Iron Nanoparticles Coated with Amphiphilic Polysiloxane Graft Copolymers: Dispersibility and Contaminant Treatability

SUPPORTING INFORMATION

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TABLE S1. Weight fractions of the three different repeat units of APGC used to optimize the APGC composition.

Sample*	% Weight fractions		
	PDMS	PEG	AA
70/25/5	70	25	5
62/36/2	62	36	2
72.5/21/6.5	72.5	21	6.5
67/29/4	67	29	4
65/32/3	65	32	3

APGC concentration used was 15 gL^{-1}.

*Weight fraction was selected based on mole fraction needed for reactions to take place.

TABLE S2. Summary of TCE degradation reaction rate constants with bare NZVI and CNZVI .

	Observed Reaction Rate K_{obs} (h^{-1})	Surface Normalized Reaction Rate k_{SA} ($L\ m^{-2}\ h^{-1}$)	Correlation Coefficient R^2
Initial TCE = 30 mgL^{-1}			
Bare NZVI	0.389	0.016	0.999
CNZVI	1.90	0.076	0.987
Initial TCE = 15 mgL^{-1}			
Bare NZVI	0.332	0.008	0.997
CNZVI	0.424	0.011	0.902
Initial TCE = 1 mgL^{-1}			
Bare NZVI	0.278	0.007	0.985
CNZVI	0.317	0.008	0.986

Average NZVI particle diameter = 35 nm; NZVI surface area = 25 m^2g^{-1}; NZVI surface area concentration in test solution (ρ_A) = 37.5 m^2L^{-1}.

TABLE S3. Peak Assignments and wave numbers for FTIR spectra of polymer before hydrolysis (PDMS/ PEG / tBA), polymer after hydrolysis (PDMS/ PEG/ AA), and CNZVI.

Peak Assignment	**PDMS /PEG/tBA (cm^{-1})**	**PDMS /PEG/AA (cm^{-1})**	**CNZVI (cm^{-1})**
O-H stretch		3200-3500	3050-3550
-CH_2 (asymmetric)	2957	2960	2962
-CH_3 stretch	2900	2898	2879
-CH_2 (symmetric)	2861	2868	2869
C=O stretch	1732	1712	
-COO stretch (asymmetric)			1556
-COO stretch (symmetric)			1456
C-O-C stretch	1256		
$(C\text{-}O)_{COOH}$ stretch		1260	1261
C-O-C (broad)	1010-1093	1015-1105	1016-1085

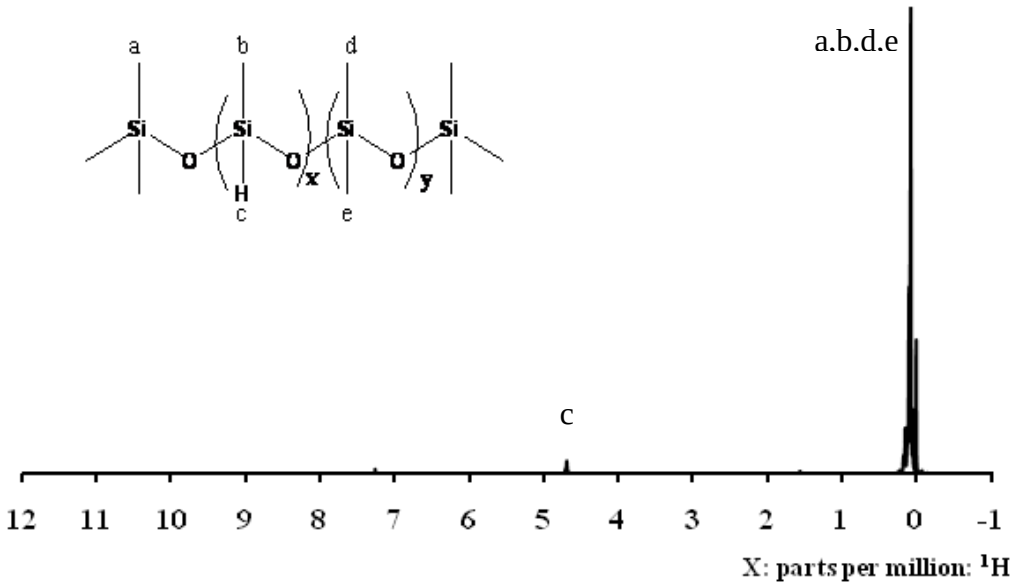

FIGURE S1. ^{1}H NMR of PDMS. PDMS is one of the raw materials used in the synthesis of APGC. The methyl group peaks are identified as a, b, d, and e, and hydride group is identified as c. The hydride group was hypothesized to react with PEG and tBA to form the copolymer (APGC).

