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Impact of enhanced-flushing reagents and organic-liquid distribution on mass removal and mass-discharge reduction

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Abstract

A series of column and flow-cell experiments was conducted to investigate the impact of non-uniform organic-liquid distribution on the relationship between reductions in contaminant mass discharge and reductions in source zone mass under conditions of enhanced-solubilization flushing. Trichloroethene was used as the model organic liquid, and SDS (sodium dodecyl sulfate) and ethanol were used as representative enhanced-flushing reagents. The results were compared to those of water-flood control experiments. Concentrations of trichloroethene in the effluent exhibited multi-step behavior with time, wherein multiple secondary periods of quasi steady state were observed. This non-ideal behavior was observed for both the water-flood and enhanced-flushing experiments. For all flow-cell experiments, the later stage of mass removal was controlled by the more poorly-accessible mass associated with higher-saturation zones. The profiles relating reductions in contaminant mass discharge and reductions in mass exhibited generally similar behavior for both the water-flood and enhanced-flushing experiments. This indicates that while the rates and magnitudes of mass removal are altered by the presence of a solubilization-reagent solution, the fundamental mass-removal process is not. The profiles obtained for the flow-cell systems differed from those obtained for the column systems, highlighting the impact of source-zone heterogeneity on mass-removal behavior.

Keywords

Enhanced flushing; DNAPL; mass flux; source zone

1. Introduction

Organic-liquid contaminants such as chlorinated solvents and hydrocarbon fuels occur at many hazardous waste sites. It is well known that the presence of immiscible organic liquids in the subsurface serves as long-term sources of contamination and significantly increases the time and the cost of site remediation. Enhanced in-situ flushing using a reagent solution (e.g., surfactants, cosolvents) that increases the apparent solubility of organic contaminants and hence the rate of mass removal via enhanced solubilization (as opposed to mobilization) is one possible method for remediation of such contaminated source zones. Recently, the reduction in mass discharge achieved with a given remediation effort has become a key metric for evaluating the effectiveness of source-zone remedial actions (e.g., Rosenbloom et al., 1993; Freeze and McWhorter, 1997; DiGiulio et al., 1999; Rao et al., 2002; Newell et al., 2003; Stroo et al., 2003; DiFilippo and Brusseau, 2008).

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Several studies based on flow-cell experiments have been conducted to examine the influence of immiscible-liquid distribution and material-property heterogeneity on mass removal and mass-discharge reduction under conditions of aqueous or enhanced-solubilization flooding (e.g., Powers et al., 1998; Walker et al., 1998; Taylor et al., 2001; Brusseau et al., 2000, 2002; Conrad et al., 2002; Saenton et al., 2002; Fure et al., 2006; Suchomel and Pennell, 2006; Brusseau et al., 2008; Kaye et al., 2008; Zhang et al., 2008; DiFilippo et al., 2010). With the exception of DiFilippo et al. (2010), these studies focused either on water floods or enhanced-solubilization floods, and did not compare behavior for the two systems. DiFilippo et al. (2010) compared mass-discharge-reduction versus mass-reduction profiles for two source configurations for cases of enhanced-solubilization (tween-80) and water flooding. They observed similar profiles for both the surfactant and water floods for both configurations. Similar results were reported for column experiments conducted for enhanced-solubilization and water flooding (Carroll and Brusseau, 2009; Tick and Rincon, 2009). The purpose of the study reported herein was to further investigate the impact of enhanced-solubilization flooding on mass removal and mass discharge reduction for systems with non-uniform organic-liquid distributions.

2. Materials and Methods

The column was constructed of stainless steel and was 1 cm in diameter and 7 cm long. The rectangular flow cell was constructed of stainless steel and tempered glass, with dimensions of 40 cm long by 20 cm high by 2.6 cm wide. The flow cell was equipped with multiple, evenly spaced injection/extraction ports on each end. In addition, three ports were evenly spaced at the top of the flow cell to allow injection of organic liquid. Water-tight seals were made with Teflon and silicone sealant.

Three natural sand media with different median particle diameters were used for the flow-cell experiments, 713 μm (20/30 mesh), 359 μm (40/50 mesh), and 172 μm (70/100 mesh) (Unimin Corp.). A homogenized mixture of these sands was used as one porous medium for the column experiments (referred to as “mixed sand”). This mixed sand has a median grain diameter of 0.34 mm and a uniformity coefficient of 3.5. A soil (Hayhook) with ~15% silt and clay content was used as a second medium for the column experiments. This soil has a median grain diameter of 0.26 mm and a uniformity coefficient of 16. Trichloroethene (TCE), ACS reagent grade (99% purity, Aldrich), was used as the organic liquid. Sodium Dodecyl Sulfate (SDS) and ethanol (both reagent grade) were used as enhanced-solubilization reagents. The organic liquid was dyed with Sudan IV (Aldrich) at a concentration of 100 mg/L.

