

## Groundwater Remediation in Cold Regions

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Sorption characteristics of partially soluble hydrocarbons (Toluene, Naphthalene and Xylene) on various adsorbent materials have been investigated at 40 °C to facilitate the development of a permeable reactive barrier (PRB) to treat oil-contaminated surface and sub-surface waters in cold regions. Inverse modelling has been utilized using the computer program CXTFIT to determine the variable parameters, axial dispersion coefficient and porosity. A set of partial differential equations was solved to describe the solute flow with appropriate initial and boundary conditions in order to develop a model to predict the future PRB and its performance in the field. The results indicated that the sorption capacity of the reactive media in fixed bed is only up to 35-63 % of the equilibrium sorption capacity. It was also found that the ADRE equation using Freundlich isotherms can best predict the column behaviour.

### 1. Introduction

Accidental oil spills on frozen grounds of Antarctica and Arctic are not uncommon because the energy generation is largely dependent on fuel used in the generators leading to various contaminated sites of variable size range depending upon the size of spill and site hydrodynamics. Although, these spilled hydrocarbons are immobile in the frozen grounds for most of the winter months, they become highly mobile during warmer summer melt season posing a threat to contaminate the coastal waters (Snape et al, 2006). Permeable Reactive Barrier, an in situ passive treatment technology that removes dissolved contaminants from polluted water through subsurface emplacement of reactive materials has been utilized to remediate contaminated sites in such sensitive environments (Woinarski et al, 2003).

Various studies have shown that GAC can successfully remove hydrocarbons from water (Arora et al, 2011). But it has problem of particle breaking over time and is quite expensive. Zeolites are hydrated aluminosilicate minerals with a characteristic cage-like structure. Natural zeolites occur as particles with millimeter or greater diameters and are free of shrink-swell behavior, a property which makes them well suited for use in cold regions. All natural zeolites have the ability to perform cation exchange. This property can be exploited by modifying their surface chemistry, thus enabling them to retain compounds like anions and non-polar organics. Therefore, the potential of raw and various modified forms of zeolite were investigated for hydrocarbon sorption (Toluene, Naphthalene and Xylene) in cold conditions (40 °C). The equilibrium isotherms for these materials were studied to identify the most suitable materials and breakthrough curves of selected materials were studied by performing fixed bed column experiments. Though, the understanding of exchange processes gained from batch tests is theoretically sufficient to describe and predict exchange performance, in practice this understanding is not directly applicable to dynamic systems of flow through porous media. Therefore a model was developed to enable the prediction of a material's performance in the field (fixed bed mode) from the equilibrium data alone without the need for extensive fixed bed column tests.

### 2. Materials and methods

The tested materials included raw St. Cloud Zeolite (a Clinoptilolite), Zeopro (Commercially available ammonium and potassium loaded zeolite), Hydrophobic Zeolite (raw zeolite coated with

octadecyltrichlorosilane) and Surfactant modified Zeolite (raw zeolite covered with hexadecyltrimethylammonium, HDTMA).

### 2.1 Adsorption equilibria

Adsorption isotherms of HC sorption on all the studied materials at 40 °C were obtained using batch equilibrium tests with known concentrations of hydrocarbon solution. The initial and final concentrations of the Toluene, Naphthalene and Xylene in the solution were analyzed by HPLC.

### 2.2 Breakthrough Curves

Fixed bed column experiments for HC sorption were conducted using a vertical glass column of 120 mm height and 35mm internal diameter. The known concentration of HC solution was introduced in the column in up flow direction at various flow rates. The water samples were collected at column exit at appropriate intervals and analyzed for HC concentration. The tests were carried out in duplicate at 40 °C.

### 2.3 Modeling

Sorption isotherms: Freundlich isotherm model was used to describe the sorption of HC's on studied materials:

$$q = K_f \cdot C^n \quad (1)$$

and can be linearized as follows:

$$\log q = \log K_f + n \cdot \log C \quad (2)$$

Where 'q' is the solute concentration on solid surface and 'C' is the solute concentration in solution. The terms Kf and n are constants for a given system (Li, et al. 2000).

