



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

Presently, the increasing awareness of environmental problems has encouraged the practice of more efficient liquid waste management and the reuse of process water. One way to solve this problem is *ion exchange process*, which is a specific type of adsorption. The application of ion exchange process in the industries can be classified under four general headings:

1. *Purification and ion removal process* – the undesirable ions are removed by exchange for an acceptable ion which appears in the effluent.
2. *Recovery process* - the desired product is not usually retained on the exchanger to be subsequently displaced by another suitable ion.
3. *Metathesis* – the replacement of one ion (cation or anion) of a single electrolyte by another by means of ion substitution using an exchanger in the appropriate ionic form.
4. *Separation* – the ion exchange is achieved by allowing the exchanger to take up a quantity of mixed ions which is far less than the total exchange capacity of the exchanger. The mixture is then resolved into separate zones within the column by continuous displacement with a solution of another ion.

Furthermore, the capacity of ion exchange process has been attributed to a combination of many factors such as the operating conditions, the specific or affinity for such ions of ion exchanger, etc. For this reason, the kinetic adsorption of ion exchange process is important to concern (Harland, 1994).

2.1 Fundamentals of Ion-Exchange Resins

2.1.1 Classification

Ion exchange resins are classified into four main types: strongly acidic cation resin, strongly basic anion resin, weakly acidic cation resin, and weakly

basic anion resin, all of which are dependent on the functional groups of the resins. Examples of resins and their properties are shown in Table 2.1.

Table 2.1 Types and properties of some resins (Harland, 1994)

Resin type	Structure	Functional group	pH range	Thermal stability (°C)
Strong acid	Gel	$-\text{SO}_3^-$	0-14	120
	Macroporous	$-\text{SO}_3^-$	0-14	120
Weak acid	Gel	$-\text{COO}^-$	4-14	120
	Macroporous	$-\text{COO}^-$	4-14	120
Strong Base (type1)	Gel	$-\text{N}(\text{CH}_3)_3^+$	0-14	80(Cl)
	Macroporous		0-14	40(OH)
Strong Base (type2)	Gel	$-\text{N}(\text{CH}_3)_2$ ($\text{CH}_2\text{CH}_2\text{OH}$)	0-14	60 (Cl)
	Macroporous		0-14	40(OH)
Weak Base	Gel	$-\text{N}(\text{CH}_3)_2$	0-9	100
	Macroporous		0-9	100
	Gel	polyamine	0-9	100

The terms *strong acid* and *strong base* defined in electrolyte chemistry meaning a strong cation resin in the acid form or a strong anion resin in the base form, completely dissociate to give free hydrogen ions (H^+) and hydroxide (OH^-) ions respectively at any pH.

2.1.2 Crosslinking

Crosslinking provides the fundamental chemical bonding between adjacent polymer chains, thus, giving the resin its inherent physical strength. The degree of crosslinking also governs the extent of swelling of the dry ion exchange resin upon absorbing water. The more weakly crosslinked the resin, the greater the swelling and water uptake.

2.1.3 Mechanisms

The rate of ion exchange reaction is a complex function of several physico-chemical processes such that the overall reaction rate may be influenced by the separate or combined effects of:

1. Concentration gradients in both phases.
2. Electrical charge gradients in both phases.
3. Ionic interactions in either phase.
4. Exchanger properties (structure, functional group).
5. Chemical reactions in either phase.

Three fundamental rate determining mechanisms that control the overall rate of ion exchange reactions on organic exchangers are shown in Figure 2.1.

