CHAPTER 8

Challenges in Groundwater Remediation with Iron Nanoparticles: Enabling Colloidal Stability

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8.1   Introduction

Zero-valent iron (ZVI)-based remediation is an attractive treatment option as iron is inexpensive, non-toxic and environmentally compatible. Nanoparticles are attractive for remediation of various contaminants because of their unique physiochemical properties (Zhang, 2003, 2005). Reactivity of the nanoparticle increases with an increase in surface area (Gotpagar et al., 1997; Li et al., 2003). In recent years, microparticles (mZVI), iron filings and ZVI nanoparticles (nZVI) have been used for the removal of various groundwater contaminants including chlorinated compounds (Matheson and Tratnyek, 1994; Boronina et al., 1995; Orth and Gillham, 1996; Roberts et al., 1996; Campbell et al., 1997; Liang et al., 1997; Tratnyek et al., 1997; He and Zhao, 2005; Tee and Bhattacharyya, 2005; Huang and Zhang, 2006; Liu and Lowry, 2006; Cheng et al., 2007), pesticides (Singh et al., 1998; Feitz et al., 2005; Joo and Zhao, 2008; Thompson, 2008), heavy metals (Boronina et al., 1995; Powell et al., 1995; Roberts et al., 1996; Blowes et al., 1997; Fiedor et al., 1998; Ponder et al., 2000; Alowitz and Scherer, 2002), nitrate (Huang et al., 2003; Huang and Zhang, 2005; Bezbaruah et al., 2008), and explosives (Gregory et al., 2004; Oh et al., 2005) in water. The typical mode of chlorinated contaminant degradation by ZVI is reductive dehalogenation (Matheson and Tratnyek, 1994), as shown below (Eq. 1).

$$R\text{-}Cl + Fe^{0}(s) + H^{+} \rightarrow Fe^{2+} + R\text{-}H + Cl^{-} \tag{1}$$

Due to their small particle size (< 100 nm, Wang and Zhang, 1997) and high reactivity, nZVI have also been used in the remediation of contaminated soils (Martin et al., 2008), sediments (Zhang and Frankenberger, 2006), and biosolids (Li et al., 2007).

Advantages of nZVI over other ZVI such as microparticles (mZVI) and iron filings include a higher reactive surface area [22-54 m^2g^{-1} for nZVI (Ponder et al., 2000; Chen et al., 2004; Liu et al., 2005; Li et al., 2006; Bezbaruah et al., 2008) and 1 m^2g^{-1} for mZVI (Bezbaruah et al., 2008; Thompson, 2008)], faster and more complete reactions, and better injectability into the aquifer (Cantrell et al., 1995; Wang and Zhang, 1997). The effectiveness of nZVI for groundwater remediation depends upon the effective delivery of the nanoparticles to the water/contaminate interface without flocculation and severe oxidation. While nZVI are easier to be injected than mZVI, the nZVI still agglomerate because of interparticle attraction due to magnetic and van der Waals forces. The agglomerated particles behave more like mZVI and settle out. The particles also get attached to aquifer materials such as sand grains. These characteristics of nZVI reduce the effective surface area available for contaminant degradation.

On the basis of the relevant literature, there exists a need for an efficient nZVI delivery vehicle that is easy to synthesize in the laboratory and mass produce when scaled-up. The authors suggest that one of the requirements for such a delivery vehicle be the commercial availability of the raw materials. Maintaining the stability of the nanoparticles for a long time without agglomeration should be the primary objective (Lu et al., 2007). The main difficulty for the use of pure metal nanoparticles (e.g., nZVI) arises from their high reactivity towards dissolved oxygen and oxygen containing compounds. However, oxidation is the main mechanism of decontamination by nZVI. So, it is important to protect the nZVI from non-target oxidation while allowing oxidation by targeted contaminants. It would further be desirable to create an affinity of the modified nZVI towards the target contaminants (Saleh et al., 2005). There exist a number of possible techniques for the stabilization of nZVI (Kim et al., 2003; Lu et al., 2007). A polymer or surfactant coating on nZVI that provides electrosteric (rather than electrostatic) repulsion to balance the magnetic and van der Waals attractive forces is needed (Sousa et al., 2001; Shen et al., 1999; Lu et al., 2007; Saleh et al., 2008).

This chapter introduces the current status of knowledge on surface modification of nZVI, followed by descriptions of an on-going work on nZVI stabilization using amphiphilic polysiloxane graft copolymers (APGCs) which will be easy to mass produce at a low cost from commercially available starting materials. Treatment of nZVI with APGCs has been found to enhance colloidal stability of nanoparticle in water, and the magnitude of the enhancement is a function of APGC chemical composition.

8.2   Current Status of nZVI Surface Modification

There are at least three possible approaches to achieving colloidal stability of nanoparticles: (1) modification of the nanoparticle synthesis process, (2) post-synthesis modification of nanoparticles, and (3) application of a physical stimulus. Among these

approaches, the post-synthesis modification of the nanoparticles has been investigated most extensively. Some studies related to surface modifications are briefly reviewed below.

Size is one of the most important parameters that control the dispersion characteristics of particles (Logan, 1999). Colloid transport through soils is easiest for particles having sizes less than 50 nm and greater than 3 nm (Logan, 1999). However, the Tufenkji-Elimelech model (Tufenkji and Elimelech, 2004), which considers the effect of hydrodynamic forces and van der Waals interactions between the colloidal particles and soil/sediment grains, predicts that the optimal particle size for effective flow of nZVI in groundwater is between 200 and 1000 nm (Hydutsky et al., 2007; Phenrat et al., 2007). Particles smaller than 200 nm undergo collisions with aquifer particles (soil grains) more frequently than their larger counterparts because the smaller particles are subjected to Brownian motion (Hydutsky et al., 2007). Phenrat et al. (2007) reported that iron nanoparticles behave as a ferromagnet once the size exceeds 15 nm which leads to aggregation of the nanoparticles.

