Application of Emulsified Zero-Valent Iron to Marine Environments

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ABSTRACT: Contamination of marine waters and sediments with heavy metals and dense non-aqueous phase liquids (DNAPLs) including chlorinated solvents, pesticides and PCBs pose ecological and human health risks through the potential of the contaminant to bioaccumulate in fish, shellfish and avian populations. The contaminants enter marine environments through improper disposal techniques and storm water run-off. Current remediation technologies for application to marine environments include costly dredging and off-site treatment of the contaminated media. Emulsified zero-valent iron (EZVI) has been proven to effectively degrade dissolved-phase and DNAPL-phase contaminants in freshwater environments on both the laboratory and field-scale level. Emulsified Zero-Valent Metal (EZVM) using metals such as iron and/or magnesium have been shown in the laboratory and on the bench scale to be effective at removing metals contamination in freshwater environments. The application to marine environments, however, is only just being explored. This paper discusses the potential use of EZVI or EZVM in brackish and saltwater environments, with supporting laboratory data detailing its effectiveness on trichloroethylene, lead, copper, nickel and cadmium.

INTRODUCTION

Significant laboratory and field research has demonstrated that zero-valent metals will reductively dehalogenate dissolved chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) to ethene (Quinn et. al., 2005). Permeable reactive barriers (PRBs) containing zero-valent iron as the reactive material have been shown to be effective in treating plumes of dissolved chlorinated solvents (O'Hannesin and Gillham, 1998; Vogan et al., 1999). . PRB technology is passive and requires no energy; however, it still relies on transport of dissolved chlorinated solvents to the barrier for treatment. The use of zero-valent iron PRBs in highly oxidizing conditions or in brackish/saltwater environments is considered impractical because of the aggressive corrosion of the metal. In the oxidative nature of marine environments, the seawater competes with the relatively low concentration of contaminants for electrons on the surface of the reactive metal, rendering it ineffective at both degradation of the chlorinated solvents and the removal of the metal contaminants.

Emulsified zero-valent iron (EZVI) on the other hand does not have this disadvantage because the reactive metal is protected from the corrosive marine environment via a hydrophobic oil membrane. EZVI is composed of a food-grade surfactant, biodegradable oil, water, and zero-valent iron particles (either nano- or micro-scale iron), which form emulsion droplets that contain the iron particles in water surrounded by an oil-liquid membrane. Figure 1 includes a schematic and a magnified image of an emulsion droplet. Since the exterior oil membrane of the emulsion particles has similar hydrophobic properties as chlorinated compounds, the emulsion attracts the contaminants and pulls them into its interior reactive zone for degradation.

