TETRACHLOROETHYLENE MIGRATION AND REMEDIATION BY SURFACTANT-ALCOHOL IN TWO-DIMENSIONAL SATURATED LAYERED SAND LABORATORY EXPERIMENT

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ABSTRACT

Surfactant-alcohol remediation have been reviewed by many researchers as an innovative technology to remediate tetrachloroethylene (PCE) from the subsurface. However, the application of surfactant-alcohol remediation to layered sand conditions is still obscurity and its implementation is limited due to flow sensitivity to site characterization. The laboratory experiment was performed in assessing the efficiency of surfactant-alcohol remediation through two-dimensional (2-D) saturated layered sand contaminated with tetrachloroethylene (PCE) spill. The 2-D physical model consist of front clear glass for easy visualization of 2-D PCE migration and framed with aluminum material has been developed. The type of sand use is fine sand and coarse sand. The laboratory investigation of PCE remediation in 2-D saturated layered sand using three different surfactant solutions. The first solution consist of 4 % surfactant, the second solution consist of 8 % surfactant and the third solution consist of 4 % surfactant and 15 % n-butanol. The PCE migration has been captured and analyzed to evaluate the dominant mechanisms and efficiency of PCE remediation. The laboratory experimental results shows that the dominant mechanism of PCE remediation in 2-D saturated layered sand using surfactant-alcohol treatment is solubilization and mobilization mechanisms. The solubilisation mechanisms are govern by the properties of surfactant itself where the surfactant are soluble in water due to the oxygen atom that are capable in forming hydrogen bond with the water molecules. The oxygen atom in surfactant are the hydrophilic head which is water lover attach to water and the other atom with the hydrophobic tail which is water hate attach to PCE. The interfacial tension between PCE, water and sand are lod because the surfactant molecules are surround PCE. The addition of co-surfactant, n-butanol in surfactant solution help in the formation of microemulsion which increase the number of micelles thus increase the solubilisation and mobilization of PCE. The reduction of total density of the microemulsion result in the PCE migration to the upward direction following its low density compared to water density. This shows that the prevention of uncontrolled downward migration of PCE are possible. The effect of microemulsion in lowering the interfacial tension between PCE, water and sand has result in no residual PCE left at the PCE source zone. The results of this study shows that surfactant-alcohol are very efficient solution to remediate PCE in 2-D saturated layered sand.

ABSTRAK

Pemulihan surfaktan-alkohol telah dikaji oleh ramai penyelidik sebagai teknologi yang berinovasi untuk menyingkirkan tetrachloroethylene (PCE) dari subpermukaan. Walau bagaimanapun, penggunaan pemulihan surfaktan-alkohol kepada keadaan pasir yang berlapis masih kabur dan perlaksanaannya adalah terhad disebabkan oleh alirannya yang sensitif terhadap pencirian tapak. Satu eksperimen makmal telah dijalankan untuk menilai kecekapan pemulihan surfaktan-dipertingkatkan di dalam dua dimensi (2-D) lapisan pasir yang tepu yang tercemar dengan tumpahan tetrachloroethylene (PCE). 2-D fizikal model yang mengandungi gelas jelas didepan untuk penglihatan yang jelas untuk 2-D pergerakan PCE dan dibingkaikan dengan bahan aluminium telah dibangunkan. Jenis pasir yang digunakan adalah pasir halus dan pasir kasar. Kajian eksperimen pemulihan PCE di dalam 2-D lapisan pasir tepu menggunakan tiga larutan surfaktan-dipertingkatkan yang berbeza. Larutan pertama mengandungi 4 % surfaktan, larutan kedua mengandungi 8 % surfaktan dan larutan ketiga mengandungi empat peratus surfaktan dan lima belas peratus n-butanol. Pergerakan PCE dirakamkan dan dianalisa untuk menilai mekanisma utama dan keberkesanan pemulihan PCE. Keputusan eksperimen menunjukkan mekanisma utama pemulihan PCE di dalam 2-D lapisan pasir tepu menggunakan pemulihan surfactant-alkohol adalah ditadbir oleh sifat surfaktan itu sendiri dimana surfaktan tersebut adalah larut dalam air disebabkan oleh atom oksigen yang dapat membentuk ikatan hydrogen dengan molekul air. Atom oksigen di dalam surfaktan adalah kepala hyrodrophilic dimana ia adalah suka dengan air lampir dengan air dan atom yang lain dengan ekor hydrophobic dimana ia benci air lampir dengan PCE. Ketegangan dalam permukaan antara PCE, air dan pasir dikurangkan kerana molekul surfaktan mengelilingi PCE. Pertambahan pembantu surfaktan, n-butanol di dalam larutan surfaktan menolong pembentukan mikroemulsi dimana pertambahan jumlah micelles yang menyebabkan pertambahan perlarutan dan pergerakan PCE. Pengurangan jumlah ketumpatan microemulsi menyebabkan pergerakan PCE ke arah atas disebabkan ketumpatannya yang rendah daripada ketumpatan air. Ini menunjukkan pencegahan pergerakan PCE kebawah yang tidak dapat dikawal adalah boleh. Kesan dari microemulsi ini dalam mengurangkan ketegangan dalam permukaan antara PCE, air dan pasir telah menyebabkan tiada serpihan PCE tertinggal di dalam zon sumber PCE. Hasil kajian ini menunjukkan surfaktan-alkohol adalah larutan yang cekap untuk memulihkan PCE dari 2-D larutan pasir tepu.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