Bare nZVI do not disperse in aqueous media and are susceptible to excessive oxidation by non-target compounds (Giri et al., 2001; He and Zhao, 2005; Krajangpan et al., 2008). As a result, they are not suitable for groundwater remediation. Nanoparticle surface modification and/or functionalization are essential for enabling effective groundwater remediation using nZVI. The motivation behind most efforts to surface modify nanoparticles is to increase their injectability into the subsurface and increase their reactivity towards contaminants. Surface modification is expected to inhibit agglomeration, and thereby, maximize the reactive surface area for contaminant remediation. Surface modification and functionalization are widely practiced on nanoparticles used for biomedical applications. Different types of modifiers have been used to modify nanoparticle surfaces for biomedical purposes, such as carboxylate-functional compounds (Sahoo et al., 2005), phosphate-functional compounds (Portet et al., 2001; Mutin et al., 2003), silica (Johnson et al., 1996; Alcala and Real, 2006), gold (Lin et al., 2001), dextran (Lee et al., 2002), polyethylene glycol (Kim et al., 2001; Paul et al., 2004), polyvinyl alcohol (Nishio et al., 2004), alginate (Kroll et al., 1996), and chitosan (Lee et al., 2005).

To avoid agglomeration, surfactants or polymers are often used to modify nanoparticle surfaces during or after the synthesis of the particles. Papell (1965) invented the ferrofluids which are now used to increase the colloidal stability of magnetic nanoparticles. Water or oil-based ferrofluids are commercially available, and they are usually stable at pH < 5 (acidic ferrofluid) or pH > 8 (alkaline ferrofluid). By controlling the surface charge and using specific surfactants, stability of ferrofluids can be enhanced (Lu et al., 2007). Kim et al. (2005) coated iron oxide nanoparticles (~15 nm) with oleic acid before dispersing them in chitosan biopolymer to make ferrofluids.

The mean hydrodynamic diameter of their coated particles in the chitosan solution was estimated to be 65 nm. The stabilized ferrofluids with different iron concentrations were stable for 30 d without precipitation.

Surfactants have been used with a varying degree of success for colloidal stabilization of nanoparticles (Rosen, 2002). The hydrophobic "tails" of the surfactants physically absorb onto the nZVI surface while the hydrophilic "heads" inhibit flocculation and allow for suspension in the aqueous medium. While surfactants enable colloidal stability in water, the highly reversible nature of surfactant absorption limits its application as an nZVI delivery system for groundwater decontamination since desorption will be favored when the nanoparticles are transported through surfactant-free groundwater. Schrick et al. (2004) used poly(acrylic acid) and anionic hydrophilic carbon supported nZVI for the removal of chlorinated hydrocarbons (Schrick et al., 2004, Saleh et al., 2005). The delivery vehicle was able to lower the aggregation and sticking coefficient of nZVI. However, poly(acrylic acid) has limited application due to reversible adsorption characteristics (Schrick et al., 2004; Saleh et al., 2005). Sun et al. (2007) used polyvinyl alcohol-co-vinyl acetate-co-itaconic acid (PV3A), a biodegradable surfactant, as a dispersant for nZVI. The addition of PV3A led to significant enhancements in particle stability and subsurface mobility of nZVI. Other effects of application of the surfactant included reduction of the mean particle size from 105 nm to 15 nm, reduction of the zeta (ζ)-potential from +20 mV to -80 mV at neutral pH, and a shift of the isoelectric point (IEP) from pH ~8.1 to 4.5. They also found that PV3A-stabilized iron nanoparticles were capable of effectively decomposing trichloroethene (TCE). Bare nZVI (prepared without PV3A) with a median diameter of 59.4 nm and a mean diameter of 105.7 nm settled in less than 1 min. However, no sedimentation of the PV3A-stabilized nZVI with a median diameter of 7.9 nm and a mean diameter of 15.5 nm was observed for over a 6-month period (Sun et al., 2007). These researchers also screened a number of commercially available polymers, copolymers and surfactants including ionic and nonionic molecules. They tested polyvinyl chloride, polyacrylic acid, polydimethylsiloxane, and polypropylene oxide as possible nanoparticle surface modifiers. PV3A with a molecular weight of 4300-4400 proved to be the best. PV3A is of food grade, nontoxic, and biodegradable because of the presence of –OH, –CO–, and –COOH groups. Song et al. (2008) stabilized CeO_2-coated SiO_2 nanoparticles with the anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), and the nonionic surfactant, polyethylene glycol (PEG). The dispersion characteristics observed under different conditions indicated better dispersion of surface-modified nanoparticles as compared to unmodified analogs. PEG is hydrophilic, and the hydrated film developed around the PEG molecule gives rise to steric stabilization (Song et al., 2008).