For the column experiments, a (macroscopically) spatially uniform residual saturation of TCE was established using standard methods described briefly as follows (e.g. Russo et al., 2009a; Mahal et al., 2010). First, organic liquid was injected into the bottom of the vertically positioned water-saturated column. Mobile organic liquid was removed prior to the initiation of water and reagent flooding by flushing several tens of pore volumes of TCE-saturated solution through the column (injected at the top) at a flow rate equivalent to a mean pore-water velocity of approximately 0.6 cm/h. Residual saturations of approximately 0.2 and 0.1 were developed for the mixed sand and Hayhook soil, respectively. A 5% SDS solution by weight and 20% and 50% ethanol solutions by volume were used for the enhanced-flushing column experiments. The flow rate used for these experiments was equivalent to a mean pore-water velocity of 0.6 cm/h. The results of these experiments were compared to water floods conducted previously for the same porous media using identical procedures (Russo et al., 2009a; Mahal et al., 2010).

Two packing configurations were created for the rectangular flow-cell experiments. The first flow-cell configuration consisted of a homogeneous pack of 20/30 sand as the matrix, with a layer of 70/100 sand placed along the bottom boundary (Figure 1A). The second configuration consisted of a matrix of 40/50 sand with lenticular lenses of 20/30 sand (Figure 1B). The TCE was injected through the top injection ports using a gastight syringe and needle. The injection needle was driven into the flow cell, creating a point injection source. Organic liquid was injected at a rate of 1 ml/min and allowed to naturally distribute within the porous media for a period of 48 h prior to the initiation of reagent or water flushing. Previous studies have reported that stable organic-liquid distributions were attained after ~24 h (e.g., Fure et al., 2006; Suchomel and Pennell, 2006; Kaye et al., 2008; DiFilippo et al., 2010).

The initial distributions of TCE generated for the two systems are shown in Figure 1. It is observed that a zone of residual saturation in the matrix existed above a local region of higher saturation (pool) that resided above the lower-permeability layer for configuration 1. Conversely, two pools were present for configuration 2, with a zone of residual saturation located in between. A 5% SDS solution was used for the enhanced-flushing experiments conducted with the flow cell. The flow rate used for these experiments was equivalent to a mean pore-water velocity of 10 cm/h. Two replicate experiments were conducted for configuration 1. In addition, an experiment was conducted for configuration 2 using a slower flow rate, equivalent to 1 cm/h.

Effluent samples (2.5 ml) were collected with a glass syringe and injected into a 10-ml glass vial. The samples were analyzed immediately using an ultraviolet-visible spectrophotometer (Shimadzu 1601) at a wavelength of 210 nm (quantifiable detection limit of ~1 mg/l). The effect of SDS and ethanol on TCE absorbance was negated through the use of relatively high dilution factors (>10), as confirmed by comparison of calibration curves developed with and without the presence of the SDS/ethanol.

3. Results and Discussion

The trichloroethene elution curves obtained for the column experiments are presented in Figures 2 and 3 for the mixed sand and Hayhook soil, respectively. As would be expected given the relatively uniform distribution of trichloroethene within the columns, the concentrations initially coincide with the aqueous or apparent solubility. The length of time for which concentrations remain at this level is observed to vary as a function of the solubilizing power of the reagent solution, denoted by the magnitude of the enhancement factor (see Figure 1). The elution curves for each of the various solutions are similar for the two porous media in terms of both relative elution positions and general profile shapes. The replicated experiments show good reproducibility (see Figure 3).

The trichloroethene elution curves exhibit multi-step behavior with time, wherein multiple secondary periods of quasi steady state are observed. This non-ideal behavior was observed for both the water-flood and enhanced-flushing experiments. However, the temporal extent of these secondary periods is significantly shorter for the enhanced-solubilization systems compared to the water floods. Such non-ideal behavior has been observed in prior column experiments, even for very ideal porous media (Russo et al., 2009a; Mahal et al., 2010). The observed behavior is considered to be a manifestation of non-ideal dissolution phenomena, wherein hydraulic accessibility of the organic liquid changes during the dissolution process, as mediated by the fluid distribution and pore-network configuration at the pore scale (Russo et al., 2009a,b). Experiments conducted using high-resolution imaging methods have demonstrated for example that the distribution of non-wetting fluids (such as

trichloroethene) is heterogeneous at the pore scale for systems with apparently uniform spatial distributions at the column scale (e.g., Russo et al., 2009b).