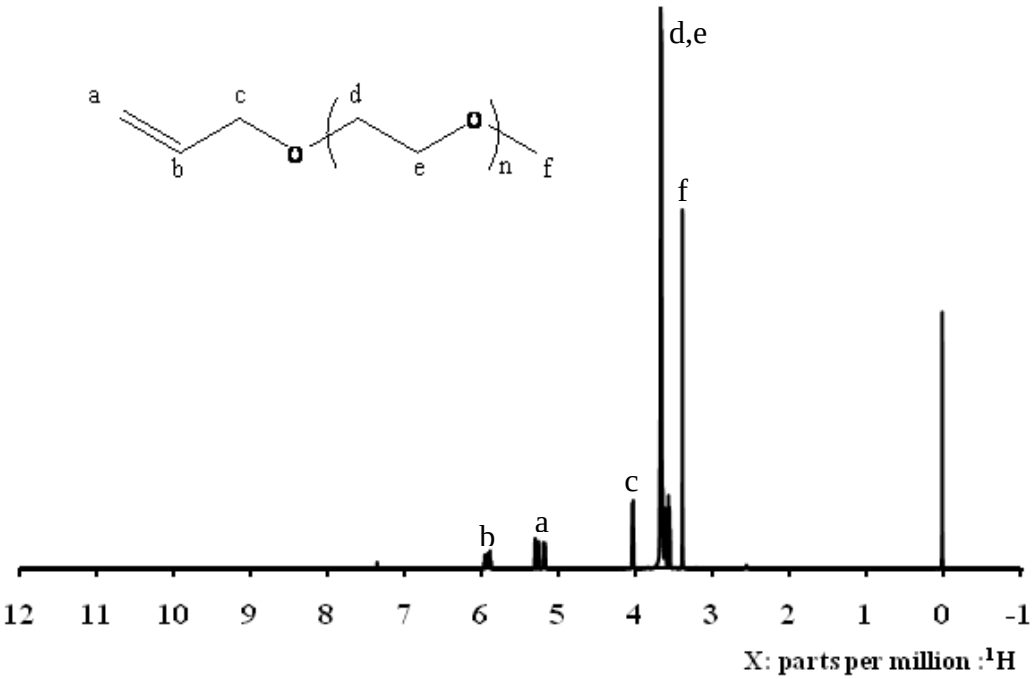

FIGURE S2. ^{1}H NMR of PEG. PEG is one of the raw materials used in the synthesis of APGC. Here a and b are double bonds from allyl PEG, c, d, e, and f represent the methylene (CH_2) groups. The double bonds present here were expected to react with the hydride groups from PDMS.

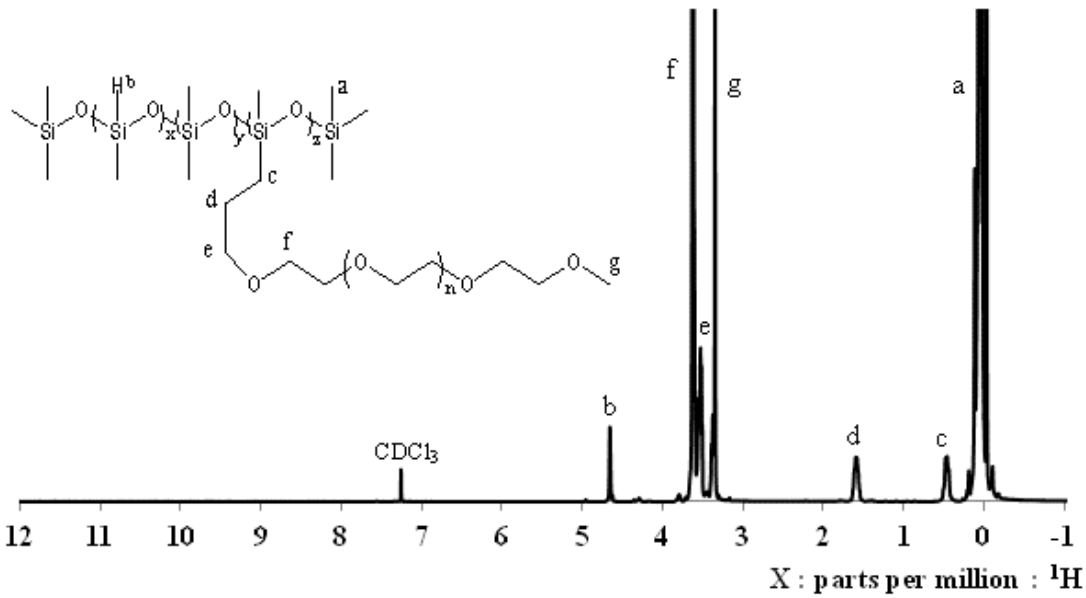

FIGURE S3. ^{1}H NMR of the hydrosilylation product of PDMS and PEG. Here b is the hydride group remaining after hydrosilylation which was expected to react later with the double bonds from tBA. The peaks at δ 5.2-5.4 corresponding to allyl peaks in PEG (peaks a and b in **Figure S2**) disappeared. The peaks at a and g represent methyl groups, and c, d, e, and f are methylene groups.

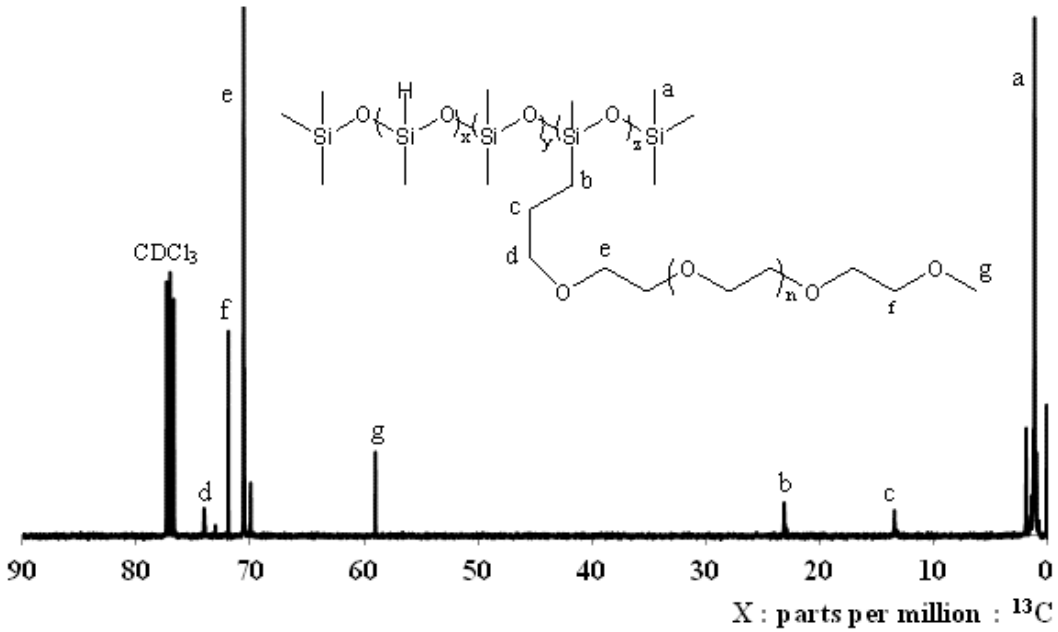

FIGURE S4. ^{13}C NMR of the hydrosilylation product of PDMS and PEG. The double bond carbon peak of starting material PEG at δ 110-130 ppm was gone. The new methylene peaks at b and c indicate that the reaction between PEG and PDMS has taken place. The peaks at a and g are methyl groups, and the peaks at d, e, and f represent -OCH_2.