1-D	-	One dimensional
2-D	-	Two-dimensional
3-D	-	Three-dimensional
API	-	American Petroleum Institute
ASTDR	-	Agency for Toxic Substance and Registry Disease
ASTM	-	American Society for Testing and Materials
Br	-	Bromine
CAS	-	Chemical Abstract Services
CBA	-	Cost-to-benefit analysis
CEC	-	Cation exchange capacity
CONNE	-	Connection
CHEMP	-	Chemical
DCE	-	cis-1,2-dichloroethylene
PCE	-	Tetrachloroethylene
DOE	-	Department of environment
ELEME	-	Element
EQA	-	Environmental Quality Act
GENER	-	Generation
IARC	-	International Agency for Research on Cancer
ICP-OES	-	Inductively Plasma Optical Emission Spectrometry
INCON	-	Initial condition
IPP	-	Image Pro-Premier
ISB	-	In situ bioremediation
ISCO	-	In situ chemical oxidation
ISCR	-	In situ chemical reduction
ISTT	-	In situ thermal treatment

ITRC	-	Interstate Technology and Regulatory Council
IUPAC	-	International Union of Pure and Applied Chemistry
LCD	-	Liquid crystal display
LNAPL	-	Light non-aqueous phase liquid
MESH	-	Meshmaker
MINC	-	Multiple interacting continua
MODFLOW	-	Modular finite-difference flow model
MT3D	-	Three-dimensional multi-transport
MULKOM	-	Research code for nonisothermal multiphase, multicomponent flows of Newtonian and non-Newtonian fluids
NAPL	-	Non-aqueous phase liquid
NAWC	-	Naval Air Warfare Center
NX	-	Grid direction x-axis
NY	-	Grid direction y-axis
NZ	-	Grid direction z-axis
PCBs	-	Polychlorinated Biphenyls
PCE	-	Tetrachloroethylene
REEs	-	Rare-earth elements
ROCKS	-	Keyword for porous media properties in T2VOC
RPCAP	-	Relative permeability and capillary pressure
RT3D	-	Three-dimensional reactive transport
RZ2D	-	Two-dimensional radially symmetry mesh
RZ2DL	-	Two-dimensional mesh
SEE	-	Steam-enhanced remediation
SG	-	Specific gravity
STMVOC	-	Nonisothermal transport of air, water and volatile organic compound
TCE	-	Trichloroethylene
T2VOC	-	TOUGH module for three-phase flow of water, air and a volatile organic compound
TIMES	-	Keyword for specified printout times in T2VOC

