Mass transfer simulation of main species in swine biogas slurry in bipolar membrane electrodialysis

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Abstract. The aim of this model is to study the mass transfer of main species in swine biogas slurry in bipolar membrane electrodialysis. We developed a two-dimensional steady-state model composing three compartments. In this model, Nernst-Planck equation and Hagen-Poiseuille equation are combined for mass transfer and Faraday’s law is for the electrolyte current density. The model considers local electroneutrality condition and does allow cations and anions pass through membranes. The set of equations with boundary conditions and initial values are calculated by the finite element numerical method with COMSOL Multiphysics. This model can be able to predict the distribution of electrolyte potential, the ion flux and the ion concentration distribution. The two parameters, cell voltage and inlet velocity, are indicated to have influences on the process of bipolar membrane electrodialysis treatment on swine biogas slurry.

1. Introduction
Electrodialysis relying on external electric field and ion exchange membrane has been widely applied in seawater desalination[1], heavy metal ions removal in industrial wastewater[2] and sewage treatment[3]. It has advantages of simple operation, high recovery rate and environmental protection[4]. In denitrification and dephosphorization process, electrodialysis is applied in concentrating nitrogen and phosphorus in sewage[5-6]. The concentrated sewage is then treated by chemical precipitation[7-8] and steam stripping[7-9]. Due to rich nitrogen and phosphorus content in livestock wastewater, electrodialysis can help realize resource recovery, which attracts more attention from all over the world.

Bipolar membrane electrodialysis with three-compartments is applied in separating ammonium and phosphate from livestock wastewater[10-11]. This system has been widely used in acid and base production in industry. Due to the complex composition of livestock manure, it is helpful to explore ion concentration distribution and electrolyte potential with simulation.

Mass transfer in electrodialysis has widely been studied with the Nernst-Planck equation on condition of local electroneutrality[12-13]. However, combined with non-equilibrium thermodynamic equations (Maxwell-Stefan, Nernst-Planck equation etc.), many researches consider Poisson equation so that mass transfer at nanometer scale can be explored[14]. For fluid flow, based on fluid dynamics, the Navier-Stokes and continuity equations are used to conjunct the velocity in convection[15]. To simplify the solution, some models assume a developed flow field between parallels with parabolic velocity profile[13]. In addition, with the improvement of computer processing capacity, these equations can be solved with multi-physics modelling platforms on basis of the finite element method. Besides, a concentration gradient at membrane-solution interface, polarization, should be considered[16].

Mass transfer and hydrolysis of bipolar membrane are two inevitable and essential problems in studying the ion separation in this scheme. The hydrolyzation of bipolar membrane is mainly affected
by the current density and time[17]. With increasing concentration of acid and alkali whose hydrogen and hydroxide ions are provided by the hydrolyzation, the current efficiency decreases and energy assumption increases. This in turn limits the degree of bipolar membrane hydrolysis. Thence, the bipolar membrane hydrolysis is not discussed under a steady-state system.

This work aims to obtain the distribution of ion concentration and flux and figure out the voltage distribution in free electrolyte. To simplify this model, biogas slurry is assumed to be a fully ionized multi-ion scheme with simulation of ammonia nitrogen, total phosphorus calcium and magnesium concentration. Therefore, mass transfer of main species in swine biogas slurry in bipolar membrane electrodialysis is recognized.

2. Model development

2.1. Definition of model geometry

Figure 1. shows a schematic graph of model geometry which is the repeating unit of BMED system. This unit consists of three membranes including two selective membranes (a CEM and an AEM) and a bipolar membrane (BM). In the CEM, cations especially monovalent cations have high elective permeability and anions have low. The AEM has the opposite characteristics. Besides, the middle BM consists of a layered ion-exchange structure composed of a CEM joined to an AEM[18]. There is a thickness of 2nm at the junction of the two membranes, which is distribute to a membrane boundary for its too small scale [19]. The adjacent left and right domain of the bipolar membrane are concentrate channels, where become acid and alkali rooms when hydrogen and hydroxide ions are dissociated from the bipolar membrane. The leftmost and rightmost domain are dilute domains where salt is to be removed.

The composition and concentration of model influent refer to swine biogas slurry having parameters listed in Table 1. In order to view performance of ammonium and phosphate in this system, simulating biochemical chemical oxygen demand with glucose is negligible so that the inlet becomes a multi-ion system. Parameters of this model are listed in Table 2.

