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## Research article

## Synthesis, characterization and performance of high energy ball milled meso-scale zero valent iron in Fenton reaction

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## ABSTRACT

Understanding contaminant degradation by different sized zero valent iron (ZVI) particles is one important aspect in addressing the long-term stability of these particles in field studies. In this study, meso zero valent iron (mZVI) particles were synthesised in a milling time of 10 h using ball milling technique. The efficacy of mZVI particles for removal of phenol was quantitatively evaluated in comparison with coarse zero valent iron (cZVI) and nano zero valent iron (nZVI) particles. Phenol degradation experiments were carried out in sacrificial batch mode at room temperature independently with cZVI, nZVI and mZVI under varied pH conditions of 3, 4, 6, 7, 8 and 10. Batch experiments substantiating the reactivity of mZVI under unbuffered pH system were also carried out and compared with buffered and poorly buffered pH systems. mZVI particles showed consistent phenol degradation at circum-neutral pH with efficiency of 44%, 67%, and 89% in a span of 5, 10 and 20 min respectively. The dissolved iron species and residual iron formation were also measured as a function of pH. Unbuffered systems at circum-neutral pH produced less residual iron when compared to buffered and poorly buffered systems. At this pH, oxidation of  $\text{Fe}^{2+}$  produced a different oxidant Ferryl ion, which was found to effectively participate in phenol degradation.

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## 1. Introduction

Highly recalcitrant organic compounds released from various chemical and food processing industries are threatening the subsurface and the associated aquifers (Tisa et al., 2014; Weber et al., 2015; Islam et al., 2015; Erto et al., 2014; Nyenje et al., 2013). Permeable reactive barriers (PRBs) have become a standard technology for subsurface remediation with coarse zero valent metal, particularly iron, being the most commonly used reactive media (Ansaf et al., 2016; Erto et al., 2011; Moraci and Calabrò, 2010; Hashim et al., 2011; Liang et al., 2000). In contrast with soluble iron salts such as  $\text{FeSO}_4$ , coarse zero valent iron (cZVI) with particle size in the order of 0.2–5 mm possesses myriad advantages such as easy availability as a recyclable material with meager cost and ability to degrade both inorganic and organic contaminants (Pereira and Freire, 2006; Liu et al., 2015). cZVI also lessens the deleterious effects of  $\text{SO}_4^{2-}$  that can be expected post-treatment in  $\text{FeSO}_4$  system. However, cZVI application suffers from restraints such as large amount of secondary sludge production due to

precipitation of iron hydroxides and iron carbonates, constrained working pH, slow reactivity and low propensity to directly target the contaminants in the subsurface matrix (USEPAa, 2005). Moreover, cZVI particles are not easily injectable by simple direct push methods in contaminated sites and therefore sustainable remediation may not be possible.

Nano zero valent iron particle (nZVI), a successful alternative over the construction grade cZVI is proving its efficacy in environmental clean-up because of the size which is typically less than 100 nm (Kong et al., 2016; Xie et al., 2016; Chen et al., 2014; Jabeen et al., 2013; Gomes et al., 2015). Larger surface area, high density of reactive sites on its surface and the ease of dispersion via injection are the predominant factors for the success of nZVI particles though they are cost competitive (Tratnyek and Johnson, 2006). The severe limitation in the usage of nZVI is its quick agglomeration that deters the delivery of nZVI dispersions to the target contaminants in the subsurface (Ambika et al., 2016; Phenrat et al., 2007). Agglomeration decreases the specific surface area which in turn leads to reduction in reactivity (Nurmi et al., 2005). nZVI particles are prone to passivation even before injection especially when mixed with oxygenated water and hence transport of nZVI particles into the subsurface becomes a challenging task. It has been reported that

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the transport of unmodified nZVI is limited only to a few meters (Krajangpan et al., 2013). Addition of stabilizers to nZVI suspension is highly recommended to limit the Vander Waals forces of attraction that promote agglomeration and to achieve proper dispersion (Quinn et al., 2005; Saleh et al., 2007; Phenrat et al., 2011; Krajangpan et al., 2012).

Sun et al. (2007) used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A) stabilized nZVI for treating TCE contaminated aquifer which prevents agglomeration. Though no significant toxicity issues were reported by nZVI particles, addition of such stabilizers can impart toxicity and hence the application may not be really eco-friendly. Another important aspect that is commonly neglected is the method of production of nanoparticles. Knowing that conventional nZVI production using hazardous sodium borohydride and other reducing agents incurs huge cost, raises safety concerns, generates toxic gases and waste streams, it becomes imperative to investigate other alternatives for large scale production of particles equivalently efficient as nZVI (Li et al., 2006).

While lower reactivity and injection challenges are the drawbacks of cZVI, high reactivity, low selectivity and long term instability are the drawbacks of nZVI particles. Meso zero valent iron particle (mZVI) which falls between cZVI and nZVI can overcome the bottlenecks of cZVI and nZVI in field applications such as the size, mobility, stability against agglomeration, injectability and reactivity. It is anticipated that the effectiveness of ZVI technology can be maximized and made sustainable with the use of mZVI particles produced by mechanical means of ball milling. Ball milling can overcome the serious drawbacks of conventional chemical synthesis and simultaneously provide particle size in a mesoscale regime. The top down approach of ball milling, where bulk iron scraps are precisely broken down into convenient sizes, is particularly advantageous for large scale production of such particles. Specific surface area, being the only parameter that distinguishes the three forms of iron, can be easily controlled by milling time. The huge quantum of ferrous scraps from different industries can be effectively recycled for bulk production of mZVI particles.

