

Application of Nanoscale Zero-valent Iron for Wastewater Treatment

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Abstract-Nanoscale zero-valent iron (nZVI) is an effective tool for wastewater treatment. It has a great potential to reduce subsurface contaminants, heavy metals and a plethora of hazardous materials. This engineered nanoparticle shows tremendous potential in the environmental sector, being a relatively cleaner wastewater remediation technology. Numerous laboratory and field techniques have been performed by researchers and scientists across the globe to assess its effectiveness. The technology has reached commercial status in many countries worldwide, however is yet to gain universal acceptance. The report presents a brief overview of nanoscale zero-valent iron and summarises our contemporary knowledge on nZVI aqueous corrosion and the recognized mechanisms for wastewater treatment. Various techniques of nZVI synthesis and methods to enhance the performance of nZVI, such as improving the aqueous mobility of nZVI are also discussed.

Keywords-zero-valent iron, wastewater remediation, aqueous corrosion, performance, mobility.

I. INTRODUCTION

A. Overview of Nanoscale Zero-valent Iron

Zero-valent iron is elemental metallic iron, and refers to the zero charge carried by each Fe atom. It acts a bulk reducing agent, converting oxidized materials – which may be toxic and soluble in water – into immobile solid forms, releasing soluble Fe^{+2} in their place, which further oxidizes to Fe^{+3} . This characteristic permits the use of ZVI for effective and reliable reduction of waterborne contaminants.

Engineered nanomaterials have great potential in remediation of polluted waters [1]. In comparison to conventional macroscale materials, nanomaterials exhibit significant improvements in surface area as a function of mass. Since a smaller mass of material can achieve the same objective, the consumption of both raw materials and energy is minimized with significant associated cost savings. Most importantly, owing to their colloidal size, subsurface deployment via injection is possible at almost any location and depth in terrestrial groundwater systems with rapid treatment of contaminants [2]. Nanoscale zero-valent iron is the most widely studied nanomaterial for wastewater mainly because of its cheap cost, environmental compatibility and high reactivity.

B. Basic chemistry for aqueous corrosion of iron

Metallic iron (Fe^0), also referred to as zero-valent iron, is highly prone to corrosion in aqueous media. Its corrosion occurs primarily through an electrochemical process, with

anodic and cathodic components. The anodic reaction involves the dissolution of Fe^0 (forming soluble ionic products or insoluble oxide/hydroxide) and is coupled with reduction of redox amenable species at the cathode. In natural waters, the primary components available for corrosion reactions are dissolved oxygen (DO) and water, with the former being thermodynamically favoured [3].

C. Environmental reactivity

During aqueous corrosion both Fe^0 and Fe^{2+} are an active source of $\text{Fe}^{3+}_{(\text{aq})}$, H_2 and various precipitates such as $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ and green rusts. It is these corrosion reactions and the product(s) thereof which are responsible for the reductive transformation and/or physical removal (sorption or enmeshment) of exposed chemical species. As surface precipitated iron oxide/hydroxide is initially porous, the material can develop a “core-shell” structure during the early stages of reaction with both sorption (at the oxide/hydroxide) and chemical reduction (at the metallic iron oxide/hydroxide interface) able to occur simultaneously [4]. Consequently, Fe^0 that is introduced to an environmental system (whether as granular or nZVI) will already have a film of surface oxide acquired directly after synthesis. Therefore, it is very clear that although this nanomaterial is referred to as being metallic, each particle exists in natural conditions with a thin but encapsulating layer of surface oxide ([5], [6]).

D. Recognised mechanisms

The most recognised mechanism by which Fe^0 and Fe^{2+} solid materials remove contaminants from groundwater is via chemical reduction, and typically requires the contaminant to be adsorbed or in close proximity (electronic range) of the iron surface. For the treatment of organic contaminants, such as chlorinated organics and polychlorinated biphenyls, removal generally occurs via the reductive degradation of the chemical, i.e. the contaminant is physically destroyed. In comparison, for the treatment of many heavy metals and radionuclides removal typically occurs via immobilization [7]. Considering the significant geochemical perturbation caused by nZVI injection, subsurface treatment zones are often highly metastable, and even a gradual reversion in groundwater conditions toward a pre-injection state may be enough for significant remobilisation to occur. This is a key issue which may limit the development of the technology.

II. SYNTHESIS OF NANOSCALE ZERO-VALENT IRON

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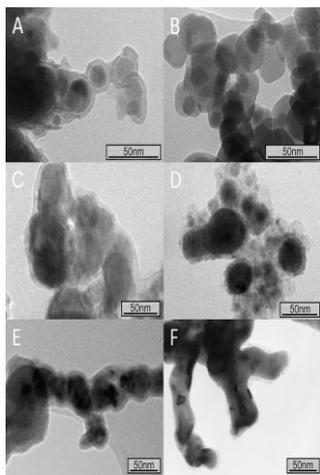


Fig.1 Transmission electron microscopy (TEM) images of different iron nanoparticles manufactured or purchased by the authors for this review. (A) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride [11]; (B) nanoscale magnetite, purchased from Sigma-Aldrich [12]; (C) NANO FER STAR, purchased from NANO IRON, s.r.o. [12]; (D) nZVI synthesised by the carbothermal reduction [12]; (E) nZVI synthesised by the reduction of aqueous Fe^{2+} using green tea polyphenols [13]; and (F) nZVI synthesised by the reduction of aqueous Fe^{2+} using sodium borohydride then annealed under vacuum (at least 10^{-6} mbar) at 500°C for 24 hours [14].

