

Development in the use of Nano Zero Valent Iron (NZVI) process for ground water remediation: A perspective

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Abstract: The last ice age ended and modern human civilization begun around 7000 years ago and in these 7000 years we have seen some of the extreme transmutations in the environmental like rise in sea level, increase in global temperature, shrinking of ice sheets and ocean acidification. These extreme events clearly indicate that the emergence of mankind and the rapid development of civilization has become the greatest threat to the survival of our beloved planet. With the industrial revolution and advancement in technology, the use of synthetic products have become extremely handy. However, most of these products are non-biodegradable and very harmful to get rid off. This degrades our ecosystem and leads to pollution of natural resources, such as soil, water, and air. Though there has been much energy spent focusing attention toward the broader environmental and climate problems that plague the Earth today, issue specifically concerning the decontamination of water requires more attention.

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1. Introduction

Water is an exceptionally vital resource: it transports nutrients and chemicals within the biosphere to all forms of life, and it plays a pivotal role in maintaining the ecosystem. Also, despite the seemingly abundant presence of water on Earth, only a minute fraction of it is potable for humans—fresh water only makes up approximately 2.5% of all water. Therefore, protection of water quality deserves immediate attention in order to ensure our collective health. This article discusses the major development of Nano Zero Valent Iron technology in order to save the water from contamination.

Water pollution can be broadly classified into two general categories: indirect and direct pollution. Indirect contamination is result of pollutants entering the water supply from the ground, or even from the atmosphere as rain. Often, ground water is contaminated through many diverse, modern agricultural practices that utilize a number of harmful chemicals, such as fertilizers and pesticides. Direct pollution is the release of contaminating waste directly into urban water from factories, refineries, or waste treatment plants. Though these practices are often controlled, regulation is very far from perfect and pollutants still find their way into clean water. As a result, the type and degree of contamination is hugely variable at any geographical location. Moreover, pollutants are added to water from air through atmospheric pollution, which is caused by emissions from automobiles, factories, and households (Cicheon & Pier, 1999).

2. Methods

Due to the global increase in polluting and contaminating activities, environmental degradation has progressed beyond natural limits, leading to irreversible ecological damage. Natural resources are continuously becoming depleted, and current levels of human consumption cannot be maintained. These devastating consequences necessitate new global measures to restore the quality of our soil, water, and air, in order to foster an environment conducive to healthy human habitation. Therefore, in addition to preventive measures that can limit and control future degradation, we need to immediately implement prudent remediation steps, through new technology and initiatives, to ensure the survival of the human environment.

Environmental remediation, by definition, is the removal of toxic pollutants that have reached our natural resources. While soil, water, and air remediation all have unique importance, the remediation of ground water is especially pressing. Ground water quality is determined by the quality of soil, water and air present on the surface, as wherever surface water makes its way into ground water, the organic chemicals and pathogens present in the surface soil or air inevitably enter alongside the water. To combat this issue, many clever techniques have been adopted to clean up contaminated ground water.

Ground water remediation techniques are varied, spanning across biological, chemical, and physical treatment technologies. The most effective approach utilizes a combination of all of these diverse technologies. Some of the biological treatment

techniques include bioaugmentation, bioventing, biosparging, bioslurping, and phytoremediation. Chemical treatment techniques include ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation, and surfactant-enhanced recovery. A common physical method involves pumping the water upwards to treat it at the surface. Although useful in certain remedial scenarios, the pump-and-treat technology has many limitations, creating logistical and financial problems (Hemut et al, 1996; Hyman & Dupont, 2001).

3. Results

One notable ground water remediation technique involves an *in situ* treatment that uses a permeable reactive barrier (PRB) (Blowes D.W., 2000; Thiruvengatachari R., 2008). A PRB is a trench in the subsurface that is filled with reactive material to collect and decontaminate plumes of ground water within the subsurface, essentially creating a passive treatment system. Ultra-fine millimeter to micron-sized particles of zero valent iron (ZVI), such as metallic iron, can be used as a very effective reactive material for this technique. As the contaminant moves through the ZVI particle barrier, reactions transform the contaminants into less harmful (non-toxic) or immobile species, and thus remediate the water. The primary removal methods include sorption and precipitation, chemical reactions, and biological mechanisms that are mediated using ZVI. In particular, ZVI usage in small-scale field studies has demonstrated complete treatment of Cadmium (Cd), Chromium (Cr), Cobalt (Cu), Nickel (Ni), nitrates (NO_3), phosphates (PO_4) and sulphates (SO_4) (Wilkin et al., 2005).