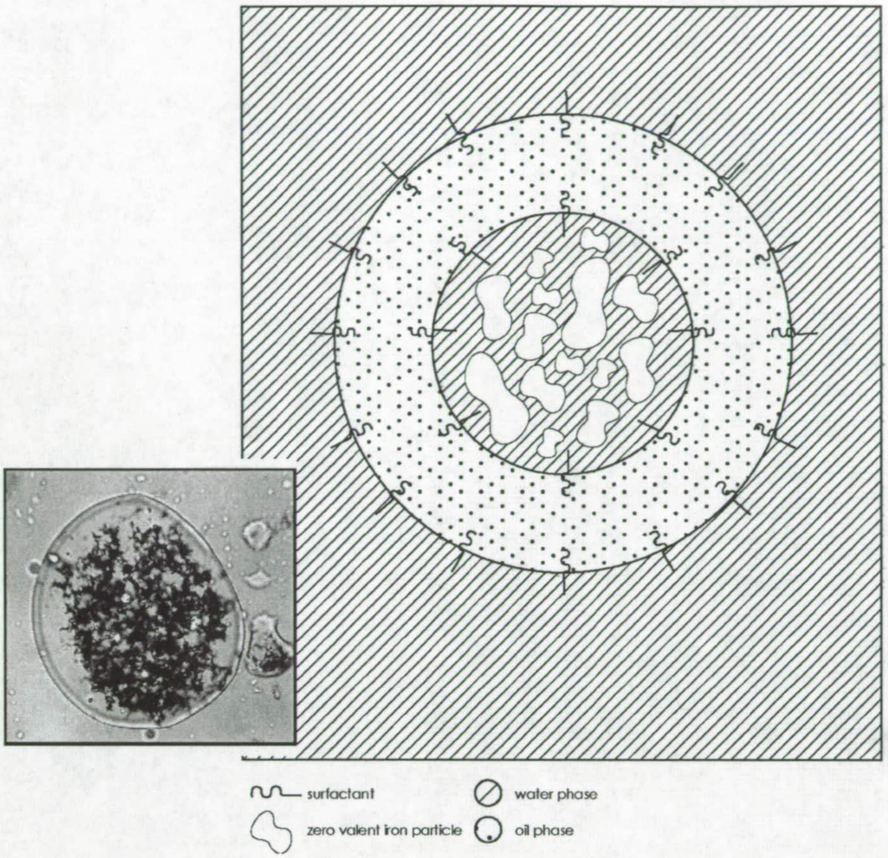

Figure 1: Magnified image and schematic of emulsion droplet

Of the 1200 sites in the United States on the National Priority List approximately 63% contain heavy metals contamination. Lead, chromium, cadmium and copper were found at 15, 11, 8, and 7 % of the sites respectively (Mulligan et al., 2001), with cadmium, lead, mercury, nickel and zinc considered by the US EPA to be the most hazardous. Because heavy metals are not biodegradable, they remain a persistent, noxious contaminant within the environment with the potential for bioaccumulation (EPA, 1999). The removal of lead and cadmium was of specific interest recently to the US Navy, where the use of seawater to flood torpedo tubes initiated corrosive action on the ship's interior causing lead and cadmium to leach into the now onboard seawater. Due to international law, the overboard dumping of this now heavily contaminated seawater was not permissible.

The removal of heavy metals from seawater or brackish water matrices is a unique challenge. It requires a system that is resistant to the corrosive nature of seawater while removing specific ions that are in a relatively low concentration compared to naturally occurring seawater salts. Zero-valent iron (Fe^0) and zero-valent magnesium (Mg) have previously been shown to effectively remove heavy metals contamination (Milum, 2004). The basic mechanism appears to be reduction of contaminant metals followed by the subsequent precipitation of their insoluble forms. Fe^0 undergoes oxidation to Fe^{2+} and then to the Fe^{3+} state. Magnesium also undergoes oxidation from Mg^0 to the Mg^{2+} state. Particulate Fe^0 has been shown to reduce Cr^{6+} to Cr^{3+} rapidly, which can then form $Cr(OH)_3$ and subsequently precipitate out of solution, greatly reducing the concentration of dissolved chromium (Cantrell et al, 1995). Lead is also reducible and undergoes reduction from Pb^{2+} to Pb^0 in the presence of either zero-valent iron or zero-valent magnesium. The challenge arises when using these zero-valent metals in the presence of naturally occurring seawater salts that instantly corrode the iron or magnesium surface, inhibiting or greatly minimizing its reducing capability.

Once again, the key to using Fe^0 or Mg^0 in brackish or saltwater systems is to protect the reductive power of these two reactants by encapsulating it in an oil-liquid membrane. In this way, only the contaminants that have the ability to pass through the oil membrane into the reactive emulsion interior will come into contact with the zero-valent metal reactant. Emulsion liquid membrane (ELM) technology has been employed as a remediation technique for the removal of metals from wastewater as both extraction and stripping processes are performed in a single operation (Raghuraman *et al.*, 1994). The ELMs are made by forming an emulsion between two immiscible liquids, such as oil and water, and are often stabilized by a surfactant. The materials to be transported through it must dissolve in the membrane, diffuse through the membrane, and reverse the dissolution on the other side (Chakravarti *et al.*, 2000). Results for the removal of heavy metals from solution using oil and water emulsions have been demonstrated and have been shown to concentrate the contaminate in the interior of the emulsion droplet (Raghuraman 1994, Chakravarti 2000, Sznejer 1999).

We have demonstrated the application of the combination of these two technologies through the use of emulsified zero-valent metals (EZVM) to treat seawaters with heavy metal contamination and chlorinated solvents. This paper discusses the potential use of EZVI or EZVM in brackish and saltwater environments, with supporting laboratory data detailing its effectiveness on degrading trichloroethylene, and immobilizing lead, copper, nickel, and cadmium.

MATERIALS AND METHODS

TCE Degradation in Seawater. Laboratory studies were performed to establish the effectivity of the EZVI to degrade TCE in saltwater. An emulsion consisting of 80 ml of corn oil, 100 ml of deionized water, 22 g of micro-scale iron, and 3 ml of Span 85 (a food grade surfactant) was prepared. Based on calculations for previous kinetics studies on the rate of TCE degradation in EZVI, headspace vials were set up in the following manner. To each vial 2.0 g of emulsion were added. To these vials, 5 ml of ocean water or deionized water were added. The solution was swirled by hand. The mixture was allowed to passivate for 2 hours. At this point 100ul of a 14,500-mg/l solution of TCE in methanol was added to all the vials. The vials were sealed and placed upon a shaker table until analysis.

