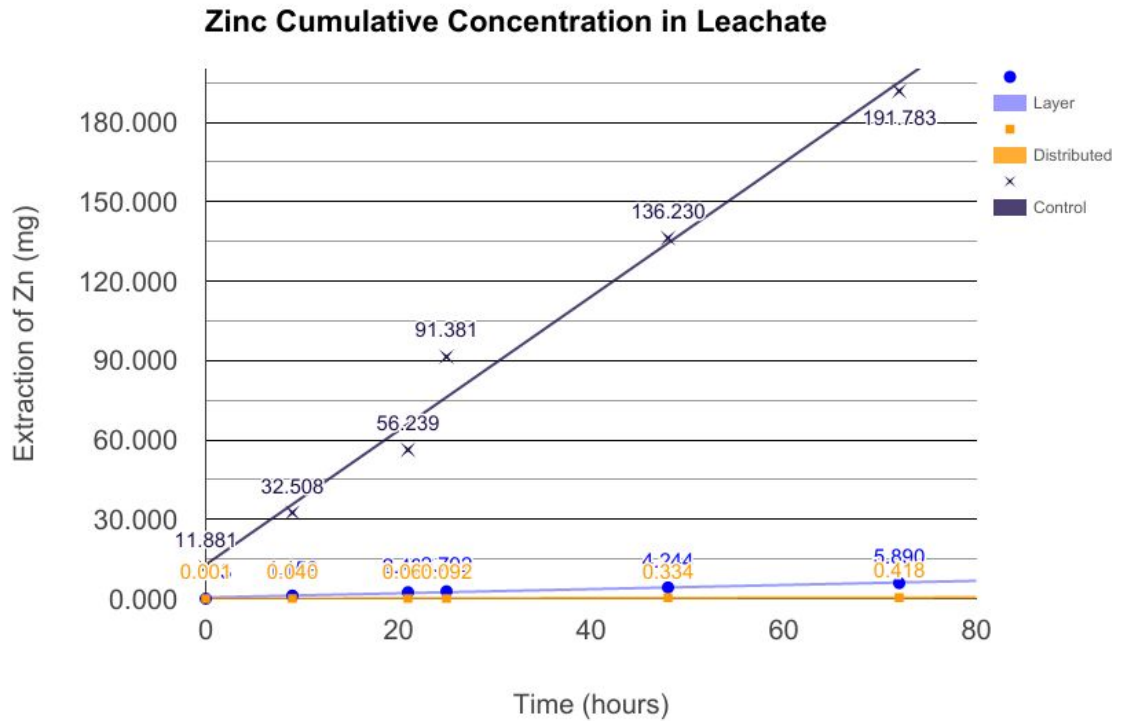
As shown from Table 8, all the results were statistically significant except for those from Rhizon B.

Tukey Test	Rhizon A	Rhizon B	Rhizon C
Layer vs. Distributed	0.994	0.793	0.673
Layer vs. Control	0.002 (P<0.01)	0.082	0.008 (P<0.01)
Distributed vs. Control	0.002 (P<0.01)	0.246	0.043 (P<0.05)

Table 9: Statistical results after running the Tukey-Kramer test.