Table 1. The main ingredient content (mg/L) of pig biogas slurry.

| COD       | NH3-N | TP   | Ca^{2+} | Mg^{2+} |
|-----------|-------|------|---------|---------|
| 4000-5000 | 600-700 | 100-120 | 100    | 40      |

Table 2. Parameters of this model.

| Name | Value | Description       | Name    | Value       | Description       |
|------|-------|-------------------|---------|-------------|-------------------|
| Vtot | 2[V]  | Total potential drop | D_{K^+} | 1.96e-9[m^2/s] | Diffusion coefficient |
| vavg | 0.01[m/s] | Average flow velocity | D_{Cl^-} | 2.03e-9[m^2/s] | Diffusion coefficient |
| cMem | 50[mol/m^3] | Membrane concentration | D_{SO4}^2- | 1.07e-9[m^2/s] | Diffusion coefficient |
### 2.2. Theories

In this model, hydrolysis originating from the bipolar membrane is neglected in a steady state system. Because the generated hydrogen and hydroxide ion concentration is closely related to current density and time. Due to the principle of conservation of mass, ion mass balance in the unit is given by

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot N_i = r_i
\]

where \(c_i\), \(N_i\) and \(r_i\) are the ion concentration, the ion flux and source term. \(N_i\) is described by Nernst-Planck (NP) equation according to diffusion, electromigration and convection.

\[
N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi + c_i u_i
\]

where \(D_i\), \(u_i\) and \(z_i\) are the diffusion coefficient, species mobility and charge number of species, while \(\phi\) and \(u\) denote electrolyte potential and fluid velocity respectively. Due to Nernst-Einstein, \(u_i\) is calculated.

\[
u_i = \frac{D_i}{RT}
\]

There is an assumption that the salt in solution is dissociated exhaustively, i.e., the concentration of dissociated cations and anions are related by local electroneutrality condition except for the nanoscale condition which isn’t thought in this model.

\[
\sum z_i c_i = 0
\]

Within the membrane, fixed ions distribute uniformly and ion flux follows Nernst-Planck equation the same as that in solution. The fixed charge of an IEM is also taken into account with local electroneutrality condition.

\[
\sum z_i c_i + \rho_{fix} = 0
\]

The current density, \(i\), is calculated using Faraday’s law, where \(F\) is the Faraday constant.

\[
i = F \sum z_i N_i = F \sum z_i (-D_i \nabla c_i - z_i u_i F c_i \nabla \phi)
\]

Conservation of charge is also taken into account.

\[
\nabla \cdot i = 0
\]

In some cases, fluid dynamics is described by Navier-Stokes equation coupled with continuity equation. To simplify, a parabolic flow profile is assumed in the parallel channel. The fluid velocity is given by Hagen-Poiseuille equation[13].

\[
v(x) = \frac{v_0}{(1 - \left(\frac{x}{h}\right)^2)}
\]

where \(v_0\) and \(h\) denote respectively the maximum fluid velocity and half of channel thickness. In this model, average fluid velocity is used instead of the maximum one.
2.3. Boundary and initial conditions
At the inlets, different species which distribute uniform have the same concentration in each channel. There is no speed component in x direction, and the component in y direction is equal to fluid velocity.

\[ c_i(x,0) = c_i,0 \]
\[ v_x = 0, v_y = v_i \]

At the end of channels, diffusion flux and electromigration flux are ignored.

\[ D_i \frac{\partial c_i}{\partial y} = 0, y = L \]

When setting the exit and entrance of the fluid, both ends of ion exchange membranes (including the bipolar membrane) are considered closed with no changes in the number of ions in y direction.

Based on a symmetrical system, the species concentration in the leftmost and rightmost boundary is consistent.

\[ c_{i,x=0} = c_{i,x=4n+3H} \]

The inlet boundaries between ion exchange membranes and free electrolyte are set up in the following way, on basis of electrolyte potential, current density and ion flux.

We have the following relation between electrolyte potential and ion concentration. The potential shift caused by Donnan law occurs at the diffusion boundary layer (DBL). Ion concentration is related by the continuity of potential drop.

\[ \varphi_s = \varphi_m + \frac{RT}{z_i F} \ln \left( \frac{c_{i,m}}{c_{i,s}} \right) \]

where the subscripts m and s denote membrane and solution, i.e., \( c_{i,m} \) and \( c_{i,s} \) are ion concentration in the membrane and free electrolyte, respectively.

The normal current density in free electrolyte domain is equal to that in the membrane. The flow of ions from free solution into the membrane is continuous so that the ion flux keeps constant. The current density and the ion flux have the following relations.

\[ n \cdot i_s = n \cdot i_m \]
\[ n \cdot N_s = n \cdot N_m \]

3. Results and discussion

3.1. Concentration distribution in channels
Figure 3. shows the concentration profile of different ions in channels at constant cell voltage and velocity (0.02V, 0.01m/s). As is known to all in the past, concentration increases in dilute channels and decreases in concentration channels[20]. The boundary layers with high gradients forms close to membrane surfaces. In these areas, the ion concentration is influenced by the freely distributed counterions.

Figure 3. Concentration distribution at half of the unit height at a constant cell potential (2V) and inlet speed (0.01m/s): (a) cations;(b) anions.

