MODELING OF LACTIC ACID ADSORPTION

ISOTHERM ON AMBERLITE IRA-96

ION EXCHANGE RESIN

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A Thesis Submitted in Partial Fulfillment of the Requirements for the

Degree of Master of Engineering in Chemical Engineering

Suranaree University of Technology

Academic Year 2014

แบบจำลองของเส้นไอโซเทิร์มการดูดซับกรดแลกติกบนเรซินแลกเปลี่ยนประจุ AMBERLITE IRA-96

นางสาววรรณวิสา สดใส

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2557

MODELING OF LACTIC ACID ADSORPTION ISOTHERM ON AMBERLITE IRA-96 ION EXCHANGE RESIN

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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เปลี่ยนประจุ AMBERLITE IRA-96 (MODELING OF LACTIC ACID ADSORPTION
ISOTHERM ON AMBERLITE IRA-96 ION EXCHANGE RESIN) อาจารย์ที่ปรึกษา :
อาจารย์ ดร.ธีระสุต สุขกำเนิด, 129 หน้า.

วิทยานิพนธ์นี้ทำการศึกษาถึงเส้นไอโซเทิร์มการดูดซับของกรดแลกติกบนเรซินแลก
เปลี่ยนประจุที่อยู่ในสารละลายกรดแลกติก และสร้างแบบจำลองทางคณิตศาสตร์ของเส้นไอ
โซเทิร์มการดูดซับของกรดแลกติก เรซินแอมเบอร์ไลท์ไออาร์เอ 96 ถูกเปลี่ยนให้อยู่ในรูปของคลอ
ไรด์ไอออนและถูกใช้ในการทดลอง อุณหภูมิของการดูดซับ ถูกศึกษาที่อุณหภูมิ 25 องศาเซลเซียส
และ 40 องศาเซลเซียส ในการทดลองการดูดซับแบบระบบกะโดย ทำการศึกษาเส้นไอโซเทิร์มการ
ดูดซับที่พีเอช 2 ซึ่งมีค่าต่ำกว่าค่าการแตกตัวของประจุของกรดแลกติก และ เส้นไอโซเทิร์มการดูด
ซับที่พีเอช 4 และ 5 ซึ่งมีค่าสูงกว่าค่าการแตกตัวของประจุของกรดแลกติก ที่แต่ละอุณหภูมิของ
การดูดซับ ผลการทดลองแสดงให้เห็นว่า ปริมาณของกรดแลกติกที่ถูกดูดซับที่พีเอช 4 และ 5 มีค่า
สูงกว่า ปริมาณของกรดแลกติกที่ถูกดูดซับที่พีเอช 2 เพราะที่พีเอช 4 และพีเอช 5 มีความเข้มข้นของ
ประจุสูง อันเนื่องมาจากการแตกตัวของกรด จากผลกระทบของอุณหภูมิที่พีเอช 5 สูงกว่าที่ค่าพีเอช
อื่นๆพบว่าปริมาณของกรดแลกติกที่ถูกดูดซับลดลงเมื่ออุณหภูมิเพิ่มขึ้น ดังนั้นการดูดซับกรดแลก
ติกโดยการแลกเปลี่ยนประจุเป็นกระบวนการคายความร้อน

ดังนั้นแบบจำลองของเส้นไอโซเทิร์มการดูดซับของกรดแลกติกบนเรซิน แอมเบอร์ไลท์ไอ
ออาร์เอ 96 ได้รวมผลกระทบของการ ดูดซับของกรดที่แตกตัวเป็นประจุและการดูดซับของกรดที่ ไม่
แตกตัวเป็นประจุที่เกิดขึ้นและนำมาเปรียบเทียบกับผลของการทดลอง ในงานวิจัยนี้มีแบบจำลอง 2
ลักษณะที่ใช้เพื่อแสดงความสัมพันธ์ โดยแบบแรกเป็น physical-physical model และแบบที่สอง
คือ physical-chemical model แบบจำลอง physical-physical model ใช้แบบจำลอง การดูดซับ
ทางกายภาพเพื่อ แสดงความสัมพันธ์ทั้ง การดูดซับ ของกรด ที่แตกตัวเป็นประจุ และการ ดูดซับของ
กรดที่ไม่แตกตัวเป็นประจุที่เกิดขึ้นบนเส้นไอโซ เทิร์มการดูดซับ แบบจำลอง physical-chemical
model ใช้แบบจำลอง การดูดซับ ทางกายภาพเพื่อ แสดงความสัมพันธ์ทั้ง การดูดซับของกรด ที่ไม่
แตกตัวเป็นประจุ และใช้แบบจำลอง การดูดซับ ทางเคมีเพื่อแสดงความสัมพันธ์ของ การดูดซับของ
กรดที่แตกตัวเป็นประจุที่เกิดขึ้นบนเส้นไอโซ เทิร์มการดูดซับ สมการแลงเมียร์ , สมการฟรุนดริช
และสมการ BET ถูกนำมาใช้ในแบบจำลองทางกายภาพ สัมประสิทธิ์การเลือก และ สเตอริค แมส
เอ็คชั่น ถูกใช้ในแบบจำลองทางเคมี สำหรับการเปรียบเทียบกับผลการทดลองแบบจำลองแลงเมียร์-
แลงเมียร์และแบบจำลองฟรุนดลิช -สเตอริค แฟคเตอร์ เป็นแบบจำลองที่ดีสำหรับการแสดง

ความสัมพันธ์บนเส้นไอโซ เทิร์ม การดูดซับที่พีเอช 2 เพราะการดูดซับของกรดที่ไม่แตกตัวเป็น ประจุจึงมีอยู่มาก ค่า AAD อยู่ที่ 0.0154 ถึง 0.1063 แบบจำลองฟรุนดลิช-สเตอริค แฟคเตอร์ เป็น แบบจำลองที่ดีสำหรับการแสดงความสัมพันธ์บนเส้นไอโซ เทิร์มการดูดซับที่พีเอช 4 และพีเอช 5 ค่าAAD อยู่ที่ 0.0147 ถึง 0.3199 ผลการทดลองแสดงให้เห็นว่า ผลกระทบของอุณหภูมิที่ขึ้นอยู่ กับค่าคงที่สมดุลของการแตกตัวของกรดสามารถไม่นำมาพิจารณาได้ สำหรับการ แสดง ความสัมพันธ์ของการดูดซับกรดแลกติกบนเรซินแลกเปลี่ยนประจุ

สาขาวิชาวิศวกรรมเคมี   ลายมือชื่อนักศึกษา_____

ปีการศึกษา 2557   ลายมือชื่ออาจารย์ที่ปรึกษา_____

WANWISA SODSAI : MODELING OF LACTIC ACID ADSORPTION
ISOTHERM ON AMBERLITE IRA-96 ION EXCHANGE RESIN. THESIS
ADVISOR : TERASUT SOOKKUMNERD, Ph.D., 129 PP.

ION EXCHANGE RESIN/LACTIC ACID/ADSORPTION ISOTHERM

The study on the adsorption isotherm of lactic acid by ion exchange resin in
lactic acid solution and the model of lactic acid adsorption isotherm were investigated
in this thesis. Amberlite IRA-96 was converted into their Cl^- form and used in all
further experiment. The adsorption temperature was studied at 25 °C and 40 °C. From
the batch adsorption experiment, the adsorption isotherm was obtained at pH 2 which
was lower than pKa of lactic acid and at pH 4 and 5 which was higher than pKa of
lactic acid at the adsorption temperature. The experimental results showed that the
amount of lactic acid adsorbed at pH 4 and 5 was more than the amount of lactic acid
adsorbed at pH 2 because of the higher ion concentrations from dissociated acid at pH
4 and 5. The effect of temperature at pH 5 was higher than those at other pH; the
amount of lactic acid adsorbed decreased with increasing temperature so the
adsorption of lactic acid on this ion exchange is an exothermic process. The capacity
of adsorption isotherm observed was higher than the reported maximum capacity of
the resin.

Then, the modeling of lactic acid adsorption isotherm on Amberlite IRA-96 by
combining effect of dissociated acid adsorption and undissociated acid adsorption was
performed and correlated with the experimental results. There are two types of models
investigated in the thesis. The first model is physical-physical adsorption model and

the second type is physical-chemical adsorption model. In the physical-physical adsorption model, the physical adsorption model was used to correlate both dissociated acid adsorption and undissociated acid adsorption on the adsorption isotherm. In the physical chemical adsorption model, the physical adsorption model was used to correlate for undissociated acid adsorption and the chemical adsorption model was used to correlate for dissociated acid adsorption on the adsorption isotherm. The Langmuir equation, Freundlich equation and BET equation is used for the physical adsorption model. The selectivity coefficient and steric mass action (SMA) is used for the chemical adsorption model. From the fitting of experimental resuls, the Langmuir-Langmuir model and the Freundlich-steric factor model are good for correlation the adsorption isotherm at pH 2 because the undissociated acid adsorption is the predominant one with the average absolute deviation (AAD) is from 0.0154 to 0.1063. The Freundlich-steric factor model is good for correlation the adsorption isotherm at pH 4 and pH 5 with the average absolute deviation ranging from 0.0147 to 0.3199. The results also show that the effect of temperature dependent on dissociation constant of lactic acid can be neglected for the correlation of lactic acid adsorption on ion exchange resin.

