MOBILIZATION OF NANO ZERO VALENT IRON (n-ZVI) PARTICLES IN SUBSURFACE

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Abstract

Mobility and stability of nano Zero Valent Iron (n-ZVI), in subsurface, for in-situ remediation of groundwater, has been an issue of concern. This may be enhanced by adding various surfactants to n-ZVI slurry. This study was conducted to determine the effect of surfactants like Poly (Acrylic Acid) (PAA), anionic part of Sapindus mukorossi (reetha) extract and Tween 20, at different volume percentages, on the stability and mobility of n-ZVI slurry, through sand and loamy sand column. Results indicate that PAA-modified n-ZVI slurry had maximum mobility and stability through both the soil column followed by reetha-modified and Tween 20 modified n-ZVI slurry.

***Index Terms**: Nano Zero Valent Iron (n-ZVI), Ground Water, In-Situ Remediation, Polyelectrolytes, Surfactants.*

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1. INTRODUCTION

In the recent years there has been an increasing interest in the in-situ remediation of groundwater contaminated with chlorinated solvents and heavy metals by direct injection of nano zero valent iron (n-ZVI) [1-5]. The in-situ injection technology is more advantageous as compared to the traditional passive processes like “funnel and gate” or the permeable reactive barrier (PRB) processes [6]. They react with contaminants in the source zone and substantially reduce remediation cost and time [6]. n-ZVI have high reactivity with contaminants due to their high surface volume and are relatively resistant to fouling from groundwater contaminants [7, 8]. However, high reactivity alone is not enough to appoint this promising technology as a good in-situ remediation tool. Simultaneously, n-ZVI needs to be properly dispersed in water for it to migrate through the water-saturated media to the contaminated zone. With relatively high values of ionic strength of groundwater reduction of electrostatic repulsion between particles is favored and colloidal agglomeration of n-ZVI in water is enhanced [8]. The agglomeration of this n-ZVI is a key technical failure this promising technology faces, due to which the delivery of the n-ZVI to contamination sources in soil and groundwater offers a great challenge [9-10]. It is due to the direct inter particle interactions like van-de-Waals force and magnetic interactions these nano-irons agglomerates which reduce the specific surface area and interfacial free energy, eventually reducing its reactivity [10].

In order to overcome the drawback in the transport property of n-ZVI a common strategy to increase the repulsive electrostatic forces have been studied and implemented. The use of certain polymeric materials to stabilize n-ZVI in water is reported in several studies. The use of a wide variety of polymers including poly acrylic acid (PAA), polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A), polyaspartate (PAP), Tween 20 and biopolymer such as soy proteins, starch, and carboxymethyl cellulose (CMC) [9-13, 25].have been reported so far. PAA is the first polymer used to stabilize the dispersion of n-ZVI for the field remediation whereas CMC has been recently introduced [14]. By the virtue of the presence of a polar anchoring groups (e.g., –COOH, –OH, –C O) and a stabilizing hydrocarbon chain in the polymers, it can act effectively in stabilizing n-ZVI in water. The anchoring group gets attached onto the surface of n-ZVI and the long hydrocarbon chain can move freely in water to obtain various desired configuration. When these flexible chains overlap the electrostatic and steric repulsion between particles is produced and thus stabilizes the particle under certain conditions [15]. Saponin is one of the most commonly known plant based surfactants. Saponin is largely found in plants like Sapindus mukorossi, soyabean [16], Quillaja bark [17] and Fagonia indica [18].

In this paper, we explore the use of three surfactants namely Polyacrylic Acid (PAA), Tween 20 and anionic extract of Reetha (Sapindus mukorossi) in order to improve the motility of nano iron slurry in porous media as compared to n-ZVI without surfactants along with the stability of prepared nano iron slurries.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals used in this work are AR grade unless otherwise specified. Except for anionic extract of reetha, the other two surfactants are commercial products. Polyacrylic acid (PAA) was procured from Otto Chemika; Tween 20 (Polyoxyethylene sorbitan monolaurete) was obtained from Sigma Life Science. The chemicals for the preparation of nanoiron particles were FeSO4·7H2O from Loba Chem and NaBH4 from Loba Chem. The Cation exchange resin used for preparation of anionic reetha extract was DOWEX 50 X8(Na) obtained from Loba Chem.Sand and loamy soil were obtained form the local areas of Dhanbad. They were sieved through 2mm sieve, washed with distilled water and heated in the oven before use.

