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Transient reactive transport model for physico-chemical transformation by electrochemical reactive barriers

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Abstract

A comprehensive model that integrates coupled effects of chemical, physical, and electrochemical processes, is necessary for design, analysis, and implementation of the electro-remediation of groundwater under flow conditions. A coupled system of equations to solve for transport and multiple reactions in an electrochemical reactor is numerically intensive due to highly stiff nature of reaction model formulation. In this study, the focus is to develop an efficient model for reactions associated with the transport and physico-chemical transformation in an electrochemical reactor. The model incorporates effects of transport mechanisms as well as chemical and electrochemical reactions. Model verification is provided for pH profiles under different electrolyte compositions in two sets of reactors; a batch and a flow-through reactor. The model is able to predict the concentration of species during the electrochemical remediation process with a close correlation to experimental data ($R^2 = 0.99$ for batch and $R^2 = 0.78$ for flow-through reactor.) Imposing polarity reversal to the system will cause fluctuation of pH, however, the trend stays the same as if no polarity were applied. Ultimately, volumetric charge flow is introduced as a unique parameter characterizing the electroremediation reactor for operating purposes.

Keywords

pH modeling; Electrochemical remediation; Groundwater remediation; Physico-chemical modeling

1. Introduction

Electrokinetic remediation is a valuable process for treatment of contaminated groundwater because of its environmental compatibility, versatility, energy efficiency, and low required maintenance [1–6]. The redox potential of the solution is altered during electrolysis, which can be manipulated to induce contaminant transformation and/or degradation reactions [7,8]. Electrochemical processes were initially investigated for oxidation of phenolic compounds in industrial wastewater [9–11]. The method was expanded for removal of various organic and inorganic contaminants for *in situ* groundwater remediation [2,4,5,12,13]. Research was focused on the influence of the electrode material, electrolyte composition, current density, and pH monitoring on remediation efficiency. Charge transfer through electrode/electrolyte interface induces electrode surface reactions through oxidation or reduction. In dilute

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solutions, pH alteration is the inevitable result of electrode/electrolyte interface charge transfer. Water electrolysis results in development of an acidic and basic regions in anode and cathode compartments, respectively. In addition to the concern for effluent pH of the remediation process, the shift in pH can influence the removal efficiency of the targeted species (e.g. [4,14–16]). This is mainly explained by effects of pH on chemical speciation as well as inducing physicochemical processes such as precipitation/dissolution, adsorption and ionic exchange between solid matrix and electrolyte (e.g. [17–19]). For groundwater treatment, pH and redox shifts can be manipulated to support various transformation/degradation mechanisms (e.g., electro-Fenton) while maintaining the neutral pH value of the treated water [16,20,21].

The electrochemical systems utilizing these reactions can be designed as pump-and-treat utilizing either batch or flow-through systems, reactive barriers, or *in situ* flow-through reactors implemented in the remediation wells. Conventional pump-and-treat systems need to extract relatively large volumes of water with relatively low contaminant concentrations and usually the non-aqueous part of the contamination is not targeted, therefore, they are inefficient for removing contaminants from the subsurface. *In situ* flow-through reactors can provide redox condition in the subsurface, with single or multiple wells, which will eliminate the cost of pumping, and target both the aqueous and non-aqueous contaminants. A schematic diagram of a proposed configuration for field implementation is presented in Fig. 1.

A major concern for *in situ* implementation of electrochemical treatment is the sustainability of process and system over operational duration. Experiments can assess transformation rates for target contaminants, however, long term performance is difficult to evaluate. Models will validate the chemistry and physics of the system, and will facilitate design, analysis, and implementation.

Models to predict the behavior of the system during the electrochemical remediation process are essential for understanding the experimental results. The reactive solute can be subjected to a variety of chemical reactions such as acid-base reaction, oxidation-reduction, complexation, sorption/desorption, and dissolution-precipitation. Development of theoretical transport models to incorporate extraction of heavy metals under electric field from fine grained soils has been well studied (e.g. [22–25]). However, due to highly stiff nature of common reaction model formulation, the number of ion fluxes to be calculated, and the iterative method to implicitly solve the coupled partial differential equations, the simulations are numerically intensive [26].

This paper, focuses on developing a reaction model for batch reactor and a one-dimensional model to predict the pH alteration within an electrochemical remediation flow-through reactor. Validation of model is chosen to be based on the pH alteration as it is one of the main characteristics that can ultimately define the system. This study implements an efficient reaction model to reduce computational time for reactions associated with the process in a batch setup. Ultimately, the transport and reaction equations are solved sequentially in order to reduce the required computational power for the flow-through reactor calculations. The model includes electrochemical surface reactions, precipitation

reaction, and acid-base reaction in addition to the transport mechanisms. The verification of this model is presented by evaluation of pH from studies on electrochemical transformation under batch and flow reported by Ciblak et al. [21] and Rajic et al. [4], respectively.

