# Advanced electrochemical oxidation for the simultaneous removal of manganese and generation of permanganate oxidants

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## Supplemental Materials

A simple mathematical model was developed to describe the electro-oxidation of $Mn^{2+}$, to higher valence state cations, under idealised conditions and assumptions. The subsequent formation of insoluble manganese hydroxides, principally $MnO_2$, is likely to occur due to thermodynamic stability in circumneutral conditions. The following model development will use generic terms for the dissolved manganese ($Mn^{2+}$) and oxidised insoluble forms of manganese ($Mn^{3,4,5+}$), as indicated by the subscripts "SOL" and "INS", respectively. The model is derived through a mole balance of: (i) the electrochemical reaction and, (ii) the anolyte vessel [*see Fig. S1*].

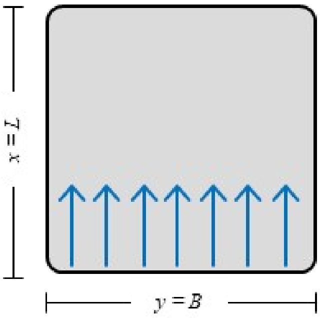

***Fig.S1** Electrode surface, of length L and width B, whereby water is assumed to be plug flow.*

Firstly, the model considers just the electrochemical reactor and more specifically the area of the reactor occupied by the electrode. Therefore, the moles of $Mn_{INS}$ are accounted for by those entering (*IN*), exiting (*OUT*), generated at the electrode surface (*GEN*), consumed (by either reduction at the cathode, general instability or further oxidation to soluble $Mn^{7+}$ species) (*CONS*), as well as the accumulation within the electro-active volume of the reactor (*ACC*), as follows:

$$IN - OUT + GEN - CONS = ACC \qquad \textbf{[Eq. S1]}$$

The above *[Eq.1]* is defined within the boundaries of the electrode volume, which can be of arbitrary width (*B*), inter-electrode gap ($\delta$) and length (*L*). It is also important to highlight two important assumptions that are made:

*(1) Plug flow reactor, i.e. no water flow velocity variations and perfect mixing*
*(2) The system and kinetics are completely mass transfer/diffusion limited*

The *IN, OUT, GEN, CONS* and *ACC* terms from [*Eq. S1*] are defined as:

$$IN = Q_V \cdot C_{INS}(x,t) \qquad \textbf{[Eq. S2]}$$

$$OUT = Q_V \cdot C_{INS}(x + \Delta x,t) \qquad \textbf{[Eq. S3]}$$

$$GEN = k_m \cdot B \cdot \Delta x \cdot C_{SOL}\left(x + \frac{\Delta x}{2},t\right) \qquad \textbf{[Eq. S4]}$$

$$CONS = k_d \cdot B \cdot \delta \cdot \Delta x \cdot C_{INS}\left(x + \frac{\Delta x}{2},t\right) \qquad \textbf{[Eq. S5]}$$

$$ACC = 0 \qquad \textbf{[Eq. S6]}$$

Where $Q_V$, $C_{OX}$, $k_m$ and $k_d$ represent the volumetric flow rate [m$^3$/s], molar concentration [mole/m$^3$], mass transport coefficient [m/s] and degradation coefficient [s$^{-1}$], which are assumed to be first-order kinetics. The above [*Eq. S2-6*] correspond to oxidised insoluble forms of manganese (Mn$^{3,4,5+}$) species, such as $MnO_2$, at an arbitrary cross section of the electrode, at a distance $x$ from the inlet boundary ($x=0$) at some time $t$, at an arbitrary thickness $\Delta x$. When [*Eq. S2-6*] are inputted in to [*Eq. S1*], the general rate balance becomes:

$$Q_VC_{INS}(x,t) - Q_VC_{INS}(x + \Delta x,t) + k_mB\Delta xC_{SOL}\left(x + \frac{\Delta x}{2},t\right) - k_dB\delta\Delta xC_{INS}\left(x + \frac{\Delta x}{2},t\right) = 0$$

***[Eq. S7]***

When divided by $\Delta x$, equation [*Eq. S7*] becomes:

$$\frac{Q_VC_{INS}(x,t) - Q_VC_{INS}(x + \Delta x,t)}{\Delta x} + k_mBC_{SOL}\left(x + \frac{\Delta x}{2},t\right) - k_dB\delta C_{INS}\left(x + \frac{\Delta x}{2},t\right) = 0$$