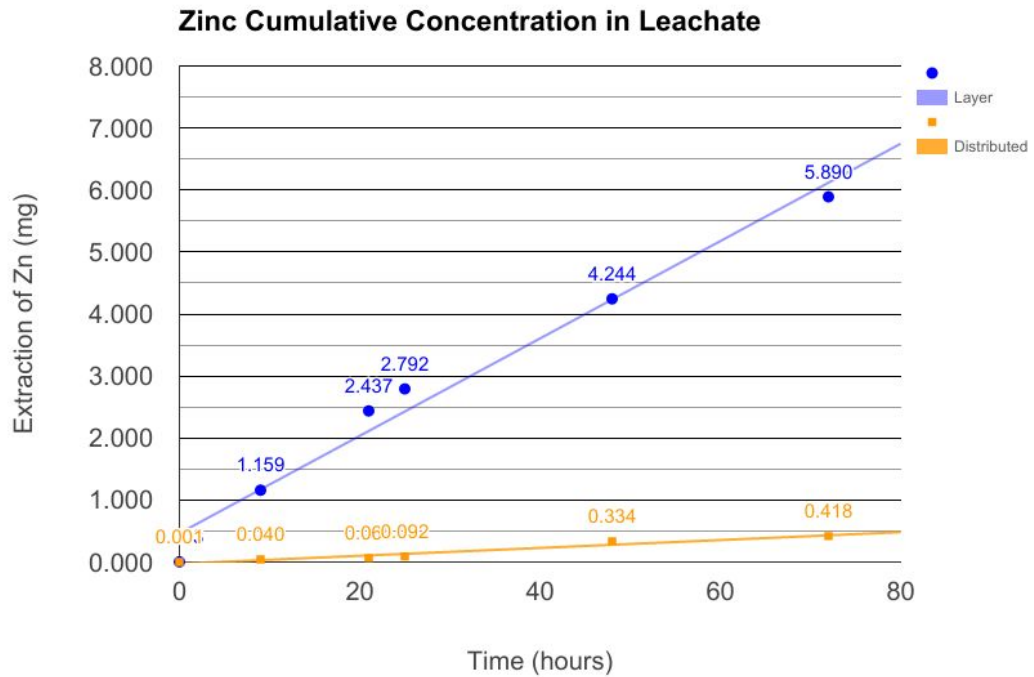
After running the Tukey-Kramer test, it shows rhizon B didn't show any significance for any comparison and there is no significance when comparing the layer vs. distributed application method. However, the significance lies when comparing the different application methods to the control. This means that having nZVI in the soil significantly stabilizes zinc, but the application method does not matter.

5.4.2 Column Leachate



Graph 3: Cumulative zinc concentrations found in the outflow leachate in all columns including the control.

Graph 3 shows the significant amount of zinc still found in the leachate of the control column when there was no nZVI applied. The control column contained 11.9 mg of zinc in the leachate in the beginning and ended with 191.8 mg at the end of the experiment. This means the control had 480 times more zinc in the cumulative leachate than compared to the better nZVI application (distributed) which had 0.418 mg of zinc at the end.



Graph 4: Cumulative concentrations of zinc found in the leachate of the columns where nZVI was applied in a layer and evenly distributed.

Graph 4 compares the concentration of zinc between the two application methods without the control. After comparing the two different application methods, the concentration of zinc found in the leachate was less in the column with nZVI distributed within the contaminated soil, making it the better remediation application option.

From the beginning at 10 hours, in the column where the nZVI is distributed, the concentration of zinc in the leachate is about 0.04 mg, while in the column with nZVI in a layer at 10 hours, the concentration of zinc in the leachate was over 1 mg. And finally, at the end of the experiment at hour 70, the concentration of zinc from the column where nZVI is distributed is about 0.4 mg, while the column with nZVI in a layer at hour 70 is almost 6 mg. This means having nZVI in a layer had 15 times more zinc in the leachate than when having nZVI distributed.

After running the one-way ANOVA, having nZVI in the soil proved to be statistically significant with $P = 0.002$. Yet, just as the pore water showed, the

