

Modelling of Transport Phenomena and Effect of Applied Electrical Field on Heavy Metals Recovery during Application of the Electro-remediation Process

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Abstract: A mathematical model for the simulation of contaminant such as heavy metals removal from soils by electric fields was performed in 2-D geometry. The model describes the coupled transport of mass and charge of species subjected to an electric field. Transport mechanisms included are electro-osmosis, electrophoresis, pressure driven convection, electromigration, and diffusion. The computer model developed using COMSOL Multiphysics computes the time evolution of several state variables, including the spatial distributions of the electrical potential and pressure, and the species velocity and concentrations profile. It allows the prediction of the system response under different conditions and helps in achieving an understanding of the fundamental phenomenological behavior, as well as speeding up the design of field applications by showing the effect of varying key process parameters on the overall level and rate of contaminant removal.

Keywords: Electrokinetic Phenomena, Electric Field, Heavy Metals, Porous Media, Modelling

1. Introduction

The recovery of heavy metals from industrial process wastes has received great attention in recent years. In fact, most heavy metals are very toxic and cause great environmental damage [1, 2]. Toxic heavy metals in solid wastes are leached by rainwater, which in turn contaminates the soil as it migrates through the subsurface. The heavy metal-contaminated soil is a recipe for disaster since it contaminates not only the ground water supply but also the crops grown on this soil. In order to protect the public health and the environment, more stringent legislations and a considerable attention have been focussed on the development of cost effective, in-situ technologies for treating heavy metal contaminated-soils. Conventional technologies

such as washing, flushing, bioremediation, thermal desorption and soil vapour extraction cannot achieve a sufficiently in removing heavy metals from soils of low permeability [3, 4]. Therefore current research tends to propose potential alternatives to enhance the remediating ability of conventional processes.

A relatively new and potentially important in situ technique, referred to as electro-remediation, has emerged in which an electric field is applied across electrode pairs placed in the ground. As the fine grained soils possess a surface charge, usually negative, they are surrounded by a layer with a higher density of positive charges, the electric double layer. When an electric field is applied, the usually negative charged particles move towards the electrode of the opposite charge. The fluid, commonly with cations, is driven towards the negative electrode. Electro-remediation thus involves the well-known electrokinetic phenomena of electro-osmosis, electrophoresis and electromigration (Figure 1). Thus the contaminants in the liquid phase in the soil are moved under the action of the electric field, to wells where they are then pumped out. Therefore, an understanding of the fundamental behavior of the fluid flow in microchannels is of considerable importance in the research fields of micro and nanofluidics.

Electro-osmotic transport can be induced by an external electric field in capillary or porous plug systems where the electric polarization (charging) of solid surfaces occurs. Due to the fixed surface charge at the solid interface, an oppositely charged region of counterions develops in the liquid to maintain the electroneutrality of the solid/liquid interface. This screening region is denoted as the electrical double layer (EDL) because ideally it consists of opposite charges, some of which are bound while others are mobile. The electric field generated force causes the fluid in the double layer (EDL) to move, which in turn, sets the bulk liquid in motion by viscous interactions [5, 6].

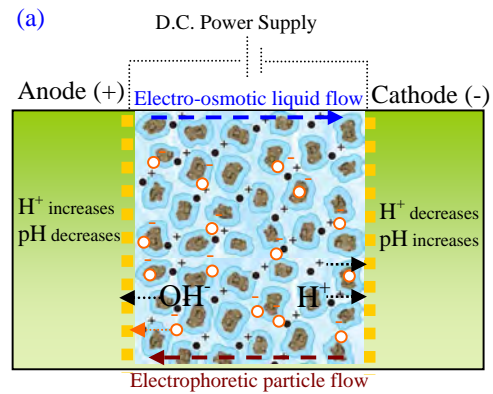
Electro-osmosis generally will dominate over pressure driven convection in low permeability soils, provided they have a finite charge.