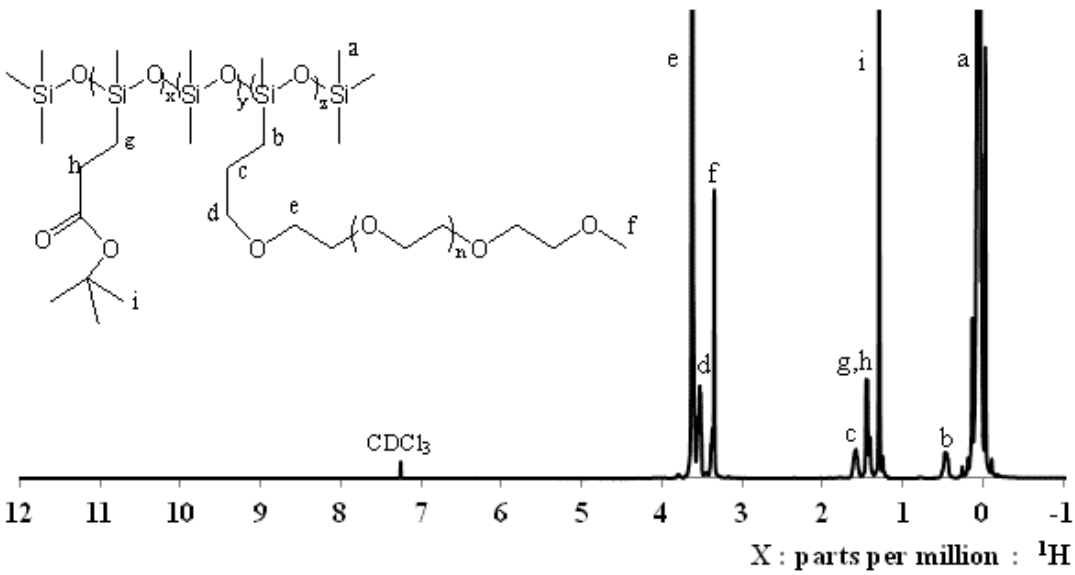

FIGURE S5. ^{1}H NMR of the hydrosilylation product of PDMS-graft-PEG and tBA. This is the precursor to APGC. The absence of a hydride peak at δ 4.8 ppm indicate the completion of the hydrosilylation reaction. This PDMS/PEG/tBA was hydrolyzed to get APGC. The peaks at a, f, and i represent methyl groups. The peaks at b, c, d, e, g, and h represent methylene groups.

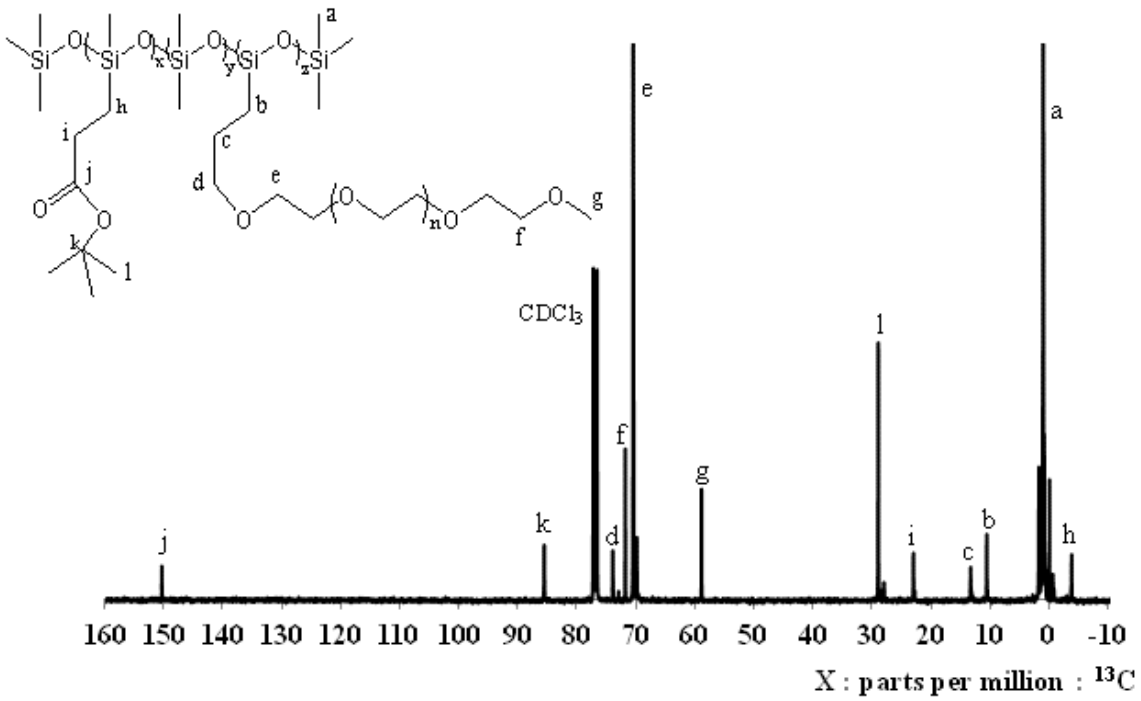

FIGURE S6. ^{13}C NMR of the hydrosilylation product of PDMS-graft-PEG and tBA. The double bond carbon peak of starting material tBA at δ 110-130 ppm disappeared. The peaks at h, i, l, and k are new carbon peaks from grafted tBA. The peak at j represents the carbonyl group from acrylate.

