

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

This chapter consists of three parts, ion-exchange equilibrium and kinetics; mode of applications; and model development. Although most related work is mentioned in the first part, a few are discussed in the other sections.

2.1 Ion-Exchange Equilibrium and Kinetics

2.1.1 Ion-Exchange Equilibrium

Equilibrium of an adsorption on ion exchangers has been investigated for many years. One important equilibrium parameter is equilibrium constant, K . It has been known that pH, temperature and exchanged ions, directly, affect the equilibrium constant.

The equilibrium adsorption of L-glutamic acid on a weak basic ion exchanger was studied by Yoshida and Kishimoto (1995). It was found that the equilibrium depends on the initial concentration of L-glutamic acid and can be significantly affected by pH of the solution. The adsorption of L-glutamic acid can be explained by the acid/base neutralization reaction as in Equation 2.1.



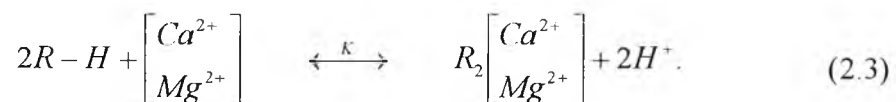
where $R-N$ denotes a tertiary amine fixed in the resin phase. In this work, the equilibrium constant, K_{HCl} , and concentration of H^+ in the resin phase, Q_{HCl} , were determined from Equation 2.2.

$$q_{HCl} = \frac{Q_{HCl}K_{HCl}C_{HCl}}{1 + K_{HCl}C_{HCl}}, \quad (2.2)$$

where q_{HCl} and C_{HCl} are concentration of hydrochloric acid in the resin phase and solution and were obtained from experimental data.

2.1.2 Ion-Exchange Kinetics

When an ion in a solution approaches an ion exchange resin, it encounters a stagnant film of the solution around the resin. The ion must pass through this film before diffusing into the pores or mesh openings to the active exchange sites. The ion then replaces an ion of the similar charge and the displaced ion now diffuses out of the resin into the bulk solution. The diffusion of an ion from the exterior of the resin through the surface is called *film diffusion* while the diffusion of an ion within the pores of the resin is called *pore or intraparticle diffusion*. The exchange process is usually represented by a chemical reaction. For example, a resin in the hydrogen ion form, $R-H$, is used to exchange Ca^{2+} or Mg^{2+} from a solution. The exchange process can be represented by Equation 2.3.



Boyd *et al.* (1982) found that diffusion either inside the resin or through the stagnant film around the resin can be the rate-determining step of the exchange process. At a concentration of the solution less than 0.003 M, the diffusion through the stagnant film controlled the exchange rate. On the contrary, at a solution concentration above 0.1 M, the exchange rate was determined by the rate of diffusion inside the resin. Intraparticle diffusion was also found to be the rate-determining step of the Cu^{2+} removal by a chelating ion exchange resin in the work of Kwon *et al.* (1992).

Recently, Xu and Chuang (1996) studied the kinetics of acetic acid esterification over ion exchange catalysts. In the experiment, methanol

was added to dilute acetic acid solutions and reacted with the acid in water to form methyl acetate and water. The reaction is shown in Equation 2.4.



The authors presented a model that can be used in the design of a catalytic distillation column to remove low concentrations of acetic from wastewater. The model is shown in Equation 2.5

$$\frac{dC_{MeAc}}{dt} = k_1(C_{MeOH}C_{HAc} - \frac{C_{MeAc}C_{H_2O}}{K}) \quad (2.5)$$

where K denotes the equilibrium constant, k_1 denotes the rate constant and C denotes the concentration of a species.

2.2 Modes of operation

Several modes of operation have been used in the ion-exchange process. They can be summarized into three categories: batch operation, fixed-bed operation and fluidized-bed operation. Each of the categories along with its related work is presented here.

