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Transport and retention of polymer-stabilized zero-valent iron nanoparticles in saturated porous media: Effects of initial particle concentration and ionic strength

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ABSTRACT

This study investigated the transport and retention of polyacrylic acid and polyvinylpyrrolidone stabilized zero-valent iron nanoparticles (PAA-ZVIN and PVP-ZVIN) in saturated porous media. The transport experiments were conducted in sand packed columns. The breakthrough curves (BTCs) and retention curves of ZVIN were analyzed. Results of transport experiments showed that increasing initial particle concentration and ionic strength led to a decrease in ZVIN transport. The zeta potentials and hydrodynamic diameters of PAA-ZVIN were apparently more negative compared to PVP-ZVIN. Results indicated that some mechanisms such as aggregation, ripening, and surface roughness had considerable impact on ZVIN retention in porous media.

1. Introduction

Zero-valent Iron Nanoparticles (ZVIN) have recently attracted a great deal of attention in environmental clean-up issues due to their high surface area resulting in high reactivity with various hazardous compounds (e.g. nitrate, Chromium (VI), reactive dyes, metronidazole, arsenic (V)) [1–5]. In addition, their cost-effective features and low toxicity danger levels have created a great interest in utilizing the above-mentioned particles in environmental remediation [6,7]. In the past, remediation techniques related to zero-valent iron dealt with permeable reactive barriers (PRB) against the path of contaminant flow. It is noteworthy to say that such remediation approach was rather expensive and suffered from several operating limitations. Subsequently, the direct injection of ZVINs in subsurface environments with the aim of reacting in the contaminating source was realized to be a proper solution to overcome the limitations of the latter technique [8].

Generally, before applying ZVIN to the in situ remediation method, it was hypothesized that ZVINs in nano-sized particles are able to pass successfully through porous media containing a wide range of pore sizes from nanometer to micrometer without any attachment and deposition. However, some column experiments have reported that bare or unmodified ZVINs are either immobile or at least low mobile at subsurface environments [9]. Some research states that bare ZVIN particles are prone to rapid agglomerating which leads to a decrease in their reactivity and mobility [10–12]. The agglomeration of ZVIN particles is attributed to the magnetic attraction forces between particles [13]. It is likely that increasing repulsive forces between nanoparticles is an effective strategy for providing a stable ZVIN suspension. In addition, limiting or preventing aggregation and settling of nanoparticles are vital prerequisites for particle transport.

Up until now, plenty of stabilizers like polyacrylic acid (PAA) [14], carboxymethyl cellulose (CMC) [15], zeolite [16], and polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A) [17] have been used to enhance repulsive forces and improve colloidal stability of ZVIN. The extent of repulsive forces imposed by each adsorbed polymer on ZVIN depends on the density of charges and its concentration [18]. Among the afore-mentioned polymers, the first polymer applied for stabilizing a ZVIN suspension was PAA. One of the studies regarding the effect of PAA on ZVIN transport was reported in 2004 [19], where Mallouk et al. stated that PAA can play the role of a vehicle to enhance the transport of ZVIN in porous media. Another research on PAA-ZVIN transport conducted by Raychoudhury et al. [20] stated that PAA-ZVIN could pass easily through the sand packed columns. Although PAA was used as a stabilizer of ZVIN, the effects of polyvinylpyrrolidone (PVP-25K) on stabilization of ZVIN suspension were not discussed fully.

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To the best of our knowledge, no article has so far reported PVP-ZVIN transport in porous media. In addition, based on our research, no comparison between the transport of PAA-ZVIN and that of PVP-ZVIN in porous media has been carried out.

There are several physical factors such as the initial particle concentration [21], the flow velocity [22], the grain size of porous media [23], the depth of porous media [24], as well as some chemical factors such as the ionic strength and the cation types [25], the pH of groundwater [26], and the organic matter [27] which affect a nanoparticle transport in subsurface environments. Among these factors, the initial concentration of nanoparticles is a key factor on particle transport because some mechanisms like aggregation are caused by the interaction between particles at high concentrations. However, most studies have been carried out at low particle concentrations (30 < mg/L), while particle concentration in a typical groundwater remediator is high. In addition, numerous studies have examined particle transport in either distilled water or low ionic strength, which are irrelevant to natural groundwater chemistry [11]. In most studies on groundwater, the concentration of monovalent cations (e.g. Na^+ and K^+) and divalent cations (e.g. Ca^{2+} and Mg^{2+}) are approximately 1–10 mM and 0.1–2 mM, respectively [25].

Although many studies have been conducted on stabilized-ZVIN transport, the studies which focus on transport and retention and the mechanisms affecting ZVIN transport and retention through porous media are taking rudimentary steps. The objective of this study is, therefore, to investigate the transport and retention behavior of two polymer-stabilized ZVINs which have shown a perfect function in the case of environmental clean-up. Especially, the influence of initial particle concentrations and different ionic strengths on ZVIN transport and retention were evaluated. Therefore, particle transport and retention were carried out by means of injecting both of the stabilized ZVIN suspensions at various initial concentrations (0.1, 0.5, and 2 g/L) and a wide range of ionic strengths (1, 10, and 100 mM NaCl plus 1 mM $NaHCO_3$) in some saturated sand columns. Finally, this research provides some essential information concerning the dominant mechanisms influencing ZVIN transport and retention in sand packed columns applicable for in situ remediation.