The trichloroethene elution curves obtained for the flow-cell experiments are presented in Figures 4 and 5 for configurations 1 and 2, respectively. The effluent concentrations are much higher in the presence of enhanced-flushing solutions as is expected. The initial concentrations are lower than $C/C_0 = 1$ for all of the experiments, in contrast to the results obtained for the column experiments. The behavior observed for the flow-cell systems is caused by their macroscopically nonuniform initial trichloroethene distributions and the associated dilution effects.

The elution curves for both water-flood and enhanced-flushing experiments exhibit multi-step behavior (Figure 4). For all of the flow-cell experiments, the later stage of mass removal was controlled by the more poorly-accessible mass associated with higher-saturation zones. This is illustrated with the images collected after approximately nine pore volumes of flooding, which show the contaminant mass remaining in the system is associated solely with the pool regions (Figure 1). This behavior is attributed to the impact of non-uniform distributions of organic liquid and associated flow-field heterogeneity, as observed in prior experiments (e.g., Brusseau et al., 2000, 2002; Fure et al., 2006; Brusseau et al., 2008; DiFilippo et al., 2010).

Examining the relationship between reductions in contaminant mass discharge and reductions in mass is an expeditious means by which to assess the fundamental dissolution and mass-removal process. Among the advantages of this approach is that mass removal is normalized to initial mass, which accounts for differences in parameters such as flow rate, initial mass, and solubilities among different experiments. The mass-discharge-reduction versus mass-reduction (MDR-MR) profiles for the column experiments are presented in Figures 6 and 7 for the mixed sand and Hayhook soil, respectively. For all experiments, significant reductions in mass discharge did not occur until relatively large fractions of mass (~0.3–0.5) were removed. In addition, the relationships all exhibit generally convex-downward profiles. This behavior, in conjunction with the behavior observed for the elution curves, indicates that mass removal during the initial stage of flooding was not significantly constrained by mass-transfer limitations. This is consistent with the initial conditions of the experiments, wherein trichloroethene was distributed uniformly within homogeneously packed columns, i.e., a “homogeneous” source.

The MDR-MR relationships obtained for the flow-cell experiments are different from those obtained for the column experiments (Figures 8 and 9). For the flow-cell experiments, the reductions in mass discharge began at smaller mass-reduction fractions (~0.1–0.2). In addition, the shapes of the profiles are more sigmoidal compared to those of the column systems. The flow-cell systems, with their permeability variability and nonuniform initial trichloroethene distributions, represent heterogeneous sources compared to the column systems. MDR-MR relationships similar to those observed herein for the flow-cell systems have been observed in prior flow-cell (e.g., Fure et al., 2006; Brusseau et al., 2008; DiFilippo et al., 2010) and field (Brusseau et al., 2013) studies. Inspection of Figures 5 and 9 shows that generally similar behavior was observed for the experiments conducted at slower and faster pore-water velocities, indicating that flow rate had minimal impact on overall behavior.

Estimating or predicting the MDR-MR relationship is of great interest for assessing the effectiveness of remedial actions. Several source-depletion functions and models have been developed in this regard. A simple function, described by $MDR = MR^n$, has for example been used (e.g., Rao et al., 2002). The smooth profiles produced with such a function do not

accurately represent the measured profiles obtained for the experiments reported herein. This suggests that more complex functions are likely to be required to represent the behavior anticipated for heterogeneous systems, as has been noted previously (e.g., Brusseau et al., 2008; DiFilippo et al., 2010).

4. Summary

A series of column and flow-cell experiments was conducted to investigate the impact of non-uniform organic-liquid distribution on the relationship between reductions in contaminant mass discharge and reductions in source-zone mass under conditions of both water flooding and enhanced-solubilization flushing. Contaminant elution curves exhibited multi-step behavior, wherein multiple secondary periods of quasi steady state were observed. This non-ideal behavior was observed for both the water-flood and enhanced-flushing experiments. For all of the flow-cell experiments, the later stage of mass removal was controlled by the more poorly-accessible mass associated with higher-saturation zones.

The profiles relating reductions in contaminant mass discharge and reductions in mass exhibited generally similar behavior for both the water-flood and enhanced-flushing experiments (conducted with two different solubilization reagents). This was true for both the column and flow-cell systems. This indicates that while the rates and magnitudes of mass removal are altered by the presence of a solubilization-reagent solution, the fundamental dissolution and mass-removal process is not. The MDR-MR profiles obtained for the flow-cell systems differed from those obtained for the column systems, highlighting the impact of source-zone heterogeneity on mass-removal behavior.