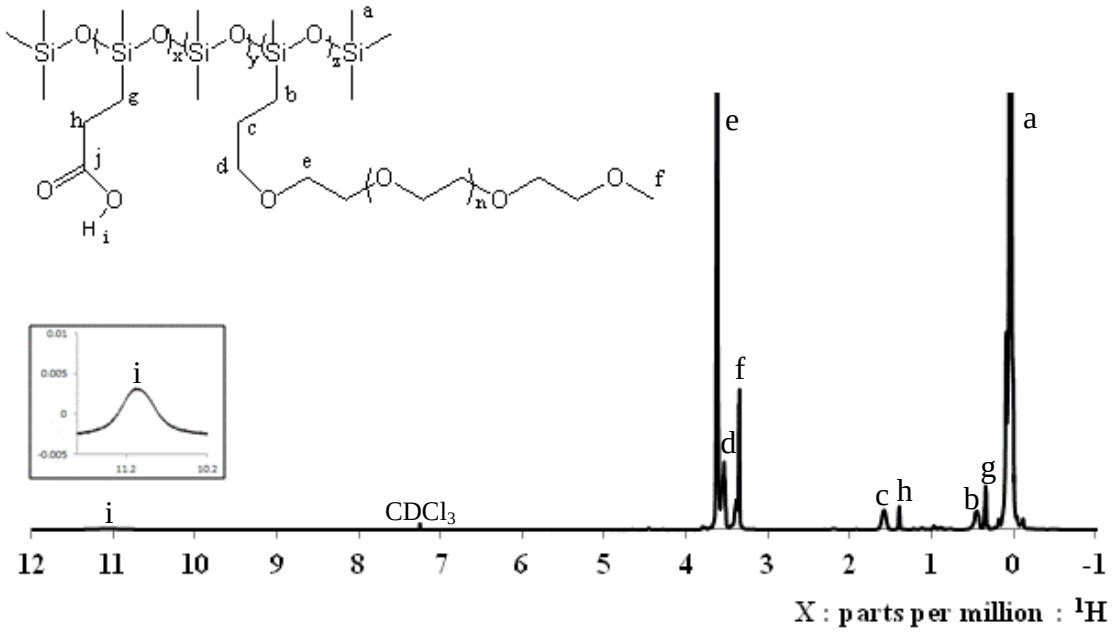

FIGURE S7. ^{1}H NMR of the final product (APGC). The carboxylic acid proton peak can be observed at i (peak i is enlarged in the inset). The peaks at a and f represent methylene groups. The peaks at b, c, d, e, h, and g represent methyl groups.

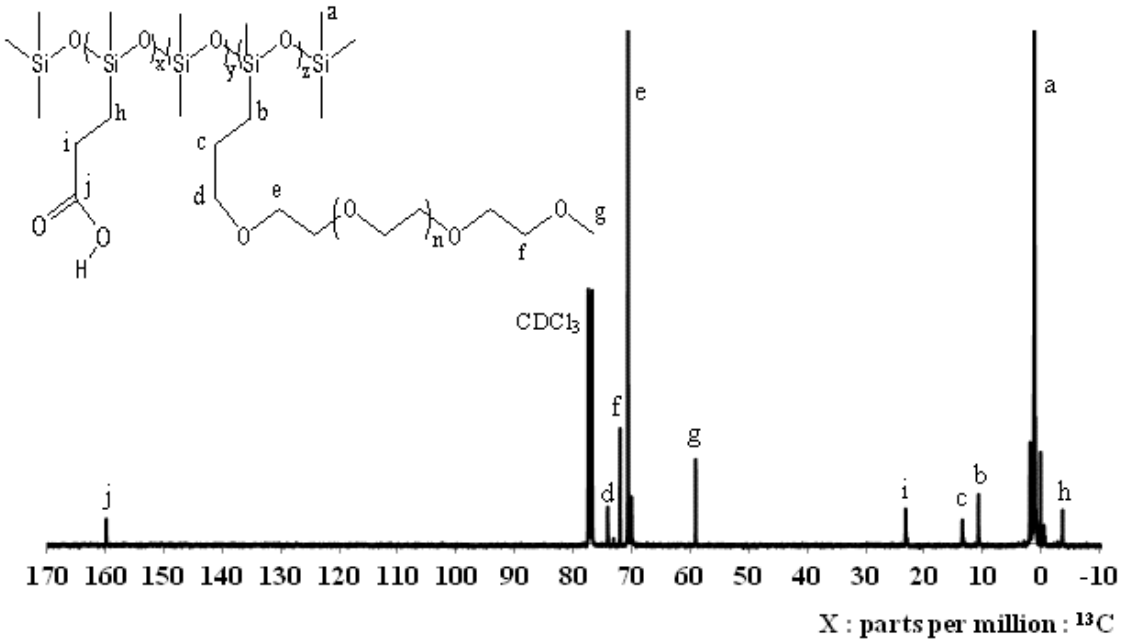

FIGURE S8. ^{13}C NMR spectrum of APGC (after hydrolysis). This ^{13}C NMR was done to verify the results obtained with ^{1}H NMR (FIGURE S7). The tert-butyl CH_3 peak at δ 29.0 ppm and the tertiary carbon from acrylate at δ 85.7 ppm disappeared. The tert butanol group was hydrolyzed and the singlet carbonyl group at j could be seen indicating the completion of hydrolysis forming APGC with carboxylic acid anchoring groups. The anchoring groups were expected to attach to the NZVI surface.