More recently, nano-structured zero valent iron (NZVI) has been studied and recognized for its usefulness in ground water remediation due to its surface area (Mueller et al., 2012). Both ZVI and NZVI reductively decompose halo alkanes, which are some of the main contaminants of ground water, into safer compounds. However, the distinguishing factor between the two is that the effective surface areas of nanoparticles have a much greater order of magnitude than those of micro-particles. For instance, if a 10 micron spherical particle is replaced by a 100 nanometer one, then the surface area increases by a factor of ten thousand, making a huge impact on reaction rates, as reactions depend upon available surface area. This makes NZVI more effective than the conventional ZVI. In fact, previously unachievable reactions by macro-sized ZVI, such as the decomposition of trichloroethylene, are now possible using NZVI. NZVI has also been found to promote the

degradation capabilities of naturally present microbes that can also degrade contaminants.

NZVI particles can be made by reducing an iron salt—such as Fe(II) chloride (iron chloride with iron in the oxidation state +2)—with a strong reducing agent, such as sodium borohydride, in solution phase. When Fe(II) reduces to Fe(0), black particles form and the reaction mixture instantly darkens (Stefaniuk et al., 2016; Shi et al., 2011). The resulting particles are retrieved by vacuum filtration, washed in ethanol, and dried for storage (Wang et al., 2006). The particles are usually susceptible to aerial oxidation, but the washing performed with ethanol prevents such aerial oxidation. A thin oxide layer of about a few nanometers in size inevitably forms in NZVI. This oxide layer is extremely useful as it functions as the protective layer that inhibits the propagation of uncontrolled oxidation into the interior of the particle. In fact, the actual particle is a core-shell structure in which the core is a zero valent metal. The shell, on the other hand, is an oxide layer where the iron is either in the Fe(II) or Fe(III) state, depending on the extent of oxidation. To ensure that the proper products have formed, electron microscopy, coupled with spectroscopic studies, can characterize and verify the uniformity of the nano zero valent metal formation. The zero valent state is crucial for the reductive decomposition of halogenated compounds. NZVI has now become commercially available as slurries to be used in PRBs.

Some of the most common contaminants found in the ground are carbon tetrachloride, chloroform, hexachlorobenzene, tetrachloroethene, and vinyl chloride—all anthropogenic contaminants created from modern, human activities. Fe(0) can oxidize to Fe(II) and reduce these halogenated compounds and chlorinated contaminants to less harmful, and chemically degradable, products. In addition, ground water is also commonly contaminated with heavy metals such as mercury, nickel, cadmium, lead and chromium salts. Heavy metals or metal ions will adsorb onto the surface of NZVI or the metal ion's oxidized ferrous surface. These adsorbed and immobilized metals precipitate from the ground water plumes and then can be removed.

4. Discussions

Another fascinating finding is the use of bimetallic nanoscale particles (BNPs) in the kinetics of the redox reactions involved in contaminant remediation (Carroll et al., 2013). The reactivity of the nanoscale iron particles can be significantly enhanced by depositing a small amount—less than 0.1%—of a noble metal, such as palladium, platinum, nickel, and silver, on the surface of the iron. This creates bimetallic nanoscale particles which increase the value of the degradation rate constant of tetrachloroethylene

by one hundred fold compared to when only NZVI is employed.

Considerable research and development has transpired to invent novel technologies for controlling water contamination as well as promoting water remediation; however, we are still far behind in controlling the damage. Given that ground water pollution is a result of soil, water and air pollution, measures therefore need to be taken from all directions and approaches in order to achieve success. Though water remediation technologies have come a long way, there is still much more to improve. Despite its many benefits, NZVI has not achieved commercial recognition for a number of reasons. Rapid aggregation, the potential for NZVI to reduce water flow, and unforeseen interactions between NZVI, ground water constituents and chemical equivalents required for the NZVI reaction, have posed serious challenges to the widespread use of NZVI water remediation. There is furthermore a high cost of manufacturing associated with NZVI nanoparticles, and the open use of nano-sized materials has, in general, generated significant health concerns. The particularly toxic and invasive nature of materials in nanoforms is still not fully investigated, and the health effects are not fully known or understood. Many speculate that because of their small size, nanomaterials may be able to enter the human body and potentially pass through the blood brain barrier. Airborne and water borne particles can be lodged in body tissues—especially lungs and endothelial layers—and cause unforeseen health challenges.

In order to reduce harmful effects and better understand the benefits, additional research is required across all related disciplines, from nanoscale studies to field studies. Deeper knowledge of the chemical and physical properties of these nanoscales will ultimately lead to more expansive trial and development in field studies—field studies that can enhance our current estimations of ground water health before and after the injection of NZVI. Through these studies, NZVI production can be further developed, and its role in water remediation can be further validated. NZVI holds much potential, but until these serious concerns are adequately addressed, the wide-scale use of such a new technology cannot be embraced with open arms.

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