He and Zhao (2005) reported on the use of water-soluble starch for the stabilization of palladized iron (Fe-Pd) nanoparticles. The modified nanoparticles were

used for the dechlorination of TCE and polychlorinated biphenyls. The starch-modified nanoparticles showed less agglomeration and were present as discrete particles as opposed to dendritic flocs for unmodified particles. The starch-modified nanoparticles remained suspended in water after 24 h, and only partial precipitation was observed after 48 h. In contrast, the bare nanoparticles agglomerated and precipitated within a few minutes. Starch is a branched, hydrophilic polymer containing ~20% amylase units. It was hypothesized that iron-starch interactions and formation of intra-starch iron clusters played a fundamental role in nanoparticle dispersion and stabilization. A significant improvement in the reactivity of the starch-modified Pd-Fe nanoparticles towards TCE and polychlorinated biphenyls (PCB) was observed. The researchers reported a 37-fold increase in the surface area normalized reaction rate (k_{SA}) for TCE degradation using starch-modified Fe-Pd nanoparticles as compared to bare particles.

Gu et al. (2005) examined a method to produce monodispersed submicron-sized polymer coated Fe_2O_3 particles referred to as "magnetic polymer particles." They conducted soap-free emulsion polymerization, during which Fe_2O_3 nanoparticles were heterocoagulated onto precipitated polymer nuclei and fixed to the nuclei through the introduction of vinyl groups on the Fe_2O_3 surface. To chemically fix the nanoparticles to the polymer, a vinyl group was introduced into the primary surface modification reaction with methacryloxypropyltrimethoxysilane (MPTMS) and methacryloxypropyldimethoxysilane (MPDMS). The colloidal stability of the polymer coated particles was improved by adding the ionic monomer, sodium p-styrenesulfonate (NaSS), during polymerization. The researchers concluded that the addition of the ionic surfactant to the soap-free emulsion polymerization might have improved the surface potential and raised the dispersion stability of the polymer coated Fe_2O_3 particles. Further, it was observed that the NaSS addition changed the zeta-potential, and consequently, raised the stability of the particles.

Jun et al. (2005) coated magnetite nanocrystals (4-12 nm) with a multifunctional ligand system to provide high stability of the particles. The ligand, 2,3-dimercaptosuccinic acid (DMSA), was used for the synthesis of the coated nanocrystals. They found that the DMSA coated Fe_2O_3 nanocrystals were fairly well dispersed in aqueous media. DMSA forms a stable coating on the Fe_2O_3 surface by chelation through a carboxylic acid group. Further stabilization was achieved through intermolecular disulfide cross-linking (Jun et al., 2005).

Ponder et al. (2000) synthesized supported Fe-nanoparticles using polymeric resin, silica gel or sand as a support material. They studied the rates of remediation of Cr(VI) and Pb(II) using both the modified and unmodified nZVI. Their modified particles showed high reactivity for a longer time compared to unmodified nZVI. Colloidal stability of the modified nZVI was not reported.

Wu et al. (2005) used cellulose acetate to coat nZVI. The goal was to preserve the chemical nature of nZVI by inhibiting iron oxidation by non-target compounds until the particles are in contact with the chlorinated contaminant stream. The nanoparticles were mixed with a cellulose acetate-acetone solution and then formed into a ~100 μm thick porous membrane by phase inversion. The membranes contained ~6.3 weight percents of nZVI. The nanoparticles existed in the membrane as dispersed agglomerated clusters allowing good access by the target contaminant to nZVI surfaces. The polymer supported nanoparticles had better dechlorination compared to bare nanoparticles. The researchers explored an interesting possibility of synergy in the form of contaminant pre-concentration in the polymer due to organic partitioning. This concept was important because successful pre-concentration and subsequent contaminant degradation would enable nZVI treatment for low concentration contaminant situations.

Mohapatra et al. (2006) synthesized superparamagnetic nanosized magnetite particles by controlled coprecipitation of Fe^{2+} and Fe^{3+} in the presence of highly hydrophilic poly(vinylalcohol phosphate) (PVAP). They found that the polymer concentration affected the particle size, size distribution, and colloidal stability. The aqueous suspension of magnetite, prepared using an 1% PVAP solution, was stable for 4 weeks at pH 5–8 (Mohapatra et al., 2006).

Iron oxide nanoparticles were surface modified by Somaskandan et al. (2008) with hydrophilic ligands. The ligands facilitated excellent stability of the nanoparticles (for several weeks) in water and different buffer solutions. The surface modified iron oxide nanoparticles also showed excellent solubility in polar solvents. Based on previous work, hydrophilic dopamine hydrochloride and dopamine-PEG were used to modify nZVI (Shultz et al., 2007).

Tiraferri et al. (2008) studied the colloidal stability of nZVI modified by the biodegradable polymers alginate, potato starch and guar gum, and compared them with commercially-available unmodified and sodium polyaspartate-modified nZVI. They found good electrophoretic mobility of the guar gum coated particles at different pH while experiments with alginate and potato starch did not give good results. Colloidal stability with guar gum coated nanoparticles was observed for 20 min and it was found to be better than the bare nanoparticles. However, the concentration of nZVI was low in their experiment, and the coated particles settled much faster when the ionic strength of the aqueous medium increased (Tiraferri et al., 2008). Guar gum is a naturally occurring water-soluble polysaccharide that consists of β-D-mannopyranose and α-D-galactopyranose units. Guar gum was found to aid in lowering the hydrodynamic radius of nanoparticle aggregates from 300 nm to 200 nm as the guar gum concentration increased from 0.05 to 0.5 g L^{-1}; however, size reduction was not observed beyond 1 g L^{-1}. Guar gum is already in use as a dispersing and stabilizing agent for many industrial applications (Bradley et al., 1989; Wang et al., 2000). It is also being investigated using

stability enhancement experiments involving magnetorheological fluids (Fang et al., 2005; Wu et al., 2006). Its low cost and "green" attributes are appealing in a nanoparticle dispersant (Tiraferri et al., 2008).