School of <u>Chemical Engineering</u>   Student's Signature_____

Academic Year 2014   Advisor's Signature_____

ACKNOWLEDGEMENT

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SYMBOLS AND ABBREVIATIONS

L^- = Lactate ion, $CH_3CHOHCOO^-$

LH = Lactic acid, $CH_3CHOHCOOH$

K_{aAH} = Equilibrium constant for dissociated acid in the liquid

phase, $mol \cdot m^{-3}$

C_0 = Initial concentration of lactic acid in the liquid

phase, $mol \cdot m^{-3}$

C_A = Concentration of acid ion in the liquid phase, $mol \cdot m^{-3}$

C_B = Concentration of counterion of resin in the liquid

phase, $mol \cdot m^{-3}$

C_{L^-} = Concentration of lactate ion in the liquid

phase , $mol \cdot m^{-3}$

C_{H^+} = Concentration of hydrogen ion in the liquid

Phase, $mol \cdot m^{-3}$

C_{Cl^-} = Concentration of chloride ion in the liquid phase, $mol \cdot m^{-3}$

C_{LH} = Concentration of lactic acid in the liquid phase, $mol \cdot m^{-3}$

C_{OH^-} = Concentration of hydroxide ion in the liquid phase, $mol \cdot m^{-3}$

SYMBOLS AND ABBREVIATIONS (Continued)

C_{A^-} = Concentration of dissociated acid in the liquid

phase, $\text{mol} \cdot \text{m}^{-3}$

C_{AH} = Concentration of undissociated acid in the liquid

phase, $\text{mol} \cdot \text{m}^{-3}$

C_T = Concentration of lactic acid in the liquid phase from

measurement at equilibrium, $\text{mol} \cdot \text{m}^{-3}$

C_{eq} = Concentration of adsorbate in the liquid

phase at equilibrium, $\text{mol} \cdot \text{m}^{-3}$

C_i = Concentration of adsorbate ion in the liquid phase

at equilibrium, $\text{mol} \cdot \text{m}^{-3}$

C_j = Concentration of counter ion of resin in the liquid phase

at equilibrium, $\text{mol} \cdot \text{m}^{-3}$

H_2O = Water

OH^- = Hydroxide ion

H^+ = Hydrogen ion

K_w = Equilibrium constant for dissociated water in the liquid

phase, $\text{mol} \cdot \text{m}^{-3}$

K_{AB} = Equilibrium constant for ion exchange resin, $\text{mol} \cdot \text{m}^{-3}$

K_{LCl} = Equilibrium constant for ion exchange resin, $\text{mol} \cdot \text{m}^{-3}$

SYMBOLS AND ABBREVIATIONS (Continued)

ν_A and ν_B	=	Characteristic charge of acid ion and counterion of resin
$\nu+$ and $\nu-$	=	Characteristic charge of dissociated electrolyte
ν_{Cl^-}	=	Characteristic charge of chloride ion ($\nu_{Cl^-}=1$)
ν_{L^-}	=	Characteristic charge of lactate ion ($\nu_{L^-}=1$)
ν_i	=	Characteristic charge of adsorbate ion
ν_j	=	Characteristic charge of counterion of resin
I	=	ionic strength of the solution
Q	=	Active sites of the resin
Q_T	=	Total concentration of lactic acid in the solid phase, $mol \cdot kgdryre\sin^{-1}$
Q_A	=	Concentration of ion(dissociated acid) in the solid phase, $mol \cdot kgdryre\sin^{-1}$
Q_B	=	Concentration of counterion in the solid phase, $mol \cdot kgdryre\sin^{-1}$
Q_{AH}	=	Concentration of molecule (undissociated acid) in the solid phase, $mol \cdot kgdryre\sin^{-1}$
Q_{L^-}	=	Concentration of lactate ion in the solid phase , $mol \cdot kgdryre\sin^{-1}$

SYMBOLS AND ABBREVIATIONS (Continued)

Q_{Cl^-} = Concentration of chloride ion in the solid

phase , $mol \cdot kgdryre\sin^{-1}$

Q_{LH} = Concentration of lactic acid in the solid

phase , $mol \cdot kgdryre\sin^{-1}$

Q_{eq} = Concentration of adsorbate in the solid phase

at equilibrium , $mol \cdot kgdryre\sin^{-1}$

Q_i = Concentration of adsorbate ion in the solid phase

at equilibrium , $mol \cdot kgdryre\sin^{-1}$

Q_j = Concentration of counterion of resin in the solid phase

at equilibrium , $mol \cdot kgdryre\sin^{-1}$

Q_{max}^{IE} = Maximum concentration of ion (dissociated acid) in the solid

phase , $mol \cdot kgdryre\sin^{-1}$

Q_{max}^{LH} = Maximum concentration of molecule (undissociated acid) in

the solid phase , $mol \cdot kgdryre\sin^{-1}$

Q_{max}^{AH} = Maximum concentration of molecule (undissociated acid) in

the solid phase , $mol \cdot kgdryre\sin^{-1}$

Q_{max} = Maximum concentration of adsorption in the solid

phase, $mol \cdot kgdryre\sin^{-1}$

SYMBOLS AND ABBREVIATIONS (Continued)

W	=	Weight of dry resin, kg dry resin
V	=	Volumn of solution, m^3
K	=	Parameter constant in Langmuir equation
K_{IE}	=	Parameter constant in Langmuir equation for ion exchange adsorption, $m^3 \cdot mol^{-1}$
K_{LH}	=	Parameter constant in Langmuir equation for molecular adsorption, $m^3 \cdot mol^{-1}$
K_{AH}	=	Parameter constant in Langmuir equation for molecular adsorption, $m^3 \cdot mol^{-1}$
k, n	=	Parameter constant in Freundlich equation
i	=	Ion of solution for ion exchange resin
j	=	Counterion of resin for ion exchange resin
S_j^i	=	Selectivity coefficient for ion exchange of counterion of resin and acid ion.
S_B^A	=	Selectivity coefficient for ion exchange of acid ion and counterion of resin
$S_{Cl^-}^{L^-}$	=	Selectivity coefficient for ion exchange of lactate and chloride ion
σ_i	=	Steric factor
σ_A	=	Steric factor of acid ion

SYMBOLS AND ABBREVIATIONS (Continued)

σ_{L^-}	=	Steric factor of lactate ion
$q_{uniquac}$	=	External surface area of uniquac model
K_S	=	Equilibrium constant for first layer
K_L	=	Equilibrium constant for upper layer
C	=	Parameter constant in BET equation
C_S	=	Solubility of the solute
HCl	=	Hydrochloric acid
H_3O^+	=	Hydronium ion
Cl^-	=	Chloride ion
AH	=	Undissociated acid
A^-	=	Dissociated acid
ΔH_{AH}^o	=	Enthalpy change of dissociation acid
μ_i	=	Chemical potential of the species i
a_i	=	Activity of the species i
f_i	=	Fugacity of the species i
γ_i	=	Activity coefficient of the species i
X_i	=	Molar concentration of the species i
Z_i	=	Charge on the species i
α_i	=	Effective diameter of the hydrated ion i

SYMBOLS AND ABBREVIATIONS (Continued)

K_a = Dissociated acid equilibrium constant of lactic acid

T = Temperature

ΔC_p = Heat of capacity change of lactic acid

A′andB′ = The value of the thermodynamic functions for the dissociation

of lactic acid

K_{ad} = Equilibrium constant for adsorption

ΔH_{ads}° = Heat of adsorption

ΔG^0 = Gibbs free energy change

ΔH^0 = Enthalpy change

ΔS^0 = Entropy change

CHAPTER I

INTRODUCTION

1.1   Significance of the Problem

Presently, the world is facing problem with global warming. One cause of this problem is the non-biodegradable plastic. Therefore, the thesis focuses on the purification of lactic acid which would assist in development of biodegradable plastics. Lactic acid, which is the raw material for one of the biodegradable plastics, polylactic acid (PLA). Lactic acid has many advantages; for example, lactic acid is used in the food industry, the production of pharmaceutics and cosmetics. The development of new purification process which is not expensive and more efficient than conventional methods is necessary. There are several methods for separation of lactic acid, such as the solvent extraction method and the electrodialysis method. For the solvent extraction method, the solvent used is quite toxic. For the electrodialysis method, cells adhering to membranes was leading to low flux and decreasing efficiency (Nomura Y, Iwahara M, Hongo M, 1987).   One of the prominent purification methods of lactic acid is the adsorption on ion exchange resin. In this thesis, the adsorption isotherm of lactic acid on ion exchange resin and its modeling by chemical engineering theory is investigated. The study on adsorption isotherm of lactic acid by ion exchange resin and the development of a model for the description of ion exchange equilibrium and adsorption in lactic acid solution is studied.

1.2   Research Objectives

The overall objective of this research is to study the adsorption isotherm of lactic acid on ion exchange resin and to develop a model for the description of ion exchange equilibrium in lactic acid solution. The specific objective of this research are:

1.2.1. To study the effect of pH on the adsorption isotherm of lactic acid on ion exchange resin.

1.2.2. To study the effect of temperature on the adsorption isotherm of lactic acid on ion exchange resin.

1.2.3. To study the parameter of a model for the description of ion exchange equilibrium in lactic acid solution.

1.3   Scope and Limitations

In this thesis, adsorption isotherm of lactic acid on ion exchange resin and its modeling by the chemical engineering theory is investigated. The study on the adsorption isotherm of lactic acid on ion exchange resin and the development of a model for the description of ion exchange equilibrium in lactic acid solution is investigated. Amberlite IRA-96 anion exchange resin is applied to the recovery of lactic acid from lactic acid solution. The adsorption isotherm of lactic acid at pH 2, 4 and 5 and 25 °C and 40 °C is obtained. The model is used to correlate the adsorption isotherm of lactic acid. The objective function for a model was fitted by non-linear regression with lsqnonlin which is a built in function in Matlab.

1.4   Outcomes of the Research

1.4.1   Equilibrium data for ion exchange resin between Amberlite IRA-96 anion exchange resin and lactic acid obtained from lactic acid solution. This equilibrium data is represented as adsorption isotherms.

1.4.2   Models for description of complex composition in equilibrium of ion exchange in solution. In the models, the effect of pH and temperature of the solution are considered. The correlation of the models is expressed in adsorption isotherms.
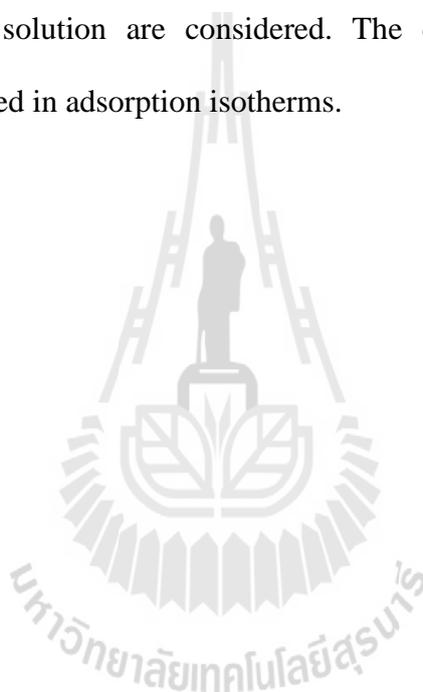
CHAPTER II

LITERATURE REVIEW AND THEORY

Lactic acid (LA) based polymers, is a good alternative for substituting conventional plastic produced from petroleum oil because of low emission of carbon dioxide that contributes to global warming, have been widely used. Lactic acid can be manufactured by chemical synthesis or carbohydrate fermentation. The recovery of lactic acid is rather difficult due to its chemical behavior due to its strong affinity to water and low volatility. Therefore, the lactic acid purification is the most cost-intensive and energy-intensive processing step. The improvement of separation process is of interest in order to reduce the costs of lactic acid purification. There are various separation techniques for lactic acid separation from fermentation broth. Lactic acid can be purified either by precipitation of metal lactates followed by a neutralizing reaction with sulfuric acid or by esterification with alcohol, distillation and hydrolysis of the formed ester, or by electro-dialysis. Besides, the ion exchange technique is widely used in bio-separation and several different ion exchangers. Thus, the ion exchange technique for lactic acid separation is interested. The use of ion exchange technique depends on various factors such as pH, temperature and sorbent characteristics such as microporosity and chemical properties. The literature review and theory are presented in this chapter.