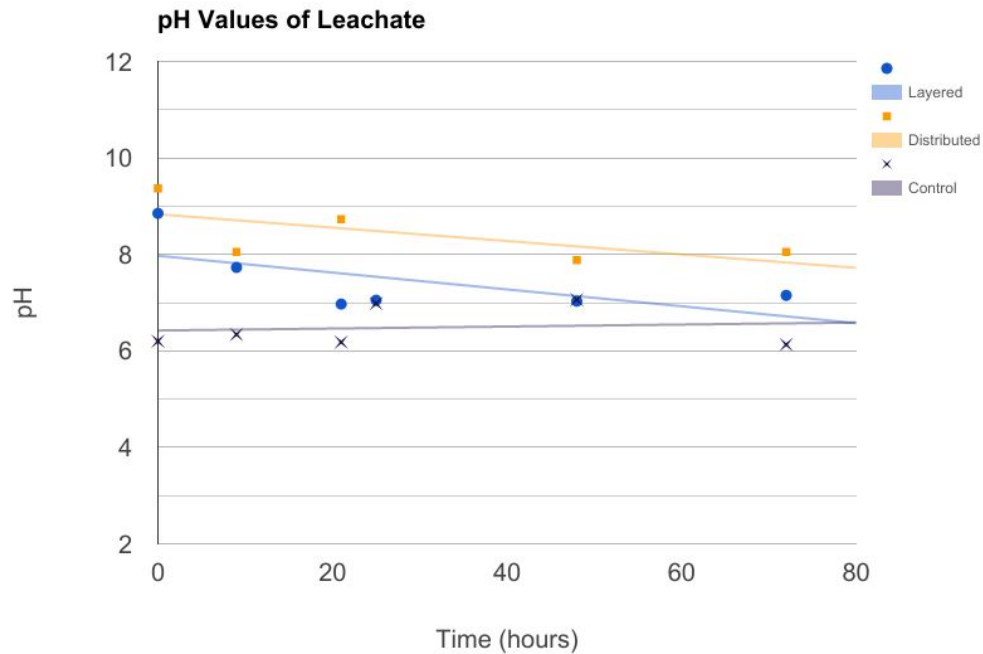
significance only laid when comparing the different application methods with the control. For instance, when comparing the layered method to the control, $P= 0.005$, and distributed against control was $P= 0.004$. Yet, when the two methods were compared with each other, $P= 0.99$, which is not statistically significant. For the pore water, having the nZVI layered was more statistically significant, but for the leachate, the distributed method had more significance. Nonetheless, both methods were significant when compared to the control, but not when compared to each other. This shows again, that having nZVI in the soil, regardless of how it is applied, will significantly stabilize zinc in the soil, ending up with less zinc in the pore water and groundwater.

1-Way ANOVA	Leachate
P Value	0.002 ($P<0.01$)

Tukey Test (Comparing Applications)	Leachate P Value
Layer vs. Distributed	0.993
Layer vs. Control	0.006 ($P<0.01$)
Distributed vs. Control	0.004 ($P<0.01$)

Table 10: 1-Way ANOVA and Tukey-Kramer test results for the leachate zinc concentrations show a significant amount of zinc is stabilized when comparing the applications to the control, but not when comparing the applications to each other.

5.4.3 pH of the Leachate



Graph 5: Different pH values taken at different hours throughout the experiment from the leachate of both columns including the control.

Overall, from Graph 5, it seems there was a higher pH value from the column where the nZVI was evenly distributed within the contaminated soil compared to when it was left as a single layer in the column. Having the nZVI in the soil, regardless of application, increases the pH when compared to the control. As we know, increased pH also helps nZVI sorption and it decreases the mobility of zinc. The average pH value for the column with nZVI evenly distributed was 8.42, with the highest pH level recorded at 9.37. As for the column with nZVI as a single layer, the average pH was 7.46, with the highest pH recorded at 8.85. Although not a severe difference, it is obvious the column with nZVI distributed showed more alkaline properties compared to

nZVI as a single layer. When compared to the control, the nZVI clearly had a more alkaline pH, as shown from Graph 5, which is what is expected. Also, compared the the pH of the rhizons, the leachate had a higher pH overall. The average rhizon pH was 6.44 while the average leachate pH was 7.94. This signifies that the solution becomes more alkaline as it moved through the column.

6. Discussion

Perhaps the most important thing to focus on when dealing with soil chemistry and remediation is the fractionation and speciation of the contaminant, since that is what determines its mobility, leachability, bioaccessibility, and bioavailability in the environment. Also, determining certain physicochemical properties such as Eh and pH, and assessing the content of organic matter, secondary minerals, or other compounds are equally important, as they can determine what the fractionation or speciation of the metal is. The mobility of a substance is often associated with how risky it is, since a greater mobility correlates with its ability to spread to other areas, making previously safe ecosystems toxic. It is after these properties are understood that a better understanding for how to solve the problem of contaminant remediation can be achieved. Furthermore, knowing the pH, type of nZVI, zinc species, and contact time will all have significant influence on the stabilization of zinc and help understand the remediation process (Kržišnik et al., 2013).