2.2.1 Batch Operation

Although batch operation is the simplest mode, its efficiency is limited by the selectivity of the resin under equilibrium. Manantapong (1997) studied the adsorption kinetics of the ion exchange process with this operation. The work concentrated on the exchange of sodium ions from a solution with hydrogen ions on Dowex50-8X resins. The reaction can be explained by Equation 2.6.



where RSO_3H and RSO_3Na are defined as the resin phase occupied by H^+ ions and Na^+ ions, respectively. In Manantapong's work, it was shown that the adsorption equilibrium was reached faster when a higher mixing rate was applied. In addition, increasing the initial concentration resulted in an increase of the solution uptake in the resin phase.

2.2.2 Fixed-Bed Operation

In fixed-bed operation, solution passes through ion-exchange resin, which is packed in a column, in the downflow direction. That makes the top of the column capture most of the ions, and the bottom receives the leftovers; therefore, it is the bottom part that accomplishes the final purification and determines the purity of the effluent. The exchangers always continue contacting the fresh so this mode achieves high efficiency. Kenneth

and Howard (1979) studied effects of different ionic mobility in a column. A model with several parameters was proposed and tested against the experimental data. Dowex50W-8X resins were used in the study. An equilibrium relation, an ionic diffusion coefficient in the resin, dispersion coefficients, boundary layer, thickness, ion-exchange capacity, bed void fraction, and particle dimensions were obtained experimentally. These data were then used in the model, which gave a good agreement with the observed data. Zhao and Sengupta (1996) used the fixed-bed operation to remove and recover phosphate from industrial wastewater. The operation was quite efficient even though the waste contained other competing chloride, bicarbonate, sulfate and dissolved organic matter.

2.2.3 Fluidized-Bed Operation

Fluidized-bed operation allows a bed of solid particles to be lifted and agitated by a rising stream of a fluid. With an increase in a flow rate, particles move apart and the bed starts to expand. The void fraction after the bed is fully fluidized can be calculated by Equation 2.7.

$$L = L_0 \left(\frac{1 - \varepsilon_0}{1 - \varepsilon} \right), \quad (2.7)$$

where

- L = height of fluidized bed
- L_0 = height of solid bed
- ε_0 = porosity or volume fraction of voids in bed of solids
- ε = bed void fraction during the fluidization.

The expanded bed allows channeling or passage of the solution through the enlarged spaces between the particles and, therefore, provides less efficient contact compared with fluidized bed operation. Manantapong (1997) studied the behavior of the fluidized-bed operation. Dowex50W-8X resins

were used in this study. In Manantapong's work, the work was developed a model to predict the rate of Na^+ adsorbed on the resin. The model is shown in Equation 2.8.

$$r = \frac{dq}{dt} = k_1 \left[\frac{q_t}{1 + \frac{h}{k_2 c}} - q \right], \quad (2.8)$$

where q represents the concentration of NaCl in the resin phase, q_t represents a total exchange capacity of the resin, c represents concentration of NaCl in the solution, and h represents hydrogen concentration in the solution phase. In the model, it was found that the rate constant k_1 is 0.092 s^{-1} and the equilibrium constant k_2 is 0.67 for the batch operation and k_1 is 0.006 s^{-1} and k_2 is 0.02 for the fluidized-bed operation. The results show that k_1 for the batch operation is higher than that of the fluidized-bed operation because the batch is nearly perfectly mixed.

2.3 Model Development

A model to describe the characteristics of ion exchange in a fluidized-bed column can be developed based on results from three types of experiment, namely: response time experiment, no adsorption experiment, and adsorption kinetics from batch experiment. The following assumptions have been made for the development.

1. Resin beads are uniform spheres.
2. Ion exchange is not accompanied by volume changes in the spheres.
3. Concentration profiles within the beads, before the adsorption, are uniform.
4. Anions are excluded from the resin phase.
5. There is equilibrium between the solid and liquid phase.