Saleh et al. (2005) showed that amphiphilic triblock copolymers with an A-B-C triblock microstructure are effective delivery systems for nZVI. High molecular weight amphiphilic polymers show essentially irreversible absorption and, thus, are more suitable as a delivery system for groundwater remediation (Velegol and Tilton, 2001; Braem et al., 2003). The triblock copolymers were produced using atom transfer radical polymerization (ATRP) in conjunction with post-polymerization ester-hydrolysis and sulfonation steps. The results of the research demonstrated enhanced colloidal stability and an increased affinity for a water/organic interface provided by the amphiphilic triblock copolymer. The poly(methacrylic acid)-block-poly(methylmethacrylate)-block-poly(styrenesulfonate) contains an anchoring block (polymethacrylic acid), hydrophobic block (polymethylmethacrylate), and hydrophilic block (polystyrenesulfonate). The hydrophilic group imparts good colloidal stability, and the hydrophobic group gives the particle better affinity for the organic contaminant and resists the access of water to the nZVI surface. The novel polymer architecture creates a thermodynamic affinity of the modified nZVI for the water/contaminant interface. However, kinetic studies showed a decrease in the rate of contaminant degradation by the polymer-modified nZVI as compared to unmodified nZVI (Saleh et al., 2007). The reduction in the contaminant degradation rate was attributed to low permeability of the contaminant through the film absorbed onto the nZVI. The synthesis method used by this research group to produce the triblock copolymer structure is sensitive to impurities and oxygen. The process is relatively slow. Further, polymerization catalyst residues can be difficult to remove from the copolymer.

Recently, the same research group studied the effect of ionic strength on the mobility of the modified nZVI (Saleh et al., 2008). They measured the change of surface charge as a function of concentration of Na^+ and Ca^{2+} ions with three different surface modifiers. They used the high molecular weight (MW) (125 kg mol^{-1}) poly(methacrylic acid)-b-(methyl methacrylate)-b-(styrene sulfonate) triblock copolymer (PMAA-PMMA-PSS), low MW (2–3 kg mol^{-1}) polyaspartate biopolymer, and sodium dodecylbenzene sulfonate surfactant (SDBS, MW = 348.5 g mol^{-1}) to determine the effect of electrosteric and electrostatic repulsions on particle stabilization. The negative surface potential of nZVI increased due to surface modification, and the particle hydrodynamic diameter also increased moderately. The group conducted column studies to simulate a groundwater environment. They concluded that, in typical groundwater containing 0.5-1.0 mM Ca^{2+} or Mg^+, polyaspartate and SDBS (both low MW) will not enhance mobility of nZVI in the aquifer. However, the triblock copolymer, PMAA-PMMA-PSS, would provide the electrosteric repulsions to inhibit attachment to sand grains under typical groundwater conditions. Electrosteric repulsion

is known to remain strong even at high ionic strengths where the electrostatic double layer becomes insignificant (Pincus, 1991; Biesheuvel, 2004; Saleh et al., 2008). Electrosteric stabilization provides the best interparticle repulsion and, hence, the best nZVI dispersion in groundwater.