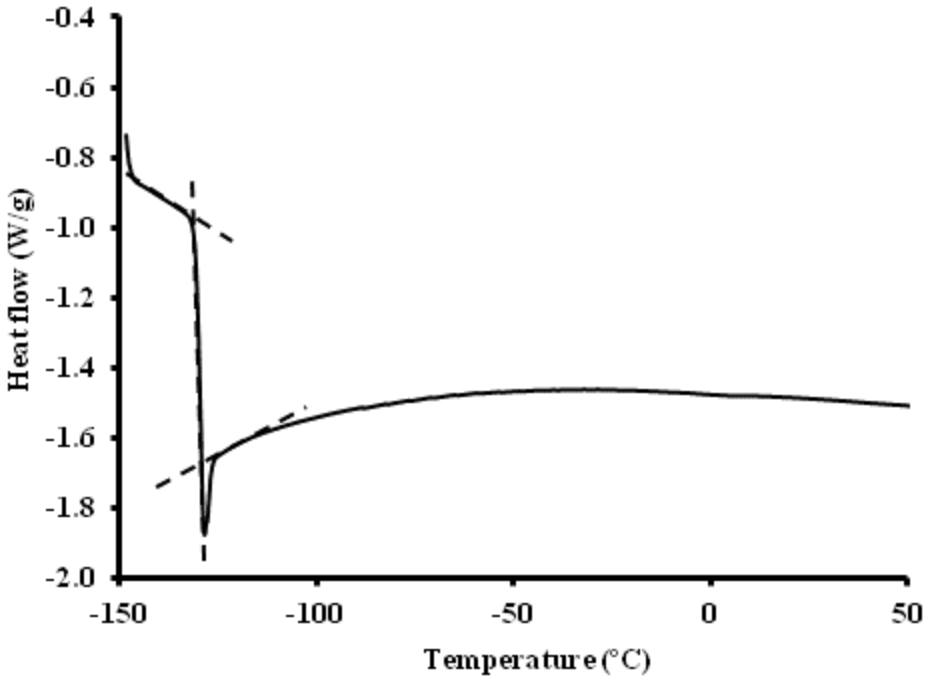

Figure S9. DSC thermogram of PDMS.

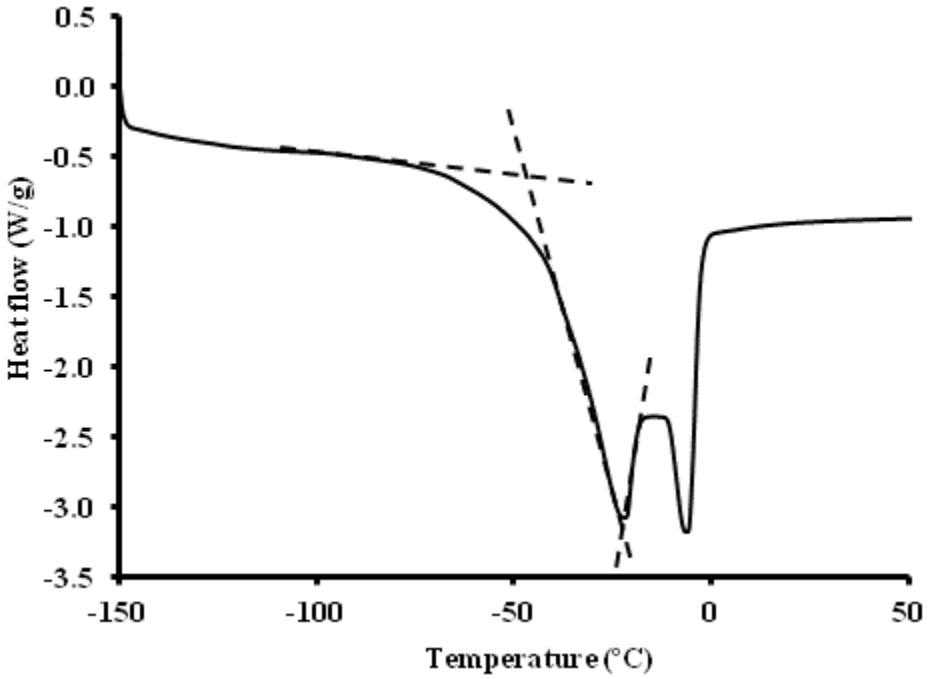

Figure S10. DSC thermogram of PDMS/PEG graft copolymer.