2.1   Type of Acid

The type of acid can be divided into two types:

2.1.1 Strong Acids

Strong acid have ionize completely or nearly completely in aqueous solution. In dilute solutions, strong acids donate their acidic proton(s) to water to make hydronium ions. Reaction involving the strong acids can be written with a regular forward arrow which represents the irreversible reaction.   For example, the reaction of gaseous hydrogen chloride with water shows that hydronium ion is produced in aqueous solution

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{2.1}$$
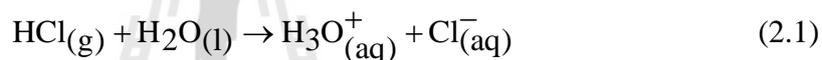
2.1.2 Weak Acids

Weak acids have ionize slightly in dilute solution. Reaction involving the weak acids is written with a forward/backward arrow to indicate that the ionization reaction is reversible. For example, the reaction of acetic acid with water shows that the acetic acid molecules remain unionized.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^-_{(aq)} \tag{2.2}$$

Table 2.1 Some Important Acids (Burns, 1999)

Strong Acids		Weak Acids	
Name	Formula	Name	Formula
Hydrochloric acid	HCl	Phosphoric acid	H_3PO_4
Hydrobromic acid	HBr	Carbonic acid	H_2CO_3
Hydroiodic acid	HI	Acetic acid	CH_3COOH
Sulfuric acid	H_2SO_4	Citric acid	$C_3H_5(COOH)_3$
Nitric acid	HNO_3	Lactic acid	$CH_3CHOHCOOH$
Perchloric acid	$HClO_4$	Boric acid	H_3BO_3

2.2 Dissociation of Acid and Chemical Thermodynamics of Acid Dissociation

The dissociation of acid can be divided into two types:

2.2.1 Strong Acid

A strong acid is an acid that completely dissociates into ions. The dissociation of strong acid can be written

$$HCl \rightarrow H^+ + Cl^- \tag{2.3}$$

2.2.2 Weak Acid

A weak acid is only partially dissociates into its constituent ions. The type of weak acid can be divided into two classes:

2.2.2.1 Polyprotic Acid Dissociation

For polyprotic acid, there is more than one ionizable H^+ atom per molecule. The dissociation of polyprotic acid can be written as

$$H_2S \leftrightarrow H^+ + HS^- \tag{2.4}$$

$$HS^- \leftrightarrow H^+ + S^{2-} \tag{2.5}$$
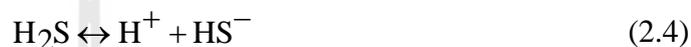
2.2.2.2 Monoprotic Acid Dissociation

In monoprotic acid, there is only one ionizable H^+ atom per molecule. The dissociation of monoprotic acid can be written as

For the acid dissociation:

$$AH \leftrightarrow A^- + H^+ \tag{2.6}$$

$$K_{aAH}(T) = \frac{C_{H^+}C_{A^-}}{C_{AH}} \tag{2.7}$$

Although H^+ is usually referred as hydrogen ions in aqueous solution, hydronium ions (H_3O^+) is actually the ion appearing in the true solution.

Where AH is the undissociated acid, A^- is the dissociated acid, H^+ is the hydrogen ion, C_{H^+} is the concentration of hydrogen ion in the liquid

phase ($\mathrm{mol}/\mathrm{m}^3$), C_{AH} is the concentration of undissociated acid in the liquid phase ($\mathrm{mol}/\mathrm{m}^3$), C_{A^-} is the concentration of dissociated acid in the liquid phase ($\mathrm{mol}/\mathrm{m}^3$) and K_{aAH} is the equilibrium constant for dissociated acid in the liquid phase ($\mathrm{mol}/\mathrm{m}^3$).

The thermodynamic equilibrium constant (K_{aAH}) can be defined by

$$K_{aAH}(T) = \frac{C_{H^+} C_{A^-}}{C_{AH}} \bullet \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{AH}} \tag{2.8}$$

Where γ_i is activity coefficient of the species i. For an ideal solution, the activity coefficient can be assumed equal to 1. The reference state used here is 1 m concentration in this thesis (John et al., 1999).

$$K_{aAH}(T) = \frac{C_{H^+} C_{A^-}}{C_{AH}} \tag{2.9}$$

The acid-dissociation equilibrium constant (K_{aAH}) can be defined by

$$pKa_{AH}(T) = -\log_{10} K_{aAH}(T) \tag{2.10}$$

The effect of temperature on the equilibrium constant can be explained by chemical thermodynamic of the Van't Hoff equation (Smith et al., 2005). The Van't Hoff equation can be followed

$$\left(\frac{d\ln K_{aAH}}{dT}\right) = \frac{\Delta H_{AH}^{\circ}}{RT^2} \tag{2.11}$$

If enthalpy change of dissociated acid (ΔH_{AH}°) is negative, the equilibrium constant decreases as the temperature increases. Conversely, this enthalpy change is positive, the equilibrium constant increases as the temperature increases.

2.3   Electrolyte Solution

An electrolyte is a solution that is able to conduct electricity. To meet this criteria, a solution must contain ions. Commonly, electrolyte solutions contain acids, bases, or salts as their ionic solute. Electrolyte solutions are normally formed when a salt is placed into a solvent such as water. The individual components dissociate due to the thermodynamic interactions between the solvent and solute molecules in a process called solvation. In the electrolyte solution, the solute dissociates into cations and anions(Prausnitz et al., 1999). A useful measure is the equivalent conductance and the conductance per mole of charge (Sandler, 2006).

2.3.1 Type of Electrolyte Solution

The electrolyte solution can be divided into two types:

2.3.1.1 Strong Electrolyte

A strong electrolyte is a strong acid, a strong base and salt (some species). A strong electrolyte is an acid, base or salt that completely dissociates into ions and its equivalent conductance is high but decreases only slowly with increasing concentration (Sandler, 2006).

2.3.1.2 Weak Electrolyte

A weak electrolyte is a weak acid and a weak base. A weak electrolyte is an acid or base that only partially dissociates into its constituent ions and its equivalent conductance is less than that of strong electrolyte at any concentration but increases rapidly as a concentration decreases (Sandler, 2006).

Consider electrolyte $M_{\nu+}X_{\nu-}$ that dissociated electrolyte according to

$$M_{\nu+}X_{\nu-} \leftrightarrow \nu^+ M^{Z+} + \nu^- M^{Z-} \tag{2.12}$$
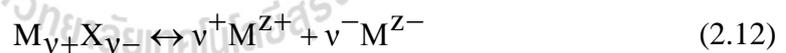
The dissociation (or ionization) equilibrium constant is

$$K(T) = \frac{a_+^{\nu+} a_-^{\nu-}}{a_{MX}} = \frac{X_+^{\nu+} X_-^{\nu-}}{X_{MX}} \bullet \frac{\gamma_+^{\nu+} \gamma_-^{\nu-}}{\gamma_{MX}} \tag{2.13}$$

Where X_i is molar concentration of the species I, $\nu+$ and $\nu-$ is the characteristic charge of dissociated electrolyte γ_i is activity coefficient of the species i. For an ideal solution, the activity coefficient can be assumed equal to 1. The

reference state used here is 1 m concentration in this thesis (John et al., 1999). The activity coefficient makes more accurate equilibrium calculation.

2.3.2 Chemical Thermodynamic of Electrolyte Solution

Excess function are thermodynamic properties of solution that are in excess of those of an ideal (or ideal dilute) solution at the same conditions of temperature, pressure, and composition.

For the dissolved solute, the chemical potential is written

$$\mu_i = \mu_i^* + RT \ln a_i \tag{2.14}$$

Where μ_i is chemical potential of the species i, μ_i^* is chemical potential of the species i, it is independent of composition but depends on temperature, pressure, and the nature of solute and sovent and a_i is activity of the species i.

The activity of component i at some temperature, pressure, and composition is defined as the ratio of the fugacity of i at these conditions to the fugacity of i in the standard state, that is a state at the same temperature as that of the mixture and at some specified condition of pressure and composition

$$a_i(T, P, x) = \frac{f_i(T, P, x)}{f_i(T, P^0, x^0)} \tag{2.15}$$

The activity used to describe the effective concentration in an equilibrium at any given ionic strength. The activity for the species i defined as

$$a_i = \gamma_i x_i \tag{2.16}$$

Where a_i is the activity of the species i, x_i is its molar concentration, and γ_i is a dimensionless quantity called the activity coefficient. The activity coefficient and thus the activity of i depend on ionic strength.

The Debye-Huckel equation used the calculation of activity coefficients of ions from their charge and their average size. The Debye-Huckel equation defined as

$$-\log \gamma_i = \frac{0.51 Z_i^2 \sqrt{I}}{1 + 3.3 \alpha_i \sqrt{I}} \tag{2.17}$$

Where γ_i is activity coefficient of the species i, Z_i is charge on the species i, I is ionic strength of the solution and α_i is effective diameter of the hydrated ion i in nanometer (10^{-9} m) (Douglas et al., 1996).

2.4   Lactic Acid

The IUPAC name of lactic acid is 2-hydroxypropionic acid (LA). Some people call milk acid and it is the most widely occurring carboxylic acid in nature. In 1780, lactic acid was first isolated by a Swedish chemist, Carl Wilhelm Scheele. In 1881, lactic acid was first produced commercially by Charles E. Avery at Littleton, Massachusetts. L-lactic acid or (s)-lactic acid and D-lactic acid or (R)-lactic acid are forms of lactic acid (Ren Jie, 2010).

Now, lactic acid used in food, chemical, pharmaceutical and biodegradable polymers. Therefore, a lot of studies on the fermentation production of lactic acid have been done. Some substrates such as whey, soybean, milk, corn, potato, and wood have been investigated for the fermentation of lactic acid (Tong, 2004).

