SURFACTANT-ENHANCED ELECTROKINETIC REMEDIATION OF HYDROCARBON-CONTAMINATED SOILS

By

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A Thesis
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in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF SCIENCE

Department of Biosystems Engineering
University of Manitoba
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STEVEN P. THOMAS

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Abstract

Concern over soil and groundwater contamination has created a demand for new and efficient remediation technologies. Surfactant-enhanced electrokinetic remediation is an innovative technique which has the potential to remove hydrocarbons from contaminated clay soils faster and more efficiently than conventional remediation methods. The main objectives of this research were to (1) evaluate the efficiency of using surfactant-enhanced electrokinetic remediation to remove hydrocarbons from contaminated soil columns in the laboratory; (2) identify the effect of various physical and chemical factors on the performance of electrokinetic remediation; and (3) develop equations to model surfactant-enhanced electrokinetic remediation. Research was also conducted on expanding and improving the analytical methods using the relatively new solid-phase microextraction technique for the determination of hydrocarbon concentration in water.

The soil column experiments indicate surfactant-enhanced electrokinetic remediation with sodium dodecylsulfate (SDS) is dominated by electrophoretic transport of micelles. The application of a surfactant increased the current through the soil which led to increased electrolysis of water. Pore fluid flow was also significantly greater in clay columns with an applied voltage potential gradient.

Values for SDS micelle-water partition coefficients were determined as 3.19, 3.42, 3.45, 3.39, and 3.36 for toluene, ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene respectively. A new relationship between the SDS micelle-water partition coefficient and the octanol-water partition coefficient was determined to allow prediction of surfactant effects for other hydrocarbons. The optimum SDS concentration during surfactant-enhanced electrokinetic remediation should be less than 2% (w/w).

Surfactant-enhanced electrokinetic remediation was modelled by adapting the classical advection-dispersion-retardation equation to include a modified retardation factor and electrokinetic effects. The model results were highly dependent on the input parameters chosen. Modelling results indicate that electrophoretic transport of hydrocarbons in SDS micelles is the dominant factor influencing transport during surfactant-enhanced electrokinetic remediation. In order to utilize electroosmotic flow, the voltage potential gradient should be greater than 1 V/cm.

Surfactant-enhanced electrokinetic remediation is still an emerging technology and a greater understanding of the factors involved is necessary before decontamination can be confidently applied in the field. However, this research significantly adds to the knowledge of surfactant-enhanced electrokinetic remediation.

"I have yet to see any problem, however complicated, which, when you looked at it in the right way, did not become more complicated."

Anderson's Law,

Ground Water Monitoring and Review,

Fall 1994 p.148-158

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List of Symbols

A = cross sectional area

B = Thomas ratio factor

C = hydrocarbon concentration in the solution phase

C_{cmc} = apparent hydrocarbon solubility at the CMC

C_{mic} = concentration of hydrocarbon in surfactant micelles expressed as amount per volume of solution

CMC = critical micelle concentration

C_{sat} = apparent hydrocarbon solubility in solution at a particular surfactant concentration greater than the CMC

C_{soil} = concentration of hydrocarbon sorbed onto the soil

C_{surf} = surfactant concentration

C_w = concentration of hydrocarbon in the aqueous phase expressed as amount per volume of solution

dE/dx = voltage potential gradient

dh/dx = hydraulic gradient

D^* = coefficient of molecular diffusion for the solute in the porous medium

D_o = permittivity of the pore fluid

DS_{mic} = moles of surfactant in micellar form per volume of solution, i.e., (C_{surf}-CMC)

D_x = hydrodynamic dispersion coefficient in the x direction

EC = electrical conductivity

f_{HCmic} = fraction of hydrocarbon in surfactant micelles

f_{oc} = weight fraction of organic carbon

I = current

J_x = the mass of solute per cross-section area transported in the x direction per unit time

K = the distribution constant of the analyte on the SPME fibre

K_d = distribution coefficient

K_{eo} = coefficient of electroosmotic permeability

K_h = hydraulic conductivity

K_i = coefficient of water-transport efficiency

K_{mc} = micelle-water partition coefficient expressed in concentration-based units

K_{mm} = micelle-water partition coefficient expressed as a dimensionless mole fraction ratio

K_{oc} = partition coefficient of a compound between organic carbon and the aqueous phase

$K_{oc,\ cmc}$ = modified partition coefficient of a compound between organic carbon and the aqueous phase taking into account surfactant effects

K_{ow} = octanol-water partition coefficient

LOD = limit of detection

M_o = mass of contaminant added to the system

MSR = molar solubilization ratio

n = porosity

n_{mol} = number of moles sorbed by the SPME fibre

N = the mean occupancy number of the organic molecules in SDS micelles at saturation