TMVOC	-	Numerical simulator for three-phase non-isothermal flow of water, soil gas and a multicomponent mixture of volatile organic chemicals
TOUGH2	-	Transport of unsaturated groundwater and heat
USBM	-	United States Bureau of Mines
USGS	-	United States Geological Survey
VC	-	Vinyl chloride
VOC	-	Volatile organic compound
WHO	-	World Health Organization
WHO2	-	World Health Organization Guidelines for Drinking Water Quality 1993/96
WN	-	When necessary
XRD	-	X-ray diffraction
XYZ	-	Rectilinear grid
ZVI	-	Zero valent iron

LIST OF SYMBOLS

K	-	Hydraulic conductivity
k	-	Intrinsic permeability
ρ	-	Fluid mass density
g	-	Acceleration due to gravity
μ	-	Dynamic (absolute) viscosity
σ	-	Surface tension
h	-	Height of capillary rise
r	-	Radius
$\emptyset$	-	Contact angle
P_c	-	Capillary pressure
P_N	-	PCE pressure
P_w	-	Water pressure
Vn	-	Arbitrary flow region
Γ_n	-	Surface area
n	-	Inward unit normal vector
M_K	-	Mass of component K per unit porous medium volume
ϕ	-	Porosity
S	-	Saturation
X_{β}^{κ}	-	Mass fraction of component K in phase β
ρ_{β}	-	Dry bulk density of soil
X_{w}^{c}	-	Mass fraction of chemical in aqueous phase
C_{s}^{c}	-	Adsorbed mass of chemical per unit volume of soil
K_{oc}	-	Organic carbon partition coefficient
f_{oc}	-	Organic carbon fraction in the soil

ρ_R	-	Soil grain density
c_R	-	Heat capacity of soil grains
T	-	Temperature
u_g^K	-	Specific internal energy of component K in gas phase
F_β	-	Phase fluxes
$k_{r\beta}$	-	Relative permeability of phase β
μ_β	-	β phase dynamic viscosity
, P_β	-	Fluid pressure in phase β
k_o	-	Absolute permeability at large gas pressure
b	-	Klinkenberg b-factor
$\mathrm{J}_\mathrm{g}^\kappa$	-	Diffusive mass flux of component K in gas phase
h_β	-	β phase specific enthalpy
q^c	-	Rate of heat generation per unit volume for chemical
λ	-	Rate constant related to half-life, $T_{1/2}$
C_u	-	Coefficient of uniformity
C_c	-	Coefficient of conformity
D_{10}	-	The effective particle size of 10% passes
D_{30}	-	The effective particle size of 30% passes
D_{60}	-	The effective particle size of 60% passes
k	-	Permeability
q	-	Water flow rate
A	-	Sample area
i	-	Hydraulic gradient
Q	-	Volumetric discharge
K	-	Proportionality constant (hydraulic conductivity
Δh	-	Difference in height
ΔL	-	Difference in length
q	-	Specific discharge
J	-	Hydraulic gradient
v	-	Kinematic viscosity
R	-	Reynold number
V	-	Velocity vector

F	-	Mass flux of solute per unit area per unit time
D_f	-	Diffusion coefficient
dc	-	Different in concentration
dx	-	Difference in distance
dt	-	Difference in time
D^*	-	Effective diffusion coeeficient
w	-	Empirical coefficient
a_L	-	Dynamic dispersivity
v_x	-	Average linear viscosity
D_L	-	Longitudinal coefficient of hydrodynamic dispersion
C	-	Contaminant concentration
C_o	-	Initial contaminant concentration
L	-	Flow path length
C^*	-	Sorbed contaminant mass per bulk dry soil mass
K_d	-	Distribution coefficient
θ	-	Volumetric moisture content
v_c	-	Contaminant velocity
$X_{nA,nB}$	-	Aggregates mole fraction forming surfactant and alcohol molecules
nA	-	Surfactant molecules
nB	-	Alcohol molecules
X_{A1}	-	Mole fraction of single dispersed surfactant
X_{B1}	-	Mole fraction of single dispersed alcohol
μ_o	-	Standard chemical potential on the same spesies
a	-	Surface area of one micellized surfactant
G_f	-	Surface free energy formation
γ	-	Surface tension of oil water interphase
ΔA	-	Change in interfacial tension area of microemulsion
ΔS	-	Change in entropy system

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

Dense non-aqueous phase liquid (DNAPL) are organic compounds that are denser than water and cannot mix with water. The DNAPL tends to sink below groundwater table and stop when it reaches impermeable layer. The penetration of DNAPL into an aquifer makes them difficult to locate and remediate.