8.3 Surface Modification with Amphiphilic Polysiloxane Graft Copolymers

8.3.1 Hypothesis

Considering the requirements of an effective delivery system for nZVI, functionalized amphiphilic polysiloxanes are an ideal class of polymers for the application. Figure 8.1 provides a schematic representation of amphiphilic polysiloxane graft copolymers (APGC) that could be easily synthesized and used for nZVI modification. The hydrophobicity of the polysiloxane polymer backbone provides protection of nZVI surfaces from excessive oxidation by creating a barrier to water while also creating an affinity of the coated nanoparticles for the water/contaminant interface, as illustrated schematically in Figure 8.2. Since polysiloxanes have a very low glass transition temperature (-120°C) and are highly soluble in most hydrocarbons, they will readily allow permeation of organic contaminants, such as trichloroethene, to the Fe° nanoparticle surface providing fast, efficient contaminant remediation. Additionally, the versatility of the hydrosilylation reaction used to produce the polymers will enable tailoring of the chemical structure to enhance contaminant specificity.
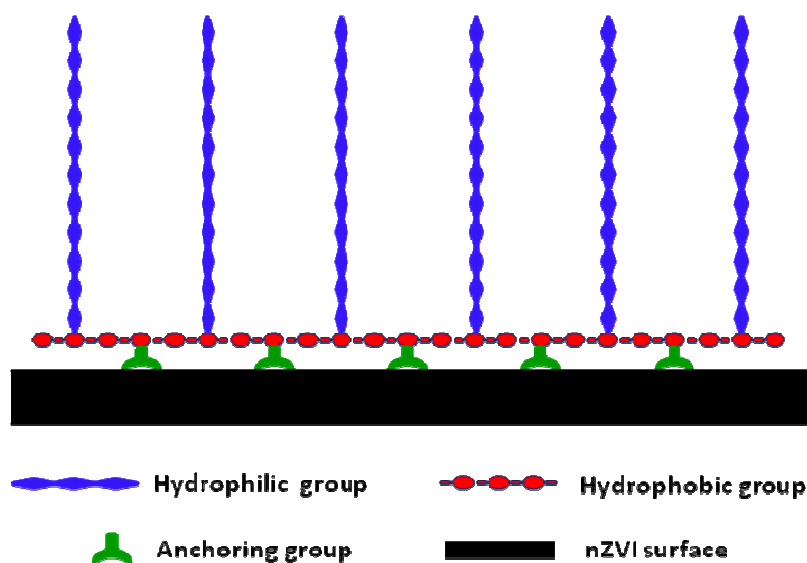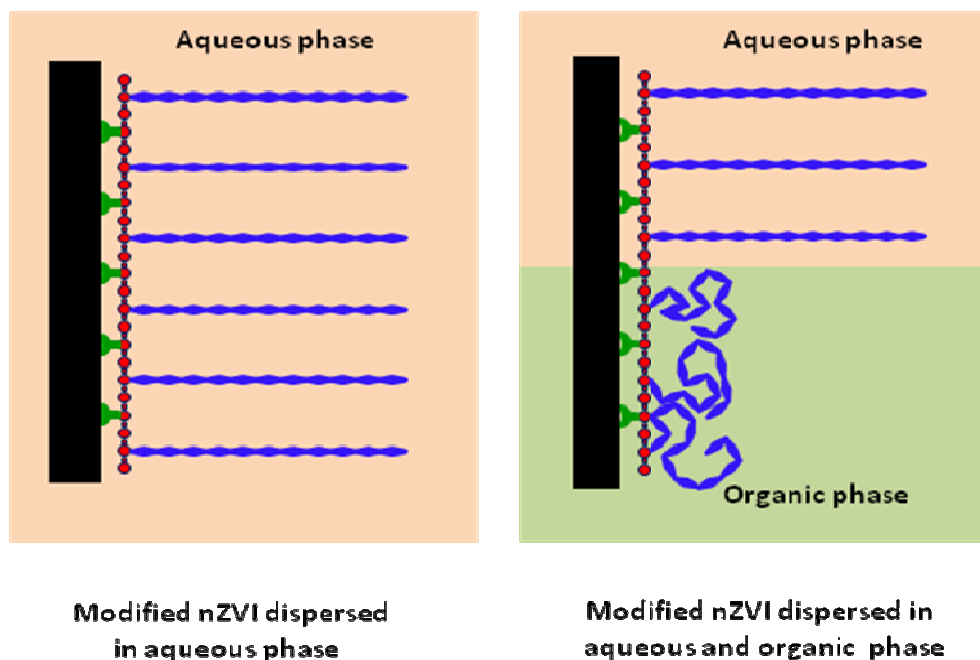

Figure 8.1 A schematic representation of amphiphilic polysiloxane graft copolymers.

8.3.2 Rationale

In addition to possessing the ideal characteristics for an nZVI delivery system, this class of polymers can be easily synthesized from a wide variety of commercially available starting materials. For example, Gelest Inc. (Morrisville, PA, USA) sells a variety of poly(dimethylsiloxane-co-methylhydrosiloxanes) copolymers with varying methylhydrosiloxane contents and molecular weights as well as poly(methylhydrosiloxane) homopolymers of varying molecular weights. With regard to precursors for the generation of hydrophilic polymer grafts, Clariant (Charlotte, NC, USA) sells an array of monovinyl-terminated PEGs of varying molecular weights. Thus, with this class of graft copolymers, extensive structure-property relationships can be developed by varying the polysiloxane backbone molecular weight, hydrophilic polymer graft content and molecular weight, as well as the anchoring group content.

Figure 8.2 A schematic representation of the modified nZVI in water and at the water/contaminant interface.

8.3.3 Experimental Methods

Synthesis and Characterization of nZVI. nZVI were synthesized using a borohydride reduction method (Liu et al., 2005) with a slight modification (Bezbaruah et al., 2008; Thompson, 2008). $NaBH_4$ (Alfa Aesar, Ward Hill, MA, USA) solution was

199

added drop-wise to an Fe(SO$_4$)•7H$_2$O (Alfa Aesar) methanol (BDH, supplied by VWR, West Chester, PA, USA)/water solution, resulting in a suspension of black iron particles. The iron particles were subsequently vacuum-filtered and washed with ethanol to remove excess borohydride. The iron particles were then vacuum-dried at 120°C under the nitrogen environment. After drying, the particles were passivated by allowing air to slowly bleed over them for 12 h. Fine nZVI powders were obtained by grinding the resulting black iron clusters. The nZVI powder was stored in a glovebox (Innovative Technology Inc., Newburryport, MA, USA) under the nitrogen environment.

Characterization of the modified nZVI was done using transmission electron microscopy (TEM, JEOL JEM-100CX II, JEOL Ltd., Tokyo, Japan). A concentrated nZVI sample was prepared in ethanol, sonicated, and placed on a Formvar®-coated copper grid (300 mesh) for analysis at an accelerating voltage of 80 kV. X-ray diffraction (XRD) of the modified nZVI was conducted using a Philips X'Pert MPD with Cu Kα X-ray source. Analyses were carried out at 40 kV and 30 mA with a scan range from 20˚ to 80˚. The Brunauer-Emmett-Teller (BET, ASAP 2000, Micromeritics, Norcross, GA, USA) specific surface area of the synthesized nZVI was determined by N$_2$ gas absorption.

Synthesis and Characterization of APGCs. APGCs were synthesized using PtO$_2$-catalyzed hydrosilylation. The reaction scheme involving commercially-available hydride-functional polysiloxanes and commercially-available monofunctional vinyl compounds is shown in Figure 8.3.
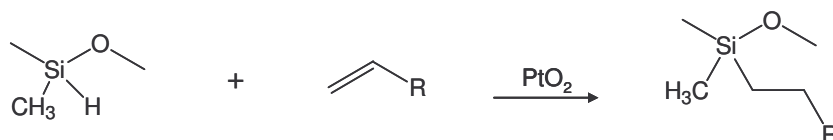
Figure 8.3 Hydrosilylation between hydride-functional polysiloxanes and monofunctional vinyl compounds.