### 2.4 Reactive transport in the Column:

The advection-dispersion equation (ADE) for the transport of a non-reactive solute in the axial direction can be expressed as: (Freeze and Cherry, 1979)

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} \quad (3)$$

The loss of solute from solution due to adsorption can be described by including an additional term in Eqn 3 to describe the effect of the rate of change in solute concentration in the solid phase. Equation 3 then becomes the advection-dispersion-reaction solute transport equation (ADRE), which is:

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial q}{\partial t} \quad (4)$$

$$\frac{\rho_b}{n} \frac{\partial q}{\partial t}$$

The term  $\frac{\rho_b}{n} \frac{\partial q}{\partial t}$  is the rate of change in solution concentration due to sorption processes, where  $\rho_b$  is the bulk density of the column material,  $D_l$  is the axial dispersion coefficient,  $x$  is the distance taken along the flow path,  $n$  is porosity and  $v$  is the average pore velocity.

In this study, three approaches (models) were utilized to determine 'q' values:

i) Under equilibrium conditions, where the sorption occurs instantaneously and local equilibrium between the liquid and solid phase solute is maintained, and the spread of the breakthrough curve is governed by axial dispersion only. The local equilibrium can be described by a linear relationship between solute concentrations in solid (q) and aqueous phases as (C):

$$q = K_d C \quad (5)$$

where  $K_d$  is a constant and commonly known as the distribution coefficient.

ii) A more realistic approach is to describe the relationship between fluid and solid phase solute concentrations by the Langmuir or Freundlich sorption isotherm. The Freundlich isotherm equation relates the solute concentrations in solid and aqueous phases as Eqn 1.

iii) For non-equilibrium sorption, mass transfer processes govern the rate of exchange, which is proportional to the distance the system is from the equilibrium, which for particle diffusion is the difference between the average concentration in the zeolite and the concentration at the particle surface that is in equilibrium with the solution (Helfferich, 1962). A linear driving force (LDF) relation is commonly used to approximate the particle diffusion controlled rate of mass transfer from the liquid to solid phase as (Helfferich, 1962):

$$\frac{\partial q}{\partial t} = \frac{60D_p}{4d_p^2} (q_e - \hat{q}) \quad (6)$$

where  $q_e$  is zeolite loading at the particle surface that is in equilibrium with the solution,  $\hat{q}$  is the average solid concentration,  $D_p$  is particle diffusion coefficient and  $d_p$  is the mean particle diameter.

Mathematica, a general purpose mathematical program (Wolfram, 1996) was used to solve the set of partial differential equations 3, 4, 5 and 6 to describe the solute flow through an adsorbent column, with appropriate initial and boundary conditions in order to develop a model to describe laboratory scale column tests, and provide a basis for the future development of a model to predict the performance of a PRB.

### 3. Results

Figures 1-3 show the sorption equilibria for all the materials tested for Toluene, Xylene and Naphthalene sorption. The Freundlich isotherm fitted the data best over the whole concentration range. The results indicate that Hydrophobic zeolite had better uptake capacity followed by SMZ, zeopro raw zeolite.