2. Model development

A system subjected to gradients experiences deviation from its equilibrium. Hydraulic, electric, thermal, or chemical gradients induce transport mechanisms. The resulting flux of matter and energy through the electrolyte is categorized into two general types of coupled and uncoupled fluxes [27]. Uncoupled fluxes result from application of a potential gradient of the same type as the transported matter, *e.g.* charge transport due to electric gradient (migration.) However, coupled fluxes refer to dissimilar type of imposed gradient as the transported matter, *e.g.* fluid transport due to electric gradient (electroosmosis.) The model equations are developed assuming that the fluxes are linear and homogenous functions of their causing phenomena. The behavior of the system is described in one-dimensional model under dilute solution assumption. High Peclet number of the solution results in advection to be the dominant transport mechanism.

2.1. Physicochemical phenomena

2.1.1. Chemical reactions—Homogeneous phase reactions included in the model are aqueous complexation reactions, redox reactions, and acid/base reactions, which often are assumed to be at equilibrium. Using equilibrium model concept, any reversible reaction deviated from its equilibrium state, can proceed towards either product(s) or reactant(s) with an extent of ξ [28]. The equilibrium model can be formulated with Eq. (1) for N_c number of species participating in N_x number of reactions, where v_{ij} is the stoichiometric constant for j^{th} species in the i^{th} reaction.

$$\sum_{j=1}^{N_c} v_{ij} c_j = 0 \quad (i = 1, \dots, N_x) \quad (1)$$

Therefore, the rate of the i^{th} reaction is generally expressed as Eq. (2), as the reaction volume remains constant.

$$r_i \equiv \frac{1}{v_{ij}} \left(\frac{dc_j}{dt} \right)_i = \frac{d\xi_i}{dt} \quad (2)$$

For each reaction, extent or degree of advancement, ξ_i is calculated in order to minimize the error. Ultimately, the concentrations of species are calculated based on the extent of the reactions (Eq. (3)).

$$c_j = c_j^0 + \sum_{i=1}^{N_x} \xi_i v_{ij} (j = 1, \dots, N_c) \quad (3)$$

2.1.2. Mass transport—In the batch reactor, the chemical and electrochemical reactions are the dominant mechanisms affecting the concentration of species, since the system is assumed completely mixed. Whereas in the flow-through reactor, the transport mechanisms are impacting the system as significantly as the chemical and electrochemical reactions.

The model for flow-through reactors with no media, assumes constant velocity operating conditions with high Peclet number, and mass fluxes are mainly driven by hydraulic gradients. However, the small contribution of dispersion is taken into consideration, as it induces mass flux at electrodes' boundaries. However, it should be noted that dispersion can be affected by electro-neutrality at the electrodes boundaries, concentration, and electrolyte ionic strength [29,30].

Mass flux for i^{th} species, N_i , is defined with a convection and dispersion term, where v is the constant operation velocity, c_i is the concentration of species i , $D_{h,i}$ is the dispersion coefficient for i^{th} species (Eq. (4)).

$$N_i = vc_i + D_{h,i} \nabla(-c_i) \quad (4)$$

2.1.3. Charge transfer—Direct electrolysis is modeled by neglecting the effects of double layer and mass transport limitations to the surface of the electrodes, due to the duration of electrolysis and presence of hydraulic gradient in the column, respectively. Assuming the charge transfer through the electrode/electrolyte surface is 100% faradaic process and the system is operating under isothermal condition, the process is described by Faraday's law (Eq. (5)), where I is the total applied volumetric current density, n is the number of participating electrons for each mole of electrolyzed species, and F is the Faraday's constant. Under this assumption all the applied electric charge is expected to participate in the electrochemical reactions and not to dissipate as heat. However, depending on the conductivity of the electrolyte, a portion of the applied current will be used to develop a thermal gradient in the system.

$$\frac{\delta c_i}{\delta t} = \frac{I}{nF} \quad (5)$$

The total charge flux in the electrolyte can be described by migrational charge flux and diffusional charge flux. The electrical conductivity of the bulk electrolyte solution, σ , is determined by Eq. (6), where z_j and u_j are the charge and ionic mobility of the j^{th} species.

$$\sigma = \sum_{j=1}^{N_c} z_j F u_j c_j \quad (6)$$

u_j is estimated by Nernst-Einstein relation with molecular diffusion coefficient (Eq. (7)).