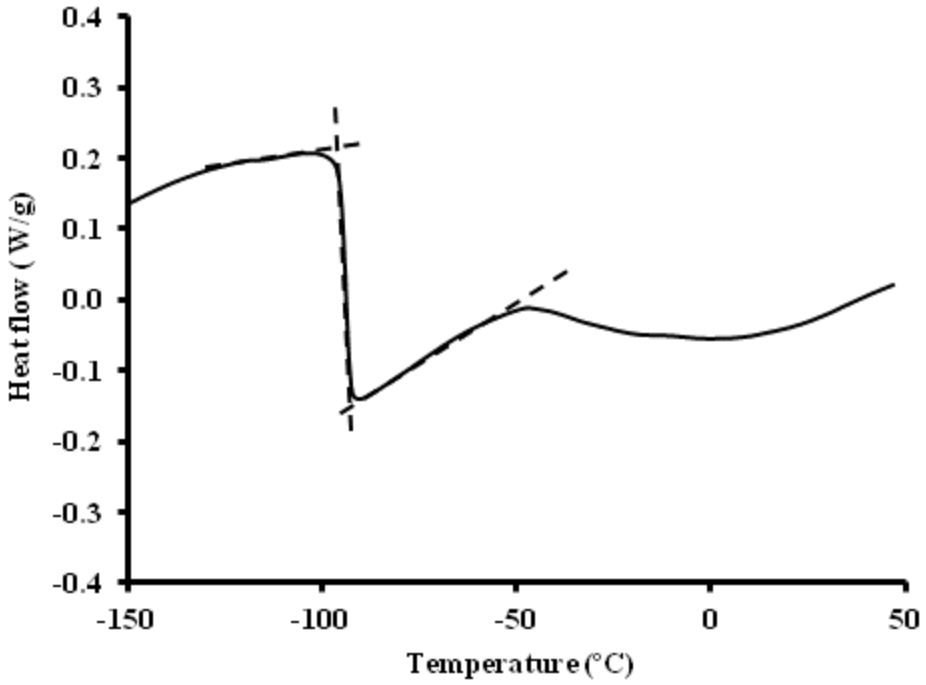

Figure S11. DSC thermogram of APGC.

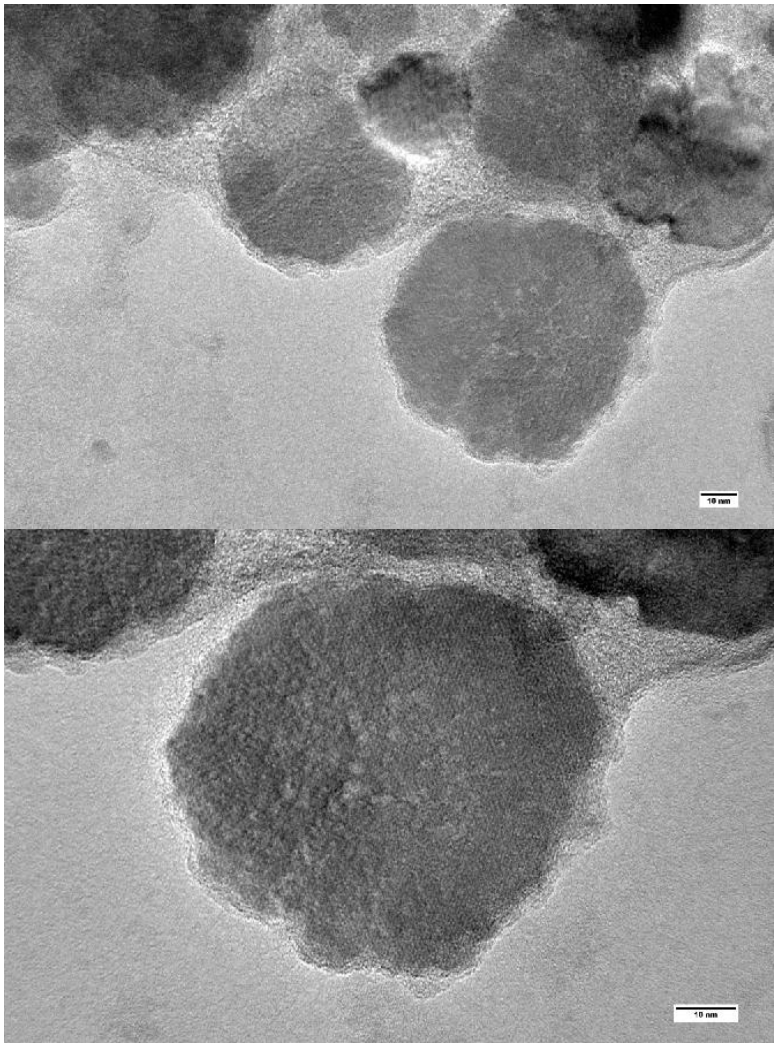

FIGURE S12. HR-TEM images showed that NZVI particles were effectively coated by APGC.

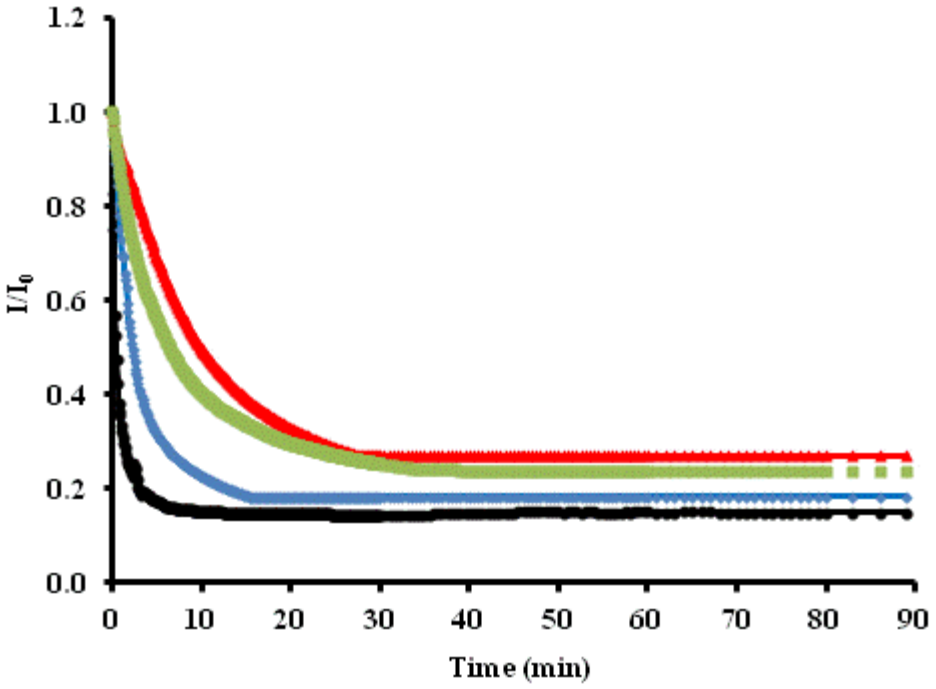

FIGURE S13. Sedimentation characteristics of bare NZVI and CNZVI with different concentration of APGC (● Bare NZVI, ◆2 g APGC L^{-1}, ■10 g APGC L^{-1}, and ▲ 15 g APGC L^{-1}). The amount of NZVI used was 3 gL^{-1} (both bare and coated). The NZVI coated with 15 g APGC L^{-1} had shown the best colloidal stability. Higher concentration (> 15 gL^{-1}) of polymer led to gel formation and the polymer could not be use for coating the NZVI particles.