6.1 Batch Experiment/Kinetic test

From the batch experiment, it was noticeable as time went on, the sorption efficiency increased, ending with over 15% sorption efficiency for nZVI with zinc at a pH of 5 and over a period of two hours. Yet, if the pH would have been higher, or the experiment was longer, the sorption efficiency would have also been greater since the sorption efficiency for iron increases with increasing pH and time. Also, if the experiment would have been longer, the experiment could have reached an equilibrium. These findings agree with another study by Violante et al (2010) which

concluded that as time went on, sorption of zinc onto ferrihydrite (a Fe-oxide) also increased. The total length of their study was 336 hours, and the entire time, the sorption continued to increase, and even resulted in an irreversible sorption reaction. Also, a study by Rieuwerts et al (1998) claimed the critical sorption pH value for Fe-oxides in regards to zinc was around 5-6.5, which is around the same pH we tested for the batch experiment.

6.2 Column Experiment for Dosage Optimization

As the dose increased, the sorption efficiency also increased, with the 5% dose stabilizing the most zinc and the 1% dose stabilizing the least amount of zinc. However, when comparing the 2% dose with the 5% dose, the difference wasn't significant. It is also more economical in the sense that less of the product is being used, and therefore saving money. So, since the difference between 2% and 5% wasn't significant, it's more economically friendly and more similar to natural conditions, the decision was 2% dose was best. In a study by Liang et al. (2014), they concluded even using a dose of 1% nZVI showed 85% removal of zinc. Another study showed using 2% made for optimal dosage of nZVI and also showed that efficiency increased with dosage increase (Shu et al., 2016), which correlates with the results from this experiment as well.

6.3 Application Methods

6.3.1 Pore Water Samples

For the pore water samples, both application methods worked well in regards to stabilizing zinc in the soil compared to the control. Also, both application methods started and ended with about the same concentration of zinc in the pore water. However, it is worth noting that in the column where the nZVI was situated in a single layer, the concentrations of zinc drop dramatically from the 0th-10th hours. This is unlike in the column where the nZVI was evenly distributed within the contaminated soil

at the top, where the levels of zinc gradually go down throughout the experiment, and not as drastically as the other application method. In this case, it seems the strategy of placing the nZVI as a single layer below the contaminated soil works more efficiently if you are seeking out an immediate positive effect of stabilizing zinc in the soil.

For both application methods, the highest concentrations of zinc are actually found in the rhizon that was situated at the bottom of the column. Likewise, the rhizon that had the lowest concentration of zinc was the rhizon situated at the top.

So, in regards to zinc concentration, both methods worked equally well, but in terms of fast effects, the column where nZVI was in a layer worked the fastest as far as reducing the concentrations of zinc in the pore water. The results from the pore water samples showed the rhizons that were closest to the bottom of the column (where the leachate was collected) contained the highest concentrations of zinc, and the rhizons that were at the top of the column had the lowest concentrations of zinc.

6.3.2 Column Leachate Samples

From the outflow volume shown in Graph 8 in the Appendix, the upwards trend in the distributed is not as pronounced as it is in the layer because the column that had nZVI evenly distributed in the contaminated soil continued to cause problems throughout the experiment including clogs in the outflow of the column (making it so not as much water was flowing out) and there were also leaks at the top of the column where the water was percolating in (also making it so not as much water was going through). These issues obviously had an effect in the final results. The control had the highest volumes of outflow. This could be due to the absence of filters, sand, or because that column didn't experience any clogs.

From the results, it seems the best method to reduce the concentrations of zinc in the leachate (or in a real-world situation, the groundwater) would be having the nZVI evenly distributed within the soil. From the beginning to the end of the experiment, the column with nZVI distributed was contained quite a lot less zinc in the leachate compared to when nZVI was in a layer (15 times less zinc). Furthermore, when comparing the distributed application to the control, the control contained 480 times

more zinc, which had a final concentration of zinc in the leachate of 191.8 mg.