Electromigration originates from the electric force exerted on ionic species, as a result of the applied voltage gradient. Transport by electromigration is only possible if the electroneutrality balance, which is imposed when a system is at equilibrium, is broken by the exchange of the electrons at the electrodes, as a result of electrochemical reactions. The electron transfer at the electrodes produces electromigration which acts to restore electroneutrality [7]. The migration velocity is proportional to the product of the species ionic charge and the local electric field. In cases where a significant fraction of the contaminant is in charged form, electromigration is likely to dominate over other transport mechanisms.

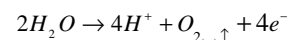
Electrophoresis refers to the movement of solid particles suspended in a liquid under the influence of an electrical field. The solid particles acquire a surface charge either from their own intrinsic surface ionization such as in the case of clays, or by the adsorption of polyelectrolytes, surfactants or ions onto their surface. In the case of colloids the surface area of the particles is large relative to the volume of the particles and therefore electrostatic repulsions dominate over the Van der Waals interaction. The electrostatic repulsion force arises from the electrical double layer, which, between adjacent particles, prevents the particles coagulating or agglomerating. When an electric field is applied across a colloidal suspension the charge on the particle interacts with the field and the particles move towards the electrode of opposite charge. This is analogous to electro-osmotic movement in which an electrical double layer (EDL) exists at the phase boundary between the solid and liquid phases. In this case, however, the direction of movement is in the opposite sense [8].

Other common physicochemical phenomena that are also present are: species diffusion in solution; chemical reactions in the bulk liquid; precipitation or dissolution of solid species; interactions with the soil such as adsorption, ion exchange; and electrochemical reactions. The complex interactions between all these phenomena make it difficult to extrapolate the response of a system from previous experimental observations or practical experience. Significant efforts have therefore been devoted to the

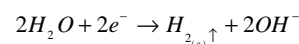
development of a mathematical model of the electro-remediation process. Therefore, a computer model has been developed herein to simulate the electro-remediation process in 2-D geometry. The computer model developed using COMSOL Multiphysics computes the time evolution of several state variables, including the spatial distributions of the electrical potential and pressure, and the species velocity and concentrations profile. It allows the prediction of the system response under different conditions and helps in achieving an understanding of the fundamental phenomenological behavior, as well as speeding up the design of field applications by showing the effect of varying key process parameters on the overall level and rate of contaminant removal.



Anode reaction



Cathode reaction



(b)

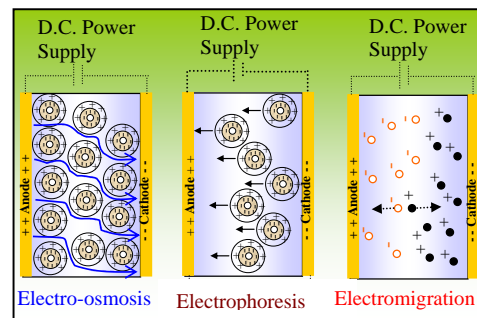


Figure 1: (a) Schematic representation of electro-remediation (b) with the different mechanisms occurring when negatively charged particles are placed in an electrical field (adapted from [9, 10, 11]).

2. Use of COMSOL Multiphysics

2.1. Governing Equations

The contribution of each transport mechanism to the species flux is derived from the corresponding phenomenological relationship [5] and extended to an isotropic porous medium using a capillary model. Electrokinetic phenomena are the result of the coupling between hydraulic and electrical potential gradients in fine grained soils [12-15]. The bulk liquid velocity v is described as the sum of the contributions due to electro-osmosis v_{eo} and due to any pressure gradient v_h in m/s. The electroosmotic velocity is calculated from the Helmholtz-Smoluchowski relation [16, 17]:

$$\bar{v}_{eo} = -\frac{\epsilon_p \epsilon_0 \epsilon_r \zeta}{\tau_p \mu} \nabla \Phi \equiv K_{eo} \nabla \Phi \quad (1)$$

where v_{eo} is the interstitial velocity due to electro-osmosis in m/s, ϵ_p the porosity, ϵ_0 the permittivity of the pore liquid in F/m, $\nabla \Phi$ the applied electrical field in V/m, ϵ_r the relative permittivity, ζ the zeta potential of the soil in V, and τ_p a nondimensional pore tortuosity factor that accounts for a nonuniform capillary path and is a number of the path and is a number of the order of but greater than 1.

