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Assessment of meso scale zero valent iron catalyzed Fenton reaction in continuous-flow porous media for sustainable groundwater remediation

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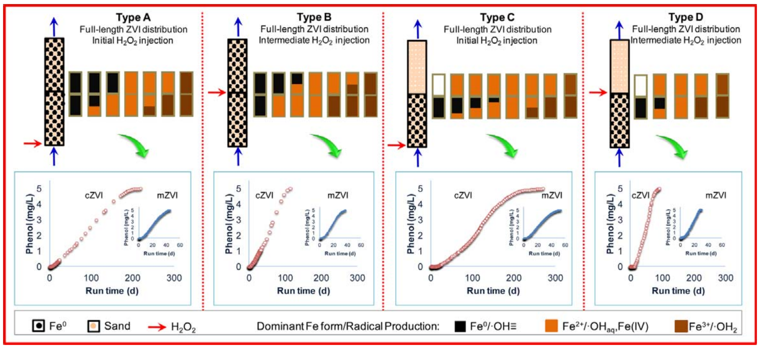
GRAPHICAL ABSTRACT



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ABSTRACT

Removal of toxic organic compounds from the subsurface with meso zero-valent iron particles (mZVI) emplaced in porous media overcomes the concerns associated with *in situ* groundwater remediation technologies. The results of the continuous column experiments with mZVI is first of its kind and provide a sound basis on Fenton reaction mediated remediation of contaminated groundwater. Columns with different configurations varying in ZVI distribution and location of H_2O_2 were investigated for factors influencing sustainable phenol removal. The performance of columns were in the ascending order of C > A > B > D where columns A and B had full-length ZVI distribution, C and D had half-length ZVI distribution, with H_2O_2 injection at initial conditions in A and C and at intermittent points in B and D. Conditions maintained in column C resulted in 61–84% more interaction between Fe^{2+} ions and H_2O_2, promoted continuous corrosion, invigorated effective Fe^{2+}-Fe^{3+} cycling, retained active iron surface area and circumvented precipitation and secondary sludge production. The breakthrough curves showed that mZVI particles extended the active corrosion stage by 5–8 times and resulted in 3–7 times increment in mg phenol removed/mg mZVI along with 80–99.8% utilization of mZVI. Additional sand-only columns proved that Fenton's oxidation in *in situ* porous media can be improvised by 14–34% without incumbent addition of ZVI particles.

1. Introduction

Application of zero-valent iron (ZVI) in permeable reactive barriers (PRB) as a method for *in situ* ground water remediation suffers from practical constraints such as feasibility, longevity and sustainability [1–4]. ZVI particles of sizes ranging from coarse to nano have been studied as catalysts in Fenton's oxidation of several groundwater contaminants including toxic organic compounds such as phenols [5–8].

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Phenol is relatively common in aqueous effluents of many chemical and pharmaceutical industries thus posing an environmental threat. Numerous studies have demonstrated phenol degradation in batch aqueous systems in the absence of porous media representing traditional Fenton's chemistry of low pH, low oxidant concentration and soluble iron (Fe^{2+}) catalyst [9]. Extrapolation of results from batch aqueous systems can deliver misconstrued data for dynamic field conditions expected in PRBs. Continuous flow aqueous systems with porous media closely address utilization of iron, active corrosion stage, formation of sludge, life-span of system and concentration of Fe^{2+}/Fe^{3+} ions into the final effluent. Residence time and half-lives measured through continuous flow aqueous systems with porous media generally are more reliable than half-lives and residence time calculated from batch studies [10,11]. Also, reaction products such as secondary precipitates tend to accumulate in batch systems whereas continuous flow experiments may remove the precipitates out of the reactive medium, a condition more representative of field PRB operation [12].

Continuous flow aqueous systems with porous media are also expected to overcome the challenges associated with *in situ* application of Fenton's process such as changes in iron surface morphology over time, precipitation of iron (oxy) hydroxides [13,14], surface passivation of ZVI, higher sorption of contaminants to non-reactive sites, delaying of electron transfer by iron oxide layers [15], high concentration of dissolved iron salts in the treated sample and formation of large amounts of iron oxide sludge. Limited work has been done till date on continuous flow aqueous systems with porous media depicting high oxidant concentration and circum-neutral pH as in field conditions. Table 1 summarizes the past continuous column investigations with respect to the form of catalyst, target pollutants and removal efficiency. As shown in Table 1, most of the studies focused only on pollutant removal but significant factors such as length of active corrosion stage, effective utilization of ZVI ions and unreacted iron contributing to secondary sludge production were neglected. It is also evident that many studies have employed traditional catalysts such as acidified iron or iron salts which immobilize soon after their injection and render an ineffective *in situ* remedial application. The table also shows that only modified Fenton's catalysts which can maintain iron in soluble form and simultaneously generate free hydroxyl radicals ($\cdot OH$) under neutral pH are effective in degrading the contaminant of interest. Hence it becomes imperative to i) choose an approach differing from traditional Fenton's reaction either by adding a co-catalyst or changing the form and size of catalyst and enhance complete utilization of the catalyst and ii) study the length of active corrosion and effective use of ZVI particles so as to eliminate secondary sludge production.

