



EFFECTS OF DIFFERENT GRAFT COPOLYMER CONSTITUENT GROUPS ON SEDIMENTATION CHARACTERISTICS OF COATED IRON NANOPARTICLES

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Introduction

In recent years, zerovalent iron nanoparticles (nZVI) have received increased interest due to their potential in environmental¹⁻⁴ and biomedical applications.⁵ The high reactivity of nZVI is due to their large surface area.²⁻⁷ However, agglomeration due to magnetic and van der Waals forces increases the effective size of nZVI and decreases specific surface area resulting in a reduction in effectiveness for various environmental applications.⁸ While bare or unmodified nanoparticles are being used for environmental remediation, their performance can be increased by suitable surface modification to reduce agglomeration.

Dispersibility of nZVI is one of the important parameters that can be manipulated by appropriate surface modification. Poly(acrylic acid) and anionic hydrophilic carbon supported nZVI has been used for chlorinated hydrocarbon remediation.⁹ However, poly(acrylic acid) has limited applications due to reversible adsorption. Ponder et al. (2000) synthesized supported nZVI using polymeric resin, silica gel or sand as the support material.¹⁰ They studied degradation rates for Cr(VI) and Pb(II) using both modified and bare nZVI. The modified particles showed high reactivity for a relatively longer period of time as compared to the unmodified nZVI. Electrosteric stabilization works better than electrostatic stabilization for nZVI surface modification.¹¹ Other researchers have used cellulose acetate,¹² starch¹³ and guar gum¹⁴ to modify nZVI to increase dispersability.

Krajangpan et al. (2008) demonstrated the use of amphiphilic polysiloxane graft copolymers (APGCs) for enhancing the dispersion nZVI in aqueous media.¹⁵ In addition to the hydrophobic polysiloxane polymer backbone and hydrophilic poly(ethylene glycol) grafts, these polymers also contained pendant carboxylic acid groups for anchoring the polymer to nanoparticle surfaces. Colloidal stability was found to be dependent on graft copolymer composition, however extensive structure-property relationships were not developed. For this study, we synthesized a series of APGCs of varying composition using high-throughput methods and determined the influence of APGC chemical structure on the sedimentation rate of nZVI treated with the APGCs.

Experimental Section

Polymer Synthesis. Library studio® was used to design an array of APGCs that were subsequently synthesized using a Symyx Batch Reactor system.

Methylhydrosiloxane-dimethylsiloxane copolymer (PDMS) and monoallyl-functional polyethyleneglycol (PEG) were dissolved in toluene. A catalytic amount of Karstedt's catalyst was added to the solution and the reaction was run for 6 h at 90°C in an N₂ atmosphere. In a second step, *tert*-butyl acrylate (*t*BA) was added and the reaction was continued for another 8h. Then, allyltrimethylsilane (ATMS) was added to the reaction mixture and the reaction was continued for an additional 8 h to yield a PDMS-PEG-ATMS-*t*BA graft copolymer. ATMS was used to inhibit gelation by consuming Si-H functionality remaining on the polymer. The solvent and the catalyst were then removed and dichloromethane was added. Trifluoroacetic acid (5 equivalence relative to *t*BA) was then added to the reaction mixture to hydrolyze the *tert*-butyl ester and produce the carboxylic acid functional graft copolymer, PDMS-PEG-ATMS-AA.

Samples were designed to have varying concentrations of hydrophobic (PDMS), hydrophilic (PEG) and anchoring (AA) groups to see their effects on colloidal stability of the modified nZVI.

Characterization. ¹H NMR and FTIR were used to monitor reaction progress. Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the copolymer. The samples were subjected to a heat-cool-heat cycle in a temperature range from -160°C to 50°C by ramping at 10°C per min.

Sedimentation study. 12 mg of nZVI was added to a 12 mL emulsion of each polymer in a 20 mL glass vial. The mixture was sonicated for 30 min and then rotated in a end-over-end shaker for 72 h to allow the copolymer to be anchored onto the nZVI. The excess polymer in the sample was removed by washing the mixture three times with deoxygenated water followed by centrifugation. Colloidal stability of the coated nZVI was monitored for at least 120 minutes using a UV-VIS spectrometer (508 nm).

Results and Discussion

APGC Synthesis. PDMS-PEG-ATMS-*t*BA and PDMS-PEG-ATMS-AA were successfully synthesized. The polymer structures are shown in **Figure 1**. The weight percentages (wt%) of PDMS, PEG and *t*BA or AA (excluding ATMS) in different polymer samples are given in Table 1.

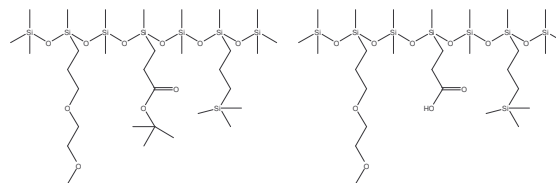


Figure 1. Structures of PDMS-PEG-ATMS-*t*BA (left) and PDMS-PEG-ATMS-AA (right)

There was only a small decrease in T_g from -85.37 to -89.01°C for samples 1 through 5 but a significant change in T_g from -67.51 to -89.01°C for sample 1Ac to 4Ac (Table 1). Again a small decrease was found in samples 6-10, but there was no significant change in T_g in samples 6Ac-9Ac.