2.3.1 A Model for the Response Time of a pH Electrode

Using a pH electrode as a means to track changes in solution does not provide an instantaneous measure of the pH in the solution. It is because there is a lag, called the *response time*, of the electrode to transfer the pH information. A model to account for the response time can be developed from Figure 2.1.

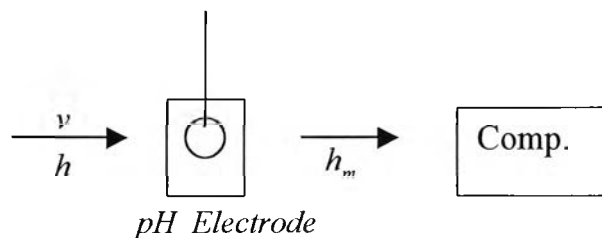


Figure 2.1 Representation of the response time experiment

The governing equation for the response time is

$$\frac{dh_m}{dt} = \alpha_e (h_0 - h_m) \quad (2.9)$$

where

- h_0 = initial H^+ concentration measured by the pH electrode, meq/ml,
- h_m = H^+ concentration measured by the pH electrode, meq/ml,
- h = H^+ concentration entering the pH electrode, meq/ml, and
- α_e = response time constant of the pH electrode, s^{-1} .

2.3.2 A model for Batch Operation with Adsorption

The notation for the diffusion in the resin particle is shown in Figure 2.2.

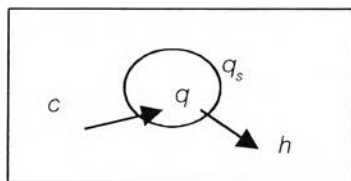


Figure 2.2 Notation for the diffusion in the resin particle

In this section, the mass balances of ions in the solution are used to determine c , q and h . The governing equations are

$$qV_R = hV_L \quad (2.9)$$

or

$$h = \beta q, \quad (2.10)$$

where

$$\beta = \frac{V_R}{V_L}, \quad (2.11)$$

which accounts the ion adsorbed/desorbed into/out of the resin, and

$$c_0 = c + q\beta = c + h, \quad (2.12)$$

which accounts for the ion balance, and

$$\frac{dc}{dt} = -\frac{dh}{dt} = -\beta \frac{dq}{dt} \quad (2.13)$$

which accounts for the change of ions with time.

Next, the concentration gradient inside the resin is accounted by Equation 2.14.

$$\frac{dq}{dt} = k_1(q_s - q) \quad (2.14)$$

Also, applying the concept of the relative volatility for a binary mixture in distillation columns, the ratio of the concentrations of cations in solution to H^+ ions on the surface of the resin is assumed to be proportional to a corresponding ratio in the liquid.

$$\frac{q_s}{q_t - q_s} = \frac{k_2 c}{h} \quad (2.15)$$

Eliminating q_s from Equation 2.14 using Equation 2.15 yields

$$\frac{dq}{dt} = k_1 \left[\frac{q_t}{1 + \frac{h}{k_2 c}} - q \right], \quad (2.16)$$

where

$$q_t = q_e \left(1 + \frac{h_e}{k_2 c_e} \right) \quad (2.17)$$

All the nomenclatures used in this part are summarized below.

- c_0 = initial concentration solution, meq/ml
- c = concentrations of Na^+ or Ca^{2+} or Mg^{2+} ion in solution phase, meq/ml
- c_e = equilibrium concentration of solution, meq/ml

h	=	concentration of hydrogen ion in the solution phase, meq/ml
h_e	=	concentration of hydrogen ion in the solution phase at equilibrium, meq/ml
k_1	=	rate constant, s^{-1} , Dr. Maurice Allen model
k_2	=	equilibrium constant, dimensionless, Dr. Maurice Allen model
q_t	=	total exchange capacity of exchange, meq/ml
q	=	concentration of Na^+ , Ca^{2+} or Mg^{2+} in the resin, meq/ml
q_s	=	concentration of Na^+ , Ca^{2+} or Mg^{2+} on surface of resin, meq/ml
q_e	=	concentration of Na^+ , Ca^{2+} or Mg^{2+} on surface of resin at equilibrium, meq/ml
V_R	=	volume of resin bed, ml
V_L	=	volume of liquid bed, ml
β	=	constant.