Table 2.2 Identification and physical-chemical properties (Ren Jie, 2010)

Identification	Physical & Chemical properties
CAS number	D/L:[50-21-5]
	L:[79-33-4]
	D:[10326-41-7]
Einecs No.	200-018-0
H.S. Code	2918.11
Formula	$CH_3CH(OH)COOH$
Melting point	L : 53°C
	D : 53°C
	D / L : 16.8°C
Boiling point	122°C(12mmHg)
Specific gravity	1.2 g/mL
Molar mass	90.08 g/mol

Table 2.3 Thermodynamic characteristics of lactic acid (Ren Jie, 2010)

Items	Characterictics
Dissociation constant (K_a)	0.000137 (at 25°C)
Heat of dissociation (ΔH)	-63 cal/mol (at 25°C)
Free energy of dissociation (ΔF)	5000 cal/mol
Heat of solution (ΔH)	1868 cal/mol (for crystalline L(+)lactic acid at 25°C)
Heat of dilution (ΔH)	-1000 cal/mol (for dilution with a large volume of water)
Heat of fusion (ΔH)	2710 cal/mol (for recemic lactic acid)
	4030 cal/mol (for L(+) lactic acid)
Entropy of solution (ΔS)	6.2 cal/mol/°C
Entropy of dilution (ΔS)	-3.6 cal/mol/°C
Entropy of fusion (ΔS)	9.4 cal/mol/°C (for recemic lactic acid)
	12.2 cal/mol/°C (for L(+) lactic acid)
Heat of combustion (ΔH_{c0})	-321220 cal/mol (for crystalline L(+)lactic acid at 25°C)
	-325600 cal/mol (for liquid racemic lactic acid at 25°C)
Heat of formation (ΔH_{f0})	-165890 cal/mol (for crystalline L(+)lactic acid at 25°C)
	-163000 cal/mol (for liquid lactic acid)
	-164020 cal/mol (for lactic acid in dilution solution)
	-164080 cal/mol (for dissociate and diluted lactic acid)
Heat of capacity (C_p)	0.338 cal/g/°C (for crystalline L(+)lactic acid at 25°C)
	0.559 cal/g/°C (for liquid lactic acid at 25°C)
Absolute entropy (S_0)	34.0 cal/mol/°C (for crystalline L(+)lactic acid at 25°C)
	45.9 cal/mol/°C (for liquid racemic lactic acid at 25°C)
Entropy of formation (ΔS_{f0})	-137.2 cal/mol/°C (for crystalline L(+) lactic acid at 25°C)
	-125.3 cal/mol/°C (for liquid lactic acid at 25°C)
Free energy of formation (ΔF_{f0})	-124980 (for crystalline L(+) lactic acid at 25°C)
	-126500 cal/mol (for liquid racemic lactic acid at 25°C)

2.4.1 Dissociation of lactic acid

Lactic acid is a monoprotic acid in weak acid and weak electrolyte. As a result, a lactic acid dissociation (or ionization) as follows:

$$LH \leftrightarrow L^- + H^+ \tag{2.18}$$

$$K_a(T) = \frac{C_{H^+} C_{L^-}}{C_{LH}} \tag{2.19}$$

For the measurement of lactic acid, both forms of lactic acid were detected. Mathematically, it can be expressed as:

$$C_T = C_{LH} + C_{L^-} \tag{2.20}$$

Where LH is the lactic acid ($CH_3CHOHCOOH$), L^- is the lactate ion ($CH_3CHOHCOO^-$), H^+ is the hydrogen ion, C_{H^+} is the concentration of hydrogen ion in the liquid phase (mol/m^3), C_{LH} is the concentration of lactic acid in the liquid phase (mol/m^3), C_{L^-} is the concentration of lactate ion in the liquid phase (mol/m^3), C_T is the concentration of lactic acid in the liquid phase from measurement at equilibrium (mol/m^3) and $K_a(T)$ is the Disociated acid equilibrium constant of lactic acid, The pKa of lactic acid is 3.86 at 25°C (Cao et al., 2002).

The equilibrium Constant Parameter can be expanded by eq 2.20 propose by Everett and Wynne-Jones (1939). The value of the thermodynamic

functions for the dissociation of lactic acids are $A' = -2578.0$ and $B' = 54.7716$ on the thermodynamics of acid-base equilibrium paper.

The thermodynamic equation follows by eq. (2.21).

$$T \log K_a = A' + \frac{\Delta C_p}{R} T \log T + B'T \qquad (2.21)$$

2.4.2 Analysis of Lactic Acid by HPLC

Lactic acid is a high boiling point then the HPLC is used for analysis lactic acid. HPLC is developed from the theory of column chromatography. The difference of adsorption is the reason of column chromatography. The technology for producing and using packing with particle diameters was developed for effect on plate heights from diffusion very slowly (Elena Katz, 1998).