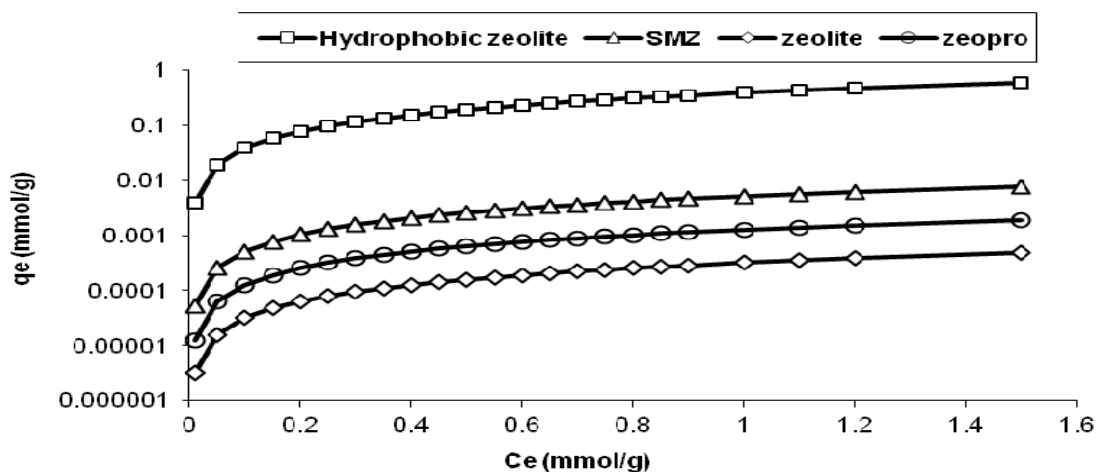


Figure 1: Sorption isotherm for toluene on Zeolite, Hydrophobic zeolite, SMZ and Zeopro

#### 3.1 Breakthrough Curves

Breakthrough curves for toluene on various materials at a temperature of 40 °C are presented in Figure 4. The figure shows that breakthrough appeared after 44 PV for hydrophobic zeolite, after 38 PV for SMZ and after 32 PV for Zeopro. Similar trends were observed for sorption of xylene and naphthalene. The results revealed that the fixed bed saturation capacities are approximately 35-63 % lower than the capacity expected from equilibrium studies depending upon the feed flow rates. One dimensional sorption equilibrium modelling was performed using distribution coefficient,  $K_d$  values and batch-estimated Freundlich constants. Solute transport modeling under non-equilibrium conditions was also performed using Freundlich constants from batch tests and the mass transfer coefficient based on the particle

diffusion coefficient estimated from kinetics data. The results show that the linear sorption equilibrium equation (Eq 4 and 5) using the distribution coefficient,  $K_d$  fails to predict the breakthrough point and curve

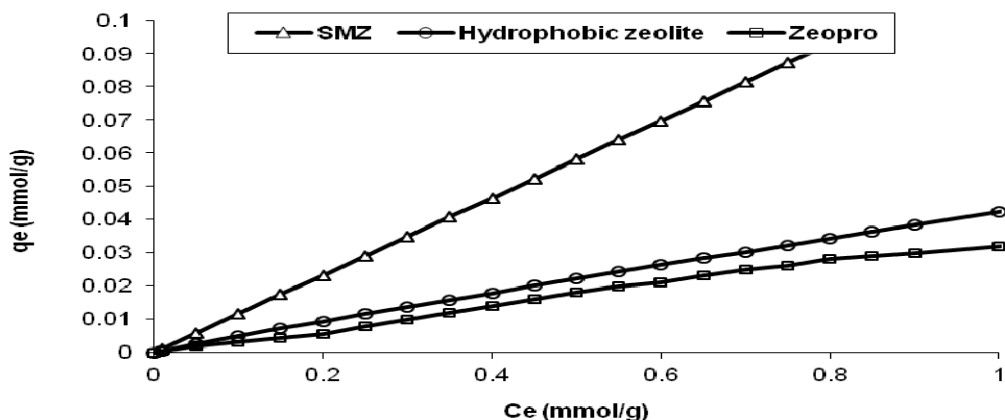


Figure 2: Sorption isotherm for Naphthalene on Hydrophobic zeolite, SMZ and Zeopro