The following is a procedure used to produce a representative APGC: 10 g of a poly(methylhydrosiloxane-dimethylsiloxane) copolymer containing 3.98 mM of hydride groups per g of polymer (HMS 151, Gelest), 10.2 mM of monoallyl-functional polyethyleneglycol (PEG, Clariant), and 10.2 mM of *tert*-butylacrylate (tBA, Aldrich) were dissolved in toluene. A catalytic amount of PtO$_2$ (Aldrich, St. Louis, MO, USA) was added, and the mixture was heated at 90°C overnight. Upon completion of the reaction, the reaction mixture was cooled to room temperature, platinum oxide removed by vacuum filtration, and the polymer isolated by vacuum stripping the toluene.

To generate the carboxylic acid anchoring groups, the *tert*-butyl ester groups of the graft copolymer were hydrolyzed as follows: 2.0 g of the polymer was dissolved in 5

mL of dichloromethane. Trifluoroacetic acid (TFA, Aldrich) was added to the solution (0.55 mL, 5 molar equivalent), and the mixture stirred at room temperature overnight. The carboxylic acid-functional graft copolymer was isolated by vacuum stripping dichloromethane (Aldrich), TFA, and *tert*-butanol. Each synthesis step was monitored using nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy. The complete synthesis procedure is represented in Figure 8.4.
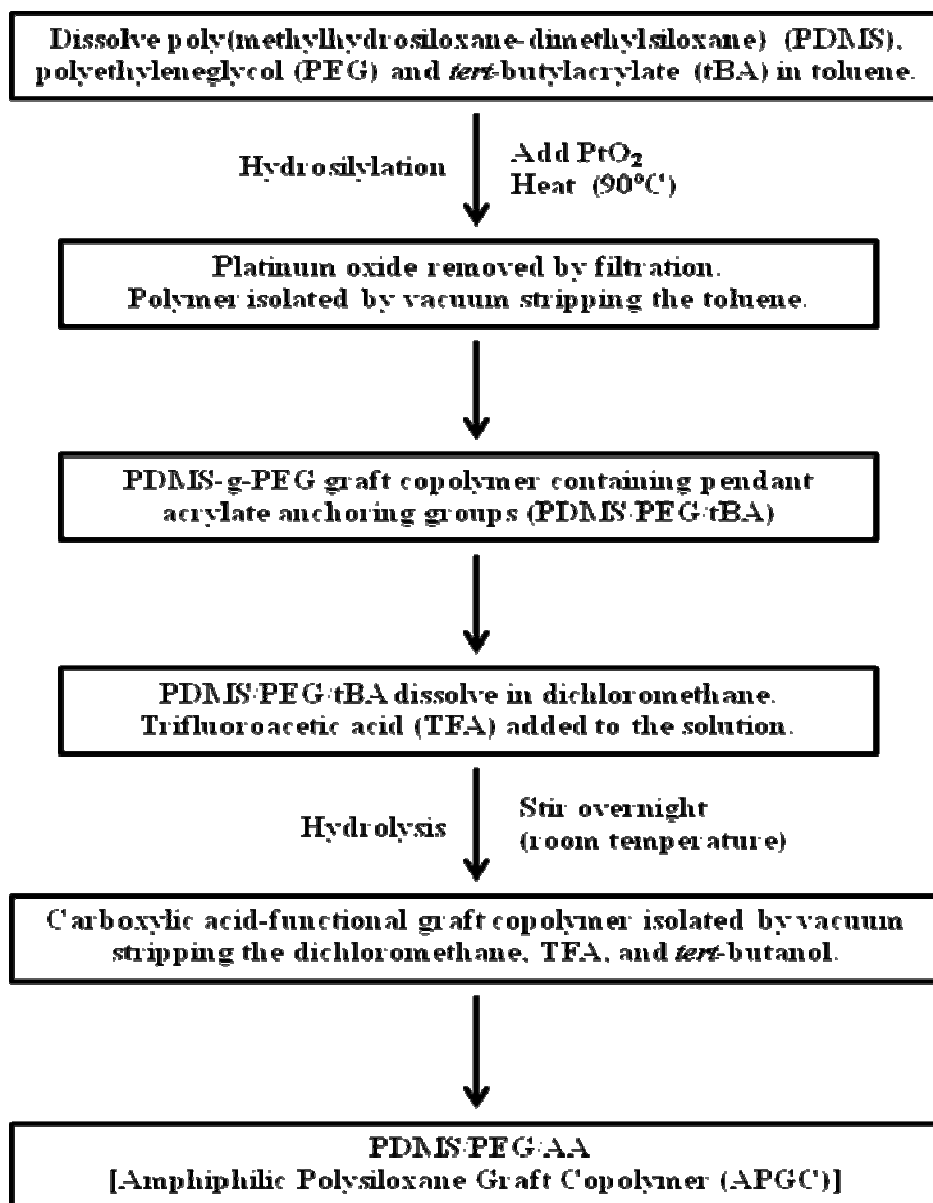

Figure 8.4 Steps in APGC synthesis.