It is clear that the line of zinc concentration for both application methods is in an upwards trend, with the concentration of zinc in the leachate increasing as time goes on. This is because it is an accumulation of zinc concentration over time. This is what would happen in groundwater in a real world scenario; metals tend to accumulate since they have nowhere else to go. Yet, although both columns followed the same upwards trend, the amount of accumulation of zinc in the leachate was less for the column where nZVI was applied evenly distributed.

Overall, when the nZVI was applied evenly distributed throughout the contaminated soil, the leachate showed less contamination of zinc, the pH was higher, and there was less outflow altogether. This is compared to when nZVI was placed in a layer, there was more contamination of zinc in the leachate, the pH was more acidic, and there was more outflow (although the outflow volumes may be caused by leaks and clogs).

The results obtained from this experiment coincide with results obtained from previous similar experiments studying the sorption efficiency of nZVI with soils contaminated with zinc. For example, a study conducted by Komarek et al (2013) claimed when using nZVI in a 1% dose, they proved to show long term stability of zinc in the soil. Another study by Liang et al (2014) showed when using 1% nZVI there was an 85% reduction of zinc within two hours of the experiment. Similarly, a study by Lee et al (2011) showed 2% nZVI in soils contaminated with zinc of concentrations of 260 ppm displayed reduced bioavailability and reduced exchangeable fractions of zinc.

Another study conducted by Mar Gil-Diaz et al (2014) showed nZVI worked efficiently in stabilizing zinc and lead in soils that were both acidic and calcareous. There was a significant decrease of the exchangeable fraction of zinc, an increase of the residual fraction, and the immobilization of zinc was described as stable for at least one month. Furthermore, not only were no negative effects observed in the soil after injecting nZVI, but there were actually positive effects in the soil, such as increased soil respiration. This is exciting news that not only does nZVI help remediate soil, but it actually creates extra benefits in the soil at the same time. In another study by the same author, they found after treating zinc contaminated soils with nZVI, the analyzed

leachate contained 72% less zinc after the treatment (Mar Gil-Diaz et al., 2014) during their column leaching experiment. Their leachates from the experiment contained less toxicity of zinc when treated with nZVI than without and the immobilization was stable.

In all of these studies, the results are consistent with one another and with the results which I obtained, which are that nZVI effectively stabilizes zinc in the soil, hence, reduces the contamination. This further backs the notion that nZVI and iron oxides make a good *in situ* soil remediation technology when dealing with zinc and other trace metals.

6.4 Sources of Error

Unfortunately, there were complications with the experiment which could undoubtedly result in sources of error. The column where the nZVI was distributed within the contaminated soil kept experiencing clogs at the outflow, preventing adequate sampling at times. Another time the sampling was being performed, the tube at the top of the column with nZVI distributed was broken, preventing any water from percolating through. Surely these errors could have interfered with the experiment, therefore, further experimentation should be done in order to acquire reliable results.

7. Conclusion

The purpose of this experiment was to demonstrate the effectiveness of nZVI in the stabilization of zinc in soil. By doing so, the sorption efficiency was tested, the dosage was optimized, and a column leaching experiment was conducted comparing two different application methods of nZVI; as a thin layer and distributed within the contaminated soil. The kinetics batch experiment showed as time went on, sorption of zinc onto nZVI increased. If the experiment was longer, an equilibrium would have been reached and the sorption efficiency would have increased as well.

The leaching experiment testing for dose optimization showed the best concentration of nZVI is 2%. As dose increased, sorption efficiency also increased, yet the difference between 2 and 5% wasn't significant, making it more economical to

experiment with the 2% dose.