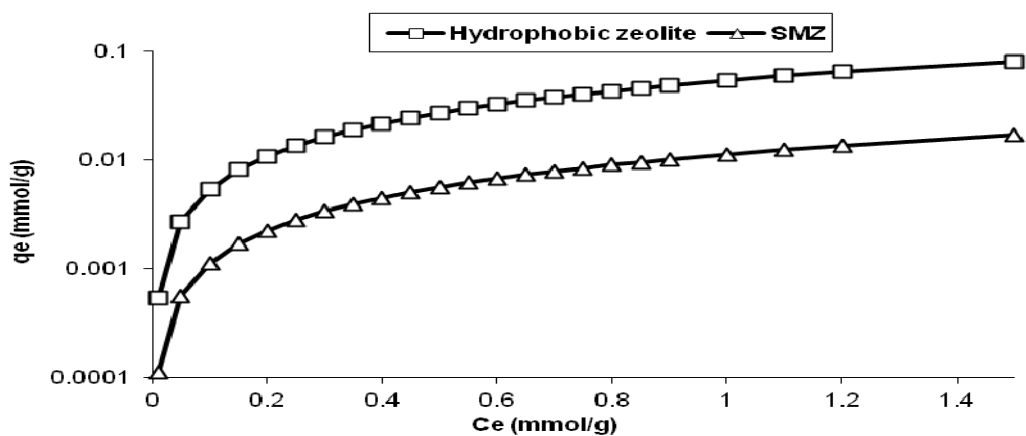


Figure 3: Sorption isotherm for Xylene on Hydrophobic zeolite and SMZ

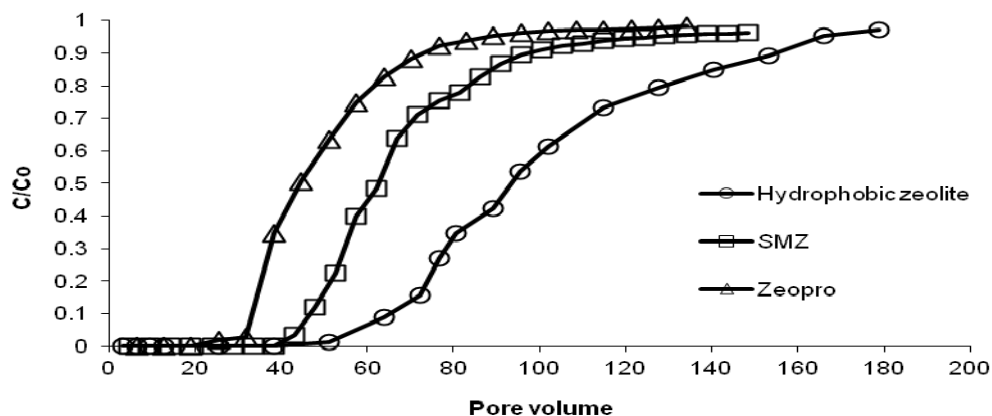


Figure 4: Toluene breakthrough curve for Hydrophobic zeolite, SMZ and Zeopro column.

shape. By using the Freundlich sorption equilibrium ADRE equation (Eq. 4 and 2, the model satisfactorily describes the experimental breakthrough point and curve shape (Figures 5 and 6). The non equilibrium mass transfer model (Eq. 4 and 6) using Freundlich parameters could not predict either the breakthrough point or the curve shape.

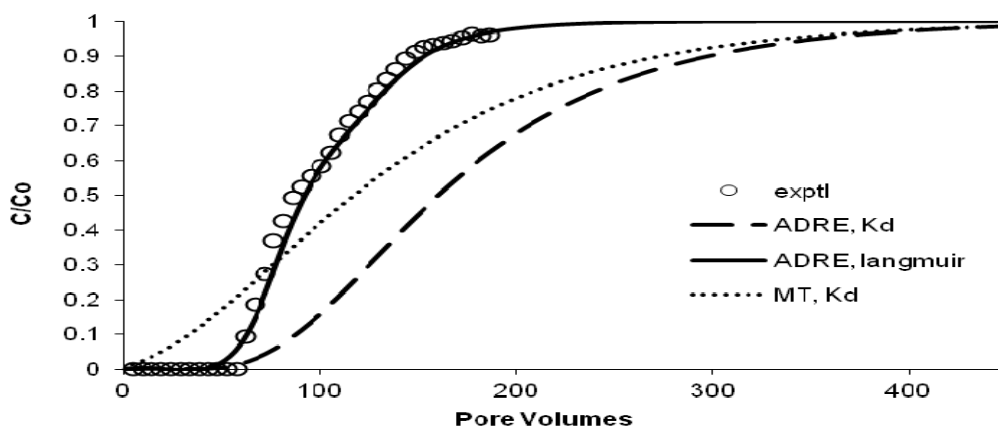


Figure 5: The experimental data for toluene breakthrough curve on hydrophobic zeolite and the curves generated by various models