The various synthesis techniques are discussed below:

A. Thermal Reduction of Ferrous Iron

The carbothermal reduction of ferrous iron has been investigated as a potential method for the manufacture of cheap and functional nZVI (Fig. 1D). The method regards the use of thermal energy and gaseous reducing agents (H_2 , CO_2 , CO , etc.) produced during the thermal decomposition of carbon-based materials (carbon black, carbon nanoparticles, hollow carbon, ultra-fine graphite powder, etc.) to drive the reduction of iron oxide nanoparticles or aqueous Fe^{2+} [12]. With high surface area carbon an extremely cheap and readily available material, it is a cheap method for the manufacture of various nZVI physicochemical forms.

B. Electrolysis

With the requirement of only Fe^{2+} salt solution, a conductive substrate, a direct current and a method to disperse electro-deposited nanoparticles, electrolysis represents an extremely simple, cheap and quick method for nZVI synthesis. The only issue is determining appropriate methods for the dispersion of newly formed metallic nanoparticles at the cathode.

C. Synthesis from Polyphenolic Plant Extracts

The most environmentally compatible process developed so far for the synthesis of nZVI is the reduction of Fe^{2+} using polyphenolic plant extracts (Fig. 1E). This method involves the preparation of a polyphenolic solution by heating specific plant extracts (coffee, green tea, lemon balm, sorghum bran, etc.) in water to near-boiling temperature, extracting the supernatant and mixing it with a Fe^{2+} solution [14].

III. OPERATIONAL DRIVERS FOR WASTEWATER TREATMENT

The structure, geochemistry and hydrogeology of each polluted site are unique. Resultantly the strategy adopted for nZVI deployment must take into account various operational parameters. Variables that may be altered to optimise nZVI performance include the particle size range, mobility, reactivity and longevity, injection strategy and the material's ecotoxicity.

A. Size of nZVI

By providing the highest surface area for reaction, the very smallest nZVI would provide the best performance for contaminant removal. However, there exists the possibility that at this size range (< 20 nm) the resultant particles are too reactive to be useful for in situ environmental applications, with reactive exhaustion likely to be achieved in a very short timescale. So, for achieving optimal nZVI performance at any given site, there is a conceptual play-off between the reactivity and longevity of the material.

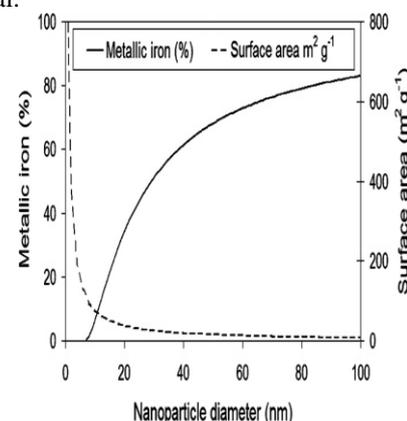


Fig. 2 Metallic iron content (%) and surface area ($\text{m}^2 \text{g}^{-1}$) calculated as a function of nanoparticle diameter. Both variables are calculated for perfectly spherical nanoparticles and are therefore not intended to directly represent empirical data.

B. Improving the Aqueous Mobility of nZVI

Limited mobility of nZVI explained by three primary mechanisms:

- (i) particle aggregation and subsequent gelation caused by poor colloidal stability;
- (ii) the formation of voluminous corrosion product precipitates from particle oxidation/corrosion; and
- (iii) particle removal from solution by interaction with subsurface components [15].

Various alternatives for improving the aqueous mobility of nZVI are

1) Surfactants:

Particle mobility and stabilisation may be improved through the use of surfactant and polymeric surface coatings. Applied to nZVI, the steric hindrances provided by such coating molecules counteract the electrical and dipolar attractions between particles and promote colloidal stability. This is only achieved when a sufficient mass of coating material or surfactant is present to form a complete micelle, resulting in its limited applicability.

2) Polyelectrolyte coatings:

As an alternative to surfactants, nZVI can be coated with high molecular weight polymers. Such an irreversible process provides a more appropriate method for increasing the hydraulic mobility of nZVI in subsurface systems. The polymer is physically or chemically grafted to the nanoparticle surface [16]. An additional benefit is that the polymer coatings may also act as an energy source to stimulate microbial activity, which may aid contaminant removal particularly in carbon limited environments. Two commonly studied materials are carboxymethyl cellulose and guar gum. Formed from cellulose and guar beans respectively, both polysaccharides are extremely cheap, non-toxic, natural water-soluble and biodegradable.

3) Improving the Mobility of nZVI for Remediation of Non Aqueous Phase Liquids

Researchers at the Kennedy Space Center (NASA) and the University of Central Florida have recently developed a new method for the treatment of non-aqueous phase liquids (NAPL) called "emulsified nZVI" (E-nZVI) [2]. It comprises of an agglomerate of nZVI particles packed into a droplet surrounded by surfactant and oil layer which forms an oil-liquid membrane. The hydrophobic membrane allows the dense NAPL to diffuse through, whereupon it undergoes reductive dechlorination by the E-nZVI in the aqueous phase. The protective membrane also allows the E-nZVI to move through the subsurface as a DNAPL, therefore improving its chances for DNAPL exposure; and operate in sites of high dissolved oxygen and/or salinity, with iron particles inside the membrane protected from corrosion. Encapsulating the nZVI in a hydrophobic membrane also protects the material from reactions with unwanted groundwater constituents such as inorganics that might otherwise act to decrease its reactive capacity.

IV. CONCLUSIONS

The global economy has experienced a nano boom over the past few decades. Theoretical and experimental evidences have proved nZVI to be highly versatile for wastewater treatment. Since the literature survey of different physicochemical forms of nZVI show discrepancies with respect to the testing parameters, a universal empirical testing framework is required. If a sound evidence of predictions of the operational drivers can be generated, nZVI will soon be at par with other wastewater remediation techniques.

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