550f Development of Triblock Copolymers as Dispersants and Interfacial Delivery Vehicles for Reactive Nanoparticulate Iron

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Insoluble pools of dense non-aqueous phase liquids (DNAPL) are a persistent source of mobile contamination in groundwater. Conventional remediation methods, including “pump and treat” methods, only address the dissolved contaminants. Since the DNAPL pools are not directly addressed by these methods, remediation is inefficient and slow. We envision a “targeted delivery” approach, inspired by analogy to targeted drug delivery technologies. Pursuing this analogy, we note that highly potent drugs can be targeted directly to diseased cells by coupling the drug to a delivery system that provides highly specific molecular recognition abilities that distinguish between healthy, non-targeted cells, and diseased, targeted cells. The alternative, non-specific systemic delivery, is highly inefficient by comparison. Can a delivery system be designed that targets remediation agents directly to the DNAPL pools, the source of the contamination, and thereby improve remediation efficiency? This study focuses on the development of a system that targets trichloroethylene pools. The remediation agents are based on protected zero valent iron nanoparticles. These have the capacity to reduce TCE to less toxic compounds. The requirement for a nanoparticle is based on the need to transport particles through microporous environments. The targeting is based on nanoparticle surface modification with environmentally responsive block copolymers prepared by atom transfer radical polymerization. One of the polymer blocks serves as the nanoparticle dispersant. These polyelectrolyte blocks are designed to effectively disperse the particles in water and to repel mineral and humic substances that the particles encounter during transport. A second, hydrophobic block serves to hinder water transport to the nanoparticle surface and preserve reactivity while the particles are dispersed in water, but this block is designed to swell in contact with TCE and anchor the particles at the TCE/water interface. This concentrates the particle reactivity at the DNAPL confined in micropores and is the basis for the targeted remediation approach. Thus, our requirement is not just for a nanoparticle dispersing agent, but for a multifunctional dispersing and delivery agent. To that end, we have developed a system based on poly(methacrylic acid)-b-poly(methyl or butyl methacrylate)-b-poly(styrene sulfonate) triblock copolymers that adsorb onto reactive iron nanoparticles and effectively disperse them in water. Adsorption of these triblock copolymers also enables transport of the nanoparticles through sand columns that are impassable to unmodified nanoparticles. Furthermore, we show that this triblock copolymer anchors the iron nanoparticles to the TCE/water interface. The evidence for this comes from the effectiveness of the polymer-coated particles as particulate emulsifiers to prepare TCE-in-water emulsions. The unmodified particles do not emulsify TCE and water. By comparing the emulsifying power of particle suspensions versus the supernatant of a centrifuged suspension, we show that the emulsification is due to the presence of the polymer-modified nanoparticles at the interface, and not due to traces of unadsorbed polymers.