2.2 Iron Based Nanoparticles

Synthesis of nanoscale zerovalent iron particles was achieved by adding 0.04 mol/L $FeSO_4 \cdot 7H_2O$ aqueous solution drop wise to a three-necked flask containing 0.08 mol/L $NaBH_4$ aqueous solution at ambient temperature [19]. The process was performed in Ar atmosphere. Ferric iron was reduced by borohydrate according to the following reaction [20]:

$$Fe(H_2O)_6^{2+} + 2BH_4^- \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow$$

Synthesized iron particles were deposited for 4 h in Ar atmosphere, and washed with ethanol. Then they were washed with deionized water after deposition for 3 h. After the preparation of nanoiron particles, the desired amount of the selected surfactant were added to the nano iron suspension and mixed vigorously.

Table 1: Recipes for different nanoiron slurry

Test No.	Type of Surfactant	Amount of surfactant added (vol %)
1	PAA	1
2	PAA	2
3	PAA	3
4	PAA	5
5	Reetha Extract	1
6	Reetha Extract	2
7	Reetha Extract	3
8	Reetha Extract	5
9	Tween 20	1
10	Tween 20	2
11	Tween 20	3
12	Tween 20	5

2.3 Preparation of Anionic Extract of Reetha

The Reetha (Sapindus trifoliata) seeds were soaked in distilled water (0.5 kg Reetha seeds/L) for two days and mashed. The extract was filtered first through a cotton cloth followed by a combination of glass–fiber prefilter and a 0.45 mm Millipore GF-C filter. Through cation-exchange column containing DOWEX 50 X8(Na) resin 50mL of the bulk Reetha extract was passed. The cation exchange columns were eluted using 50mL of Milli-Q water each, to obtain the cationic fractions of the Reetha extract [21].

2.4 Stability of Nanoiron Slurries

The stability of various nanoiron slurries was visually evaluated by gravitational sedimentation of nanoiron within. 100ml of well mixed slurry was poured into a 100 ml of glass measuring cylinder and observations were made after every hour. A control test of nanoiron slurry with no surfactant was also carried out. Test were carried out in batches of four with different concentrations of surfactants (1%, 2%, 3% and 5%) (Table1).

2.5 Column Experiments

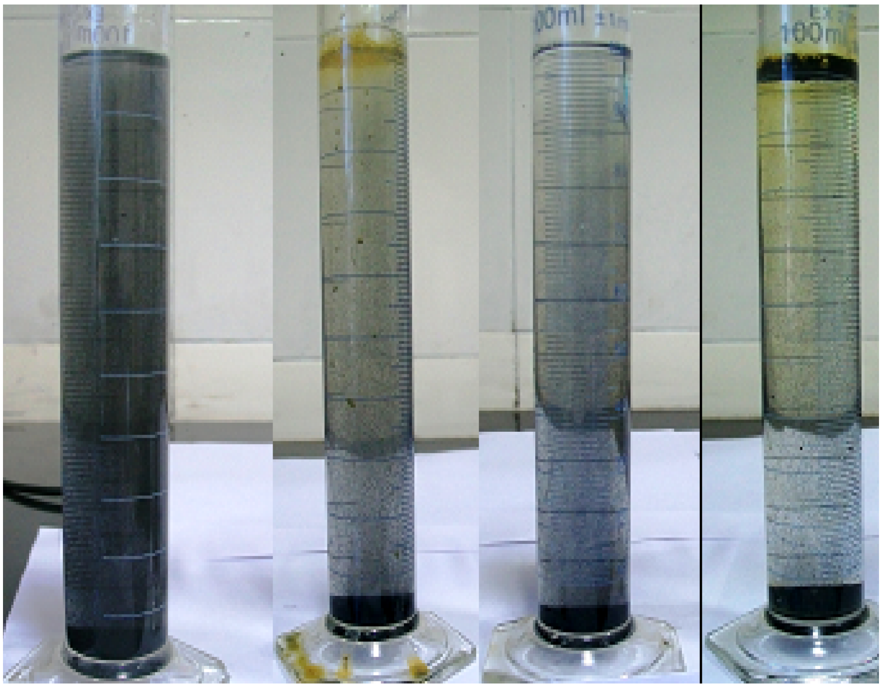
Glass burette columns were used to compare the transport behaviour of different nanoiron slurries. The experimental set up was similar to that of Schrick et al. [11] where the column ends were packed with glass wool plugs to prevent the drainage of both soil and iron particles. Columns were filled with sandy loam soil up to the height of 15 cm before the addition of nanoiron slurries. The experiments were carried out in a batch of four for all the different concentrations of surfactants and a control which comprised of only nanoiron particles. After the tests were done for sandy loam, test with sand were carried with similar experimental setup and conditions.