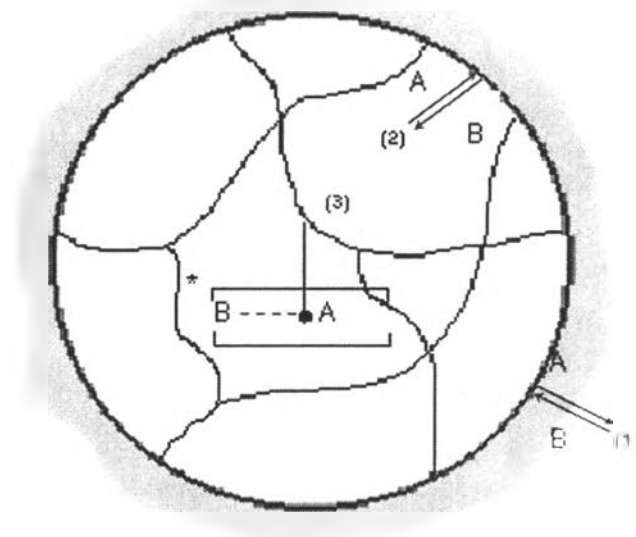


Figure 2.1 Rate determining steps in ion exchange

1. Coupled Diffusion of Counter-Ions in the “External” Solution phase

Rate in this step controlled by mass transfer in the “external” solution is interpreted as *coupled mass transfer* across the hypothetical film or *Nernst layer* surrounding the resin particles by a mechanism of diffusion called *film diffusion*.

The driving force for mass transfer is the concentration difference or the concentration gradient of counter-ions between the two boundaries of the film. If theoretical refinements are ignored for the time being, the momentary flux equation for ion A may be written in terms of Fick’s first law:

$$J_A = \frac{D_A \Delta C_A}{\delta} \quad (2.1)$$

Where

D_A = the diffusion coefficient of ion A within the resin (m^2/s)

J_A = the flux of ion A ($\text{kmol}/\text{m}^2 \cdot \text{s}$)

ΔC_A = the concentration difference of the counter-ion A (kmol/m^3)

δ = the thickness of film (m).

2. Coupled Diffusion of Counter-ions in the Resin

Mass transfer in the film and resin particles are sequential processes, and either process may be rate controlling. By a *simplified* analogy with the previous case for film diffusion, the average flux condition for transfer of ion A in the resin phase may be written:

$$\bar{J}_A = \frac{\bar{D} \Delta C_A}{r_0} \quad (2.2)$$

where

\bar{D} = the average diffusion coefficient for ions A and B within the resin (m^2/s)

ΔC_A = the concentration gradient between the interior of the resin and the resin solution interface for ion A (kmol/m^3)

r_0 = the radius of resin beads (m).

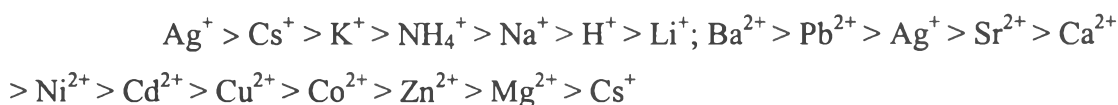
Resin phase diffusion coefficients are about one or two orders of magnitude smaller than those found in case of aqueous solutions because of the steric resistance; the hindrance effect of heterogeneity in resin structure on the ions diffused to the inside of resin.

3. Chemical Reaction Rate Control

The chemical reaction at the sites of the functional groups is shown in Figure 2.1 in terms of an imaginary transition state complex of ions A, B, and the inorganic group. Reactions between simple, freely dissociated, aqueous ions are usually very fast and therefore not rate controlling. However, some published data suggest chemical reaction rate control for the exchange of transition metal ions or complex ions is capable for strong chelation. The exchange of transition metal ions occurs by following the chelating steps: the co-ordination complex formation between the heavy metals and electron pair donating ligands, and type complex formation with iminodiacetate or phosphonate functional groups.

2.1.4 Selectivity / Affinity

Relative affinity is one of other quantities used to determine what type of cations and anions are suitable for resinous exchangers. The following sequences represent the order usually found for dilute solutions of commonly encountered ions with a strong acid cation resin ($A^+ > B^+$: the ion A has the selectivity value for a type of resin higher than that of ion B):



2.2 Theoretical Considerations of Ion-Exchange Kinetics

There are generally three basic modes in operating ion exchange process: batch, fixed-bed, and fluidized-bed operation. Each of these modes of operation and its theory is described below.