Surface Coating of nZVI. An aqueous slurry of nZVI was combined with a 10 gL^{-1} APGC solution. The mixture was sonicated for 30 min followed by gentle end-over-end rotation for 72 h to disperse the nanoparticles to allow the polymer to absorb onto the surface of the nanoparticles. The APGC-coated nZVI were then filtered and washed multiple times to remove any excess non-adsorbed APGC.

Sedimentation Rate Measurements. The colloidal stability of the APGC-coated nZVI was evaluated by measuring sedimentation rates of nanoparticle suspensions using a UV-spectrometer. The optical density at a wavelength of 508 nm was monitored over several hours to determine sedimentation rate (Krajangpan et al., 2008).

8.3.4 Results and Discussion

nZVI Synthesis and Characterization. nZVI particles were synthesized following the method enumerated earlier. The average particle diameter was determined to be approximately 35 nm with a particle size range between 10 and 90 nm (Table 8.1). Similar particle sizes have been reported by Li et al. (2006). A thin (2–5 nm) oxide shell was identified around the nZVI, which was believed to be created during particle passivation process. A similar core-shell structure has been reported by others (Nurmi et al., 2005; Li et al., 2006; Martin et al., 2008). The shell has been reported to be made of iron oxide/hydroxide and the core, zero-valent iron (Nurmi et al., 2005; Li et al., 2006). Recently, Martin et al. (2008) reported that nZVI (50–100 nm) are always surrounded by a thin shell/layer of an amorphous material. They reported it to be FeOOH. The FeOOH layer thickness was found to be 2–4 nm. The BET surface area of the nZVI synthesized during this experiment was found to be 25 m^2g^{-1} which is in agreement with others (22 m^2g^{-1} reported by Ponder et al., 2000; 36 $m^2 g^{-1}$ reported by Liu et al., 2005).

Table 8.1 Particle size distribution of nZVI synthesized.

| Particle Size (diameter, d) (nm)	Percent Present (%)	Cumulative Percentage (%)
0 < d < 10	0.00	0.00
10 < d < 20	11.22	11.22
20 < d < 30	34.15	45.37
30 < d < 40	25.37	70.73
40 < d <50	13.66	84.39
50 < d < 60	9.27	93.66
60 < d < 70	4.39	98.05
70 < d < 80	1.46	99.51
80 < d < 90	0.49	100.00
90 < d < 100	0.00	100.00
d > 100	0.00	100.00

APGC Synthesis, nZVI Surface Modification and Colloidal Stability Analysis. Carboxylic acid-functional APGC containing polyethylene glycol grafts (PDMS/PEG/AA) were successfully synthesized using the synthesis process described above. The proton absorption peaks at δ 0.4–0.5 and 1.4–1.6 ppm in the proton NMR spectrum correspond to methylene protons created as a result of hydrosilylation of the vinyl functional precursors to the hydride functional polysiloxane copolymer.

The concentration of nZVI used for determining the effect of polymer-modification on colloidal stability was based on experimentation. While 10 g nZVI L^{-1} would have been the ideal concentration for groundwater remediation (Saleh et al., 2008), the experiments in this study were conducted with the nZVI concentrations up to 3.0 g L^{-1}. Results from sedimentation studies carried out with 0.5, 1.0, and 3.0 g L^{-1} bare nZVI indicated that colloidal stability decreased with an increase in particle concentration, possibly because of more extensive particle agglomeration. As shown in Figure 8.5, most of the particles settled out in the initial few minutes of the test. The authors decided to use an nZVI concentration of 3.0 g L^{-1} for further studies.

Sedimentation rates of APGC-modified nZVI were found to vary as a function of the relative molar concentration of carboxylic acid groups to PEG grafts. Figure 8.6 displays representative data illustrating the effect of APGC composition on the sedimentation rate of nZVI. It can be seen that modification of nZVI with APGCs decreases the sedimentation rate, and the APGC with the highest concentration of carboxylic acid anchoring groups provides the highest colloidal stability.
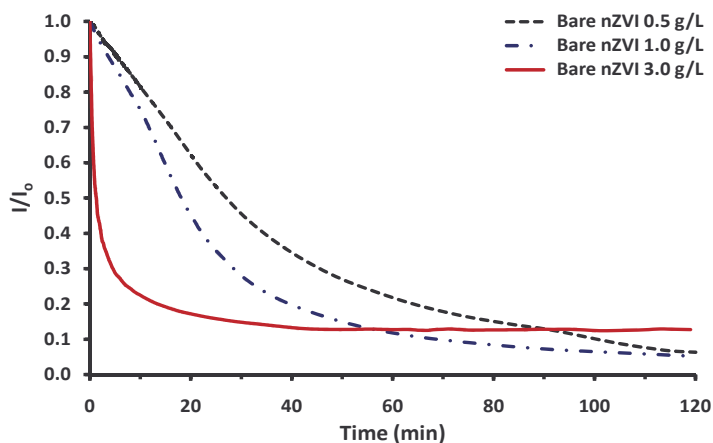
**Figure 8.5** Sedimentation of bare nZVI in water.
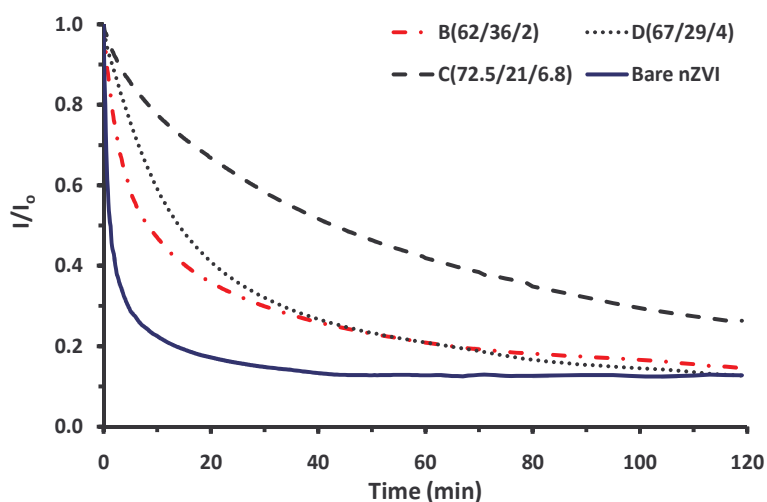
Figure 8.6 Results from nZVI sedimentation studies. B, C and D are samples of polymer with different weight percents of polydimethylsiloxane (PDMS), polyethylene glycol (PEG) and acrylic acid (AA). For example, polymer B (62/36/2) contains 62% PDMS, 36% PEG and 2% AA.