$$u_i = \frac{D_i z_i F}{RT} \quad (7)$$

Therefore, the total charge flux in the electrolytic reactor is defined by Eq. (8), where $\frac{\partial \varphi}{\partial x}$ is the imposed electric field.

$$I = -F \sum_{j=1}^{N_c} z_j D_j \frac{\partial c_j}{\partial x} - \sigma \frac{\partial \varphi}{\partial x} \quad (8)$$

2.2. Boundary and initial conditions

Batch reactor is assumed to be a spatially zero-dimensional model due to the continuous stirring condition. Therefore the initial condition should be specified with the initial concentration of the species.

A schematic view of the flow-through reactor is presented in Fig. 2. The initial condition of the electrolyte is a global equilibrium for all the species present in the electrolyte (Eq. (9)).

$$C_i(x, 0) = C_{i0} \quad (9)$$

Flux type boundary is considered for the upper bound of the reactor since the system is continuously fed with the known and constant concentrations of species, (Eq. (10)) C_{i0} . This will lead to conservation of mass within the column.

$$-D_i \frac{\partial c_i}{\partial x} + v c_i \Big|_{x=0} = c_i^0(t) v \quad (10)$$

And for the lower bound assuming a finite column with zero concentration gradient the boundary condition is described by Eq. (11):

$$\frac{\partial c_i}{\partial x}(L, t) = 0 \quad (11)$$

This condition leads to a continuous concentration distribution at $x = L$, where L is the length of the reactor.

Boundary conditions for the partial differential equations describing species transport are evaluated based on species flux and electrolysis reactions at the electrodes. Charge transfer across electrode/electrolyte interface is a heterogeneous reaction which is considered as a boundary condition in the model described by Eq. (12).

$$-D_i \frac{\partial c_i}{\partial x} + v c_i \Big|_{x=electrode} = c_i^{electrode} + \frac{I}{nF} \quad (12)$$

As was mentioned, the reactor is designed to operate under constant current condition. The physical electric setup dictates the cathode to be the grounded electrode (Eq. (14)), therefore, the electric boundary condition at the anode will be defined as Eq. (13)

$$-\sum_j z_j F D_j \frac{\partial c_j}{\partial x} - \sigma \frac{\partial \varphi}{\partial x} \Big|_{at\ 8239\ anode} = I \quad (13)$$

$$\varphi \Big|_{at\ 8239\ cathode} = 0 \quad (14)$$

2.3. Numerical solution method

Ultimately, coupled nonlinear partial differential equations (PDE) are produced with flux type boundary conditions as well as a number of algebraic equations to define the equilibrium condition in the aqueous phase. The approach for discretization of the defined reactor is implicit finite difference method (Crank- Nicolson method), with second order accuracy for spatial dimension, $O(\Delta x^2)$, and first order error for the temporal discretization, $O(\Delta t)$. Although choosing large temporal and spatial steps can lead to less accurate result, the model is stable unconditionally.

A two-step approach is implemented for the solution of the final system of partial differential equation. Reaction extents are calculated for chemical equilibrium reactions by Newton-Raphson method separately, and are substituted in the mass transport system of equations with an iterative approach [31] (Fig. 3). The accuracy of two-step approach depends on the degree of coupling between the terms. Therefore, if the time-steps are small or the terms are weakly coupled, the two-step method is a reliable solving method [26].

3. Results and discussion

The developed reaction model and the one-dimensional transport model is validated with experimental data reported by Ciblak et al. [21] and Rajic et al. [4], respectively. The result of verification is presented in separate sections due to different boundary and initial conditions imposed on each system. Ultimately, the pH prediction of model is presented

under flow condition with velocity ranging from 0.1 to 1 cm/min and external currents ranging from 10 to 120 mA.

3.1. Reaction model verification pH variations in electrochemical batch reactor

Evaluation of the reaction model is provided for pH alteration in a divided electrolyte batch reactor reported by Ciblak et al. [21]. The study was conducted to experimentally assess temporal change of electrolyte oxidation reduction potential (ORP) and pH in an electroremediation batch system [21]. The reactor consists of separate anolyte and catholyte compartments connected by a 112 Nafion® membrane, containing 0.02 M Na_2SO_4 electrolyte with mixed metal oxide (MMO)-coated titanium mesh electrodes. The anolyte and catholyte were continuously stirred with a constant speed to simulate a well stirred batch system and to avoid development of a considerable double layer on the electrode surface [21]. The setup was operated under constant volumetric current density of 112.5 mA L⁻¹. For currents on the order of milliamps used in dilute electrolyte experimental cells, there is a sufficient supply of H_2O , and adequate local convection present at the electrodes to sustain the electrolysis [32]. Therefore, a constant water electrolysis rate at the electrode/electrolyte interface is a reasonable assumption.