%RSD = percent relative standard deviation

Q = the volume flow rate

Q_{eo} = electroosmotic flow rate

R = retardation factor

R_f = modified retardation factor

R_p = radius of the charged particle

S = hydrocarbon solubility in the aqueous phase

SDS = sodium dodecylsulfate

S_i = the aqueous solubility of a compound in a complex mixture

S_{wi} = individual aqueous solubility of a compound

t = elapsed time

T_e = Thomas ratio

u_{ep} = electrophoretic mobility of the micelle

v_{eo} = electroosmotic flux

v_{ep} = electrophoretic flux or the flux of the micelles

v_h = hydraulic flux

V_{mol} = the molar volume of water (0.01805 L/mol at 25°C)

v_w = average linear groundwater velocity

V_s = volume of the stationary phase of the SPME fibre

x = distance travelled in the x direction

X_a = mole fraction of a compound in the aqueous phase

X_i = mole fraction of a compound in a complex mixture

X_m = mole fraction of compound in the micellar pseudo-phase

α = confidence limit

α_l = dispersivity

κ = diffuse double layer thickness

η = viscosity of the pore fluid

ρ_b = dry bulk density

σ = electrical conductivity of the pore fluid

ζ_{soil} = zeta potential of the soil

ζ_{mic} = zeta potential of the micelles

1.0 Introduction

1.1 Scope

Hydrocarbon contamination of soil and groundwater has become a major environmental concern in recent years due to increased environmental awareness and knowledge of the widespread occurrence of hydrocarbon contamination. Contamination by organic liquids originates from many sources ranging from leaking underground storage tanks at gasoline service stations to accidental spills at large industrial facilities. It has been estimated that hundreds of thousands of gasoline leaks to the subsurface may be presently occurring from the seven to eight million underground storage tanks found in the United States (Hoag and Marley 1986). With over half of the U.S. population depending on groundwater as a potable water supply (Putnam 1988) and the high demand for clean groundwater in Canada, the potential impact of hydrocarbon contamination is enormous.

Concern over soil and groundwater contamination along with the cost and limitations of current remediation methods has created a demand for new and efficient remediation technologies. Electrokinetic remediation with a surfactant is an innovative technique which has the potential to remove hydrocarbons from contaminated clay soils faster and more

efficiently than other techniques. However, limited research has been done in using electrokinetic remediation with a surfactant and the complicated chemical and physical interactions involved have not been adequately understood. The scope of this research is to evaluate the performance of using surfactant-enhanced electrokinetic remediation to remove hydrocarbons from contaminated soil columns in the laboratory and to identify the effect of various physical and chemical factors on the performance of surfactant-enhanced electrokinetic remediation. In addition, equations which combine electrokinetic and surfactant effects are to be developed to model contaminant transport during surfactant-enhanced electrokinetic remediation.

1.2 Surfactant-Enhanced Electrokinetic Remediation

Electrokinetic remediation is an innovative *in situ* remediation technique which promotes the movement of contaminants through soil by applying a low-level voltage potential gradient. The application of an electrical gradient causes the movement of cations (positively charged particles) which drag the pore fluid toward the negatively

charged cathode (Fig. 1.1). This bulk flow of pore fluid, referred to as electroosmotic flow, can significantly increase flow through low permeability soils. Electroosmotic flow transports the contaminants toward the cathode within the aqueous phase.

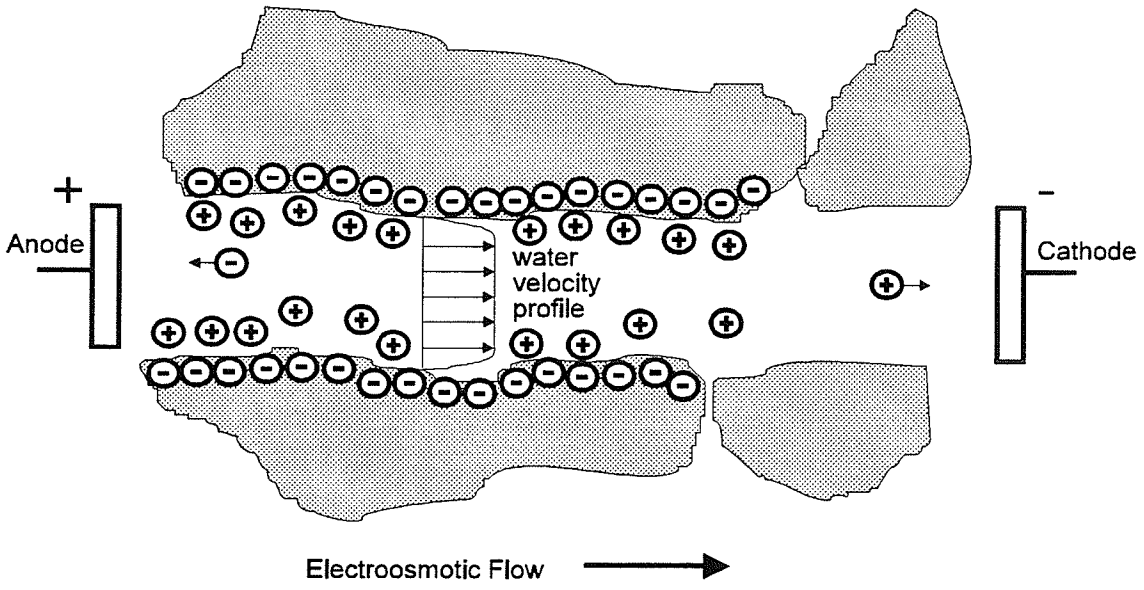

Figure 1.1 Schematic of electroosmotic flow in a charge porous media (adapted from Shapiro et al. 1989).

Another transport phenomena called electrophoretic flow occurs when combining electrokinetics with a processing fluid consisting of an ionic surfactant (enhanced electrokinetic remediation). Electrophoretic flow is the movement of charged particles toward the oppositely charged electrode with the application of a voltage potential