A flow rate of liquid sample and mobile phase stream, which are desired by pumps, carries into the column. The temperature in column influence into the interactions taking place between sample components and sorbent. The detector translates the changes in the chemical composition of the column effluent during the chromatographic run into an electrical signal. This signal can give the required information about the sample composition (Elena Katz, 1998).

```
┌──────────────┐
│   Liquid     │
│  Reservoir   │
└──────────────┘
       │
       ▼
┌──────────────┐
│  Gradient    │
│   Device     │
└──────────────┘
       │
       ▼
┌──────────┐      ┌──────────┐
│   Pump   │ ───▶ │  Sample  │
└──────────┘      │ Injector │
                  └──────────┘
                       │
                       ▼
                  ┌──────────┐      ┌──────────┐
                  │  Column  │ ◀─── │   Temp   │
                  └──────────┘      │ Control  │
                       │            └──────────┘
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                  ┌──────────┐
                  │ Detector │
                  └──────────┘
                       │
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                  ┌──────────┐
                  │ Recorder │
                  └──────────┘
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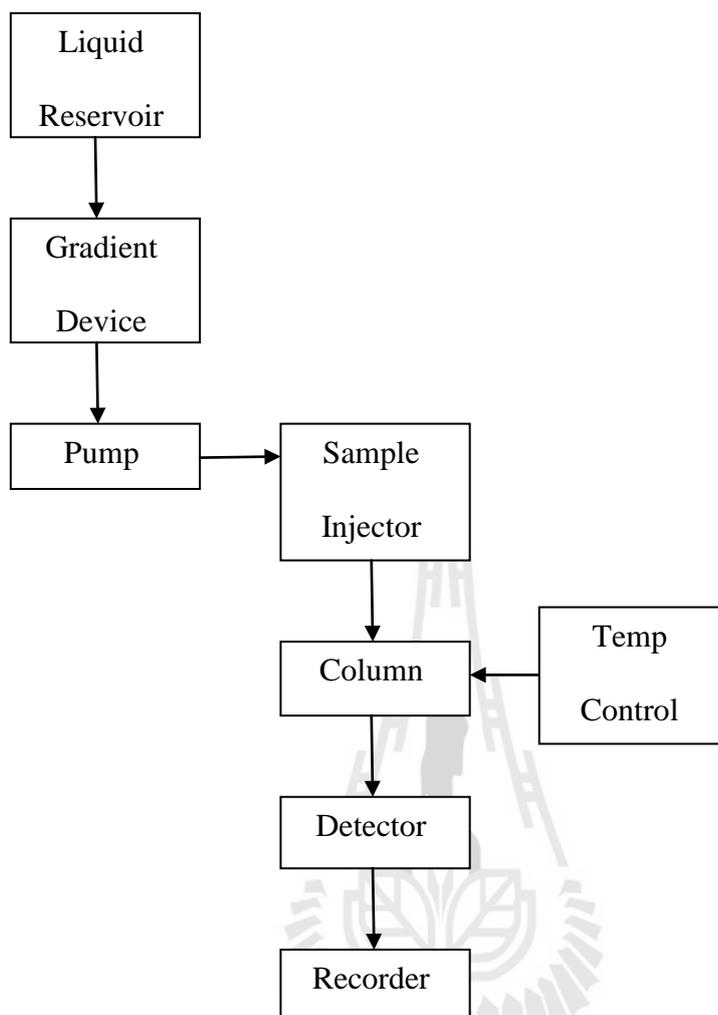
Figure 2.1 A schematic of HPLC equipment (Satinder Ahuja, 2003).

Lactic acid is analyzed by HPLC. Cao et al. (2002) analyzed by high performance liquid chromatography equipped with Aminex HPX-87H column. The column temperature was maintained at 45°C and the pressure of the column was 69 atm. UV detector is set at 210 nm. The mobile phase was 0.008 M sulfuric acid and the flow rate was 0.5 ml/min. Tong et al. (2004) analyzed by high performance liquid chromatography equipped with Aminex HPX-87H column. The column temperature

was maintained at 45°C. UV detector is set at 210 nm. The mobile phase was 0.008

M sulfuric acid and the flow rate was 0.6 ml/min.

2.5   Purification of Lactic Acid

Ther are several methods for separation of lactic acid. The purification process

of lactic acid in industial process as show in Figure 2.2.
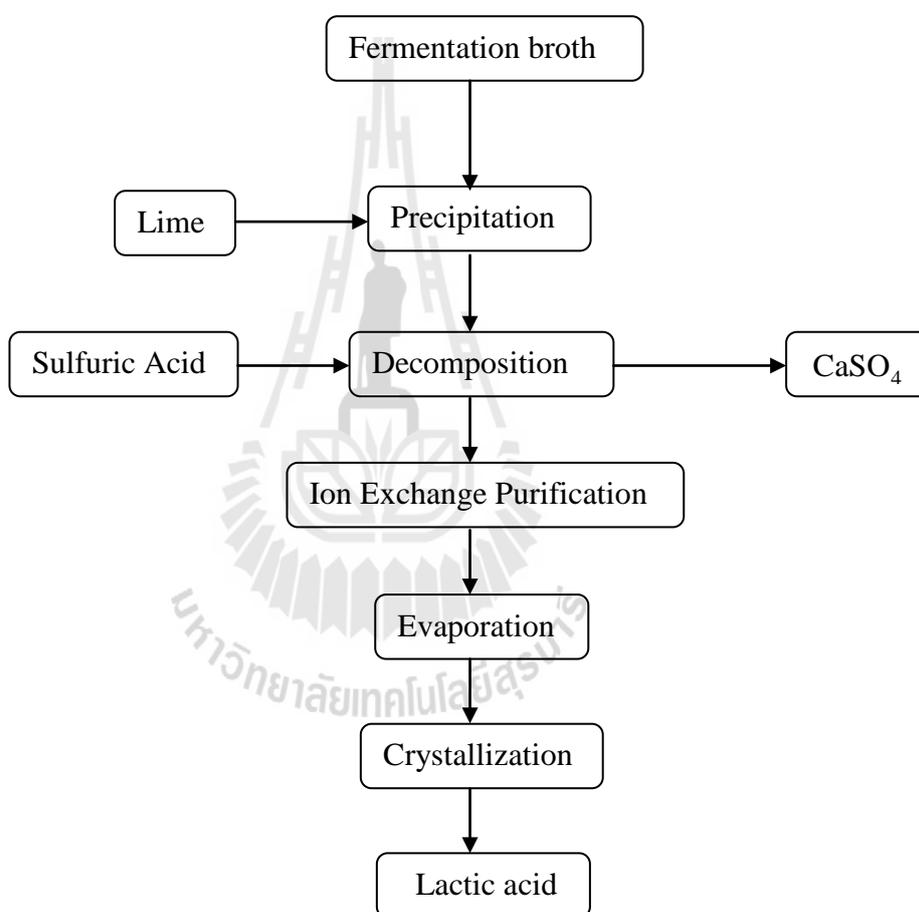
Figure 2.2 The purification process of lactic acid in industial process (Dow

Water & Process Solution).

2.5.1 Electrodialysis

In electrodialysis, electrically charged membranes are used to separate components of an ionic solution under the driving force of an electric current.

Lactic acid is separated by electrodialysis with bipolar membrane (EDBM) propose by Huang et al. (2006). The EDBM can substitute for conventional separation to produce organic acids. Hirata et al. (2005), Li et al. (2004) and Min-tian et al. (2005) analyzed the direct applications of EDBM to recovery lactic acid without pretreating fermentation broth. Wang et al. (2013) analyzed there certainly will intensify membrane fouling rapidly compared with processing the fermentation broth after pretreating. Then the pretreatment fermentation broth before feeding to EDBM equipment is a necessary. For the electrodialysis method, cells adhered membranes during the process was leading to decreased efficiency in the separation process (Nomura et al., 1987).

2.5.2 Liquid-Liquid Extraction

Extraction is a separation process in which a solute is distributed between two immiscible solvents. The distribution coefficient is related to relative solubilities of the solute in the two solvents. A sample is subjected to the extraction process by shaking it with the two solvents and then allowing them to separate (Satinder Ahuja, 2003). For the solvent extraction method, the lactic acid product has toxicity which comes from used solvent.

2.5.3 Adsorption on Ion Exchange Resin

Ion-exchange equilibria can lead to separation of cation or anions. The chromatography methods have been found very useful for this purpose. In ion-exchange chromatography, exchange equilibrium of the ions plays a major role.

2.5.3.1 Type of Resin

Resins can be classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

a) Cation exchangers

- Strong Acid Cation Resins

The resins are highly ionized in both the acid ($R-SO_3H$) and salt ($R-SO_3Na$) form of the sulfonic acid group. The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na^+ and H^+ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution.

- Weak Acid Cation Rasins

Weak acid resins are weakly dissociated. The ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO_3H) used in strong acid resins. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH. A typical weak acid resin has limited capacity below a pH of 6.0.

b) Anion exchangers

• Strong Base Anion Resins

These resins are used in the hydroxide (OH) form for water deionization. The strong base resins are highly ionized and can be used over the entire pH range. After exhaustion, the resin is converted back to the hydroxide form (regenerated) by contact with a sodium hydroxide (NaOH).

• Weak Base Anion Resins

Weak base resins are weakly dissociated. The degree of dissociation of a weak base resin is strongly influenced by the solution pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0. After exhaustion, the resin is converted back to neutralize the absorbed acid with weakly basic reagents such as ammonia (NH_3) or sodium carbonate.

2.5.3.2 Ion Exchange at Equilibrium

The ion exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counter ion which is different from that in the ion exchanger.

Counter ion exchange occurs, and the ion B in the ion exchange partially replaced by A

$$\nu_A Q_B + \nu_B C_A \leftrightarrow \nu_A C_B + \nu_B Q_A \tag{2.22}$$

Where ν_B and ν_A are the characteristic charge of counterion of resin and acid ion, respectively. C_B is the concentration of counterion of resin in the

liquid phase (mol/m^3). C_A is the concentration of acid ion in the liquid phase (mol/m^3). Q_B is the concentration of counterion of resin in the solid phase (mol/ kg dry resin). Q_A is the concentration of acid ion in the solid phase (mol/ kg dry resin).

In this reversible equilibrium, both the ion exchanger and the solution contain both competing counter ion species, counterion of resin and acid ion.

$$K_{AB} = \left(\frac{Q_A}{C_A}\right)^{\nu_B} \left(\frac{C_B}{Q_B}\right)^{\nu_A} \tag{2.23}$$

Where K_{AB} is the equilibrium constant for ion exchange resin (mol/m^3).

2.5.3.3 The Effect of pH of Solution

The resin have limited the range of pH for use. The selectivity depends on the total concentration in the aqueous phase, ion valence, size and shape. The high selectivity number has a more tightly bound of ion. The solution pH can also have a profound effect on selectivity.

2.5.3.4 The Effect of Temperature of Solution

The temperature is changed the degree of ionization will be change too. This has a much greater effect on systems that are only slightly ionized. However, a higher temperature can increase the solubility for ion in solution (Frank DeSilva and Bill Koebel, 2000).

2.5.3.5 Equilibrium Studies

Moldes et al. (2003) Analyzed the capacity of weak base and strong base anion exchange resin. The weak base resins presented higher capacities than the strong base ones in all the range of concentrations explored. The matrix of Amberlite IRA 96 is a macroreticular and the matrix of Amberlite IRA 97 is a gel. Both resin converted into their Cl^- form. In Cl^- form, the weak base resins presented the highest capacities (Moldes et al., 2003). Amberlite IRA 97 is gel in the water with the pore size is uncertain. This thesis an anionic exchange resin Amberlite IRA 96 (Cl^- form) will be used for the lactate separation process. The characteristic of the resin show in Table 2.4 and the capacity of the resin is shown in Figure 2.2.

Table 2.4 Characteristic of the resin (Moldes et al., 2003)

Resin	Manu-facturer	Matrix	Active group	Form	Basicity	Capacity (meq/g)	pH range
Amberlite IRA 900	Rohm and Haas	Macrore-ticular	Quaternary ammonium	Cl^-	Strong	4.2	0-14
Amberlite IRA 400	Rohm and Haas	Gel	Quaternary ammonium	Cl^-	Strong	3.8	0-14
Amberlite IRA 96	Rohm and Haas	Macrore-ticular	Polyamine	Free base	Weak	4.7	0-7