The reaction vials were analyzed by GC/FID for ethene production after a 48 day period. The GC/FID Purge and Trap system was set up as follows: initially an instrument blank was analyzed to ensure that the instrument, auto sampler and concentrator were functioning within normal parameters. A calibration program for ethene was set-up by injecting 50, 100, 200, 500 and 1000 ul of a 1:300 ethene:air solution into the ports of Tekmar auto sampler connected to the purge & trap. The headspace of the experimental vials was placed in the ports by removing 5ml of the headspace and placing it into an evacuated auto-sampler port. Five milliliters of room air was replaced in the vial. This process was repeated three times to make a total of 15 ml of headspace /air that was added for each discrete sample.

Heavy Metal Removal from Seawater. Micro-scale iron (1-3 μm and <10 μm) was obtained from BASF Corporation and washed with a 5% sulfuric acid solution prior to use. Magnesium (approximately 4 μm) was obtained from Hart Metals, Inc. and used as received. Lead solutions that were prepared from dried lead nitrate with 1% HNO_3. Cadmium, copper, nickel, and chromium solutions were prepared from 1000 ppm reference solutions obtained from Aldrich and Fisher Scientific. Emulsions were prepared immediately prior to use utilizing the same composition that was used for TCE analyses, with the modification that the metal mass was reduced from 22 grams to 20 grams.

To each vial, 2.0 grams of emulsion were added. To these vials, 10 ml of ocean water containing 100 ppm Cu, Cd, Ni and Pb was added. The vials were sealed and placed on a shaker table until analysis. Aliquots from the reaction vials were analyzed by inductively coupled plasma spectroscopy and atomic absorption spectroscopy on a Varian SpectrAA 20Plus Spectrophotometer. All solutions containing lead, cadmium, copper or nickel were analyzed using an air-acetylene flame atomization apparatus. Chromium samples were analyzed on the Varian SpectrAA 20Plus Spectrophotometer outfitted with a GTA 96 Graphite Tube Atomizer.

RESULTS AND DISCUSSION

TCE Degradation in a Seawater Matrix. Analytical results showed that EZVI was very effective at degrading TCE. The reaction by-products (ethene, acetylene and ethane) were produced at the same rate in seawater (e.g. 71%) as was observed in fresh water. Additionally, iron within the EZVI particles was protected from oxidation of the corrosive seawater. This can best be seen in the Figure 2. Note that the vial containing neat or un-emulsified iron has turned an orange-yellow color. This material is an oxidized form of iron and has been shown to be incapable of reducing TCE. On the other hand, the vial containing TCE, water and EZVI shows that iron contained within the emulsion droplet is still un-oxidized and continues to be capable of reducing and degrading the TCE even within a seawater matrix. The analytical results are shown in Table 1.

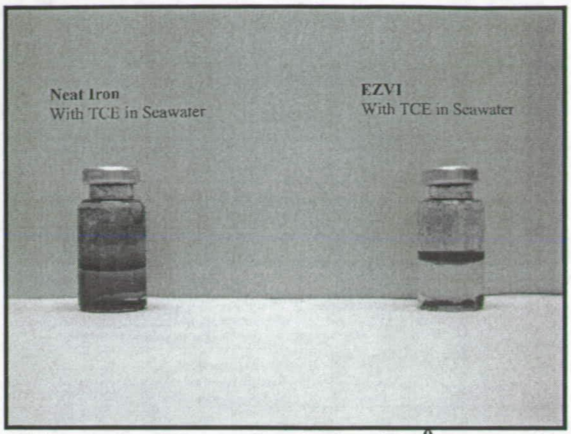

Figure 2: Photo depicting Fe^0 exposed to Seawater as neat metal and emulsified metal

Table 1: Ethene Production for TCE Exposed to EZVI in Fresh and Saltwater Environments after 48 days of Exposure

Conc. Ethene mg/l in 5ml	Area Counts	Calculated ug Ethene in 5 ml standard
Standard 0.075	6454	0.375
Standard 0.15	16650	0.75
Standard 0.3	31295	1.5
Standard 0.75	104936	3.75
Standard 1.5	213063	7.5
Sample ID with 1450 ug TCE added to 5 ml water (either salt or fresh)	**Area Counts 48 days**	**Ethene produced (ug) from 5 ml sample**
blank	0	0.24
Seawater Exp 1	51153	1.97
Seawater Exp 2	42272	1.67
Freshwater Exp 1	73965	2.75
Freshwater Exp 2	62942	2.38

R^2 = 9.98E-01 for Ethene Calibration Curve

Effectivity compared to freshwater: 71.48 %

AVG seawater Ethene Production (ug) : 1.83
AVG freshwater Ethene Production (ug): 2.56

Heavy Metal Removal from a Seawater Matrix. Analytical results indicate that for most of the heavy metals tested in this study, an emulsion formulation containing Mg^0 as the reactant gives a higher rate of removal as compared to Fe^0 as a reactant, except for copper (see Figure 3). Average removal after a five day exposure period to 100 ppm solutions of Cu, Cd, Ni and Pb were 92.5%, 81.8%, 99.6% and 98.4 % respectively. Table 2 shows a summary of the data, including standard deviations.