2.2.1 Batch Operation

In batch operation, all ion-exchange resin particles are contacted with the electrolyte solution. Therefore, the aqueous phase is considered as homogeneous phase. This application is the simplest mode, but its efficiency is limited by the

selectivity of the resin under equilibrium. Manantapong (1997) studied the adsorption kinetics of ion exchange process of sodium ions in a solution with hydrogen ions in the resin phase, and the process could be explained by the exchange equation (2.3).



RSO_3H and RSO_3Na are in the resin phase, and $NaCl$ and HCl are in the solution phase. From Manantapong's work, it was shown that the adsorption equilibrium was reached faster when a higher mixing rate was applied. In addition, the increasing the initial concentration resulted in an increase of the solution uptake in the resin phase. For the exchange of calcium ions in a solution with hydrogen ions in the resin phase, the process was represented by the exchange equation (2.4).



RSO_3H and RSO_3Ca are in the resin phase and $CaCl_2$, and HCl are in the solution phase.

Simple material balances for ions can be written as

$$\begin{aligned} \text{Mole of } Ca^{2+} \text{ going to resin} &= \text{Mole of } H^+ \text{ going to solution} \\ 2V_{Rq} &= V_L h \end{aligned} \quad (2.5)$$

$$\begin{aligned} \text{Mole of } Ca^{2+} \text{ before adsorption} &= \text{Mole of } Ca^{2+} \text{ after adsorption} \\ &= \text{Mole of } Ca^{2+} \text{ adsorbed onto the resin} + \text{Mole of } Ca^{2+} \text{ in the solution (not adsorbed by resin)} \end{aligned}$$

$$2V_L c_0 = 2V_R q + 2V_L c \quad (2.6)$$

where

V_R	=	volume occupied by the resin bed (ml of resin)
V_L	=	volume occupied by the liquid bed (ml of solution)
c_0	=	initial concentration of calcium chloride (meq/ml of solution)
h	=	concentration of hydrogen ion in the solution phase (meq/ml of solution)
q	=	concentration of calcium ion in the resin (meq/ml of resin)
c	=	concentration of calcium ion in the solution phase (meq/ml of solution)
eq	=	amount of atomic weight of ion divided by its ion charge named equivalent weight
eq	=	$\frac{\text{molar mass}}{\text{ion charge}} = \frac{\text{mole of ion}}{\text{ion charge}}$

In the batch part, a series of batch adsorption experiments was carried out in order to develop a relationship between the concentration of metal ions on the resin and in the solution at equilibrium (q^e and c^e), and an expression for the rate of adsorption (Warasinchai, 2000).

2.2.2 Fluidized-Bed Operation (Upflow Direction)

For upflow operation, the bed of solid particles was lifted and agitated by increasing the flow rate of fluid. It is perfect mixing and generally modeled as having no spatial variations in concentration, temperature and reaction rate. The void fraction of the bed can be calculated with any known height, H , from:

$$H = H_0 \left(\frac{1 - \varepsilon_0}{1 - \varepsilon} \right) \quad (2.7)$$

where

H	=	height of fluidized bed (cm)
H_0	=	height of compacted bed (cm)
ε_0	=	compacted bed void fraction, 0.41
ε	=	bed void fraction.

Manantapong (1997) and Tresattayawed (1999) studied the ion-exchange behavior of the fluidized bed operation of Na^+/H^+ and $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{H}^+$, respectively. They developed a model to predict the rate of metal ions adsorbed on the resin. The rate of adsorption 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	=	concentration of NaCl, CaCl_2 or MgCl_2 in the resin phase (meq/ml of resin)
q_t	=	total exchange capacity of the resin (meq/ml of resin)
c	=	concentration of NaCl, CaCl_2 or MgCl_2 in the solution phase (meq/ml of solution)
h	=	hydrogen concentration in the solution phase (meq/ml of solution).

2.2.3 Fixed-bed Operation (Downflow Direction)

For downflow operation, the solution is passed through the resin bed in the downward direction. The uppermost portion of the column constantly contacts with fresh electrolyte whereas the lower portions contact with the electrolyte, not adsorbed by the upper exchange. This procedure permits the resin bed to become fully exhausted, first at the top and then gradually downwards.