In the column studies, the stock solution of suspended iron nano particles (3mg/mL) were introduced to the top of the column continuously and an eluent was collected in 2ml fraction. For the analysis of this eluent 3mL of aqueous ortho-phenanthroline (Aldrich, 3mg/mL) solution was added. Complex formed was measured at 508 nm [22]. If PAA used as surfactant the analysis is carried out as follows: 2.0 ml of ortho-phenanthroline (3 mg/ mL) aqueous solution and 1 mL of 6 M HCl are mixed to each aliquot and the mixture is centrifuge at 14000 rpm for 30 minutes. The amount of iron in the supernatant is determined by absorbance at 508 nm.

3. RESULTS AND DISCUSSIONS

3.1 Stability of Nanoiron Slurries

The settling behaviour of various nano iron slurries prepared by adding different surfactants were observed for a period of 6 hours where observations were made after every hour. A distinctive result was observed after four hours which can be seen in the figure 1. For the nanoiron slurry without any surfactant almost all the nano iron particles settled down accompanied by the formation of thin lumpy layer at the top of the column. For the nanoiron slurry with Tween 20, no appreciable stability was observed. The anionic extract of reetha showed a slight improvement in stability but a yellowish colour layer was formed on top of the column which is due to oxidation of the nanoiron. A satisfactory result was observed with PAA where the n-ZVI was still found in a dispersed state with no sign of oxidation. This observation is in good agreement with report of other researches [11, 23-24] where it was reported that PAA is a good agent for enhancing the motility of n-ZVI. The effective use of other anionic surfactants like PV3A and sodiumdoceyl benzensulfonate has also been reported [13, 26]. Bearing in mind the highest level of stability offered by PAA the column studies were carried on.



Surfactant: PAA (2%) Reetha Extract (2%) Tween 20 (2%) No surfactant

Figure 1: Effect of surfactants on the dispersion of n-ZVI after settling for 4 hours.