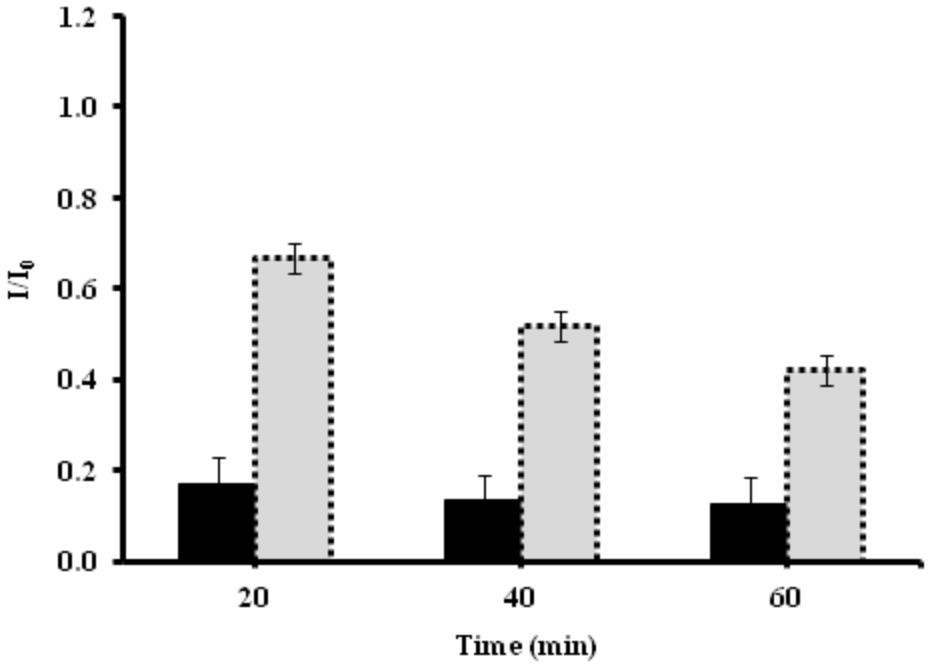

FIGURE S14. Comparison of sedimentation characteristics between NZVI coated with APGC (CNZVI) having the optimal sedimentation characteristics [plot PDMS/PEG/AA (72.5/21/6.5) in Figure 5] and bare NZVI (■ Bare NZVI, ⁙ CNZVI). The data points are connected with straight lines for ease of reading only and they do not represent trendlines. The vertical error bars indicate ± standard deviations. The concentration of APGC used for coating was 15 mgL^{-1} and NZVI was 3 gL^{-1}. I = measured light intensity, I_0 = initial light intensity.

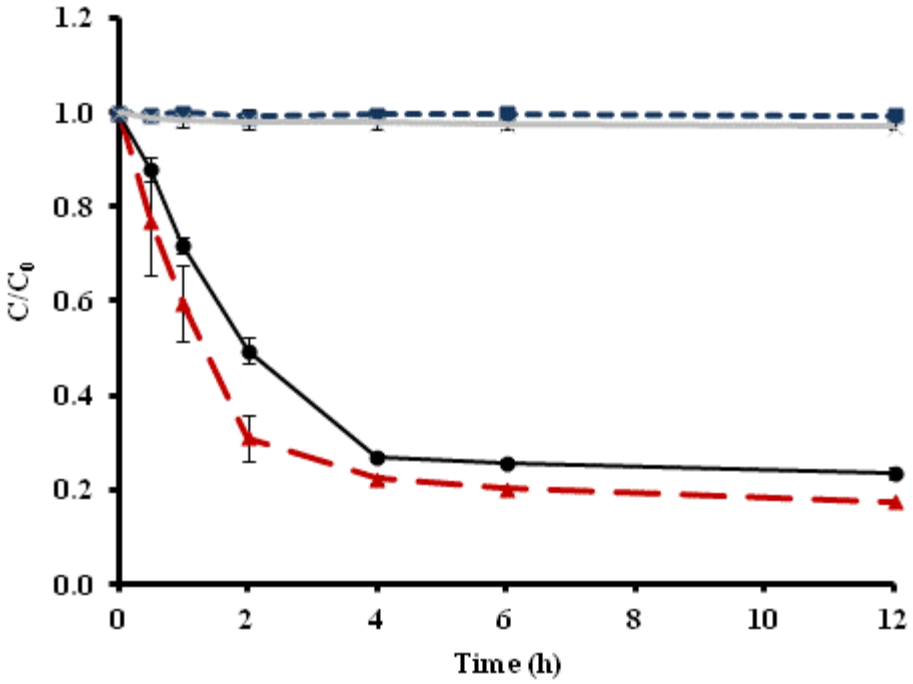

FIGURE S15. Dechlorination of TCE by bare NZVI and CNZVI. Initial TCE concentration = 15 mgL^{-1}. (CNZVI, Bare NZVI, Blank, Control). The data points are connected with straight lines for ease of reading only and they do not represent trendlines. The vertical error bars indicate ± standard deviations.