***[Eq. S8]***

When the limit ($\lim_{\Delta x \to 0} .$) is taken and derived, [*Eq. S8*] becomes:

$$-Q_V\frac{dC_{INS}(x,t)}{dx} + k_mBC_{SOL}(x,t) - k_dB\delta C_{INS}(x,t) = 0$$

***[Eq. S9]***

At this point, other assumptions that can be made include:

1. *All manganese species are homogeneously distributed*
2. *Manganese exist as either soluble or insoluble species*
3. *Total manganese is conserved, as follows:*

$$C_{INS,0} = C_{SOL}(x,t) + C_{INS}(x,t)$$

***[Eq. S10]***

The conservation of manganese equation ([*Eq. S10*]) can be rearranged and substituted into [*Eq. S9*]:

$$-Q_V\frac{dC_{INS}(x,t)}{dx} + k_mB\left[C_{SOL,0} - C_{INS}(x,t)\right] - k_dB\delta C_{INS}(x,t) = 0$$

***[Eq. S11]***

Which can be rearranged as:

$$\frac{dC_{INS}(x,t)}{k_mC_{SOL,0} - (k_m + k_d\delta)C_{INS}(x,t)} = \frac{B}{Q_V}dx$$

***[Eq. S12]***

This equation can be integrated by defining boundary conditions, with respect to just the reactor (electro-active area). The following boundary conditions are defined:

$$C_{INS}(x,t)|_{x=0} = C_{INS}(IN,t)$$

***[Eq. S13]***

$$C_{INS}(x,t)|_{x=L} = C_{INS}(OUT,t)$$

***[Eq. S14]***

When the boundary conditions are applied to [*Eq. S12*]:

$$\frac{k_mC_{SOL,0} - (k_m + k_d\delta)C_{INS}(OUT,t)}{k_mC_{SOL,0} - (k_m + k_d\delta)C_{INS}(IN,t)} = exp\left[-\frac{(k_m + k_d\delta)BL}{Q_V}\right]$$

***[Eq. S15]***

Furthermore, the above ([*Eq. S15*]) can be simplified by defining the reactor volume ($V_R$) and residence time ($t_R$) as:

$$V_R = B\delta L \qquad \textbf{[Eq. S16]}$$

$$t_R = \frac{V_R}{Q_V} \qquad \textbf{[Eq. S17]}$$

Therefore *Eq. S15* can be further simplified and rearranged to isolate for the generated oxidant concentration leaving the reaction at time *t*:

$$C_{INS}(OUT,t) = \frac{\frac{k_m}{\delta}}{\frac{k_m}{\delta} + k_d}\left(1 - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]\right)C_{SOL,0} + exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]C_{INS}(IN,t) \qquad \textbf{[Eq. S18]}$$

The same approach taken above can be used to model the generated oxidant concentration in the batch recycle reservoir, where samples are drawn for analysis during laboratory experiments. Another mole balance is undertaken, this time defining the boundaries of the reservoir as:

$$IN = Q_V C_{INS}(OUT,t) \qquad \textbf{[Eq. S19]}$$

$$OUT = Q_V C_{INS}(IN,t) \qquad \textbf{[Eq. S20]}$$

$$GEN = 0 \qquad \textbf{[Eq. S21]}$$

$$CONS = k_d V_V C_{INS}(IN,t) \qquad \textbf{[Eq. S22]}$$

$$ACC = V_V \frac{dC_{INS}(IN,t)}{dt} \qquad \textbf{[Eq. S23]}$$

Where $V_V$ is the volume of the reservoir vessel. Other terms found in [*Eq. S19-23*] are consistent with those used in [*Eq. S1-18*], at some arbitrary time, *t*. Once again, the mole balance is setup by inputting [*Eq. S19-23*] in to [*Eq. S1*]:

$$Q_V C_{INS}(OUT,t) - Q_V C_{INS}(IN,t) - k_d V_V C_{INS}(IN,t) = V_V \frac{dC_{INS}(IN,t)}{dt} \qquad \textbf{[Eq. S24]}$$

The residence time of the reservoir can be defined as:

$$t_V = \frac{V_V}{Q_V} \qquad \textbf{[Eq. S25]}$$

This can be substituted into [*Eq. S24*], as well as the $C_{INS}$ *(OUT, t)* term defined in [*Eq. S18*]:

$$\frac{\frac{k_m}{\delta}}{\frac{k_m}{\delta} + k_d}\left(1 - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]\right)C_{SOL,0} - \left(1 + k_d t_v - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]\right)C_{INS}(IN,t) = t_V \frac{dC_{INS}(IN,t)}{dt} \qquad \textbf{[Eq. S26]}$$