2.3.3 A Model for Fluidized-Bed Operation without Adsorption

The behavior of the fluidized-bed column without adsorption can be viewed as consisting of two parts. The first part is well mixed and can be represented by the CSTR model while the other part is when the liquid just passes through without any reaction and is accounted for by the PFR model.

To ensure that the model can represent experimental data well, the number of CSTRs will be varied from one to three. A schematic of the model is shown in Figure 2.3.

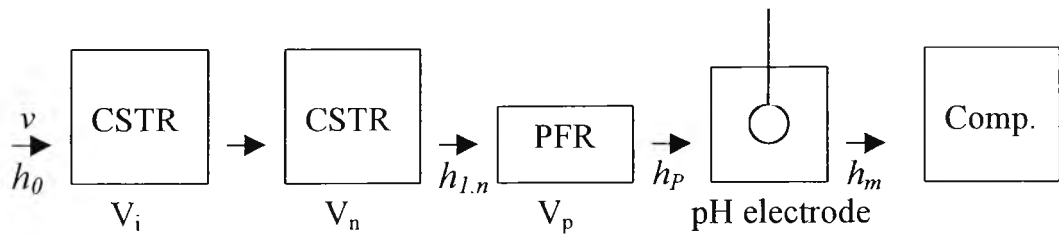


Figure 2.3 Representation of ion-exchange column without adsorption

A H^+ balance on the first CSTR gives:

$$\frac{dh_i}{dt} = \frac{v}{V_L} (h_0 - h_{1,i}) \quad (2.18)$$

A H^+ balance on the i^{th} CSTR gives:

$$\frac{dh_{1,i}}{dt} = \frac{v}{V_L} (h_{1,i-1} - h_{1,i}) \quad (2.19)$$

The effect of the plug-flow volume is

$$h_{p,(t)} = h_{1,(t-t_r)}, \quad (2.20)$$

in which

$$t_r = \frac{V_p}{v} \quad (2.21)$$

The response time of the pH electrode is shown in Equation 2.22.

$$\frac{dh_m}{dt} = \alpha_e (h_p - h_m), \quad (2.22)$$

where

- h_m = H^+ concentration measured by the pH electrode, meq/ml,
- h_p = H^+ concentration leaving the PFR, meq/ml,
- $h_{l,i}$ = H^+ concentration leaving the CSTR no. i , meq/ml,
- h_0 = H^+ concentration entering the column, meq/ml,
- v = volumetric flow rate of the solution, ml/s.,
- V_i = total volume of CSTR no. i , ml,
- α_e = the response time constant for each pH electrode,
- i = number of CSTR ($i = 1, 2$ or 3),
- t_r = residence time in plug flow volume,
- V_L = volume of liquid in CSTR, $(1-\varepsilon)V$, ml,
- V_R = volume of resin in CSTR, (εV) , ml, and
- V_p = volume of plug flow reactor, ml.

2.4.4 A Model for Fluidized-Bed Operation with Adsorption

The model for the fluidized-bed column with adsorption is shown in Figure 2.4.

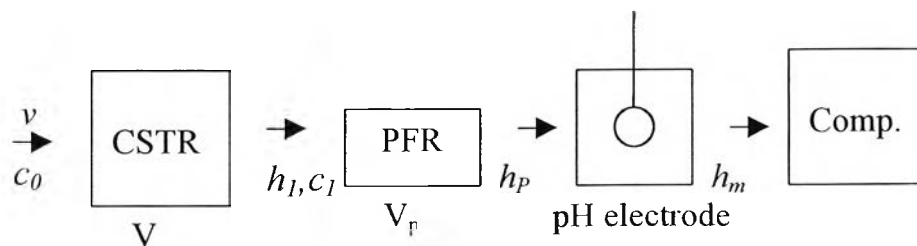


Figure 2.4 Representation of ion-exchange column with adsorption.