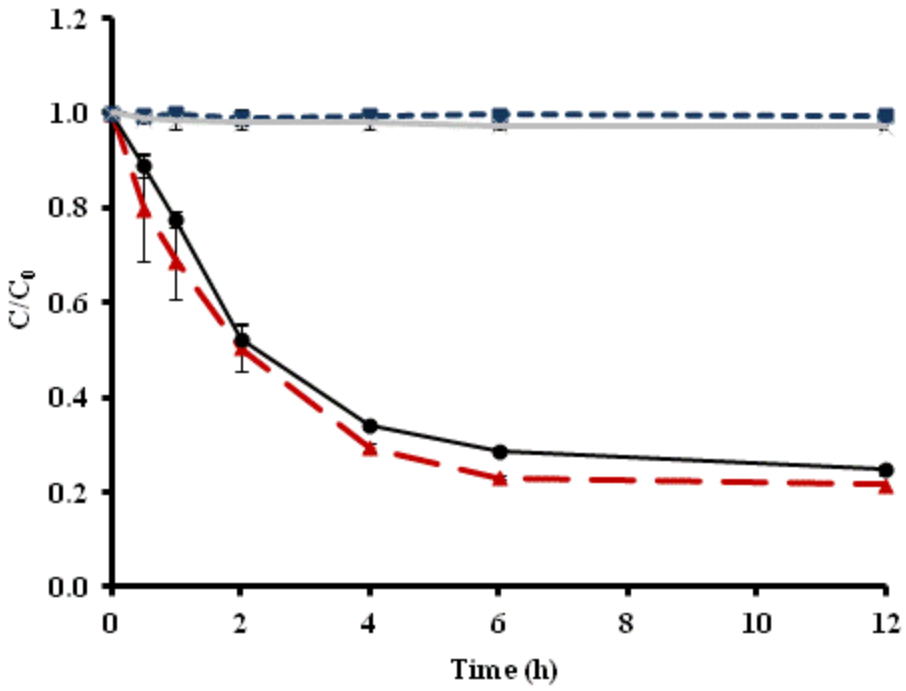

FIGURE S16. Dechlorination of TCE by bare NZVI and CNZVI. Initial TCE concentration = 1 mgL^{-1}. (CNZVI, Bare NZVI, Blank, Control). The data points are connected with straight lines for ease of reading only and they do not represent trendlines. The vertical error bars indicate ± standard deviations.

COLUMN STUDY DETAILS

A set of experiments were conducted to examine the breakthrough behavior of APGC coated nanoscale zero-valent iron (CNZVI) in columns filled with fresh quartz sand (crushed from larger pieces). Column studies were carried out in 10 cm long and 2.5 cm internal diameter glass columns as per He et al. (2009). The columns were first filled with aqueous medium (deoxygenated) and then gradually filled with quartz sand with constant patting with a glass rod to ensure proper compaction (48.86% porosity was achieved) and to avoid air pockets. During the experiments CNZVI feed solution was pumped into the quartz column with a Peristaltic pump to maintain a constant flow of 2 mL/min (down flow mode). The feed solution (0.25 g/L CNZVI in deoxygenated DI water) was stored in a tank and mixed constantly with overhead mechanical stirrer (stainless blades) for homogeneity, and purged with nitrogen to prevent oxidation of iron. Samples were collected over time at the outlet end of the columns. The results indicate that exhaustion (~90-95%) was achieved with 8-10 bed volumes passing through the fresh quartz column (**Figure S17**).

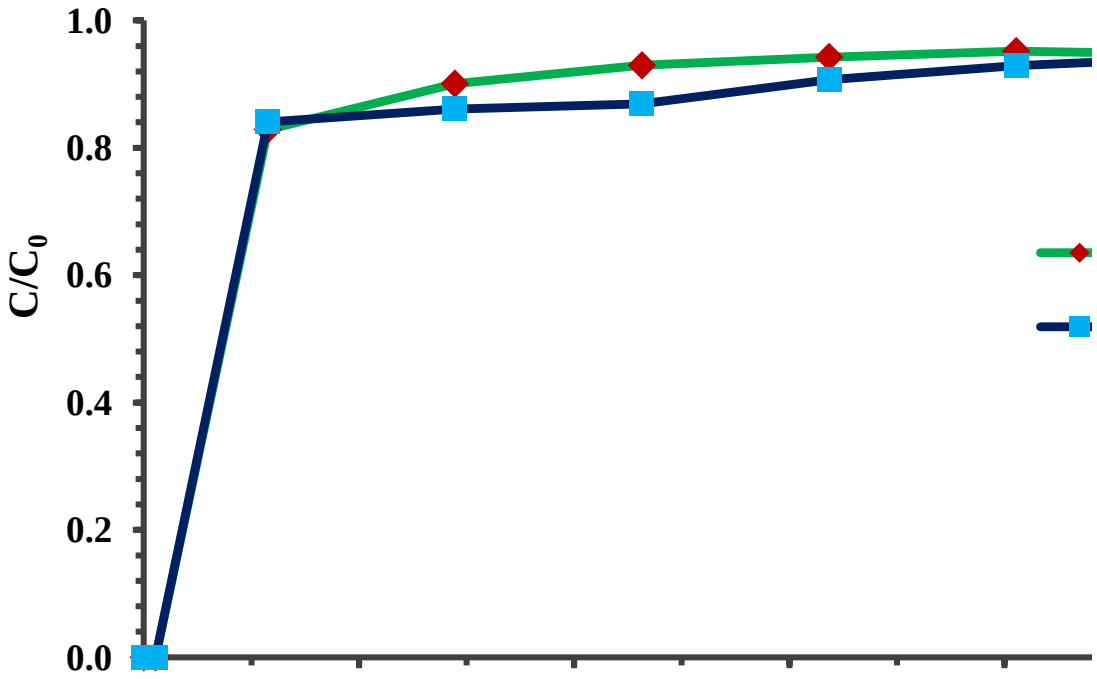

Figure S17. Quartz column study results for APGC coated NZVI.

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