In the present study, the aromatic toxic pollutant phenol is chosen as the representative organic compound. Phenolic compounds are released from various industries such as oil refineries, pharmaceutical plants, food processing and several other chemical plants (Ambika and Nambi, 2014; Nambi and Ambika, 2012; Tao et al., 2013). These persistent organic compounds cause a wide range of environmental and health problems and are recalcitrant to conventional physicochemical and biological treatment methods (Michałowicz and Duda, 2007). Advanced oxidation process such as Fenton's reaction is found to be an attractive technique that provides cost effective treatment in a short span of time (Zazo et al., 2005; Yusuf et al., 2012). The competence of mZVI particles in Fenton's advanced oxidation to degrade phenol is investigated and the results are compared with cZVI and nZVI particles. Surface morphology and size characterization of mZVI particles produced by ball milling technique, influencing key factors such as pH and oxidant generation and phenol degradation kinetics are elucidated in this study. There is only limited understanding of ZVI behaviour in unbuffered systems that can be expected in real conditions. Degradation experiments were therefore carried out in unbuffered systems and compared with buffered and poorly buffered systems. Obvious challenges during in situ treatment process with ZVI particles are formation of iron precipitates that may result in clogging of soil pores and limiting the mass transfer of the reactants to the ZVI surface. Iron speciation studies were done to compare the sustainable success rate of all three ZVI particles. The lacuna in understanding the reactivity of Ferryl species that are suspected to play a key role in the process at circum-neutral pH, is also untangled in the present study.

## 2. Experimental section

Commercial scrap iron, collected from the central workshop of IIT Madras, was initially washed with hexane and acetone followed by multiple washes with distilled and deionized water. The resultant particles were sieved for size 2 mm and stored for use as cZVI particles. The sieved cZVI particles were further reduced in size by grinding them in a high energy planetary ball mill (Fritsch P5) with iron-ball ratio as 10:1 as per standard protocols. After milling for 10 h, the resultant particles, henceforward termed as meso ZVI (mZVI) were stored in glass vials with ethanol and in zip-lock cover to avoid further oxidation. Commercial Nanofer 25S (Nano Iron, Czech Republic) was designated as nZVI particles. Surface area and size distribution of the resultant particles were determined by DLS particle size analyzer (Microtrac Bluewave, M/s. Microtrac Inc., USA). The surface morphology was studied using scanning electron microscope (SEM) equipped with a field emission gun (JEOL, JSM-6380, Japan). The spot elemental analysis of cZVI, mZVI and nZVI particles were carried out using SEM equipped with an energy dispersive X-ray analyzer (EDAX; FEI, Quanta 200, Czechoslovakia). X-ray Diffraction spectroscopy (XRD) data was collected for purified particles to ensure ZVI formation using Copper K alpha radiation with Lynx detector at an operating voltage of 35 kV and current of 25 mA supplied by BrukerAxs, USA (model D8 Discover). The AT-FTIR spectra of mZVI samples were recorded in the transmission mode at room temperature using PerkinElmer Spectrum Model 100 in the spectral range of  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  with resolution of  $1.0\text{ cm}^{-1}$ .

Phenol degradation experiments were carried out in sacrificial batch mode at room temperature as two-fold: a) independent studies with cZVI, nZVI and mZVI under varied pH conditions of 3, 4, 6, 7, 8 and 10 in order to compare the effectiveness of three different particle sizes and clarify the most effective particle for phenol degradation and b) systematic studies of mZVI reactivity in unbuffered pH system in comparison with buffered and poorly buffered pH system. In the first set of batch experiments, initial phenol concentration was varied between 5 and 60 mg/L. ZVI concentration was maintained as 20 mg/L. No effort was taken to increase the dosage of ZVI, as it is expected that the excess concentration could decrease the density of surface adsorbed  $\text{H}_2\text{O}_2$ . The experiments were carried out in 100 mL glass reactors placed on rotary shaker at a stirring velocity of 150 rpm for 60 min. At selected time intervals, aliquots (20 mL) were withdrawn and the filtered samples were analyzed for phenol concentration. Glass syringe filters of  $0.45\text{ }\mu\text{m}$  were used for cZVI and nylon membrane was used for mZVI and nZVI particles. The concentrations of residual  $\text{Fe}^0$  and total Fe in solid and aqueous phase were measured as represented in supplementary material. Both solid and aqueous phase  $\text{Fe}^{2+}$  were analyzed and  $\text{Fe}^{3+}$  was found by subtracting the  $\text{Fe}^{2+}$  concentration from total Fe concentration in respective phases. Mass balance was checked by comparing the measured total iron with initial ZVI concentration. Total organic carbon (TOC) analysis was done to ensure complete oxidation of phenol without the formation of intermediates.

The second set of batch experiments were conducted with initial phenol concentration of 5 mg/L, mZVI concentration of 20 mg/L with 3% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) addition. Parallel control experiments were performed without any form of mZVI particles and  $\text{H}_2\text{O}_2$ . The reactions of phenol with mZVI were studied by adding buffers (buffered, System A), without adding buffers (unbuffered, System B), and condition where pH was adjusted to its initial value at start of every use (poorly buffered, System C). The following solutions served as buffers at various pH: Phosphate (pH 3, 8) Sodium acetate (pH 4), Carbonate (pH 6, 7) and Ammonium (pH 10). All buffer concentrations were 1 mM unless specified. The

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