To test the versatility of the APGCs in improving the dispersibility of nanoparticles, silver nanoparticles (AgNP, 100nm, Aldrich) were also coated, and sedimentation studies carried out. The results indicated that there is no change in colloidal properties of AgNP when coated with the APGC. The sedimentation plot for the coated AgNP was essentially the same as that of the bare particles (Figure 8.7). Ag (molecular weight ~108 g mol^{-1}) is almost two times heavier than Fe (molecular weight ~56 g mol^{-1}), which may be one of the reasons why the AgNP sedimented out so fast. Change in the APGC architecture might have enhanced the colloidal stability of the particles but that was beyond the scope of the present research.

The surface coating on the nZVI was achieved by combining nZVI with APGC and rotating them in a custom made end-over-end shaker for 72 h. The mixing allowed the nanoparticles to disperse and the polymer to absorb onto the surface of the nanoparticles. The mixing time of 72 h appeared a little long, and efforts were made to shorten the mixing time. A 48-h mixing time gave similar results (Figure 8.8). The authors infer that there is a possibility of shortening the mixing time and, thus, reduce production cost of the coated nZVI. Further work is needed to optimize the mixing time.
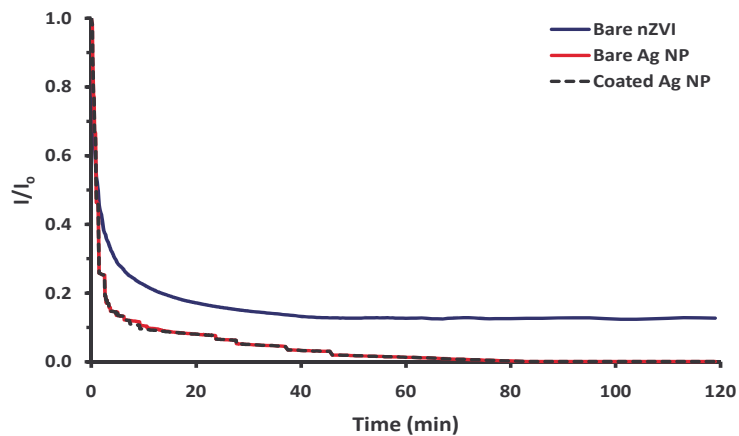
Figure 8.7 Sedimentation bare and APGC modified silver nanoparticles. The bare nZVI sedimentation curve is shown here for comparison purpose.
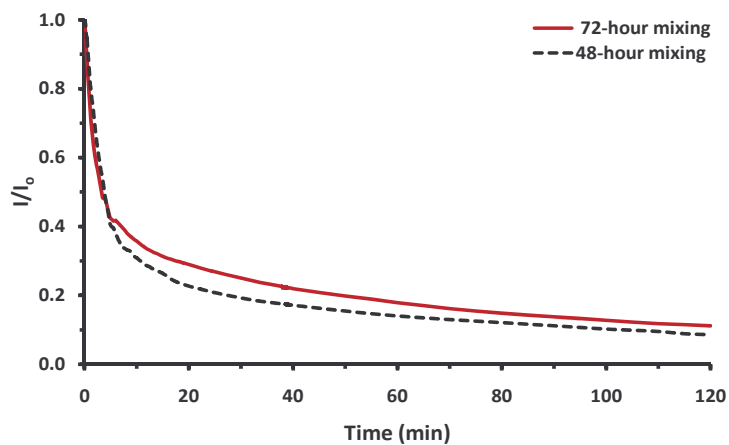
Figure 8.8 Colloidal stability of APGC modified nZVI when nZVI and APGC were mixed for different lengths of time.

8.4   Conclusions

A series of APGCs were successfully synthesized using a process that consisted of hydrosilylation of *tert*-butylacrylate and monoallyl-functional PEG to a polysiloxane copolymer containing hydride groups and subsequent hydrolysis of the *tert*-butylester groups. The APGCs were composed of polydimethylsiloxane (PDMS), polyethylene glycol (PEG) and acrylic acid (AA). The PEG hydrophilic groups promoted colloidal stability of nZVI in aqueous media. The APGC with the highest concentration of carboxylic acid anchoring groups provided the highest colloidal stability. The modified nZVI were significantly more stable than bare nZVI. The polysiloxane polymer backbone is expected to protect nZVI from oxidation by non-target compounds and create an affinity of the modified nZVI for the water/organic (specifically, non-aqueous phase liquids) interface. The polymer coating will make more nZVI reactive surface available for contaminant degradation.

8.5   Acknowledgements

8.6   References

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