Worasinchai (2000) studied the ion-exchange behavior of the fixed-bed operation of Ca^+/H^+ , Mg^+/H^+ and $\text{Ca}^{2+}/\text{Mg}^{2+}/\text{H}^+$, respectively. In this study, the previously developed model has been simplified and used to predict the rate of metal ions adsorbed on the resin.

2.3 Development of a Kinetic Model for an Ion-Exchange Column in Fixed-Bed Mode of Operation

The mechanism of ion exchange is expressed by the governing equations, which can be solved analytically or numerically. The solution is valid if it is compatible with the experimental data. The assumptions made in the derived equations are:

1. The solid particles are uniform.
2. Equilibrium exists at the liquid-solid interface.
3. There are no gradients in the solid particle, so the concentration in the solid particle is uniform.
4. The driving force involved in the mass transfer is expressible in terms of concentrations, and chloride ions in the solution do not affect the process.
5. The influence of counter-diffusion of the exchange ion from the solid particle of the solution is neglected.

2.3.1 Modeling the Response Time of pH Electrode

The hydrogen ions at the exit of the column are measured by a pH electrode, which do not provide an instantaneous measurement, because there is some lag, called the *response time*, of the electrode to detect the pH value of the solution. The model to account for the response time can be developed by examining Figure 2.2 (Worasinchai, 2000).

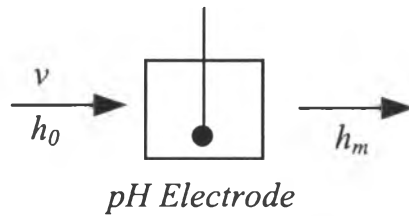


Figure 2.2 Representation of the response time experiment

The governing equation for the response time is

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

where

h_o = entering H^+ concentration (meq/ml of solution)

h_m = H^+ concentration measured by the pH electrode (meq/ml of solution)

α_e = response time constant of the pH electrode (s^{-1}).

2.3.2 Modeling Flow Characteristics of the Column (No Adsorption test) with Downflow Operation

A theory was developed to apply to the ion-exchange column performed under downflow or fixed-bed operation about the flow characteristic in the column. The mathematical model for the no adsorption test can be viewed as the non-ideal PFR, consisting of one CSTR and one ideal PFR connected in series, which is shown in Figure 2.3 (Worasinchai, 2000).

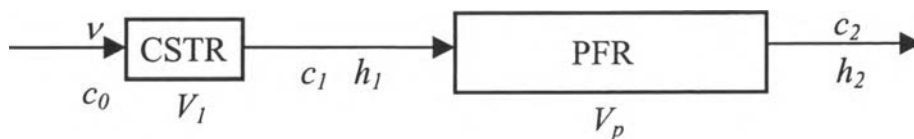


Figure 2.3 Representation of no adsorption experiment as one CSTR and one ideal PFR in series

The H⁺ balance on the CSTR was described by:

$$\frac{dh_1}{dt} = \frac{v}{V_1} (h_o - h_1) \quad (2.10)$$

where

h_o = initial hydrogen ion concentration (meq/ml of solution)

h_1 = hydrogen ion concentration at the exit of CSTR (meq/ml of solution)

v = volumetric flow rate of solution (ml/s)

V_1 = volume of CSTR (ml).

The metal ion concentration on the solid particle (q) and in the solution (c) at any time and length along the column can be determined by using the method of *characteristics for hyperbolic equations* together with a completely *implicit approach* for fixed-bed (downflow) operation.

Mathematical modeling for the no adsorption test is developed first to determine the flow characteristics of the column and then used in the adsorption kinetics part. By setting the rate of adsorption equal to zero and fitting the experimental data with the model, the volume of the CSTR can be determined.

2.3.3 Modeling Adsorption with Downflow Operation

The mathematical model developed from the no-adsorption test is used in this part with the incorporation with the rate of adsorption. The theoretical results can be compared with the experimental data after including the small volume of a CSTR into the model. Also, the non-ideal PFR, consisting of one CSTR and one ideal PFR connected in series, was applied for flow characteristic flow description, as shown in Figure 2.4 (Worasinchai, 2000).