Acknowledgments

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Figure 1 A



Figure 1B

Figure 1. Images of organic-liquid distribution and porous-media configuration for flow-cell experiments: A) Configuration 1 (single pool); Top = initial condition, Bottom = after ~9 pore volumes of flooding with SDS solution. B) Configuration 2 (two pools); Top = initial condition, Bottom = after ~9 pore volumes of flooding with SDS solution.

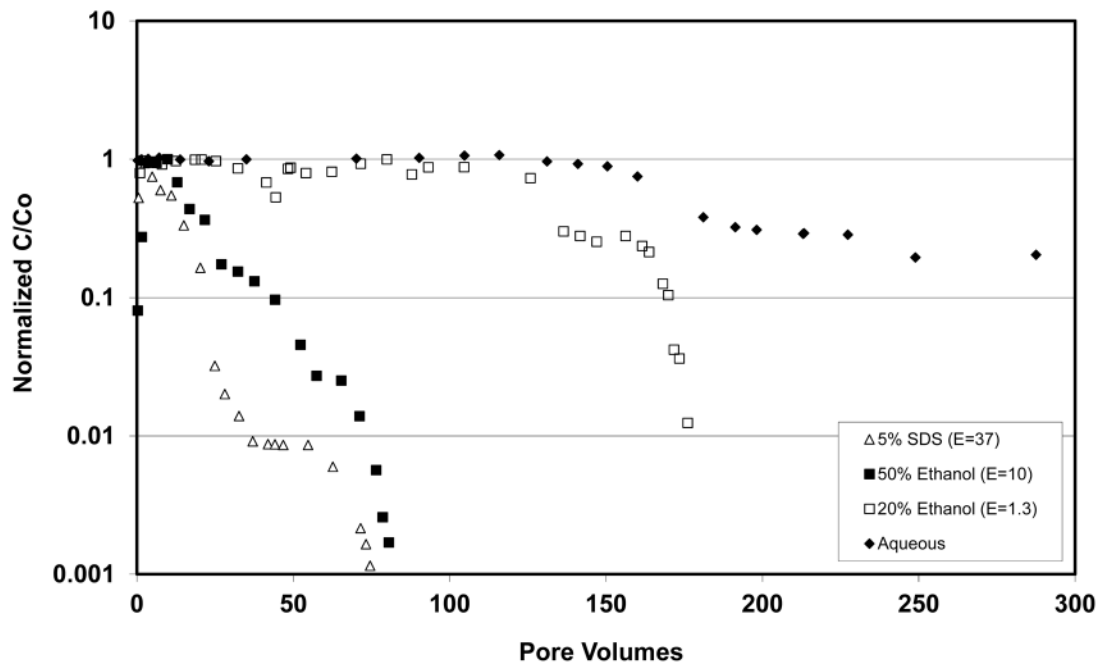


Figure 2. Effluent trichloroethene concentration as a function of pore volumes for the water-flood and the enhanced-solubilization column experiments conducted using mixed sand. The relative concentration (C/C_0) of TCE in the effluent is normalized by the enhancement factor (increase in apparent (measured) solubility compared to aqueous solubility), which is reported in the legend. Note that the concentrations for the water-flood experiment extend for several hundred pore volumes off-scale.

