Electronic supplementary

A Membrane-based Electrochemical Flow Reactor for Generation of Ferrates at near Neutral pH Conditions

Macarena A. Cataldo-Hernández, Arman Bonakdarpour, Joseph T. English, Madjid Mohseni, and David P. Wilkinson*

Department of Chemical and Biological Engineering and the Clean Energy Research Center, University of British Columbia, 2360 East Mall, Vancouver, BC, Canada, V6T 1Z3

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1. Development of an analytical model for electrochemical generation of ferrates by electrochemical flow reactor operating in batch recirculation with ferrate degradation

We express the general rate balance equation of the flow reactor as:

\[ IN - OUT + GEN - CONS = ACC \] (S1)

where \( IN, OUT, GEN, CONS, \) and \( ACC \) are the flow into, flow out of, generation in, consumption in, and accumulation in, respectively, a control volume or surface. The individual terms correspond to rates of some quantity of interest, for example the moles of Fe(VI), for a cross section of the flow reactor at some arbitrary distance \( x \) from the inlet and at some arbitrary time \( t \) with some arbitrarily small thickness \( \Delta x \). It is assumed that: 1) each cross section is perfectly mixed, 2) the reaction of Fe(III) to form Fe(VI) is a heterogeneous reaction occurring at the surface of the electrode, and 3) the degradation of Fe(VI) to form Fe(III) is homogeneous occurring uniformly throughout each cross section. As such, the terms of Equation (S1) are expressed as follows:

\[ IN = Q_V c_{Fe(VI)}(x,t) \] (S2)

\[ OUT = Q_V c_{Fe(VI)}(x + \Delta x,t) \] (S3)

\[ GEN = k_m B \Delta x c_{Fe(III)}(x + \frac{\Delta x}{2},t) \] (S4)

\[ CONS = k_d B S \Delta x c_{Fe(VI)}(x + \frac{\Delta x}{2},t) \] (S5)

\[ ACC = 0 \] (S6)

where \( Q_V \) is the volumetric flow rate of the electrolyte in \( m^3 \) s\(^{-1} \); \( c_{Fe(III)}(x,t) \) and \( c_{Fe(VI)}(x,t) \) the molar concentration of Fe(III) and Fe(VI), respectively, at \( x \) and \( t \) in mole \( m^{-3} \); \( k_d \) and \( k_m \) is the coefficients of Fe(VI) degradation (first order) \([1]\) and mass transport in \( s^{-1} \) and \( m \) s\(^{-1} \), respectively; and \( B \) and \( S \) are the electrode width and inter-electrode distance, respectively, in \( m \).

Combining Equations (S1)–(S6) gives:

\[ Q_V c_{Fe(VI)}(x,t) - Q_V c_{Fe(VI)}(x + \Delta x,t) + k_m B \Delta x c_{Fe(III)}(x + \frac{\Delta x}{2},t) - k_d B S \Delta x c_{Fe(VI)}(x + \frac{\Delta x}{2},t) = 0 \] (S7)

Dividing Equation (S7) by \( \Delta x \) gives:
\[ \frac{Q_v c_{Fe(VI)}(x,t) - Q_v c_{Fe(VI)}(x + \Delta x,t)}{\Delta x} + k_m B c_{Fe(III)}(x + \frac{\Delta x}{2},t) - k_d B c_{Fe(VI)}(x + \frac{\Delta x}{2},t) = 0 \] 

Taking the limit \( \Delta x \to 0 \) to Equation (S8) and applying the definition of a derivative gives:

\[ -Q_v \frac{dc_{Fe(VI)}(x,t)}{dx} + k_m B c_{Fe(III)}(x,t) - k_d B c_{Fe(VI)}(x,t) = 0 \] 

By conservation of mass, it is therefore developed that: 1) the total iron concentration is conserved and 2) the total iron concentration remains homogeneously dispersed. Furthermore, it is assumed that: 3) the only iron species which appear in significant concentrations are Fe(III) and Fe(VI) such that:

\[ c_{Fe(III)}(0) = c_{Fe(III)}(x,t) + c_{Fe(VI)}(x,t) \]

where \( c_{Fe(III)}(0) \) is the initial concentration of Fe(III). Thus, substituting Equation (S10) in Equation (S9), it becomes:

\[ -Q_v \frac{dc_{Fe(VI)}(x,t)}{dx} + k_m B [c_{Fe(III)}(0) - c_{Fe(VI)}(x,t)] - k_d B c_{Fe(VI)}(x,t) = 0 \]