2. Experimental

2.1. Chemicals

Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was purchased from AppliChem Co., while hydrogen peroxide (H_2O_2 35%wt) was prepared from Acros. Polyacrylic acid (M.W. = 750,000) and methanol (HPLC grade) were obtained from Sigma–Aldrich. polyvinylpyrrolidone (M.W. = 25,000), sodium borohydride (>98%, $NaBH_4$), sodium chloride, acetone (99.5%), concentrated hydrochloric acid, sodium dithionate, sodium bicarbonate and sodium hydroxide were all purchased from Merck Co. All chemicals used in this research were of chemical grades and all solutions were prepared using deionized water (DI).

2.2. The synthesis of bare and polymer-stabilized Fe^0

The synthesis procedure for bare-ZVIN was a modification from Liu et al.'s [28] method. In short, 20 mL of $NaBH_4$ solution (1.05 M) was slowly added in the constant rate of 3 mL/min under N_2 atmosphere using a dropping funnel to 200 mL of a water–methanol solution (30%, v/v of methanol) of $FeSO_4{\cdot}7H_2O$ of 0.065 M concentration and was mixed vigorously for 30 min by a magnetic stirrer at an ambient temperature. After adding the entire $NaBH_4$ solution, the mixture was stirred for an extra 30 min to help control the particle size. During the experiment, ferrous iron was reduced by sodium borohyride as a reductant to form black particles immediately. The black particles were collected by vacuum filtration and then washed three times by DI water and acetone. The prepared particles were then dried overnight under vacuum condition.

For polymer-stabilized ZVIN, 100 mL aqueous solution of $FeSO_4{\cdot}7H_2O$ (0.065 M) was added to 100 mL of polymer solution of 0.5% (w/v) of PAA and PVP and stirred vigorously by a magnetic stirrer for 30 min. The next steps in this process were similar to the one described above.

2.3. The characterization of nanoparticles

The SEM images of bare ZVIN, PVP-ZVIN and PAA-ZVIN were obtained by scanning electron microscope (SEM, S 4160, Hitachi, Japan) to assess the size and the morphology of particles. To study crystalline characteristics of ZVIN, XRD patterns of nanoparticles were obtained by X-ray powder diffraction (XRD, PW 1840, Hitachi company) at $2\theta = 15^\circ$–80°. Additionally, Cu Kα radiation source was applied. The zeta potential and hydrodynamic diameter of synthesized nanoparticles were determined by Dynamic Light Scattering (DLS, Zetasizer, Malvern, UK). It is worth mentioning that a suspension at pH, 7.5 and IS = 1–100 mM plus 1 mM $NaHCO_3$ with 0.2 g/L concentration of each ZVIN was prepared to determine zeta potentials and hydrodynamic diameters of ZVINs.

2.4. Colloidal stability

The sedimentation test was performed in quiescent condition to assess the colloidal stability of bare and polymer stabilized-ZVINs in aqueous solutions. In this regard, absorbance of 0.2 g/L of ZVIN suspension with 1 mM concentration of NaCl plus 1 mM $NaHCO_3$ and pH 7.5 at room temperature was measured via a UV–visible spectrophotometer (APEL-PD-303UV) at 508 nm wavelengths. In addition to using spectrophotometer, some images were taken using a camera in different time intervals. Then, pictures of each ZVIN suspension were compared in order to evaluate the colloidal stability of synthesized ZVIN.

2.5. Porous media

To investigate the behavior of stabilized-ZVIN, the sand with definite grain size distribution and specific gravity of 2.68 g/cm^3 was selected as a porous media. The results of X-Ray diffraction (XRD) analysis of sand showed that it consisted of a significant amount of quartz with a small amount of dolomite and goethite. In addition, zeta potentials of sand grains were measured using DLS at different IS from 1 to 100 mM. The sand was sieved gently by means of a stainless steel U.S. 30–50 Mesh to reach the size range between 0.3 and 0.6 mm. Because the metal oxides coating on the surface of the sand tends to influence the surface charge of the sand [29], the sand grains were washed by DI water, and then soaked in 0.1 M dithionate sodium solution (0.1 M $Na_2S_2O_4$) to eliminate metal oxides [30]. In order to remove organic impurities, the sand was immersed in 5% hydrogen peroxide solution (H_2O_2 5%) for 3 h, and then washed by DI water and kept in hydrochloric acid (12 N) during the night. Finally, the sand was washed by DI water to equilibrate pH.

2.6. Transport experiments

The effects of initial nanoparticle concentration and ionic strength of solution on ZVIN transport and retention were studied in saturated porous media. Transport experiments of bare and polymer-stabilized ZVINs were carried out in saturated sand packed columns with 10 cm of length and 2.5 cm of inner