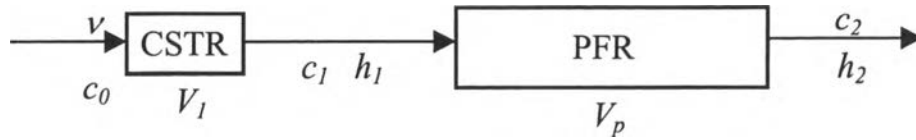


Figure 2.4 Representation of ion-exchange column as one CSTR and one ideal PFR in series

Ion (Ca^{2+}) balance on the CSTR (without reaction) can be written as:

$$\frac{dh_1}{dt} = \frac{v}{V_1} (h_0 - h_1) \quad (2.11)$$

The rate of ion uptake by solid particle can be expressed by using the batch adsorption results.

$$r = \frac{dq}{dt} = K(q^e - q) \quad (2.12)$$

where

$$q^e = \beta(c^e)^{1/n} \quad (2.13)$$

in which

- c_0 = initial substance (metals) concentration (meq/ml of solution)
- c_1 = metals concentration at the exit of CSTR (meq/ml of solution)
- c^e = metals concentration in the solution at equilibrium (meq/ml of solution)
- v = superficial velocity (ml/s)
- V_R = volume occupied by the solid particle bed in the column (ml of resin)
- V_L = volume occupied by the liquid bed in the column (ml of solution)
- q = metals concentration onto the solid particle (meq/ml of resin)

- q^e = metals concentration onto the solid particle at equilibrium
 (meq/ml of resin)
 K = rate constant (s^{-1})
 β = constant, v^*dt/V_1
 n = constant.

2.4 Method of Characteristics for Solving the Hyperbolic System of Equations for the Ion-Exchange Column

The adsorption equation for the fixed-bed operation, in the downflow direction, is very complicated and difficult to solve because the concentrations of ions in the liquid (c) and on the resin (q) depend upon both distance along the column, x , and time, t , so the *method of characteristics for hyperbolic equations* is necessary for solving this problem (Worasinchai, 2000).

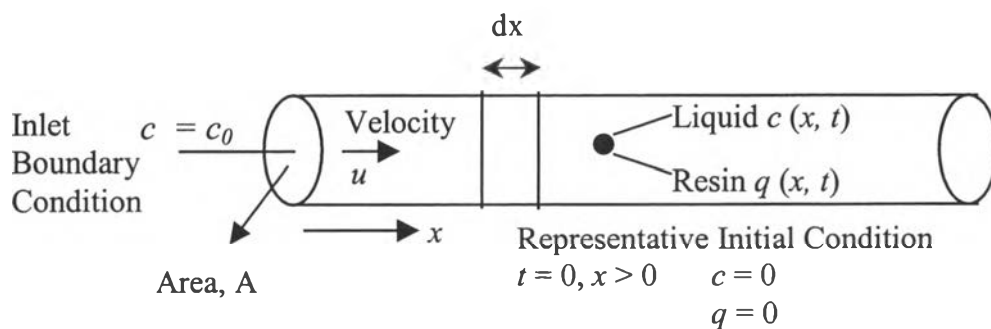


Figure 2.5 Representation of ion-exchange column in fixed-bed operation

Metal Ion Balance on Liquid

$$\text{In} - \text{Out} = \text{Accumulate}$$

$$uAc - uA\left(c + \frac{\partial c}{\partial x} dx\right) = Adx\varepsilon \frac{\partial c}{\partial t} + r(1 - \varepsilon)Adx \quad (2.14)$$

$$\varepsilon \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = -(1 - \varepsilon)r \quad (2.15)$$