When rearranged:

$$\frac{C_{INS}(IN,t)}{\frac{\frac{k_m}{\delta}}{\frac{k_m}{\delta} + k_d}\left(1 - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]\right)C_{SOL,0} - \left(1 + k_d t_v - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]\right)C_{INS}(IN,t)} = \frac{dt}{t_V} \qquad \textbf{[Eq. S27]}$$

Now, initial conditions can be defined:

$$C_{INS}(IN,t)|_{t=0} = 0 \qquad \textbf{\textit{[Eq. S28]}}$$

Which assumes that at the start of electrolysis (*t=0*), no insoluble forms of manganese are present, and manganese existing solely in the lower oxidation of $Mn^{2+}$. From this, an expression for the molar concentration of generated insoluble manganese at any time (*t*) in the sampling reservoir is obtained:

$$C_{INS}(IN,t) = X(1 - \exp(-Yt))C_{SOL,0} \qquad \textbf{\textit{[Eq. S29]}}$$

Where,

$$X = \left(\frac{\frac{k_m}{\delta}}{\frac{k_m}{\delta} + k_d}\right)\left(\frac{1 - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]}{1 + k_d t_v - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]}\right) \qquad \textbf{\textit{[Eq. S30]}}$$

$$Y = \frac{1 + k_d t_v - exp\left[-\left(\frac{k_m}{\delta} + k_d\right)t_R\right]}{t_V} \qquad \textbf{\textit{[Eq. S31]}}$$

The final expression ([*Eq. S29-31*]) relates the generation of insoluble manganese species with respect to the mass transport coefficient ($k_m$) and degradation coefficient ($k_d$), which are functions of electrical current, temperature, reaction concentration, etc.

## Water Velocity Distribution Analysis

Computational fluid dynamic models were used to confirm the water velocity flow variations within the electro-active area of the electro-oxidation reactor. The anolyte side of the electrochemical cell (along the plane of symmetry) was modelled using COMSOL Multiphysic ®. A 3-dimensional water velocity profile in the laminar flow regime was yielded, assuming fluid flow was independent of electrostatic interactions with the electrode, as well as no significant influence of ions on water velocity due to their negligible effect on water viscosity. A final assumption included that any gas (oxygen or hydrogen) possibly generated at the electrode surface would have negligible effects on water velocity due to the greater force of convection mass transport through the electrochemical cell.

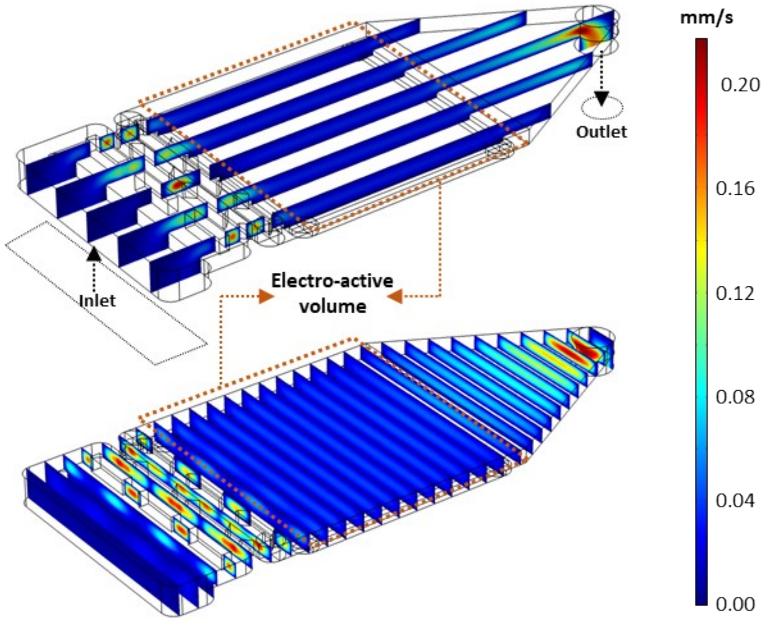

***Fig.S2*** *CFD model of electrochemical reactor flow velocity profile (38).*

The reactor's water inlet incorporated flow channels, which helped to distribute water evenly between and over the anode surface. It was observed in the CFD model that velocity was evenly distributed throughout the electro-active chamber of the cell, consequently minimising any current density variations that may exist due to highly variable flow. No stagnant areas, or dead zones, were observed in the CFD models, which helped to ensure that no accumulation of manganese was occurring within the reactor.