Amberlite IRA 67	Rohm and Haas	Gel	Polyamine	Free base	Weak	5.6	0-7
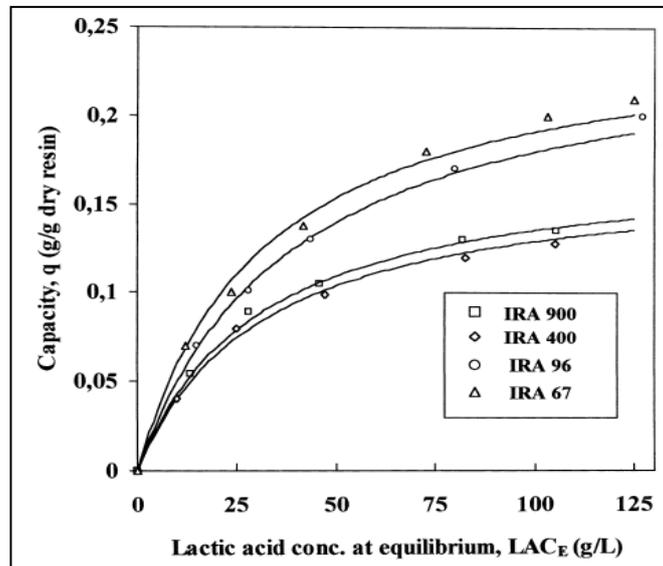
Figure 2.3 Ion exchange isotherms at temperature 25 (initial pH adjusted to 4.85 by
alkali addition) (Moldes et al., 2003).

Cao et al. (2002) analyzed the adsorption isotherm of lactic acid
at pH 2 and pH 5 by IRA-400.The equilibrium point of the dissociation of lactic acid
shifted by the change of concentrations ion. Isotherms of IRA-400 ion exchange resin
adsorbing lactic acid in Figure 2.3 the maximum adsorption capacity at pH 5 was
much higher than that at pH 2.
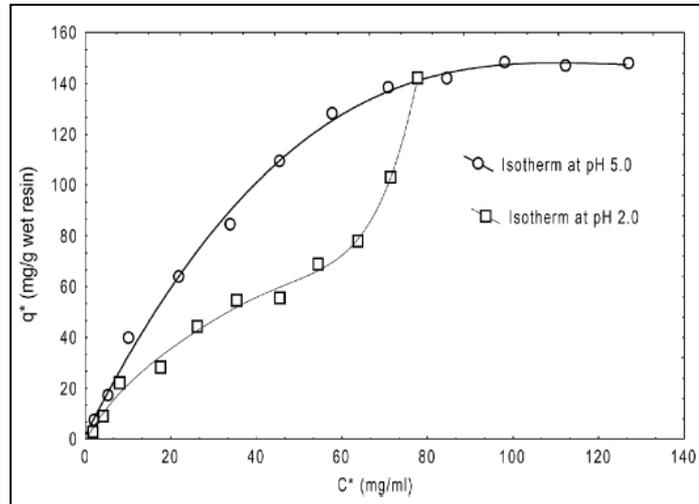
Figure 2.4 Isotherms of IRA-400 ion exchange resin adsorbing lactic acid (Cao et al., 2002).

The experiments were performed at two different temperatures at room temperature (25°C) and at the temperature at which the fermentation broth is recovered and ultrafiltration steps, i.e, 40°C. In Figure 2.4, the selectivity at 40°C was slightly higher than the selectivity of the anion exchanger at 25°C (Isabel et al., 2006)**.**
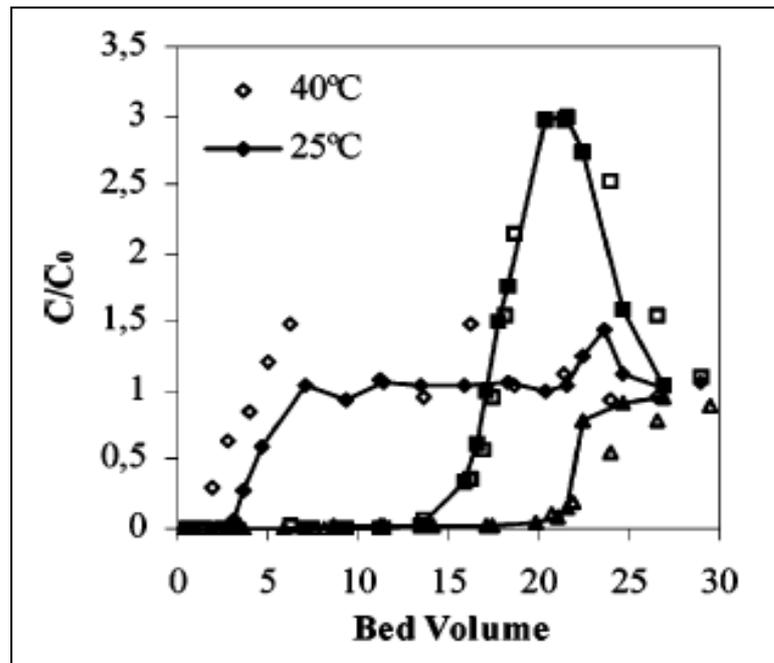
Figure 2.5 Breakthrough curves for the Lewatit S3428 column at different operating temperatures, flow rate 14 BV/h, and feed solution pH 1.2 (◊, lactate; □, phosphate; Δ, chloride).

2.5.3.6 Typical Properties of Amberlite IRA 96 resin

A.B. Moldes et al. (2003) analyzed the Amberlite IRA 96 resin presented high capacities. Amberlite IRA 96 resin was used in this thesis. Amberlite IRA 96 resin is a macroreticular weak base anion exchange resin. Typical properties of amberlite IRA 96 resin show in Table 2.5.

Table 2.5 Typical Properties of Amberlite IRA 96 resin

Physical form	Tan opaque spherical beads
Matrix	Styrene divinylbenzene copolymer
Functional group	Tertiary amine: at least 85%
Ionic form as shipped	Free base (FB)
Total exchange capacity	= 1.25 eq/L (FB form)
Moisture holding capacity	57 to 63% (FB form)
Shipping weight	670 g/L
Specific gravity	1.040 to 1.060 (FB form)
Particle size uniformity coefficient	= 1.80
Harmonic mean size	0.550 to 0.750 mm
< 0.300 mm	1.0% max
Reversible swelling	FB $\rightarrow$ Cl$^-$ = 15%

2.6 Adsorption

Adsorption is the adhesion of atoms, ions or molecules of a gas, liquid or dissolved solid to a surface. The surface is called an adsorbent. The atoms, ions or molecules are called the adsorbate. The ion exchange separation occurs in solid-liquid interface. The adsorption process are divided by the interactions between the solid and the molecular in the fluid phase as physical adsorption and chemical adsorption. The adsorption analysis is generally classified as equilibrium and kinetics. The kinetics adsorption is described per time. The adsorption at equilibrium is usually described through the adsorption isotherm (Duong D.Do., 1998). The models describing adsorption isotherms are Freundlich equation, Langmuir equation, BET equation, etc. The separation of lactic acid by ion exchange can be described by adsorption process.

2.6.1 Type of Adsorption Isotherm

Isotherms for adsorption analysis is generally classified into four main classes, according to the nature of slop of the initial portion of the curve, and thereafter into sub-groups. The main classes are S Curves, L Curves, H Curves and C Curves(Giles et al., 1960).
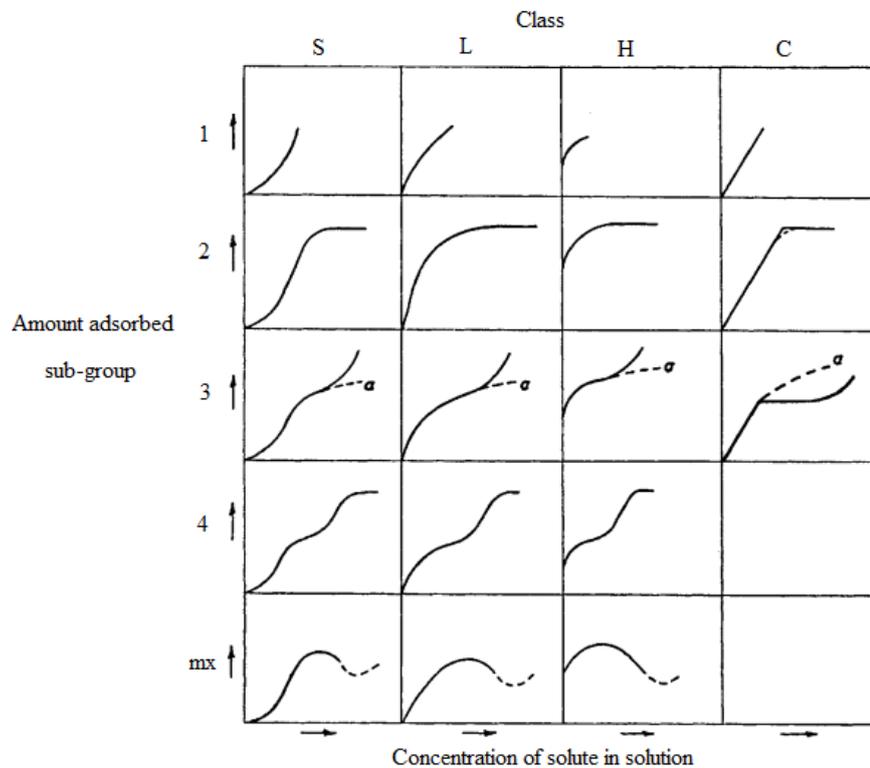
Figure 2.6 System of isotherm classification (Giles et al., 1960).

2.6.2 Thermodynamics of adsorption

The thermodynamic principles are most conveniently used in analyzing the equilibeium state. The thermodynamic relationships relevant to the study of adsorption as background to the discussion (Chi Tien, 1994).

According to the thermodynamic law, the Gibbs free energy change $\left(\Delta G^0\right)$ of adsorption is calculated as follows:

$$\Delta G^0 = -RT \ln K_{ad} \tag{2.24}$$

Where K_{ad} is the equilibrium constant for adsorption and T is absolute temperature. In study of adsorption, Eq. 2.23 has been employed for determination of ΔG^0. The relationship of ΔG^0 to enthalpy change (ΔH^0) and entropy change (ΔS^0) of adsorption can be expressed as

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \tag{2.25}$$

Substituting Eq. 2.24 into Eq. 2.23 gives

$$\ln K_{ad} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{2.26}$$

The term heat of adsorption is the heat released upon the adsorption of an adsorbate and adsorbent. The amount of heat released may be significant to the performance of the adsorption process. There are two type of heat of adsorption, the first ones is isosteric heat of adsorption and the second ones is adiabatic heat of adsorption. The heat of adsorption is calculated from the following Van't Hoff equation (Duong D.Do., 1998):

$$\left(\frac{d \ln K_{ad}}{dT}\right) = \frac{\Delta H_{ads}^{\circ}}{RT^2} \tag{2.27}$$

Where ΔH_{ads}° is the heat of adsorption. Basically the heat of physical

adsorption is of the same order of magnitude as the heat of condensation, i.e., 2.1

kJ/mol^{-1} (Sag and Kutsal, 2000), while the heats of chemical adsorption generally

fall into a range of 80 to 200 kJ/mol^{-1} (Hayward and Trapnell, 1964; Smith, 1981).

The positive value of ΔH_{ads}° implies that adsorption would be and endothermic

process, while a negative ΔH_{ads}° indicates an exothermic adsorption process (Liu and

Wang, 2009).

2.6.3 Modeling of Adsorption Isotherm

The theories, as shown later, can be extended to describe the

simultaneous adsorption of two or more components (John et al., 1998).

2.6.2.1 Langmuir Equation

$$\frac{Q_{eq}}{Q_{max}} = \frac{KC_{eq}}{1 + KC_{eq}} \tag{2.28}$$

Where Q_{eq} is the concentration of adsorbate in the solid phase

at equilibrium (mol/kg dry resin), Q_{max} is the maximum concentration of adsorption

in the solid phase (mol/kg dry resin), C_{eq} is the concentration of adsorbate in the

liquid phase at equilibrium (mol/m^3) and K is the parameter constant in Langmuir

equation.

Langmuir equation is based on four assumptions:

• The adsorption takes plase on a homogeneous surface. The

surface in homogeneous.

- Adsorbed molecules do not interact.

- All adsorption occurs through the same mechanism.

- At the maximum adsorption, only a monolayer is formed.

2.6.2.2 Freundlich Equation

Freundlich adsorption isotherm is popularly used in the description of multilayer adsorption in gas and liquid phase systems provided the range of fluid phase concentration is not too wide.

$$Q_{eq} = kC_{eq}^{1/n} \qquad (2.29)$$

Where Q_{eq} is the concentration of adsorbate in the solid phase at equilibrium (mol/kg dry resin), C_{eq} is the concentration of adsorbate in the liquid phase at equilibrium (mol/m^3) and k, n are the parameter constant in Freundlich equation.

Freundlich equation is based on assumptions (Duong D.Do., 1998):

- Freundlich equation is very popularly used in the description of adsorption of organics from aqueous streams on to activated carbon.

- Freundlich equation is also applicable in gas phase systems having heterogeneous surfaces.

- The isotherm equation does not have a proper Henry law behavior at low concentration, and it does not have a finite limit when the concentration is sufficiently high.

2.6.2.3 BET Equation

$$Q_{eq} = Q_{max} \left[\frac{CC_{eq}}{(C_s - C_{eq})\left(1 + (C-1)\left(\frac{C_{eq}}{C_s}\right)\right)} \right] \quad (2.30)$$

Where Q_{eq} is the concentration of adsorbate in the solid phase at equilibrium (mol/kg dry resin), Q_{max} is the maximum concentration of adsorption in the solid phase (mol/kg dry resin), C_{eq} is the concentration of adsorbate in the liquid phase at equilibrium (mol/m^3), C_s the solubility of the solute and C is the parameter constant in BET equation.

BET equation is based on three assumptions:

- Multilayer adsorption is possible. As a result, the forces of adsorption are much higher for the first layer and constant for the subsequent layers.
- There is again no lateral interaction as in the case of Langmuir.
- The surface in homogeneous.

In this thesis, a study of the equilibrium model on adsorption isotherm of lactic acid on ion exchange resin will be presented.

2.7 Modeling of Adsorption Isotherm of Charged Ion on Ion Exchange Resin