The pressure gradient contribution is calculated from Darcy's law:

$$\bar{v}_h = -\frac{\epsilon_p R_p^2}{8\tau_p \mu} \nabla p \equiv K_h \nabla p \quad (2)$$

where v_h is the interstitial velocity in m/s resulting from a pressure gradient, R_p^2 the average pore diameter in m, ϵ_p the porosity, and ∇p the pressure gradient in Pa/m. Again, an effective permeability coefficient K_h in $\text{m}^2/(\text{Pa}\cdot\text{s})$ is defined for convenience.

For species i , the electromigration velocity v_{ei} in m/s is given by:

$$\bar{v}_{ei} = -z_i F u_i \frac{\nabla \Phi}{\tau_p} \equiv K_{ei} \nabla \Phi \quad (3)$$

where v_{ei} the migration velocity is relative to the pore liquid, u_i is the ionic mobility, defined as the velocity resulting from a unit force per mole, z_i the charge number of species i , F Faraday's constant, and an effective mobility coefficient in $\text{m}^2/(\text{V}\cdot\text{s})$.

Finally, the contribution of diffusion to the species flux for dilute solutions is given by Fick's law

$$\bar{j}_i^d = -\frac{D_i}{\tau_p} \nabla c_i \quad (4)$$

where \bar{j}_i^d is the molar flux due to diffusion in $\text{mol}/(\text{m}^2\cdot\text{s})$, c_i the molar concentration of species i in the pore liquid in mol/m^3 , and D_i the diffusion coefficient in m^2/s .

Superposing the different mass-transfer mechanisms, the total flux of an individual species is given by

$$\bar{j}_i = (v_{eo} + v_h + v_{ei})c_i - \frac{D_i}{\tau_p} \nabla c_i \quad (5)$$

or in terms of the gradients of pressure, electrostatic potential, and concentrations by

$$\bar{j}_i = \left[(K_{eo} + K_{ei}) \nabla \Phi + K_h \nabla p \right] c_i - \frac{D_i}{\tau_p} \nabla c_i \quad (6)$$

where \bar{j}_i , is the molar flux of species i per unit interstitial area in $\text{mol}/(\text{m}^2\cdot\text{s})$.

2.2. Boundary Conditions

The external boundary is assumed to be formed by impermeable, nonreacting, nonconducting walls, so no-flux boundary conditions are imposed. For the electrodes, two classes of electrodes are defined: permeable electrodes are those where the pore liquid flows from the soil into the electrode reservoir; and impermeable electrodes. In general, the boundaries of microfluidic systems can be divided into two main groups: (i) the liquid-solid boundaries and (ii) the open boundaries. We can, for example, use: (i) the nonslip velocity conditions, (ii) the reference pressure at a specified point (the inlet and the outlet), (iii) the normal flux of ionic components equal to zero (without chemical reactions) or the normal flux of ionic components equal to the rate of the component consumption by a surface chemical

reaction (with surface chemical reactions), (iv) a specified value of electric potential (electrode surfaces) or the normal electric potential equal to zero (electric insulator surfaces), (v) the velocity profile, (vi) fixed values of ionic concentrations, (vii) the current density balance are insulating for all boundaries except the electrodes surfaces, (viii) the boundary conditions for the mass transport are insulating, except for the inlet and the outlet,etc.

3. Numerical Analysis

3.1. Geometry Modelling

Figure 2 shows a schematic drawing of the system. It consists of a contaminated porous material charged with copper ions, containing two electrodes that generate the potential difference in the system. The effect of electrochemical reactions at the surface of the electrodes is assumed to be negligible.