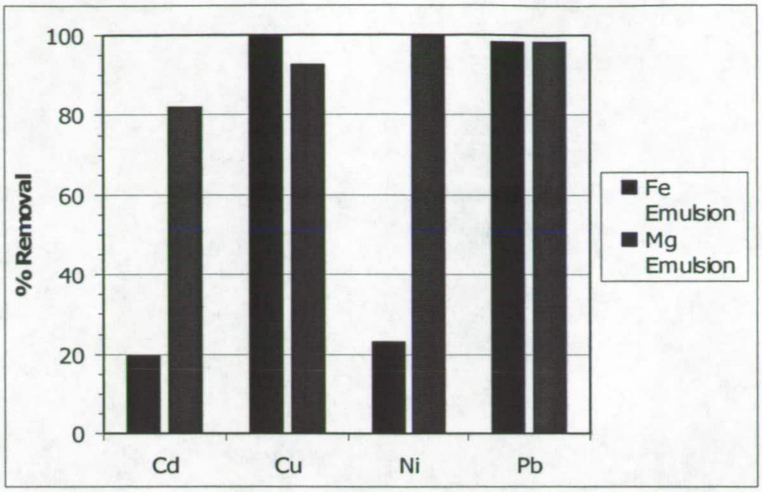

Figure 3: Matrix Effects on Metal Removal Efficiency in Seawater (10 mL of 100 ppm metal solutions in seawater exposed to 5 mL of emulsion for 5 days)

Table 2: Exposure of Various Metals in Seawater to an Mg/Oil Emulsion (C=Spiked Seawater Control and SW=Seawater Blank)

Sample	#	Abs.	Conc.	% Rem.	Avg.	sd
Cu	C	0.191	97.9	-----	-----	-----
	1	0.016	11.1	88.7	92.5	4.1
	2	0.008	5.9	94.0		
	3	0.014	10.1	89.7		
	4	0.003	2.3	97.7		
	SW	0.005	3.5	-----	-----	-----
Cd	C	0.024	109.6	-----	-----	-----
	1	0.005	21.5	80.4	81.8	3.0
	2	0.004	17.0	84.5		
	3	0.004	17.5	84.0		
	4	0.006	24.0	78.1		
	SW	0.007	26.0	-----	-----	-----
Ni	C	0.354	79.5	-----	-----	-----
	1	0.002	0.3	99.6	99.6	0.2
	2	0.001	0.2	99.7		
	3	0.002	0.5	99.4		
	4	0.001	0.3	99.6		
	SW	0.002	0.4	-----	-----	-----
Pb	C	0.087	99.66	-----	-----	-----
	1	0.005	1.63	98.4	98.4	0.3
	2	0.005	1.8	98.2		
	3	0.005	1.2	98.8		
	4	0.006	1.91	98.1		
	SW	0.006	1.99	-----	-----	-----

CONCLUSION

EZVI has been shown through laboratory testing to degrade TCE in the presence of seawater, and it has done so at a similar rate to that which was observed in a freshwater environment. In laboratory experiments, the average ethene production from the exposure of EZVI to 1450 ug of TCE was 1.83 ug in the presence of seawater and 2.56 ug in freshwater after 48 days. No other zero-valent iron-containing technology has the ability to perform as a reducing agent in a saltwater environment because of the corrosive nature of the sea salts.

EZVI containing either zero-valent iron or magnesium is also capable of removing metal ions from the complex salt matrix found in seawater. Analytical tests reveal that over 90% removal of a number of RCRA metals from aqueous solution using EZVI or EZVM can be achieved within five days of exposure. Because the reactive material, iron or magnesium, is protected by the oil-liquid membrane, it is not consumed by the salt matrix of the seawater, which would otherwise interfere with the ongoing reaction chemistry. Competitive technologies, utilizing ex situ ion exchange, fail to selectively remove ions of interest from naturally occurring saltwater ions rendering them immensely less efficient than EZVM.

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