2.7.1 Detailed Adsorption Isotherm

The dissociated acid and undissociated acid are adsorbed on the resin independently.

$$Q_T = Q_{AH} + Q_A \qquad (2.31)$$

Where Q_{AH} is the concentration of undissociated acid in the solid phase (mol/ kg dry resin). Q_A is the concentration of dissociated acid in the solid phase (mol/ kg dry resin). Q_T is the total concentration of acid in the solid phase (mol/ kg dry resin)

2.7.2 Modeling Adsorption Isotherm of Charged Ion

Table 2.6 The litilature review of modeling adsorption isotherm

2.7.2.1 Physical Physical Adsorption Model					
Model No.	Name of model	adsorption of undissociated acid	adsorption of dissociated acid	Assumption	Reference
1	Langmuir-Langmuir model	Langmuir equation	Langmuir equation	-Langmuir assumption	Phenol, (Carmona et al., 2006)
					Phenol, (Caetano et al., 2009)
2	BET-Freudlich model	BET equation	Freudlich equation	-BET assumption and Freudlich assumption - The equilibrium constant of dissociated acid constant	Phenol, (Juang et al., 2010)
3	BET-Langmuir model	BET equation	Langmuir equation	-BET assumption and Langmuir assumption - The equilibrium constant of dissociated acid constant	Phenol, (Juang et al., 2011)

Table 2.6 The litilature review of modeling adsorption isotherm (Continued)

2.7.2.2 Physical Chemical Adsorption Model					
Mode l No.	Name of model	adsorption of undissociated acid	adsorption of dissociated acid	Assumption	Reference
4	Freudlich-Selectivity model	Freudlich equation	Selectivity coefficient	-Freudlich assumption - The equilibrium constant of dissociated acid constant	Carboxylic acids, (Kanazawa, 1999) Carboxylic acids and monosulfonic acids, (Kanazawa, 2004)
5	steric factor model	-	steric mass action	-The surface is heterogeneous surface - The equilibrium constant of dissociated acid constant	Proteins, (Stuart, 2004)

2.7.2.1 Physical Physical Adsorption Model

Langmuir-Langmuir Model, the adsorption of acid on the adsorbent take place due to the dissociated acid adsorption can be expressed by Langmuir equation. The uptake of phenol into the adsorbent takes place due to undissociated acid adsorption can be correlated by Langmuir equation. Langmuir Langmuir Model is proposed by Carmona et al. (2006) and Caetano et al. (2009). The assumption of equilibrium constant of water is constant for Carmona et al. (2006) but the assumption of equilibrium constant of water is depending on temperature for Caetano et al. (2009).

The adsorption of acid on the resin beads take place due to the dissociated acid adsorption can be expressed by Langmuir equation.

$$Q_A = \frac{Q_{max}^{IE} K_{IE} C_A}{1 + K_{IE} C_A} \qquad (2.32)$$

Where Q_{max}^{IE} is the maximum concentration of ion(dissociated acid) in the solid phase (mol/ kg dry resin), K_{IE} is the parameter constant in the Langmuir equation for ion exchange adsorption $\left(m^3 / mol\right)$.

The uptake of acid into the resin beads takes place due to undissociated acid adsorption can be correlated by Langmuir equation.

$$Q_{AH} = \frac{Q_{max}^{AH} K_{AH} C_{AH}}{1 + K_{AH} C_{AH}} \qquad (2.33)$$

Where Q_{max}^{AH} is the maximum concentration of molecule(undissociated acid) in the solid phase (mol/ kg dry resin), K_{AH} is the parameter constant in the Langmuir equation for molecular adsorption $\left(m^3/mol\right)$. C_{AH} is the concentration of undissociated acid in the liquid phase (mol/ kg dry resin).

The model equation are proposed by Carmona et al. (2006) is obtained

$$Q_T = \frac{Q_{max}^{AH} K_{AH} C_T}{1 + \left(K_{aAH}(T)/K_w(T)\right) \cdot 10^{-(14-pH)} + K_{AH} C_T} + \frac{Q_{max}^{IE} K_{IE} \left(K_{aAH}(T)/K_w(T)\right) \cdot C_T \cdot 10^{-(14-pH)}}{1 + \left(K_{aAH}(T)/K_w(T)\right) \cdot 10^{-(14-pH)} \cdot \left(1 + K_{IE} C_T\right)}$$

(2.34)

The model equation are proposed by Caetano et al. (2009) is obtained

$$Q_T = \frac{Q_{max}^{AH} K_{AH} C_T}{1 + \left(K_{aAH}(T)\right)^{-1} \cdot 10^{-(pH)} + K_{AH} C_T} + \frac{Q_{max}^{IE} K_{IE} \cdot C_T \cdot \left(K_{aAH}(T)\right)^{-1} \cdot 10^{-(pH)}}{1 + \left(K_{aAH}(T)\right)^{-1} \cdot 10^{-(pH)} \cdot \left(1 + K_{IE} C_T\right)}$$

(2.35)

The model describes the removal of acid by the resin in the term of three unknown parameters (K_{IE}, K_{AH}, Q_{max}^{AH}) related to dissociated acid and undissociated acid adsorption. The maximum of percent average deviation of

Carmona et al., (2006) was 11.8. The maximum of percent average deviation of Caetano et al., (2009) was 18.

BET-Freudlich Model, the adsorption of acid on the adsorbent take place due to dissociated acid adsorption can be expressed by Freudlich equation. The uptake of acid into the adsorbent takes place due to undissociated acid adsorption can be correlated by BET equation. The BET Freudlich model is proposed by Kanazawa et al. (2001).

The uptake of acid into the resin beads takes place due to undissociated acid adsorption can be correlated by the BET equation.

$$Q_{AH} = Q_{max}^{AH} \left[\frac{C_s C C_{AH}}{(C_s - C_{AH})(C_s + (C-1)C_{AH})} \right] \tag{2.36}$$

Where C is the parameter constant in BET equation.

The adsorption of acid on the resin beads take place due to the dissociated acid adsorption can be expressed by Freundlich equation.

$$Q_A = kC_A^{1/n} \tag{2.37}$$

Where k and n are the parameter constant in Freundlich equation.

The model equation is obtained

$$Q_T = kC_A^{1/n} + \left[\frac{Q_{max}^{AH} C_s C C_{AH}}{(C_s - C_{AH})(C_s + (C-1)(C_{AH}))} \right] \tag{2.38}$$

The model describes the removal of lactic acid by the resin in the term of four unknown parameters (k, n, C, Q_{max}^{AH}) related to dissociated acid and undissociated acid adsorption.

BET-Langmuir Model, the adsorption of acid on the adsorbent take place due to dissociation acid adsorption can be expressed by BET equation. The uptake of acid into the adsorbent takes place due to undissociated acid adsorption can be correlated by Langmuir equation. The BET Langmuir model is proposed by Kanazawa et al. (2001).

The model equation is obtained

$$Q_T = \frac{Q_{max}^{IE}K_{IE}C_A}{1+K_{IE}C_A} + \left[\frac{Q_{max}^{AH}C_sCC_{AH}}{(C_s-C_{AH})(C_s+(C-1)(C_{AH}))}\right] \quad (2.39)$$

The model describes the removal of lactic acid by the resin in the term of three unknown parameters (K_{IE}, C, Q_{max}^{AH}) related to dissociated acid adsorption and undissociated acid adsorption.

2.7.2.2 Physical Chemical Adsorption Model

Freudlich-Selectivity Model, The adsorption of carboxylic acids on the adsorbent take place due to the dissociated acid adsorption can be expressed by selectivity coefficient. The uptake of carboxylic acids into the adsorbent takes place due to undissociated acid adsorption can be correlated by Freundlich equation. Freudlich Selectivity model are proposed Kanazawa et al. (1999) and Kanazawa et al. (2004). Kanazawa et al. (1999), the ion exchange equation, including a selectivity coefficient to chloride ion for each combination between carboxylate ions and anion-

exchange resins, could be used in wide ranges of concentration and pH. The ion-exchange equilibria using 16 anion-exchange resins and 9 organic acids exchange on monocarboxylic acids. Kanazawa et al. (2004), The ion-exchange equilibria using ion-exchange resins exchange on monocarboxylic acids and monosulfonic acids.

The uptake of acid into the resin beads takes place due to undissociated acid adsorption can be correlated by the Freundlich equation.

$$Q_{AH} = kC_{AH}^{1/n} \tag{2.40}$$

Where k and n are the parameter constant in Freundlich equation.

The adsorption of acid on the resin beads take place due to dissociated acid adsorption can be expressed by selectivity coefficient.

$$S_B^A = \left(\frac{Q_A}{C_A}\right)^{\nu_B} \left(\frac{C_B}{Q_B}\right)^{\nu_A} \tag{2.41}$$

Where S_B^A is the selectivity coefficient for ion exchange of acid ion and counterion of resin, ν_B is the characteristic charge of counterion of resin, and ν_A is the characteristic charge of acid ion.

The model equation is obtained

$$Q_T = k\left[\frac{C_T C_{H^+}}{K_{aAH} + C_{H^+}}\right]^{1/n}$$

$$+ \left[\frac{S_B^A}{2(W/V)}\right]\left[\frac{K_{aAH}C_T}{K_{aAH} + C_{H^+}}\right]\left[-1 + \sqrt{1 + \frac{4(W/V)Q_{max}^{ion}}{\left(S_B^A \cdot \left[\frac{K_{aAH}C_T}{K_{aAH} + C_{H^+}}\right]\right)}}\right] \tag{2.42}$$