The DNAPL is a poisonous and dangerous substance. It can cause burning in the mouth and throats, as well as causing stomach pains. Direct contact with DNAPL can cause severe skin irritation, burning sensation on the surface of the eyes, convulsions and mental confusion, kidney or liver problems, unconsciousness, and even death. The potential for significant long-term soil and groundwater contamination by DNAPL chemicals depends on their toxicity, limited solubility, and significant migration potential in soil gas, groundwater, and/or as a separate phase liquid. One of well-known source of DNAPL is tetrachloroethylene (PCE).

1.2 Background of the Problem

Tetrachloroethylene (PCE) are hydrocarbon liquids that spills or leaks into the ground and become DNAPL. Since the early 20th century, hydrocarbon has been produced and utilised widely by industrial facilities, superfund sites, military bases, dry cleaner sites, grain elevators, etc. However, hydrocarbon spill, which causes contamination to soil and groundwater, has not been realised until 1980 because of the lack of analytical methods and equipment of PCE detection.

Many researchers have come up with their research the application of surfactant-alcohol remediation through simulation, laboratory research, field demonstration. They study the solubilisation, mobilisation, displacement and physical forces analysis of surfactant in porous media to visualise the PCE removal (Pennell *et al.*, 1996; Walker *et al.*, 1998). Surfactant partitioning which involved surfactant mixture polydispersity, surfactant hydrophobicity, and interfacial tension was investigated (Cowell *et al.*, 2000).

Solubilisation increase when micelle is added to the groundwater to increase the contaminant removal rate. Mobilisation increases when interfacial tensions between PCE and groundwater are low thus release PCE from pores (Van Valkenburg, 1999). The surfactant-alcohol remediation follows the study of removal effectiveness (Ang and Abdul, 1991; Lee *et al.*, 2002; Saenton *et al.*, 2002). This be supported by studies of micelles contributing removal of hydrocarbon (Chu, 2002; Chu and Kwan, 2003).

The addition of alcohol in surfactant solution increases the solubilisation and mobilisation of PCE. Ramsburg *et al.* (2004) in their study showed that surfactant-alcohol increase solubilisation and mobilisation of PCE. At the same time, the surfactant-alcohol can control downward migration of PCE. Alcohol was found to be able to enhance oil recovery from subsurface similar with steam, but has a much better improvement in terms of capillary retention and oil phase behavior.

The type of alcohol selected for surfactant-alcohol treatment determines the efficiency of PCE remediation. In previous PCE remediation, the alcohol were 2-methyl-2-propanol (Darcy, 1856), n-butanol (Berner, 2013; Fetter, 1994; Streeter, 1962) and 1-butanol solution with low interfacial tension (IFT) solution (Bruch and Street, 1967; Ramsburg *et al.*, 2004).

1.3 Statement of the Problem

The PCE is a dangerous substances and hazardous to humans, animals, and natural habitats. This issue has encouraged many researchers to investigate the best method of PCE remediation. A study that aimed to investigate the PCE remediation has been conducted through laboratory experiment using surfactant-alcohol remediation. The investigation was performed in two-dimensional (2-D) saturated heterogeneous porous media model.

Surfactant-alcohol remediation, has been widely used in remediation of PCE worldwide. The surfactant-alcohol remediation's main goal is to remove as much PCE as possible with the least chemical in a short time. Surfactant-alcohol remediation has also been stimulated from surfactant-enhance oil recovery in the petroleum industry and has been recognised as an advanced innovation in PCE remediation technology. Surfactant-alcohol remediation challenges are finding PCE location, determining optimum surfactant solution, finding a variation of subsurface properties over treatment zone, and the risk of uncontrolled downward migration during surfactant flood (Mackay and Cherry, 1989).

