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Mobility of zero valent iron nanoparticles and liposomes in porous media

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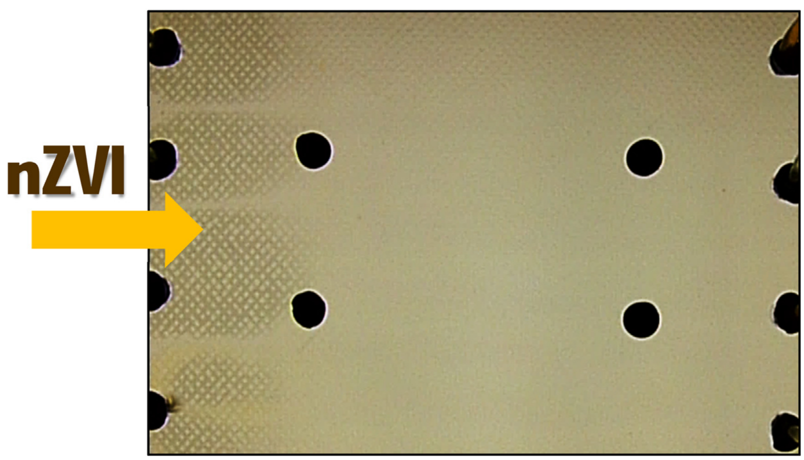
HIGHLIGHTS

- The presence of oleic phase triggers the lipid membrane disruption.
- CMC-coated nZVIs are highly mobile in any form.
- Empty liposomes co-flowing with nZVI coalesce and are trapped in pore network.
- Liposomes encapsulating CMC-coated nZVI retain, in part, their mobility.
- Trapped liposomes are easily remobilized by injecting water.

GRAPHICAL ABSTRACT



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ABSTRACT

Suspensions of zero valent iron nanoparticles (nZVI) are commonly used for the in situ remediation of groundwater contaminated with chlorinated solvents. Stable aqueous suspensions of zero-valent nano-particles (nZVI) are prepared by wet chemistry techniques and stabilized with a carboxyl-methyl-cellulose (CMC) coating. To enhance their penetration length along with their capacity to attach on oil/water interfaces, nanocomposites are prepared where the CMC-coated nZVI suspension is encapsulated in liposomes. The liposomes might be regarded as vehicles for the safe delivery of nZVI to hydrophobic pollutant targets. The integrity of synthesized liposomes membranes is evaluated with batch tests and flow-through tests in a pre-saturated with oil glass-etched pore network. For assessing the mobility and longevity of nZVI suspensions under flow-through conditions, visualization flow tests are performed on the glass-etched pore network for three types of suspensions: (i) CMC-coated nZVI; (ii) CMC-coated nZVI encapsulated in liposomes; (iii) mixture of CMC-coated nZVI and empty liposomes. The measured iron and lipid concentration breakthrough curves for all cases are interpreted by accounting for

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the transient changes caused on the particle size distribution in the suspension collected from the outlet. Albeit the CMC-coated nZVI are always very mobile, stable, and detectable in the effluent, a fraction of the liposomes or no liposomes are detected in the effluent, when injecting CMC-coated nZVI encapsulated in liposomes or mixed with empty liposomes, respectively. The flushing of the pore network with water, remobilizes the liposomes and withdraws them completely from the pore system.

1. Introduction

Most lab-scale studies and field-scale applications of nanoscale materials for soil/groundwater remediation has focused on nanoscale zero-valent iron (nZVI) and related products. The advantages of nZVI may be summarized as follows [1]:

- Fast reaction: (i) short treatment time; (ii) less cost; (iii) less exposure for workers, fauna and flora.
- Complete reduction pathway to non-toxic byproducts: (i) less exposure for workers, fauna and flora.
- In situ treatment: (i) less equipment and above-ground structures required; (ii) less costs.