It is worth mentioning that trends of ions with different valances are distinct in boundaries close to the bipolar membrane. In these areas, the concentration of monovalent ions increases but the
concentration of divalent ions decreases. From my view of point, due to the presence of the adjacent layer of the bipolar membrane, the migration flux of counterions within the bipolar membrane is not as high as that within ion exchange membranes. The diffusion of monovalent ions is dominant in the diffusion boundary layer.

Ammonium and phosphate are considered as typical cations and anions. At a constant velocity, it seems that concentration gradients become huge in the boundary layers close to the membrane surfaces for both ammonium and phosphate (Figure 4.). The voltage variable has a positive effect on concentration gradient in this layer. However, this relationship doesn’t matter in free electrolyte far from the membrane surface.

Figure 4. Concentration profile at half of the unit height for different voltages: (a) ammonium in the leftmost dilute channel; (b) phosphate in the rightmost dilute channel.

Similarly, the concentration of ammonium and phosphate close to the membrane increases obviously, which is due to the drop of speed (Figure 5.). The drop of ion concentration in the diffusion boundary layer is the concentration polarization phenomenon which limits mass transfer and increases non-Ohmic voltage. Increasing the velocity can help shorten the diffusion boundary layer’s thickness, thereby easing the concentration polarization.

Figure 5. Concentration profile at half of the unit height for different flow rates: (a) ammonium in the leftmost dilute channel; (b) phosphate in the rightmost dilute channel.

3.2. Electrical potential distribution

Figure 6. and Figure 7. show the electrolyte potential distribution along a horizontal line placed at half of the cell height. The former has the speed stable and has an increased voltage, while the latter is exactly the opposite. Results show that an increase in cell voltage results in a greater growth rate of electrical potential. However, the variable velocity has no effect on the electrolyte potential obviously.

The potential loses a lot when ions transport across membranes and is much greater than that results from ion transportation in solution. Another result in the figure is that a significant potential discontinuity occurred in the boundary between the free electrolyte and the membrane domain. The discontinuous potential difference is related to the concentration of counterions in the IEM.
3.3. Flux of ions

Figure 8. reveals migration and diffusion fluxes of ammonium and phosphate at a constant flow rate (0.01 m/s) and cell potential (2 V). Far away from the membrane in the channel, migration flux and diffusion flux have the same value. However, in the area near the membrane, ions are dominated by diffusion motion. It is so called diffusion boundary layer phenomenon. Due to the large amount of counterions distributed in the membrane, the ion flux in this area will increase significantly.

At a constant speed of 0.01 m/s, Figure 9. shows the total flux distribution of ammonium and phosphate at different voltage values of 1 V, 2 V and 3 V. As we can see, a voltage increase makes the flux of ions increase significantly. There is a detail that the increase in ion flux results from 1.5 V to 2 V is greater than the increase results from 1 V to 1.5 V. Therefore, within a certain range, increasing the cell voltage, even total electrodialysis system voltage, can obtain better ion concentration efficiency. The best ammonium and phosphate recovery efficiency may be achieved on in-depth research.

It is indicated from Figure 10. that the flow rate has no significant influence on the total flux of ammonium and phosphate when keeping the voltage 2 V. At this voltage, maintaining the influent speed at 0.01 m/s will result in higher species recovery efficiency. At the diffusion boundary layer, the greater the flow rate, the greater the ion flux gradient. Therefore, the increased flow velocity can help shorten the thickness of the diffusion boundary layer and reduce the scaling occurred on the membrane surface cooperated with partitions.
3.4. Concentration distribution in the bipolar membrane

Figure 11 shows the concentration distribution of different species within the bipolar membrane at a constant voltage (2V) and inlet speed (0.01 m/s). As we can see, cation concentration increases and anion concentration decreases in the boundary between the connected two ion exchange membranes. This may be because although we believe both cations and anions can be transferred in ion exchange membranes in this model, the diffusion coefficients of ions in the cation or anion membranes are not the same. Compared to single ion exchange membrane, the ion concentration gradient in the bipolar membrane is much larger. In my opinion, for mass transfer characteristics of electrodialysis, the counterion concentration is quite low and the concentration of ions transferred from the solution becomes high in this adjacent layer of the bipolar membrane.

4. Conclusion

The aim of this work is to develop a simulation to predict mass transfer of main species in swine biogas slurry. Based on a set of equations, this model is capable of depicting the distribution of ion concentration, electrolyte potential and ion flux. Meanwhile, setting voltage and velocity variables, some conclusions are achieved, which support higher ion concentration efficiency and lower energy assumption in actual...
experiments. Within a certain range, increasing the cell voltage can obtain better concentrate efficiency. A velocity increase leads to a small boundary layer thickness and helps slow down the scaling in the membrane surface.

This model is limited to consideration of water dissociation resulting from the bipolar membrane. In addition, the large amount of bicarbonate ions contained in the swine biogas slurry is not considered, because its balance is greatly affected by the hydrolysis of the bipolar membrane. These will be studied in recent research.

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