Metal Ion Balance on Resin

$$\text{In} - \text{Out} = \text{Accumulate}$$

$$0 = A dx (1 - \varepsilon) \frac{\partial q}{\partial t} - r(1 - \varepsilon) A dx \quad (2.16)$$

$$\frac{\partial q}{\partial t} = r \quad (2.17)$$

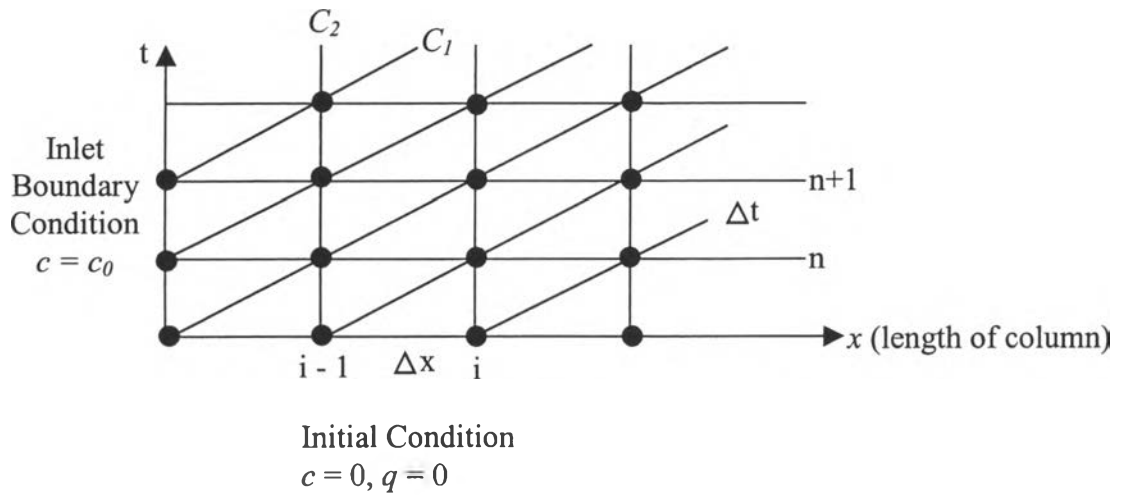


Figure 2.6 A diagram of grid points together with C_1 and C_2 direction

Characteristic directions

C_1 direction: relates to an observer travelling with the liquid

C_2 direction: relates to an observer on a fixed resin particle

$$C_1 \quad \frac{dx}{dt} = \frac{u}{\varepsilon} \qquad C_2 \quad \frac{dx}{dt} = 0$$

The partial differential equations can be written

Along C_1 :

$$\begin{aligned} \frac{dc}{dt} &= \frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} \frac{dx}{dt} \\ &= \frac{1}{\varepsilon} \left(\varepsilon \frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} \right) = \frac{-(1-\varepsilon)r}{\varepsilon} \end{aligned} \quad (2.18)$$

Along C_2 :

$$\begin{aligned} \frac{dq}{dt} &= \frac{\partial q}{\partial t} + \frac{\partial q}{\partial x} \frac{dx}{dt} \\ &= r + \left(\frac{\partial q}{\partial x} * 0 \right) = r \end{aligned} \quad (2.19)$$

The equations shown below can be used together with a completely *implicit approach* for finding the metals (Ca^{2+} , Mg^{2+}) concentration on the resin, q , and in the solution, c at any time and length along the column. Finally, the theoretical values of q and c at the exit of the column are compared with the experimental data.

$$C_1: \quad \frac{dc}{dt} = \frac{-(1-\varepsilon)r}{\varepsilon} \quad \text{along} \quad \frac{dx}{dt} = \frac{u}{\varepsilon} \quad (2.20)$$

$$C_2: \quad \frac{dq}{dt} = r \quad \text{along} \quad \frac{dx}{dt} = 0 \quad (2.21)$$

where r was given by equation (2.12).

2.4.1 Completely Implicit Approach

Fortunately, the above system of ordinary differential equations can be solved by using a *conventional finite-difference* method. Equations (2.22) and (2.23) give a completely *implicit approach* for determining the metals concentration on the resin, q , and in the solution, c at any time and length along the column. Finally, the theoretical values of q and c at the exit of the column can be compared with the experimental data. This method involves two unknowns, at time $t + dt$, which can be obtained from two equations by using the iteration method as discussed in Appendix G to find the final (real) answer. The two finite-difference equations have the values of both c and q at time $t + dt$. The equations used to predict the value of q and c at time $t + dt$ are