The column leaching experiment testing the two different application approaches showed that having the nZVI in the soil, no matter which application was chosen, positively impacted the leachate and soil pore water in terms of zinc contamination. The control, which didn't contain any nZVI, had significantly more zinc in the soil pore water and leachate at the end of the experiment when compared to having the nZVI in the soil. Specifically, the control had 480 times more zinc in the leachate and 6.3 times more zinc in the soil pore water than that of when there was nZVI in the soil. Furthermore, the best application of nZVI could be either layered or distributed, since both methods worked. For the pore water, having nZVI layered was more significant than distributed, but for the leachate, having nZVI distributed was more significant. This simply means either application method works, as both were significantly better at stabilizing zinc than compared to the control. These claims can be backed up by the one-way ANOVA and Tukey-Kramer test which was run, which proved to be statistically significant for nZVI stabilizing zinc in the soil.

The best way to avoid unnatural amounts of zinc from getting into the environment would be to prevent anthropogenic activities which cause this abnormality. Yet, since this doesn't seem to be an option in the near future, a viable remediation technique such as nZVI should be utilized to reclaim the soil and water which is contaminated with such metals, and with that, prevent it from further spreading into the environment and even organisms.

8. References

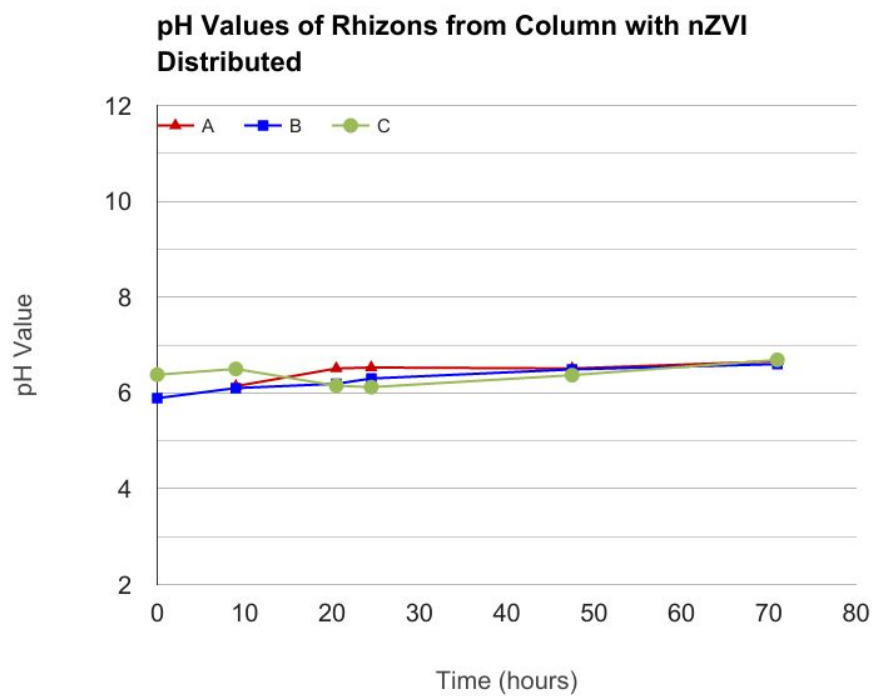
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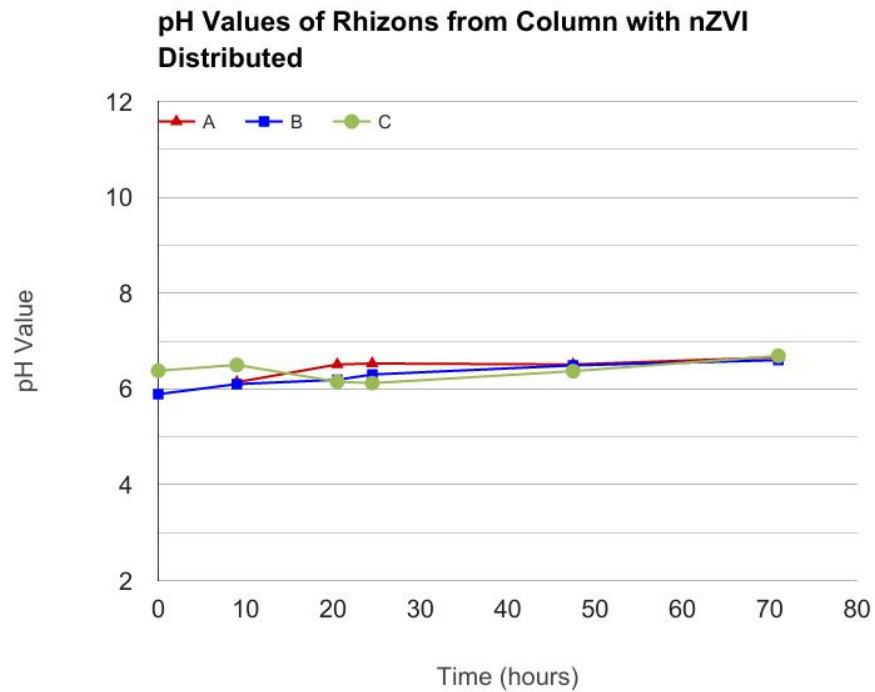
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9. Appendices