Rearranging Equation (S11):

\[ \frac{dc_{Fe(VI)}(x,t)}{k_m c_{Fe(III)}(0) - (k_m + k_d S)c_{Fe(VI)}(x,t)} = \frac{dx}{Q_v} \]

We integrate Equation (S12) and apply the following boundary conditions:

\[ c_{Fe(VI)}(x,t)|_{x=0} = c_{Fe(VI)}(IN, t) \]

\[ c_{Fe(VI)}(x,t)|_{x=L} = c_{Fe(VI)}(OUT, t) \]

where \( L \) is the length of the electrode length in m. We then obtain the following solution:

\[ \frac{k_m c_{Fe(III)}(0) - (k_m + k_d S)c_{Fe(VI)}(OUT, t)}{k_m c_{Fe(III)}(0) - (k_m + k_d S)c_{Fe(VI)}(IN, t)} = \exp \left[ -\frac{(k_m + k_d S)BL}{Q_v} \right] \]

Substituting for the reactor volume \( V_R \) and residence time \( \tau_R \) in m\(^3\) and s, respectively, where
\[ V_R = BSL \#(S16) \]
\[ \tau_R = \frac{V_R}{Q_V} \#(S17) \]

and rearranging to isolate \( c_{Fe(VI)}(OUT,t) \), we obtain:

\[ c_{Fe(VI)}(OUT,t) = \frac{k_m}{k_m + k_d} \left\{ 1 - \exp \left[ -\left( \frac{k_m}{S} + k_d \right) \tau_R \right] \right\} c_{Fe(III)}(0) + \exp \left[ -\left( \frac{k_m}{S} + k_d \right) \tau_R \right] c_{Fe(VI)}(IN,t) \#(S18) \]

Using the general balance Equation (S1) we now perform a mole balance of Fe(VI) on the entirety of the reservoir at \( t \). It is assumed that: 1) the reservoir is perfectly mixed and 2) the degradation of Fe(VI) to form Fe(III) is homogeneous, occurring uniformly throughout each cross section. As such, the terms of Equation (S1) are expressed as follows:

\[ IN = Q_V c_{Fe(VI)}(OUT,t) \#(S19) \]
\[ OUT = Q_V c_{Fe(VI)}(IN,t) \#(S20) \]
\[ GEN = 0 \#(S21) \]
\[ CONS = k_d V_T c_{Fe(VI)}(IN,t) \#(S22) \]
\[ ACC = V_T \frac{dc_{Fe(VI)}(IN,t)}{dt} \#(S23) \]

where \( V_T \) is the reservoir volume in m\(^3\). Combining Equations (S19)–(S23) leads to the following equation for the reservoir:

\[ Q_V c_{Fe(VI)}(OUT,t) - Q_V c_{Fe(VI)}(IN,t) - k_d V_T c_{Fe(VI)}(IN,t) = V_T \frac{dc_{Fe(VI)}(IN,t)}{dt} \#(S24) \]

Substituting the reservoir residence time \( \tau_T \) in s given by

\[ \tau_T = \frac{V_T}{Q_V} \#(S25) \]

and substituting \( c_{Fe(VI)}(OUT,t) \) as expressed by Equation (S18) into Equation (S24) leads to:
\[
\frac{k_m}{S} \left(1 - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right] \right) c_{Fe(III)}(0) - \left[ 1 + k_d \tau_T - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right] \right] c_{Fe(VI)}(IN,t) = \tau_T \frac{dc_{Fe(VI)}(IN,t)}{dt} \tag{S26}
\]

Rearranging Equation (S26):

\[
\frac{k_m}{S} \left(1 - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right] \right) c_{Fe(VI)}(IN,t) \left( \frac{1}{S} + k_d \right) = \frac{dt}{\tau_T} \tag{S27}
\]

We solve Equation (S27) and apply the following initial condition:

\[
c_{Fe(VI)}(IN,t) \big|_{t=0} = 0 \tag{S28}
\]