3.2 Column Studies

The column studies are carried out to measure the effects of surfactants on the overall particle transport. For n-ZVI, with no surfactant, only aqueous solution passed through the sandy loam and sand column, with the aggregated mass of nanoiron retained on the top of the column. The immobility of these nanoiron particles was mainly due to the instant agglomeration of the nanoparticles in absence of surfactants. As for n-ZVI with PAA (2%), it was observed the nanoiron particles easily passed through the sand as well and sandy loam column, with the sandy loam column offering more resistance than sand. Figure 2 and 3 gives the effect of the three surfactants PAA, reetha extract and Tween 20 on the flow of n-ZVI through both the columns as per the concentration of n-ZVI eluted from the column in constant volume. The efficiency of the surfactants followed the trend: PAA, anionic extract of reetha and Tween 40. Similar kind of trend was also observed in Schrick et al., 2004 where only 40% of Fe/PAA injected were retained in the soil columns. The flow rate of the slurries were also recorded with the Fe/PAA showing the highest flow rate of 7.5 ml/min through the sand column as compared to 6.0 ml/min through the sandy loam column. Similarly, the Reetha extract and Tween 20 modified n-ZVI observed the flow rate of 3.5ml/min and 2.3 ml/min through the sand column, respectively and 2.0 ml/min and 1.5 ml/min through the sandy loam column, respectively. The sand column observed a flow rate of Fe/PAA >10 ml/min and 1-5 mL/min in sandy loam column. Both the flow rate and the concentration of eluted nanoiron are observed to be high in case of sand column as compared to sandy loam column. The main reason being that the sandy loam has 15-20% silt, due to which, the particles impede the flow of n-ZVI slurry through the column [11]. Previous works by researchers have confirmed that PAA binding to n-ZVI creating highly negative surfaces effectively reduces the filtration removal by aquifer materials [11, 23-24]. Based upon this work, the results confirmed that the transport efficiency of n-ZVI in porous media can be enhanced by the increase of the PAA dosage.

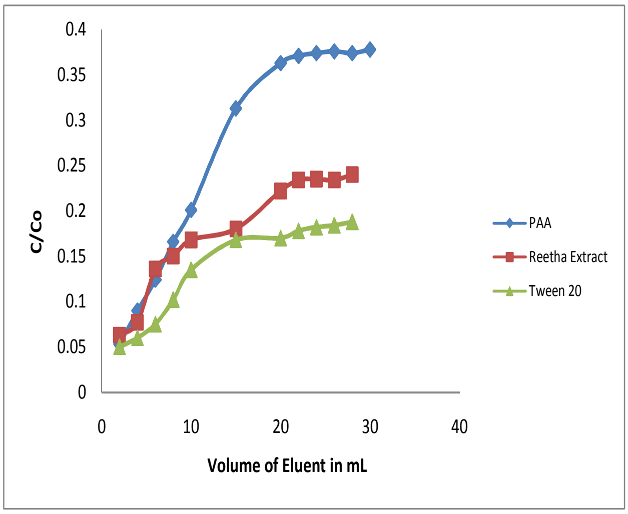


Figure 2: Effect of surfactant on the n-ZVI concentration eluted from soil column.

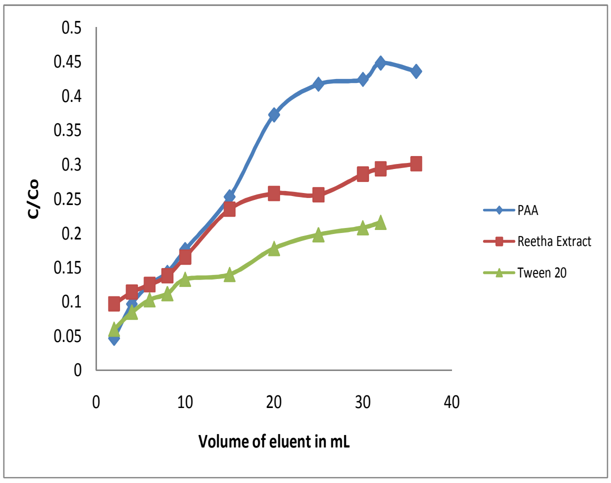


Figure 3: Effect of surfactant on the n-ZVI concentration eluted from sand column.

CONCLUSIONS

The establishment of the stability of n-ZVI slurry to enhance its motility through soil is very important for in-situ remediation of groundwater. The addition of PAA would greatly enhance the stability of nano iron slurry followed by reetha extract and Tween 20. The transport behaviour of n-ZVI is very different in different soil depending largely on their texture ad characteristics. In the real groundwater and soil condition the interception of n-ZVI is equally important for remediation purpose. Hence to minimise this interception of n-ZVI slurries due to various soil particles by the use of surfactants can show positive results in enhancing the motility of n-ZVI slurry.

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