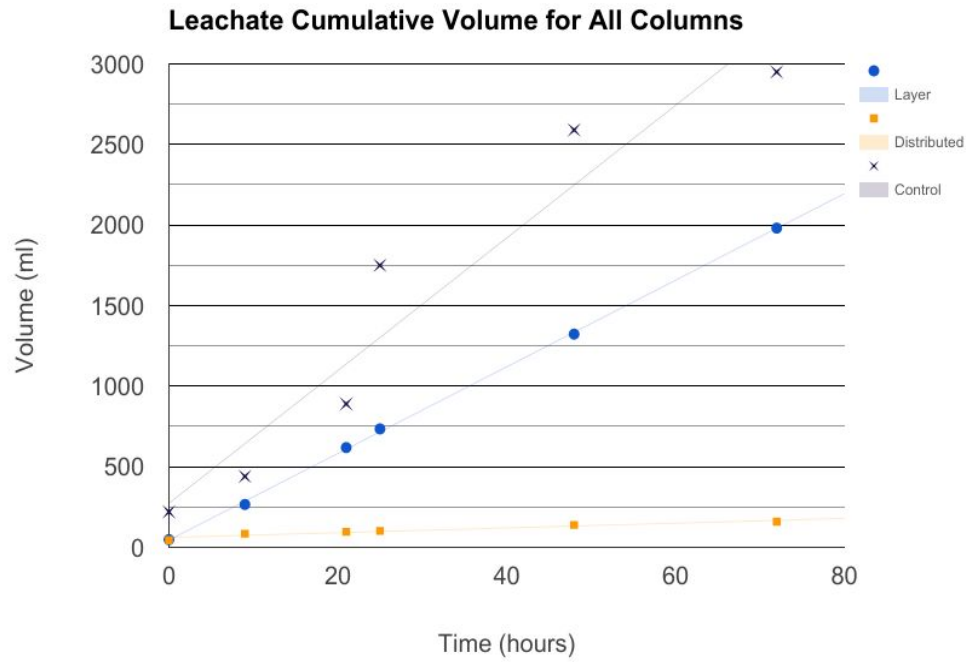


Graph 6: Different pH values taken at different hours throughout the experiment from all three rhizons from the column that had 2% nZVI distributed within the contaminated soil.



Graph 7: Different pH values taken at different hours throughout the experiment from all three rhizons from the column that had 2% nZVI in a single layer situated below the contaminated soil.

In this column, rhizon A is missing two data points because there was not enough sample to measure the pH. Throughout all three rhizons at all hours of the experiment the pH is between 6 and 7, which is relatively neutral, and at the end of the experiment for both columns all three rhizons tend to homogenize their pH levels with each other, with both columns averaging 6.44 at the end for all three rhizons.



Graph 8: Total cumulative volume collected from the leachate from all columns.

From the outflow volume shown in Graph 8, the control actually had the highest volume of water in the leachate, followed by the column with nZVI in a layer, and the column with nZVI distributed had the least outflow volume. This could be due to the several clogs and leaks that were dealt with in that column.