In field installations, sand sized particles of ZVI are selected and mixed with sand in order to reduce the quantity of ZVI usage. Coarse zero-valent iron (cZVI), the most common media used so far, has low specific surface area of 1–2 m^2/g [16] and is difficult to inject in contaminated sites; nano zero-valent iron (nZVI) possess a higher specific surface area but tend to agglomerate and form larger particles that settle into aquifer pores. Also, subsurface mobility of nZVI is limited by particle-aquifer grain attachment and more commonly by particle-particle agglomeration [17]. It is therefore necessary to select a particle size that has higher surface area and affords good hydraulic conductivity (at least five times or more than the surrounding aquifer). In this work, an intermediate particle size meso ZVI (mZVI) that falls in the range of 12–35 μm was chosen as reactive media for the Fenton's process. mZVI particles possess higher surface area and do not agglomerate as nZVI, hence only a lower total iron mass would be required in the treatment system. The earlier work by the authors proved the efficacy of mZVI particles in degrading phenol. 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. It was observed that mZVI mediated unbuffered systems showed consistent phenol degradation at circum-neutral pH with the help of radicals and non-radicals generated [5]. The authors have confirmed from the batch experiments that at circum-neutral pH of 7, $\cdot OH_{aq}$ generation would be quick compared to other radicals and the non-radical $(Fe^{IV}O)^{2+}$ formed as an intermediate has the capacity to replace the oxidising power of $\cdot OH$ radicals. However, quenching of radicals is a challenging process in continuous flow porous media systems unless special equipment with data acquisition sensors are attached to the columns. The half-life time of the radicals being very short, verifying and characterizing the radicals becomes difficult in continuous column experiments.

The current focus of the study was to investigate the emplacement of mZVI particles in porous media and its utilization in *in situ* phenol degradation via Fenton's reaction at circum-neutral pH of 7. Significant portion of this study has been dedicated to gauge the influence of the distribution of different types of ZVI and the location of H_2O_2 in continuous aqueous column studies. As the thickness of field PRBs depend upon the distribution and uniformity of ZVI particles, different configurations with respect to ZVI distribution both along the full length of the column and up to half the column length were studied. In conventional Fenton's process, the reaction between H_2O_2 and Fe^{2+}/Fe^{3+} suffers from major drawback of limited life time of H_2O_2 and its consumption for non-target purpose. In the present study, H_2O_2 addition was made at the beginning and at an intermediate point in the columns to understand if an optimal dose of H_2O_2 would suffice the entire degradation process without additional requirement of H_2O_2. The present study also tried to understand if the dissolved iron emerging from the system is capable of restoring phenol removal by mere addition of $H_2O_{2.}$ Sand-only columns (without addition of mZVI) were investigated to bring out the contribution of dissolved iron in phenol removal.

The column experiments were aimed to understand the influencing parameters in phenol degradation by comparing systems with more residence time/contact area (with mZVI particles spreading throughout the entire column) and systems with less residence time/contact area

Table 1
Summary of investigations on column experiments with respect to iron catalyst type and performance.

Catalyst	Target compound	Column dependent/Porous Media	Optimal performance	pH	Flow rate (mL/min)	References
Acidified iron (II)	Chlorinated Solvents	Columns/Soil	100% adsorption to soil, poor performance	5–7	Not mentioned	[20]
Nanofer Star nZVI	Salmonella typhimurium phage 28 B	Columns/Glass beads	36.8% virus reduction	7.75	2	[21]
ZVI	Lead	Columns/Soil	97–75% removal	5	5, 10, 15 and 20	[22]
Fe co-catalysed by Al	Isopropyl alcohol	Columns/Fe/Al catalyst	99.9%	< 3	5.5	[23]
Swarf (General purpose steel)	Azo dye Acid Red 18.	Glass Column/Swarf	26.4%	3.0	0.01	[24]
Fe^{2+}	BTEX compounds	Bubble column reactor	84–97% removal	3	2	[25]
Modified Fenton's catalyst	VOC	Column/Soil	13.6% adsorption to soils, good VOC removal	Wide pH	Not mentioned	[26]
Iron	PAH	Column/Soil	hj36–54% removal	3	Not mentioned	[27]