To obtain the concentration of Fe(VI) in the reservoir as a function of time:

\[
\frac{c_{Fe(VI)}(IN,t)}{c_{Fe(III)}(0)} = a \left[ 1 - \exp \left( - bt \right) \right] \tag{S29}
\]

where

\[
a = \frac{k_m}{S} \left(1 - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right] \right) \left( \frac{1}{S} + k_d \right) + k_d \tau_T - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right] \tag{S30}
\]

and

\[
b = \frac{1 + k_d \tau_T - \exp \left[ - \left( \frac{k_m}{S} + k_d \right) \tau_R \right]}{\tau_T} \tag{S31}
\]
2. Linearization of analytical model and fitting of linearized experimental data

2.1. Linearization of analytical model

The following is postulated to develop a simplified approximation of the analytical model expressed by Equations (S29)–(S31) such that it can be linearized:

\[ k_d \ll \frac{k_m}{S} \tag{S32} \]

\[ k_d \tau_T \ll 1 \tag{S33} \]

This work evaluating \( k_d \) using the non-linear least squares method suggests that Equation (S32) is also a reasonable postulate. Previous work with degradation of electrochemically-generated ferrates [1] suggests that Equation (S33) is also a reasonable postulate. As such, Equations (S30) and (S31) become:

\[ a \cong 1 \tag{S34} \]

\[ b \cong \frac{1 - \exp\left(-\frac{k_m \tau_R}{S}\right)}{\tau_T} \tag{S35} \]

Therefore, Equation (S29) can be expressed in the following linearized form:

\[ \ln \left[ c_{Fe(III)}(0) - c_{Fe(V)}(IN,t) \right] = a' t + b' \tag{S36} \]

where

\[ a' = -\left[ 1 - \exp\left(-\frac{k_m \tau_R}{S}\right) \right] \tag{S37} \]

\[ b' = \ln \left[ c_{Fe(III)}(0) \right] \tag{S38} \]

It is noted that \( k_d = 0 \) satisfies both postulates described by Equations (S32) and (S33) and results in the approximations described by Equations (S34) and (S35). In other words, linearization of the analytical model is equivalent to the special case where \( k_d = 0 \).
2.2. Fitting of linearized experimental data

To demonstrate this analysis, $c_{Fe(VI)}(IN,t)$ data for varying current densities, $i$, using an ion exchange membrane are shown on a $\ln [c_{Fe(III)}(0) - c_{Fe(VI)}(IN,t)]$ vs time plot (Figure S1). It is clear that data for different current densities show linear trends and can be fitted by linear regression (straight lines). For all fits the value of $R^2$ exceed 0.95 (Table S1).

Figure S1. $\ln [c_{Fe(III)}(0) - c_{Fe(VI)}(IN,t)]$ for varying current densities with an ion exchange membrane plotted as a function of time. Initial conditions: pH 7, $c_{Fe(III)}(0) = 10$ mM, $Q_V = 4.9$ L min$^{-1}$.
Table S1. Summary of statistics from linear regression analysis of linearized experimental data

<table>
<thead>
<tr>
<th>$i$ (mA cm$^{-2}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.979</td>
</tr>
<tr>
<td>7.5</td>
<td>0.957</td>
</tr>
<tr>
<td>10.0</td>
<td>0.994</td>
</tr>
<tr>
<td>15.0</td>
<td>0.993</td>
</tr>
</tbody>
</table>

The values of $k_m$ are obtained from the slopes of the linear regression analysis and are summarized in Table S2. In addition, we performed non-linear least squares method to directly fit Equation, i.e., without applying approximations (S32,S33) and linearization (S36). It is clear that regressed values of $k_m$ do not vary significantly within a 95% confidence interval for a given $i$, irrespective of whether the linear regression analysis of linearized experimental data or non-linear least squares method was employed. With the use of non-linear fitting, best optimum fitting is generally obtained when $k_d$ is 0.

Table S2. Comparison of parameters obtained by 1) linear regression analyses of linearized experimental data (“Linear”) and 2) non-linear least squares method (“Non-linear”). Reported values include 95% confidence intervals

<table>
<thead>
<tr>
<th>$i$ (mA cm$^{-2}$)</th>
<th>$k_m$ / m s$^{-1} \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Linear</td>
</tr>
<tr>
<td>5.0</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>7.5</td>
<td>10.6 ± 1.8</td>
</tr>
<tr>
<td>10.0</td>
<td>21.9 ± 1.3</td>
</tr>
<tr>
<td>15.0</td>
<td>35.8 ± 2.4</td>
</tr>
</tbody>
</table>
References