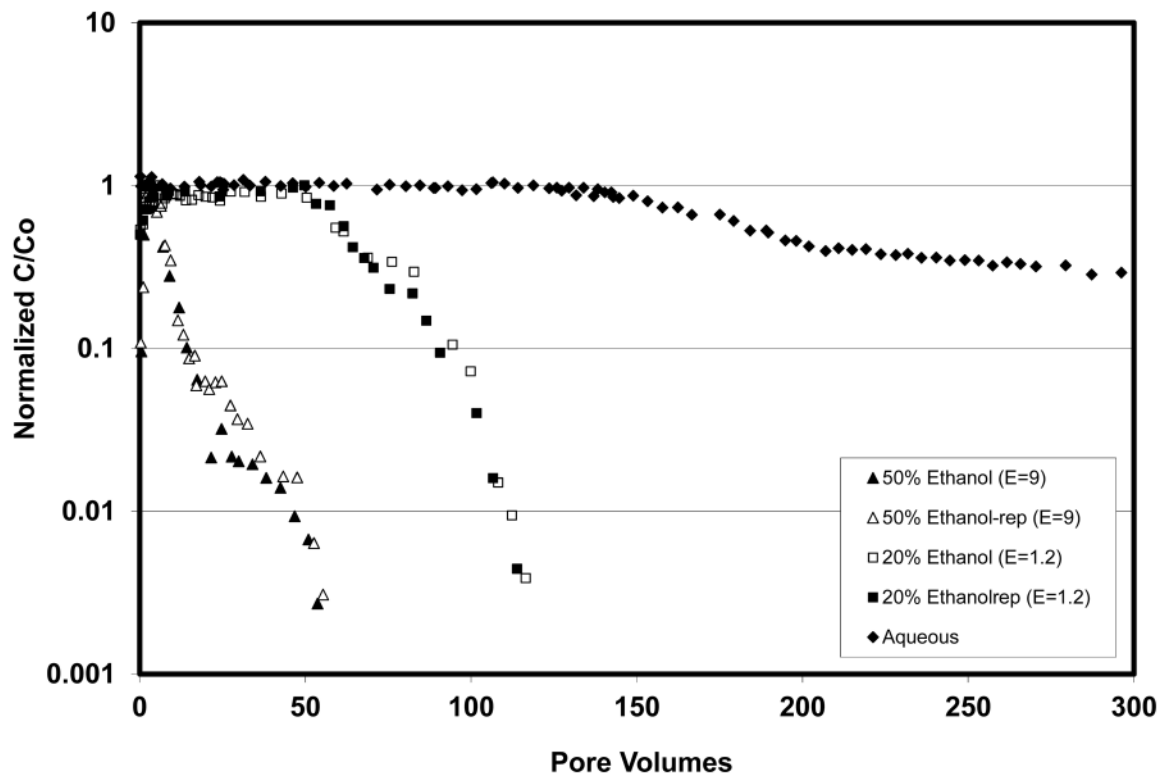


Figure 3.

Effluent trichloroethene concentration as a function of pore volumes for the water-flood and the enhanced-solubilization column experiments conducted using Hayhook soil. The relative concentration (C/C_0) of TCE in the effluent is normalized by the enhancement factor (increase in apparent (measured) solubility compared to aqueous solubility), which is reported in the legend. Note that the concentrations for the water-flood experiment extend for several hundred pore volumes off-scale.

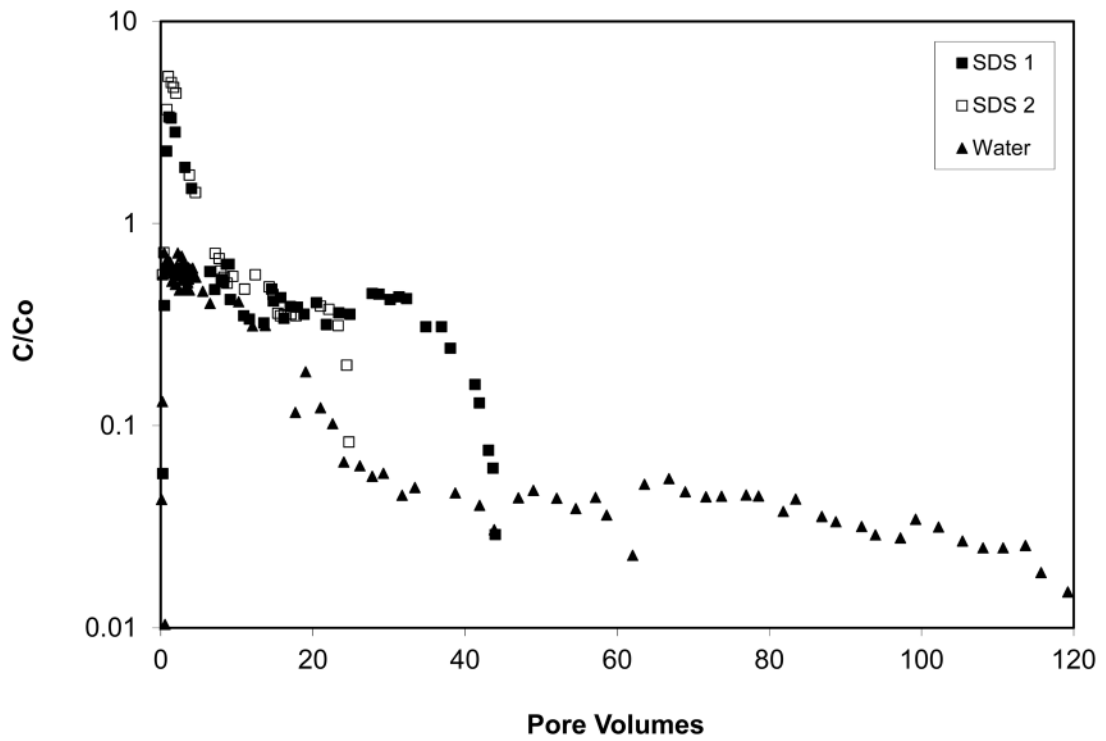


Figure 4. Effluent trichloroethene concentration as a function of pore volumes for the water-flood and the enhanced-solubilization (SDS) flow-cell experiments conducted for configuration 1. The water-flood data were reported previously by DiFilippo et al. (2010). The effluent concentrations are normalized by aqueous solubility.