Sample No	PDMS %	PEG %	<i>t</i> BA %	AA %	T _g (°C)
1	50	0	50	0	-85.37
2	50	12.5	37.5	0	-87.25
3	50	25	25	0	-89.30
4	50	37.5	12.5	0	-89.46
5	50	50	0	0	-89.72
1Ac	64	0	0	36	-67.51
2Ac	60	15	0	25	-73.53
3Ac	56	28	0	16	-84.09
4Ac	53	39.5	0	7.5	-86.71
6	80	0	20	0	-91.88
7	80	5	15	0	-92.70
8	80	10	10	0	-93.13
9	80	15	5	0	-93.67
10	80	20	0	0	-95.47
6Ac	87.5	0	0	12.5	-94.14
7Ac	85.5	5.5	0	9	-93.95
8Ac	83.5	10.5	0	6	-93.53
9Ac	82	15	0	3	-93.42

Table 1. Weight percents of constituents in copolymers synthesized and their glass transition temperature.

Sedimentation rate analysis. Colloidal characteristics of nZVIs coated with varying copolymer concentrations are shown in Figures 2 through 5. 20g/L of the graft copolymer gave the best nZVI colloidal stability. Figure 6 displays the colloidal stability of

the different polymer-coated nZVI with graft copolymer concentration of 20 g/L. Nanoparticles coated with 9Ac had the best colloidal stability. The amount of PDMS and PEG were same in 9 and 9Ac, but 9 contained tBA whereas 9Ac contained carboxylic acid as the anchoring group. This implies that the carboxylic acid anchoring group is essential for obtained enhanced colloidal stability. Further, the dispersibility of the coated nZVI not only depends on the concentration of the anchoring group but also the concentration of the PDMS and PEG. Comparison of results for 4Ac and 9Ac (Table 1 and Figures 3, 5, and 6) indicate that 4Ac had a higher concentration of the anchoring group (AA) than 9Ac, still 4Ac gave less stability than 9Ac. Sample 9Ac (Figure 3) contained the optimal concentrations of hydrophobic, hydrophilic and anchoring groups and the best colloidal stability was achieved.

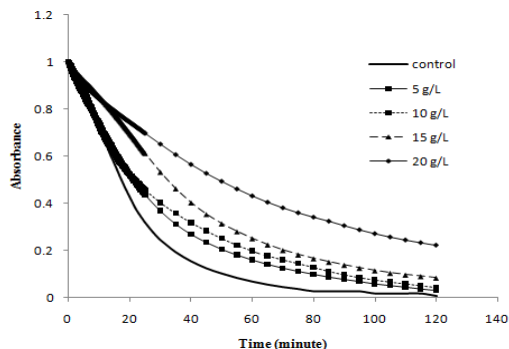


Figure 2. Sedimentation curve for sample 9

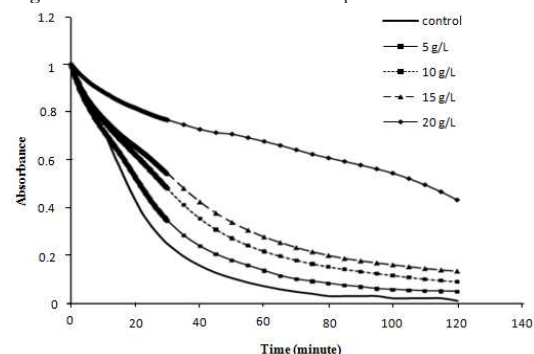


Figure 3. Sedimentation curve for sample 9Ac

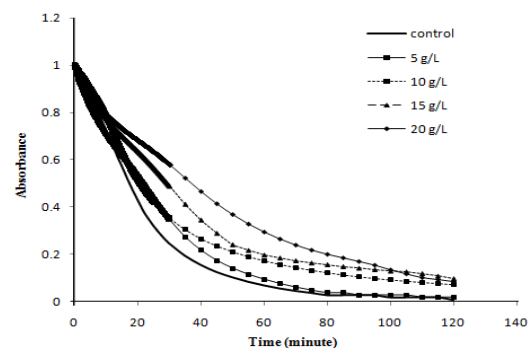


Figure 4. Sedimentation curve for sample 10.

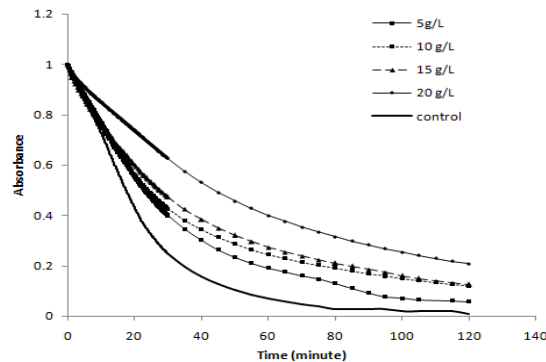


Figure 5. Sedimentation curve for sample 4Ac

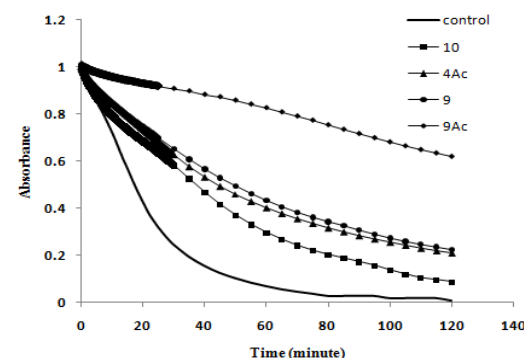


Figure 6. Colloidal stability of coated nZVI. Graft copolymer concentration was 20 g/L.

Conclusions

A series of polymers was successfully synthesized with different concentrations hydrophobic (PDMS), hydrophilic (PEG) and anchoring groups (tBA or AA). The copolymer (sample 9Ac) having 82/15/3 wt% of PDMS/PEG/AA was found to provide the best colloidal stability for zero-valent iron nanoparticles. The study is ongoing and expected to have great remediation in groundwater remediation.

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