The model is considering the concentrations of four species, H^+ , OH^- , SO_4^{2-} , and HSO_4^- .

The Nafion® membrane limits the hydroxide and hydrogen ions accessible for water association/dissociation reaction. Consequently, extreme acidic and basic conditions develop in anolyte and catholyte, respectively. The significant change in pH is observed in less than 30 min from the beginning of electrolysis reaction (Fig. 4a). However, Nafion® membranes allow a limited and selective amount of ion exchange between the two compartments, which can lead to an insignificant mismatch between the observed data and the model prediction, shown in Fig. 4a. Fig. 4b illustrates the close correlation ($R^2 = 0.99$) of the model prediction to the experimental results reported by Ciblak et al. [21]. The prediction is consistent with the well-established literature (e.g. [23,27,29,33,34]).

3.2. Reaction model prediction- effect of electrolyte composition

The batch reaction model developed with operating conditions of the study by Ciblak et al. [21] was used to assess the effect of electrolyte composition on pH alteration during electroremediation process (Fig. 5). This effect was evaluated by using NaHCO_3 and combination of NaHCO_3 and CaSO_4 to increase the electrolyte buffering capacity. This increase in buffering capacity caused a delay in the expected extreme pH in both anolyte and catholyte. However, the ultimate steady state pH reached 2 and 12, similar to sodium sulfate containing electrolyte. Additionally, the initial drop in pH is decreased by increasing the buffering capacity of the electrolyte. The combination of sodium bicarbonate, NaHCO_3 , and calcium sulfate, CaSO_4 , induced precipitation/dissolution of calcium carbonate, CaCO_3 , which caused further delay in the expected extreme alteration in pH.

3.3. pH variations in a two electrode, flow-through electrochemical reactor

The verification of the one-dimensional transport model is done using the laboratory scale test results reported by Rajic et al. [4]. The study was to evaluate trichloroethylene (TCE) electroremediation efficiency under flow condition using MMO electrodes utilizing polarity reversal method [4]. The importance of pH in this study is to assure a steady state and a neutral pH of the effluent. The electrochemical setup considered for treatment is a vertical cylindrical column with diameter of 3.8 cm and height of 10 cm with two *Ti/MMO* electrodes with 2.5 cm spacing (Fig. 2) operating under constant current of 60 mA. Similar to the operational conditions in the batch reactor, water electrolysis is the dominant electrochemical process (Eqs.(15) and (16)). The column was operated under constant velocity of 0.25 cm/min. The pH fluctuation was measured at sampling ports shown in Fig. 2. P_1 and P_2 sampling ports represent the conditions in electrode vicinity, while P_3 is considered as the effluent. The experimental data was obtained by exploring the effects of 6 cycles per hour with cathode/anode sequence as the initial configuration of the process. Electrolyte composition presents low buffered electrolyte, 0.172 g L⁻¹ calcium sulfate in deionized water [4]. The model is considering the concentrations of four dominant species affecting the pH, H^+ , OH^- , SO_4^{2-} , and HSO_4^- with their corresponding equilibrium reactions (Eqs.(17) and (18)). The model predicts a cyclic alteration of pH throughout the process, whereas the experimental data shows a consistently low pH during the electrochemical process. Due to lack of experimental data for time intervals of 5–10 min the fluctuation of the model prediction is not confirmed. The predicted alteration in the system is explained due to effects of the sudden changes in current direction. Even though an insignificant duration for charge/discharge of double layer is considered in the model, the effects of parallel direct electrolysis on the surfaces of each electrode is neglected. Although the aforementioned effect might result in less fluctuation within a smaller range in the reactor, model prediction and experimental data comparison show a good correlation ($R^2 = 0.78$) at points of measurements. Fig. 6 was obtained by comparing the experimental data and the model prediction at three different sampling ports shown in Fig. 2.

3.4. Polarity reversal effects on pH alteration,

The effect of polarity reversal on the transformation of TCE in aqueous solution was evaluated using a flow-through reactor and mixed metal oxide electrodes (MMO) and Pd

catalyst by Rajic et al. [4]. The electrolyte composition consists of 0.413 gL^{-1} sodium bicarbonate and 0.172 gL^{-1} calcium sulfate, to simulate the groundwater electrical conductivity. The effluent of the reactor was monitored for pH alteration in the experimental study after reaching steady-state condition, to check for any deviation from the natural water pH. The model results, shown in Fig. 7, predicts reaching steady state condition within less than 30 min from the start of the experiment and a slight oscillation of pH around the obtained experimental pH (7.2 [4]).