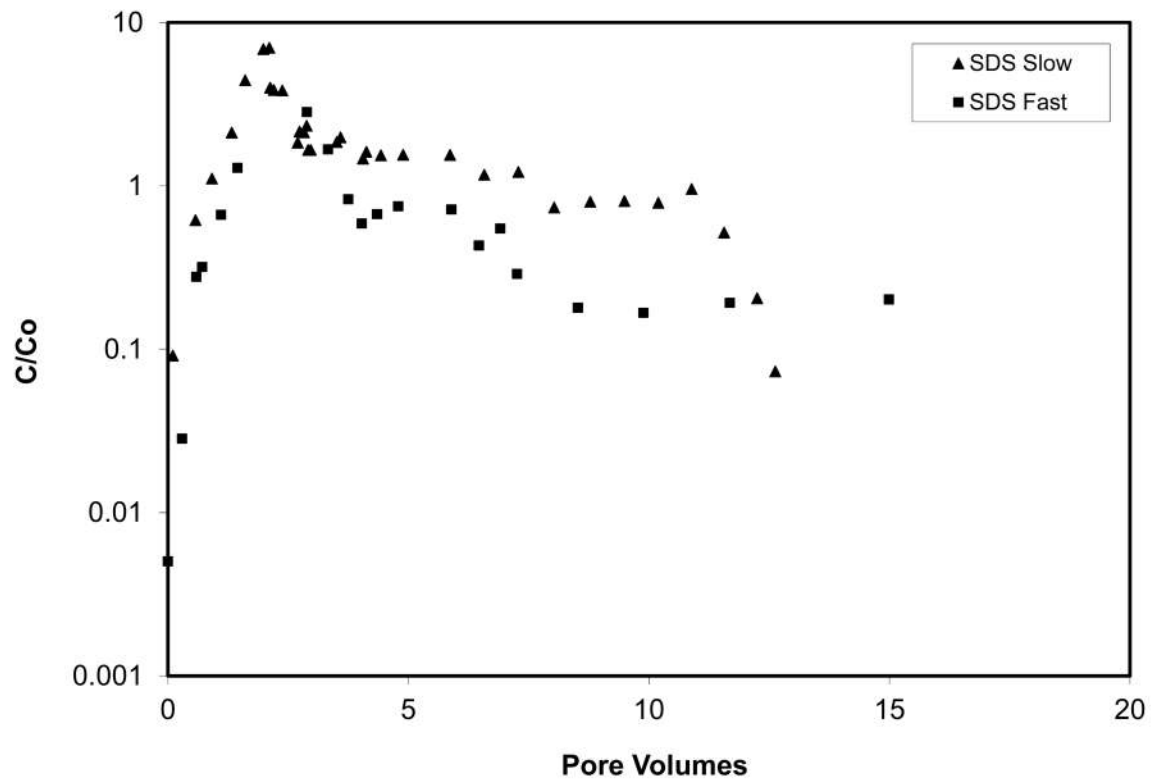


Figure 5. Effluent trichloroethene concentration as a function of pore volumes for the enhanced-solubilization (SDS) flow-cell experiments conducted for configuration 2. The effluent concentrations are normalized by aqueous solubility.