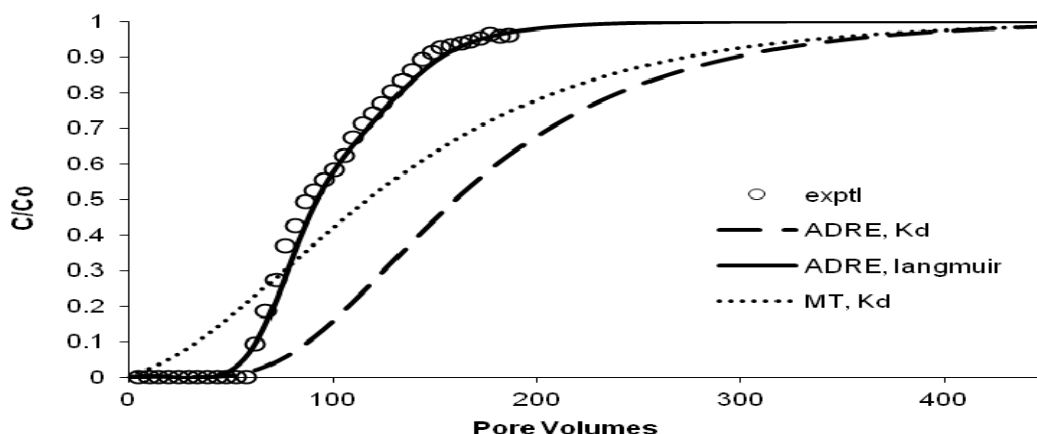


Figure 6: The experimental data for xylene breakthrough curve on hydrophobic zeolite and the curves generated by various models

### 3.2 Discussion

For a given material and the solvent system, theoretically the equilibrium and exchange parameters determined from batch and fixed bed studies should be the same (Helfferich, 1962). However, the column capacities of the studied materials are approx. 35-63 % lower than the batch estimated values which are in line with the findings of other researchers (Inglezakis et al, 2002). The lower values of the sorption capacity in fixed bed systems can be attributed to the differences in local equilibrium conditions that exist in each system. Additionally, the measured column capacity can be reduced due to the formation of hydraulic dead zones from channelling and preferential flow which physically limits the ability of solute to reach the sorption sites on a portion of sorbent particles (Hlavay et al, 1982). Flow conditions also influence the sorption characteristics (like capacities and particle diffusion coefficients) in columns (Inglezakis and Grogopoulou, 2003, Lehmann et al, 2001).

The results of this study reveal that hydrophobic zeolite and SMZ columns can successfully retain soluble hydrocarbons (toluene, xylene and naphthalene) and the one-dimensional Freundlich sorption equilibrium model can describe the column performance. But there might be a significant disparity in the hydro geological conditions in the lab scale columns and PRB in Antarctica/Arctic, where the flows will be highly dynamic and variable. The binary system consisted of only known concentrations of either toluene, xylene

or naphthalene in deionized water used in this study is relatively simple as compared to the natural waters in contaminated sites like Main Power House at Casey, old Casey and Wilkes in Antarctica or other sites in Arctic with highly variable concentrations and flow rates and significant sea spray. Though the model should be able to predict the PRB performance in field conditions, further kinetic and fixed bed studies may be necessary to describe the solute transport in complex natural systems. All these factors should be considered while designing a cold region PRB

#### 4. Conclusions

This study shows that hydrophobic zeolite and SMZ can successfully retain soluble HC's. The fixed-bed sorption parameters are significantly different from batch estimated values, with the capacity of sorbent in fixed beds approx. 35-63 % of the capacity in batch system. An equilibrium sorption model for solute transport using Freundlich parameters estimated by batch tests can successfully describe the fixed bed performance in a binary system. However, further work on uptake of HC on these materials in multi-component system may be necessary to describe the solute transport in complex natural systems.

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