Model predictions, Fig. 7, show slight decrease in the predicted effluent pH by increasing the applied current. The results reported by Rajic et al. [4] for *6 cycles per hour* and for *30, 60, and 90 mA* of applied current was *7.2, 7.2, and 7.4*, respectively. The minor difference between the prediction and the experimental data can be the result of sampling duration.

Increasing the polarity reversal frequency in the model did not result in any major deviation for the effluent pH comparing to no polarity reversal operating condition, Fig. 8. Similarly, the model predicts the system to reach steady state in less than 30 min. However, the experimental result shows slight increase in pH for *10 cycles per hour* with 60 mA applied current comparing to no polarity reversal (*7.6–7.7*).

3.5. Model prediction- flow-through reactor

The model was used to predict the effluent pH for a range of velocities and applied currents for a flow-through reactor with dimensions and electrode positions similar to Rajic et al. [4]. The range of velocities were considered 0.1–1 cm/min, and current 10–120 mA. Volumetric charge flow in *mole e^- /l* was chosen as a unique parameter for the system in this analysis. Figs. 9 and 10 are provided as a guide of operating condition for flow-through electrochemical remediation reactor depending on its application and characteristics. Fig. 9 illustrates the operating condition of the remediation reactor with high buffered electrolyte where the increasing of volumetric charge flow will result in drop of the effluent pH in respect to the initial value. Fig. 10 can be utilized in reactors with low buffer capacity, where manipulation of pH in vicinity of anode and cathode is of interest. In this setup the effluent pH was consistent within a range of 8.5 ± 0.25 .

4. Conclusion

A theoretical reaction model is developed and is coupled with 1D transport to simulate electrochemical reactions, precipitation reaction, and acid-base reaction in an electrochemical reactor for *in situ* groundwater treatment. This model can be used for implementation and maintenance purposes.

The problem with high computational power is solved with reducing the number of unknowns in the reaction model formulation to number of reactions. The transport and reaction equations are solved sequentially in order to reduce the required computational power. The model is verified by evaluation and comparison of pH profiles with experimental studies reported by Ciblak et al. [21] and Rajic et al. [4]. The model is able to predict the concentration of species during the electrochemical remediation process with a close

correlation to experimental data ($R^2 = 0.99$ for batch and $R^2 = 0.78$ for flow-through reactor).

The pH fluctuation is important for various reasons including forcing certain desired reaction pathways and/or the effluent water quality. This model can be used to manipulate the applied current condition, flow velocity, and electrolyte composition to impose a desired pH and ORP within the flow-through reactor to achieve highest removal efficiency depending on the anticipated removal pathways or the desired effluent pH. Ultimately, volumetric charge flow was introduced as a unique parameter for an electrochemical remediation flow-through reactor for operation purposes.

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Fig. 1.
General schematic view of groundwater circulation wells for installing the electrochemical remediation reactor.

Fig. 2.
Schematic view of the sampling ports and the modeled reactor (original position was vertical).

Fig. 3.
Two-step method flowchart finite difference method.

Fig. 4. (a) pH alteration in a divided electrolyte batch reactor, where the electrolyte consists of 0.02 M Na_2SO_4 ; (b) divided electrolyte batch reactor correlation plot. The experimental data is reported by Ciblak et al. [21].

Fig. 5. Reaction model prediction to assess the effects of electrolyte composition on pH alteration in anolyte.

Fig. 6. Correlation Scatter plot between the polarity reversal model and experiment reported by Rajic et al. [4].

Fig. 7.

The model prediction of the effluent for different applied current for the remediation process; for 6 cycles/h, 30mA, 60mA and 90mA are 7.2, 7.2, and 7.4, respectively. The experimental effluent pH was obtained by Rajic et al. [4].

Fig. 8.

Theoretical result of effluent pH monitoring, experimental data is obtained by Rajic et al. [4]; Electrolyte composition: 0.413 g/l sodium bicarbonate, 0.172g/l calcium sulfate; applied current: 60mA with 0, 6, and 10 cycles/h.

Fig. 9.
Effluent pH variation in respect to volumetric charge flow; Electrolyte composition: 0.413g/l sodium bicarbonate, 0.172g/l calcium sulfate.

Fig. 10.
pH variation after anode in respect to volumetric charge flow; Electrolyte composition:
0.02M calcium sulfate.