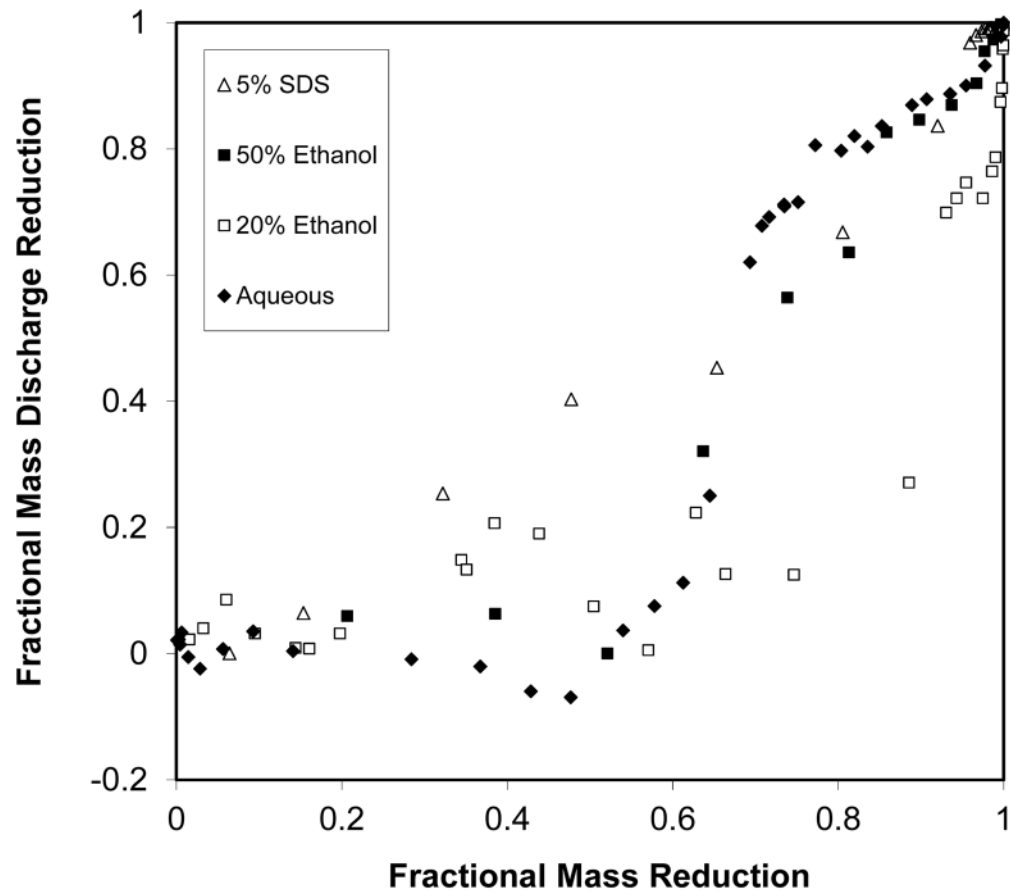


Figure 6. Mass discharge reduction versus mass reduction for the column experiments conducted using mixed sand.

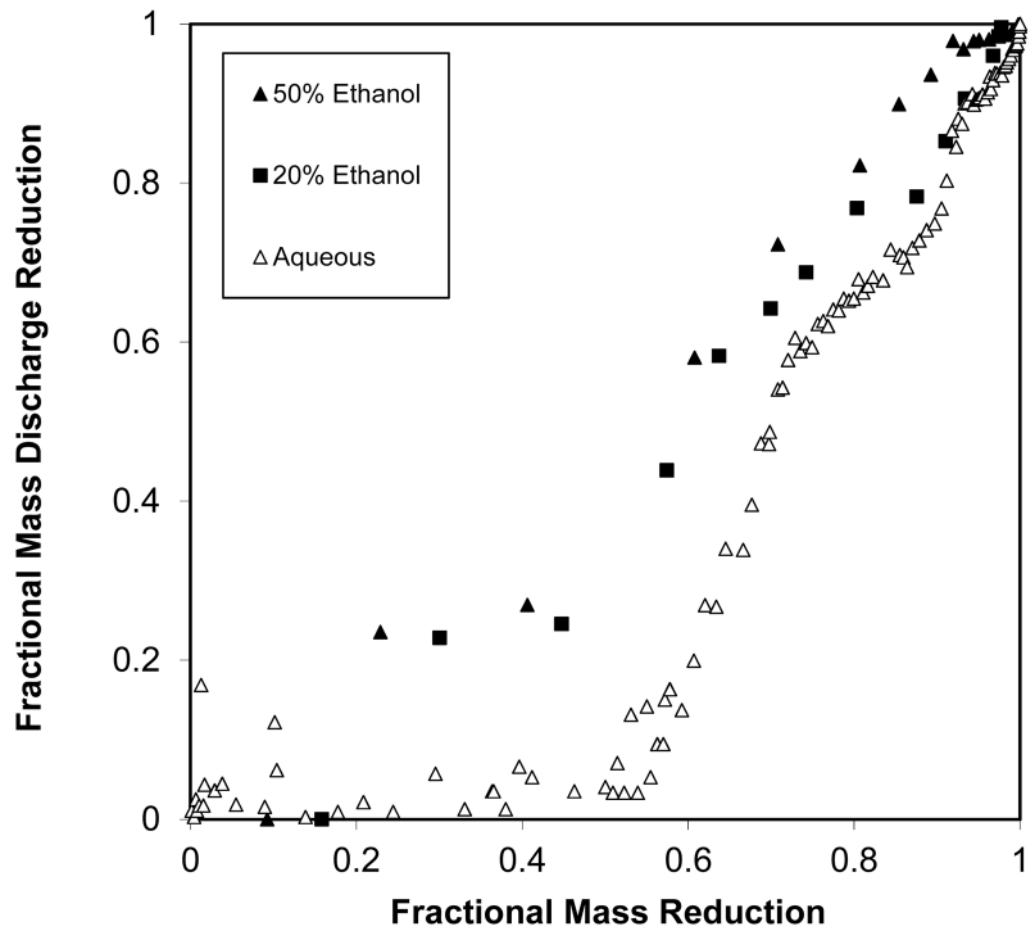


Figure 7. Mass discharge reduction versus mass reduction for the column experiments conducted using Hayhook soil.