The zero valent iron nanoparticles (nZVI) are synthesized by a variety of bottom-up and top-down methods, reported in detail elsewhere [2–7]. However, a disadvantage of nZVI suspended in aqueous media is the agglomeration of particles to each other and the fast attachment of agglomerates to the soil surface. Agglomeration may be caused by groundwater conditions (pH, ionic strength), surface properties of the particles, the age of materials, or shipping conditions [8,9]. Modifications to enhance the mobility, reactivity, or stability of nanoscale iron particles have been made by using polymers or surfactants. Surface modifiers increase the surface charge of the nanoparticles thereby providing electrostatic stabilization. They can also create a surface brush layer that engenders long-range strong steric repulsion forces, usually insensitive to high ionic strengths for which double layer repulsions would be greatly shielded.

Examples of iron nanoparticles stabilization methodologies include:

(1) Coatings such as polyelectrolyte or triblock polymers which are added in the suspension [9–14] to stabilize the iron nanoparticles and improve their mobility.
(2) Nanoparticle encasement in emulsified vegetable oil droplets (EZVI) [15] to improve their stability and reactivity (by facilitating their contact with the contaminant). The emulsions have the potential to partition into non-aqueous phase liquids (NAPLs) due to hydrophobic oil continuous phase that may be miscible with NAPL.
(3) Development of multi-functional nano-composites (MFNC) by incorporating nZVI into porous sub-micron particles (nano-composites) of silica [16,17] or carbon [18] to prevent agglomeration and couple iron reactivity with high silica/carbon adsorption capacity.
(4) The use of guar gum as a stabilizing agent of aqueous suspension to reduce the attachment efficiency of NP in soil grains [19].

Liposomes are artificially prepared vesicles composed of a lipid bilayer which encapsulate a region of aqueous solution inside a hydrophobic membrane. They can be used as vehicles for administration of nutrients, drugs and imaging agents Nanoliposomes have been recently used to encapsulate Ultra Small Paramagnetic Iron Oxide (USPIO) in order to target large quantities of NPs, and direct them to target sites by using small amounts of targeting ligands (for in vivo imaging purposes) [20]. The physicochemical properties of liposomes (size, surface charge and hydrophilicity, membrane fluidity, integrity) can be easily manipulated by using different preparation techniques and modulating the composition of the lipid bilayer or by adding specific polymeric coatings (e.g. PEG, chitosan etc.) on their surface [21]. Depending on the specific application, liposomes can be constructed to have optimal properties and release (of encapsulated materials) kinetics. In fact, by using a specific methodology, known as dried-rehydrated vesicles (DRV) technique [22], very high entrapment of USPIOs (<20 nm mean diameter) in nanoliposomes (mean diameter ∼100 nm) has been achieved [20]. Perhaps, the distribution, dispersion, and penetration of active NPs in polluted soils can be modulated in a beneficial way, by encapsulating them in nanoliposomes (Fig. 1a). In this manner, active particles (nZVI) will be released at high concentration in the areas where most pollutants reside, by enhancing the pollutant remediation efficiency. The general concept of nanoparticles delivery close to trapped NAPL ganglia, after the liposomes (Fig. 1a) membrane disruption, is shown schematically in Fig. 1b.

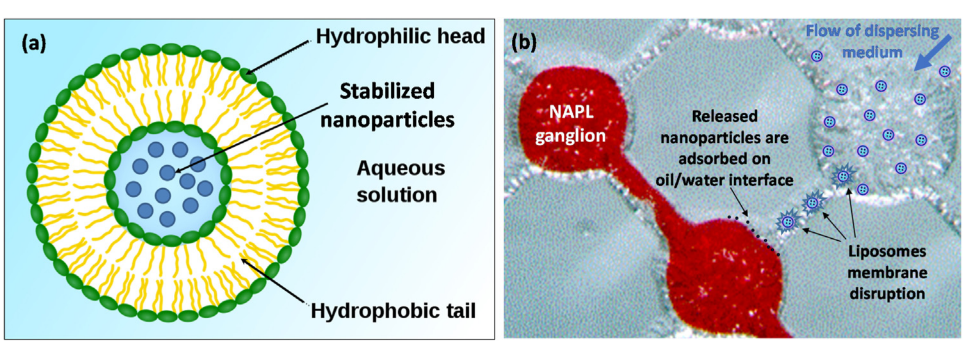

Fig. 1. (a) The general concept of a liposome encapsulating nanoparticles. (b) The liposomes are used as vehicles for the release of nanoparticles at the vicinity of NAPL/water interfacial regions.