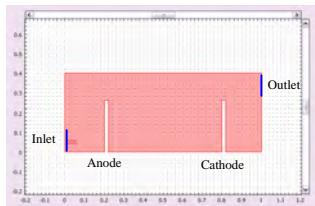


Figure 2: Schematic of the modelled domain.

3.1. Pressure and Velocity Distributions

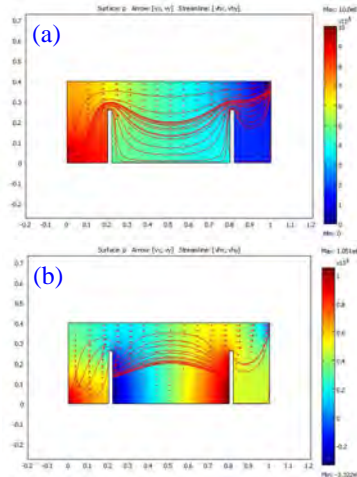


Figure 3: Pressure and velocity distributions in the cell in the case where pressure driven convection dominates over electrokinetic driven (a) and in the case where electrokinetic driven dominates over pressure driven (b). In both cases, the electrodes are impermeable.

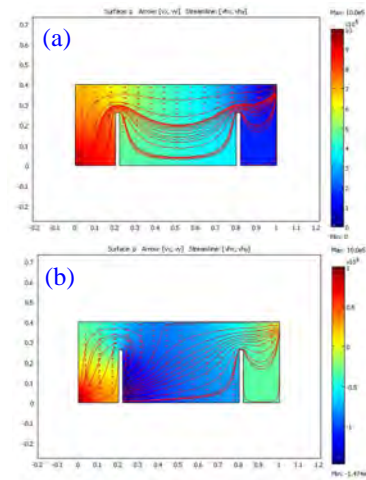


Figure 4: Pressure and velocity distributions in the cell in the case where pressure driven convection dominates over electrokinetic driven (a) and in the case where electrokinetic driven dominates over pressure driven (b). In both cases, the cathode electrode is permeable electrode.

3.2. Concentration Distributions

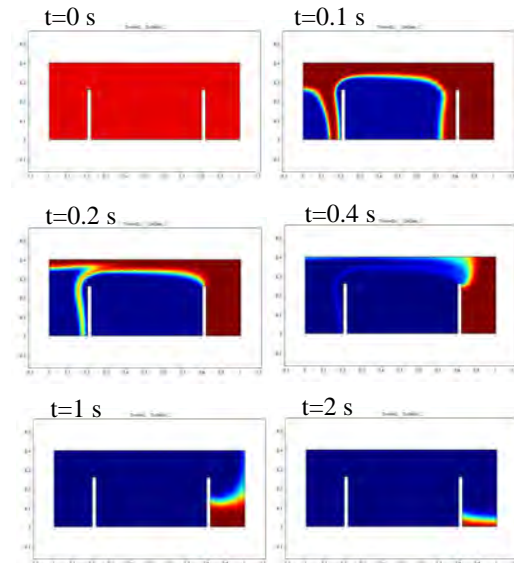


Figure 5: Concentration distributions in the cell at different times in the case where both pressure and electrokinetic forces driven are included.

The calculated concentration distributions at several times are presented in Figure 5. The advancement of the clean front due to pressure and electrokinetic forces driven can be seen from this figure.

4. Conclusions

Difficulties in the numerical solution of the electro-remediation model set out arose, not only because of the interaction between the transport of mass and charge and because the solution involves a strongly nonlinear system of partial differential and algebraic equations, but more importantly because of the development of thin boundary layers, high localized electric fields, and kinematic shocks in the solution. These latter factors result in severe constraints on the mesh resolution and the time-step size for numerical stability.

On the other hand, due to the convergence and numerical stability requirements of the Galerkin formulation, it was necessary to introduce an artificial diffusivity in order to approximate the solution for cases with high migration or convection velocities. The artificial diffusivity was added to the diffusion coefficients used in the transport equations so that the Peclet number over the computational domain for the species included in the transport equations was about 1000.

5. References

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