Along the C_1 direction, equation (2.18) becomes

$$\frac{c_{i,n+1} - c_{i-1,n}}{\Delta t} = \frac{-(1-\varepsilon)r}{\varepsilon} = \frac{-(1-\varepsilon)K}{\varepsilon} \left[\beta c_{i,n+1}^{1/n} - q_{i,n+1} \right] \quad (2.22)$$

Along the C_2 direction, equation (2.19) becomes

$$\frac{q_{i,n+1} - q_{i,n}}{\Delta t} = r = K \left[\beta c_{i,n+1}^{1/n} - q_{i,n+1} \right] \quad (2.23)$$

where

c	=	Ca^{2+} concentration in the solution (meq/ml of solution)
c_0	=	initial calcium concentration (meq/ml of solution)
$c_{i,n}$	=	Ca^{2+} concentration in the solution at time i and distance subscript n (meq/ml of solution)
$c_{i,n+1}$	=	Ca^{2+} concentration in the solution at time i and distance subscript $n+1$ (meq/ml of solution)
u	=	superficial velocity (cm/s)
x	=	length of column (cm)
q	=	Ca^{2+} concentration onto the resin (meq/ml of resin)
$q_{i,n}$	=	Ca^{2+} concentration onto the resin at time i and

		distance subscript n (meq/ml of resin)
$q_{i, n+1}$	=	Ca^{2+} concentration onto the resin at time i and distance subscript n+1 (meq/ml of resin)
dq/dt	=	adsorption rate (meq/ml of resin*s)
dc/dt	=	desorption rate (meq/ml of solution *s)
K	=	rate constant (s^{-1})
ϵ	=	void fraction of resin
β	=	constant, v^*dt/V_1
n	=	constant.

2.5 Literature Survey

Huang *et al.* (1995) simulated the ion exchange process which is classified as a fixed-bed adsorption column depending mainly on the choice of an adequate mathematical model. To develop a mathematical model that describes the adsorption process, the four following steps must be considered: mobile phase mass balance, external film diffusion, interparticle diffusion and adsorption kinetics. In general, the adsorption rate is much faster than the diffusion rate, so that equilibrium can be assumed at every local position.

Manantapong (1996) studied the behavior of exchanging of Na^+ ions on the strong-acid cation resin (Dowex50-X8), which was placed in a packed column. This column work was operated in upflow as a fluidized bed. The study of adsorption kinetics was first carried out in a batch operation, so that the concept of degree of relative volatility was suitable for describing the experimental data. The model parameters for the exchange of Na^+ and H^+ on Dowex50-X8 resin can be predicted from the theoretical derivation. In the case of upflow operation, the flow pattern agreed well with the modeling as one CSTR and one PFR in series.

Lucas *et al.* (1997) studied batch dynamics for the uptake of potassium from crude polyols on Amberlite 252, a strong acid ion exchange resin. The results were obtained over a wide range of conditions. Experimental data were analyzed using a homogeneous model with a finite solution volume. An increase of diffusion

coefficients with the resin weight used in the purification was observed. An asymptotic maximum value, approaching the value of the diffusion coefficient in bulk solution, was reached for high resin weights or low values of external concentration. The heterogeneous nature of the resin matrix and the large size of the diffusing molecule were proposed as an explanation of this behavior. The proposed purification procedure found general applicability for other polyol types, being economically and technically feasible.

Worasinchai (2000) studied the behavior of exchanging the single ion and mixed ions of Ca^{2+} and Mg^{2+} on the strong-acid cation resin (Dowex50-X8), which was placed in a packed column. This column work was operated in downflow as a fixed bed. In both batch and fixed bed operation, the Dowex50-X8 resin has a preferential adsorption of Ca^{2+} ions over the Mg^{2+} ions. The model parameters for the exchange of Ca^{2+} and H^+ on Dowex50-X8 resin behaved in a manner predictable from the theoretical derivation. In the case of downflow operation, the flow pattern was found to be adequately described by one CSTR connected with PFR in series where CSTR representing a small non-ideal segment (2.5 ml) in the ion-exchange column.