A cation balance on the CSTR gives:

$$vc_0 - vc - rV_R = V_L \frac{dc}{dt} \quad (2.23)$$

A H^+ balance in the CSTR gives:

$$-vh_1 + rV_R = V_L \frac{dh_1}{dt} \quad (2.24)$$

The effect of the plug-flow volume is the same as Equation 2.20

$$h_{p,(t)} = h_{1(t-t_r)} \quad (2.20)$$

in which

$$t_r = \frac{V_p}{v} \quad (2.21)$$

The rate of adsorption is previously shown in Equation 2.16

$$\frac{dq}{dt} = k_1 \left[\frac{q_i}{1 + \frac{h}{k_2 c}} - q \right] \quad (2.16)$$

And response time of the pH electrode was given in Equation 2.22 as

$$\frac{dh_m}{dt} = \alpha_e (h_p - h_m) \quad (2.22)$$

where

- h_m = H^+ concentration measured by the pH electrode, meq/ml,
- h_p = H^+ concentration leaving the PFR, meq/ml,
- h_{1i} = H^+ concentration leaving the CSTR no. i , meq/ml,
- h_0 = H^+ concentration entering the column, meq/ml,
- c_0 = initial concentration solution, meq/ml,
- c_1 = concentrations of Na^+ or Ca^{2+} or Mg^{2+} ion in solution leaving the CSTR, meq/ml,
- v = volumetric flow rate of the solution, ml/s.,
- V = total volume of CSTR, ml,
- α_e = the response time constant for each pH electrode, s^{-1} ,
- t_r = residence time in plug flow volume,
- V_L = volume of liquid in CSTR, $(1-\epsilon)V$, ml,

- V_R = volume of resin in CSTR, (εV), ml, and
 V_p = volume of plug flow reactor, ml.

2.3.5 Mathematical Procedure

The flow chart diagram of the numerical method used in this work is shown in Figure 2.5. In the following, the superscripts i and $i+1$ denote values at the beginning and at the end of the time-step dt , respectively. To ensure the stability of the method, the equation will be implicit in time, with as many quantities as possible expressed at the end of the time step. Then, the solver tool of Excel is used to solve the equations as shown in Equations 2.25-2.33.

Definition of constants

$$\beta = \frac{v\Delta t}{V_L}, \quad \gamma = \frac{V_R\Delta t}{V_L} \quad (2.25)$$

A cation balance on the CSTR gives:

$$vc_0 - vc_1^{i+1} - V_R r^i = V_L \left[\frac{c_1^{i+1} - c_1^i}{\Delta t} \right] \frac{dc}{dt} \quad (2.26)$$

so that

$$c_1^{i+1} = \frac{c_1^i + \beta cc_0 - \gamma r^i}{1 + \beta} \quad (2.27)$$

A cation balance on the resin gives:

$$q^{i+1} = \Delta t r^i + q^i \quad (2.28)$$

A H^+ balance on the CSTR gives:

$$h_1^{i+1} = \frac{h_1^i + r^i \gamma}{1 + \beta} \quad (2.29)$$

The rate of adsorption is:

$$r^{i+1} = \frac{dq}{dt} = k_1 \left[\frac{q_i}{1 + \frac{h^{i+1}}{k_2 c^{i+1}}} - q^{i+1} \right] \quad (2.30)$$

Effect of plug-flow volume:

$$(h_p)_t = (h_1)_{t-t_r}, \quad (2.31)$$

Where

$$t_r = \frac{V_p}{v}. \quad (2.32)$$

Response time of pH electrode:

$$h_m^{i+1} = \frac{\alpha_e \Delta t h_p^{i+1}}{1 + \alpha \Delta t}. \quad (2.33)$$