The use surfactant-alcohol remediation is important to identify and visualise their effectiveness and capabilities of PCE removal in saturated porous media. These results can be used to evaluate possible conservancy effects for an adequate dissolution of PCE. This provide characterisation and remediation to avoid the spreading of contamination. The study of mechanisms of surfactant-alcohol would give a perfect solution in improvising the PCE remediation method.

The removal of PCE using surfactant-alcohol remediation was investigated to identify, acquire, analyse, visualise, and evaluate the effectiveness of the remediation. Several parameters can be controlled to justify the success of the remediation. A comprehensive understanding of the subsurface environment, multiphase fluid flow, and the physical processes is required to prevent PCE remediation failure.

1.4 Research Objectives

This research attempts to investigate the efficiency of PCE remediation in saturated layered sand using laboratory experiment of surfactant-alcohol remediation. The findings of this research guide the development of an effective PCE remediation technology.

The research objectives (RO) can be further detailed as follows:

1. To develop the 2-D physical model filled with layered sand for PCE migration and remediation experiment.

2. To investigate the PCE remediation in 2-D saturated layered sand through laboratory experiment of surfactant-alcohol.

3. To evaluate dominant mechanisms and efficiency of PCE remediation through laboratory experiment of PCE remediation using surfactant-alcohol.

1.5 Scope of the Study

A two-dimensional physical model filled with layered soil was develop in Objective (1). The model was developed to perform the PCE remediation in Objective (2). The subsurface media characteristic is layered sand comprising two type of sand which are fine sand and coarse sand. The PCE remediation was investigated using laboratory experiment of surfactant-alcohol. There are three different surfactant solution which are 4 % surfactant solution, 8 % surfactant solution and surfactant-alcohol. All three solution applied on the same model with sequences.

The dominant mechanisms of surfactant-alcohol remediation in Objective (3) determined. The PCE migration area and the PCE penetration depth measured through qualitative measurement. The behavior of PCE migration and remediation was discussed to determine the dominant mechanisms. The performance and efficiency of surfactant-alcohol remediation evaluated.

The qualitative measurement in a laboratory experiment is different from the quantitative measurement, whereby the former does not involve the saturation data and mapping but more to providing the characteristics and the appearances such as area, perimeter, and penetration depth. In addition, qualitative measurement is inclusive of the measurement of volume calculated based on the mass balance calculation. Unlike the qualitative measurement, the quantitative measurement in laboratory experiment involves the saturation data and mapping for both PCE and water.

1.6 Significance of the Study

The study is valuable and beneficial in protecting the subsurface specific to fine sand and coarse sand from hazardous contaminant of PCE which risking human health and ecosystems. The research is favorable to the environmental protection agencies, contaminated site owner, and environmental consultant firms who want to remediate sand from PCE. The investigation consequently reduce PCE contaminant sites in preserving better soil and groundwater quality for the benefit of humans, animals, and nature.

1.7 Thesis Organisation

Chapter 1 provides the introduction to this research, which includes the research background, problem statement, research objectives, research scope, the significance of the research, and thesis organisation. Chapter 2 is a review of existing literature related to this research including the sources and effects of PCE to humans and ecosystems, theory of PCE's distribution in subsurface, and the PCE remediation technologies of surfactant-alcohol remediation

Chapter 3 provides the research methodology of surfactant-alcohol remediation. The development of 2-D physical physical model was presented together with the research design, data collection, laboratory experiment process of PCE migration and remediation using surfactant-alcohol remediation.

Chapter 4 presents the results and discussion obtained from laboratory experiment of surfactant-alcohol remediation. The PCE migration area and the PCE penetration depth during surfactant-alcohol remediation was determined. The results of PCE volumes and PCE penetration depth was compared with past existing experiment. The dominant mechanisms of surfactant-alcohol remediation was discussed. The performance and efficiency of surfactant-alcohol remediation was evaluated.

Chapter 5 presents the conclusions derived from this research and the recommendations for future studies.

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