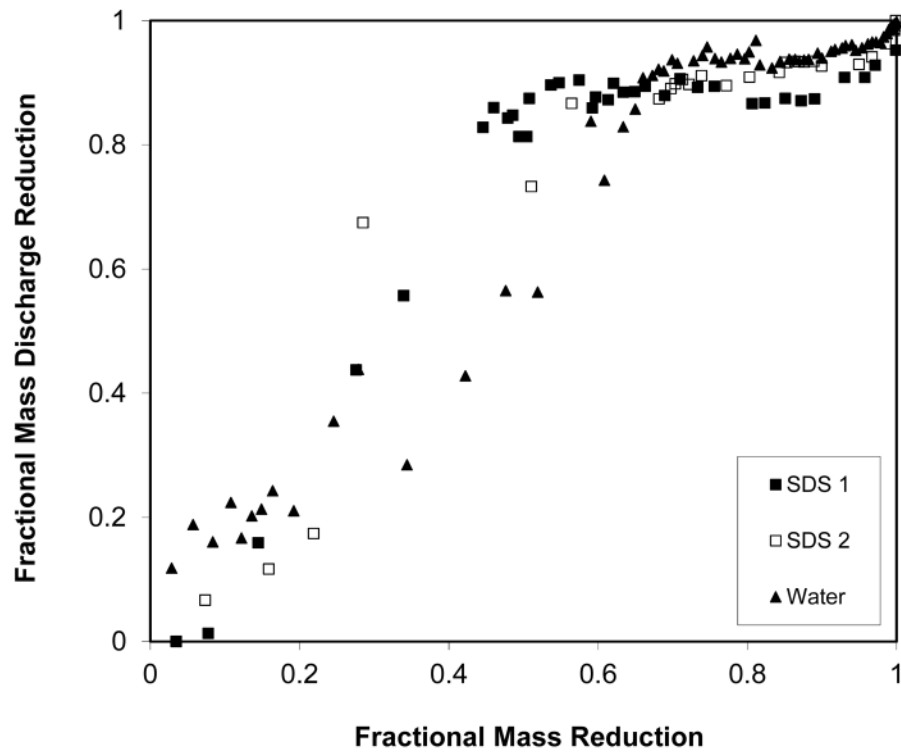


Figure 8. Mass discharge reduction versus mass reduction for the flow-cell experiments conducted for configuration 1.

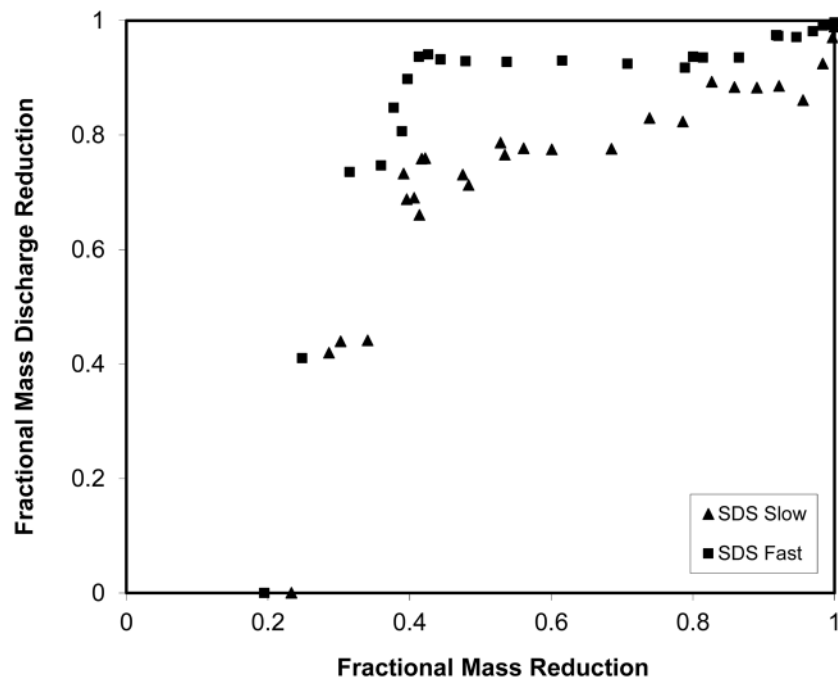


Figure 9. Mass discharge reduction versus mass reduction for the flow-cell experiments conducted for configuration 2.