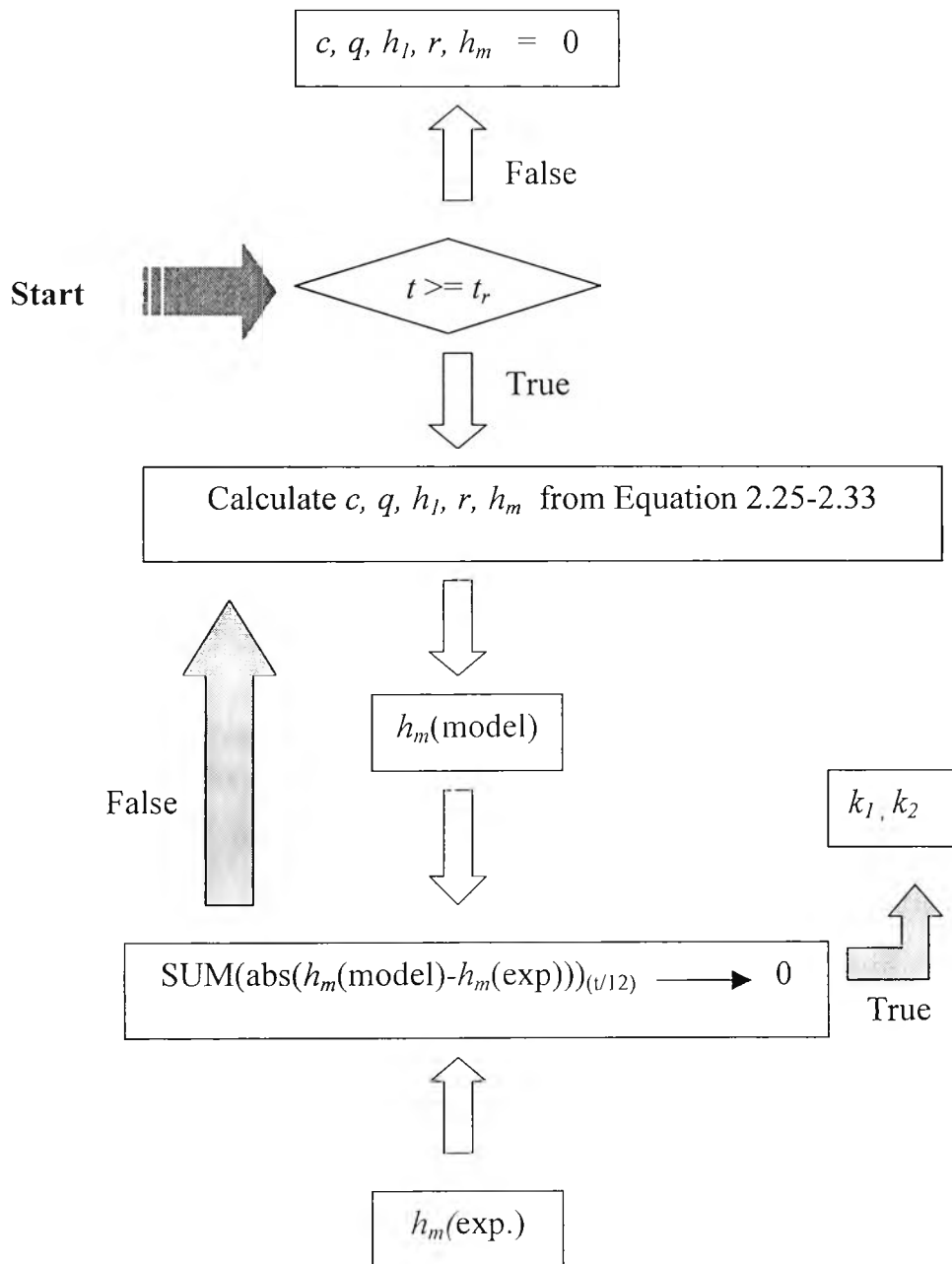


Figure 2.5 A diagram of the numerical method