The model describes the removal of lactic acid by the resin in the term of three unknown parameters (k, n, S_B^A) related to dissociated acid and undissociated acid adsorption. The correlation coefficient (R^2) values of Kanazawa et al., (2001) were from 0.80 to 1.0 except for butyrate ion. The minimum of square of error of Kanazawa et al., (2004) was 0.78.

Steric Factor Model, the steric mass action (SMA) is used for the equilibrium adsorption, a three parameter model of ion exchange is used predicts the multicomponent adsorption of protein under dilute and concentrated conditions. Steric Factor model is proposed by Stuart, (2004).

The adsorption of lactic acid on the resin beads take place due to dissociated acid adsorption can be expressed by the steric mass action (SMA).

Electroneutrality requires that:

$$Q_{max}^{IE} = Q_B + (v_A + \sigma_A)Q_A \tag{2.43}$$

Where Q_{max}^{IE} is the maximum concentration of ion in the solid phase (mol/ kg dry resin), σ_A is the steric factor of acid ion.

The model equation is obtained

$$K_{AB} = \left(\frac{Q_A}{C_A}\right)^{v_B}\left(\frac{C_B}{Q_{max}^{IE} - (v_A + \sigma_A)Q_A}\right)^{v_A} \tag{2.44}$$

The model describes the removal of lactic acid by the resin in the term of four unknown parameters (K_{AB}, σ_A, Q_{max}^{IE}) related to dissociated acid adsorption.

2.8   Nonlinear Regression

The regression models is used for experiment data from a completely randomized design. Whether, the data are observational or experimental, it is essential that the conditions of the regression model be appropriate for the data at hand for the model to be applicable.

To obtain the normal equations for a nonlinear regression model:

$$Y_i = f(X_i, \gamma) + \varepsilon_i \tag{2.45}$$

The method of least squares considers the sum of the n squared deviations.

$$E = \sum_{i=1}^{n} (Y_i - f(X_i, \gamma))^2 \tag{2.46}$$

The nonlinear regression models are usually difficult to solve (Michael et al., 2005).

The numerical methods can use to the least squares estimates. The Gauss-Newton method is used for regression parameters. Normally, the Gauss-Newton method works effectively in many nonlinear regression applications.

In this thesis, the nonlinear regression was used to fit the curve by method of lsqnonlin in MATLAB.

CHAPTER III

EXPERIMENTS AND METHODS

In this thesis, adsorption isotherm of lactic acid on ion exchange resin and its dissociation of acid and chemical thermodynamic of acid dissociation theory was investigated. The study on the adsorption isotherm of lactic acid by ion exchange resin in lactic acid solution was performed. Amberlite IRA-96 anion exchange resin was applied for the recovery of lactic acid from lactic acid solution. The adsorption isotherm for the separation of lactic acid at pH 2, 4 and 5 at temperature 25 °C and 40 °C was obtained. The adsorption models were used to correlate the adsorption isotherm of lactic acid.

3.1   Experiments

3.1.1 Resin and Chemical

An anionic exchange resin Amberlite IRA 96 (free base form) was used for the lactate separation process. The resin was commercially provided with free base on its surface. The free base form with a matrix of styrene divinylbenzene copolymer has a specific gravity of 1.040 to 1.060 (FB form) and a bulk density of 670 g/l having a harmonic mean size 0.550 to 0.750 mm. Before utilization, the resins were washed and converted into their Cl⁻ form. Resins in Cl⁻ form were obtained by washing the resins sequentially with 1 M HCl solution, distilled water, 1M NaOH

solution, distilled water, 1 M HCl solution and distilled water (until pH of DI). The resin in Cl⁻ forms were air dried and assayed for moisture by oven drying at 105 °C for 24 h (Moldes et al., 2003).

The lactic acid solution was prepared from a lactic acid commercial solution. Initial concentration of lactic acid is 78 g/l. Then, pH value was adjusted to 2 (or pH 4 and pH 5) by adding 1 M NaOH and the solution was stored at 4 °C. Before utilization, lactic acid concentration was determined by using high performance liquid chromatography (HPLC).

3.1.2 Equilibrium Experiments

A series of samples with different amounts of Amberlite IRA-96 in Cl⁻ form were prepared in flasks. Then, initial concentration of solution 78 g/l was added into each flask with a solution of 10 ml at pH 2 (or pH 4 and pH 5). Thereafter, all the flasks were shaken for 48 h in a shaking water bath at 200 rpm at 25 °C (or 40 °C). Residual lactic acid concentrations in the solution were measured by HPLC.
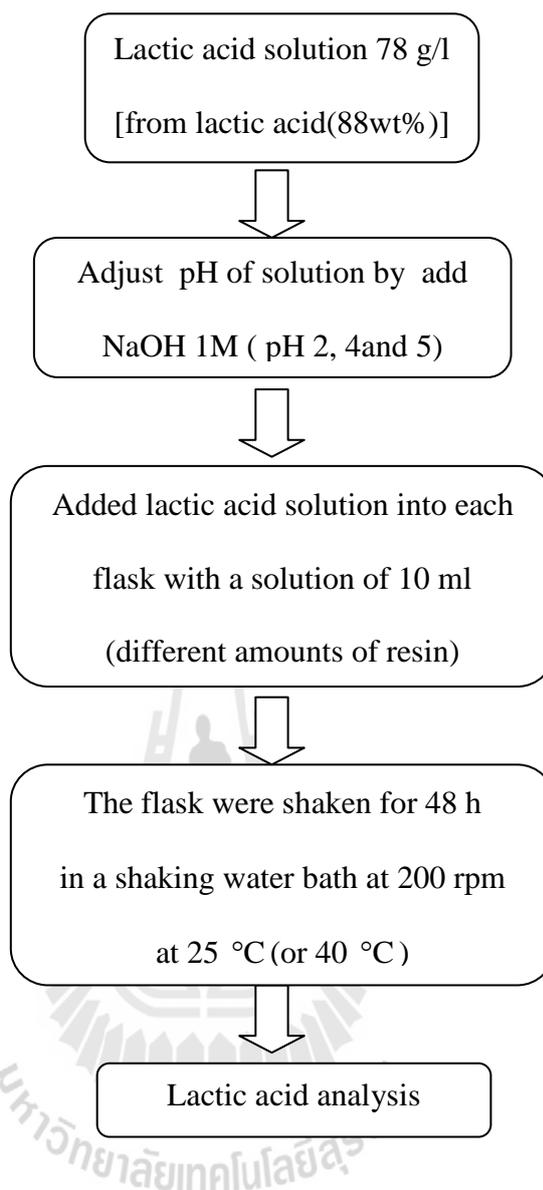
Figure 3.1 Process scheme for ion exchange of lactic acid solution.

3.1.3 HPLC Analysis of Lactic Acid

Lactic acid concentration was determined by high performance liquid chromatography equipped with a Hypersil BDS-C18 column. The column temperature was maintained at 60 °C. A UV detector was set at 210 nm. The mobile phase was 0.008 M sulfuric acid and the flow rate of mobile phase was 0.6 ml/min.

3.1.4 Analysis of Equilibrium Studies

A series of samples with different amounts of Amberlite IRA-96, in Cl⁻ form, were weighed in flasks. Then, the solution 78 g lactic acid/l was added into each flask with a solution of 10 ml at pH 2, 4 and 5. Thereafter, all flasks were shaken for 48 h in a shaking water bath at 200 rpm at 25 °C (or 40 °C). The residual lactic acid concentrations in the solution were measured by HPLC. The adsorption isotherm was presented in this thesis.

The resin-phase concentration was determined from the mass balance according to Eq. (3.1)

$$Q_T = \frac{V}{W}(C_0 - C_T) \qquad (3.1)$$

Where Q_T is the total concentration of lactic acid in the solid phase (mol/ kg dry resin), C_0 is the initial concentration of lactic acid in the liquid phase (mol/m^3), C_T is the concentration of lactic acid in the liquid phase from measurement at equilibrium (mol/m^3), V and W are the volume of the solution (m^3) and weight of dry resin (kg).

3.1.5. Detailed Adsorption Isotherm

The dissociated acid and undissociated acid are adsorbed on the resin and the total of both adsorptions is expressed in the adsorption isotherm.

3.2   Modeling

The model that used in the study two types, the first ones is dissociated acid and the second ones is undissociated acid, as show in Table 3.1. Furthermore, the equilibrium constant of dissociated acid was considered in this thesis. The lactic acid adsorption isotherm is estimated from the experimental data. The model is solved by lsqnonlin which is a built in function in the MATLAB program.
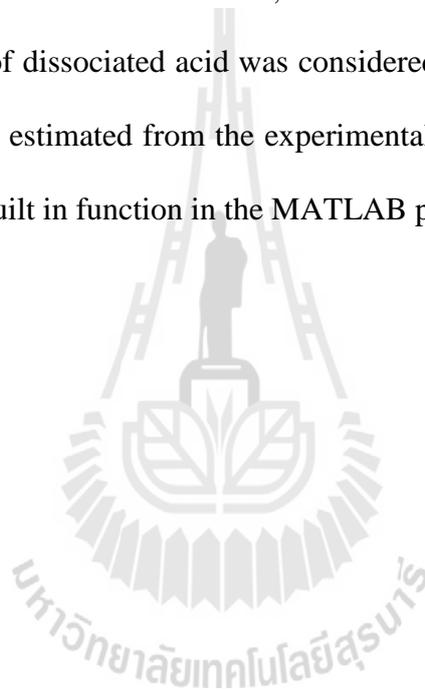
Table 3.1 The Modeling of Adsorption Isotherm

3.2.1 Physical Physical Adsorption Model				
Model No.	Name of model	adsorption of undissociated acid	adsorption of dissociated acid	assumption
1	Langmuir-Langmuir model	Langmuir equation	Langmuir equation	-Langmuir assumption -The equilibrium constant of lactic acid dissociation is assumed constant
2	Langmuir-Langmuir model+Ka(T)	Langmuir equation	Langmuir equation	-Langmuir assumption -The equilibrium constant of lactic acid dissociation depend on temperature
3.2.2 Physical Chemical Adsorption Model				
Model No.	Name of model	adsorption of undissociated acid	adsorption of dissociated acid	Assumption
3	Freudlich-Selectivity model	Freudlich equation	Selectivity coefficient	-Freudlich assumption -The equilibrium constant of lactic acid dissociation is assumed constant
4	Freudlich-Selectivity model+Ka(T)	Freudlich equation	Selectivity coefficient	-Freudlich assumption -The equilibrium constant of lactic acid dissociation depend on temperature
5	BET-Selectivity model	BET equation	Selectivity coefficient	-BET assumption -The equilibrium constant of lactic acid dissociation is assumed constant
6	BET-Selectivity model+Ka(T)	BET equation	Selectivity coefficient	-BET assumption -The equilibrium constant of lactic acid dissociation depend on temperature
7	Freudlich-Steric factor model	BET equation	Steric mass action	-Freudlich assumption -The equilibrium constant of lactic acid dissociation is assumed constant

Table 3.1 The Modeling of Adsorption Isotherm (Continued)

Model No.	Name of model	adsorption of undissociated acid	adsorption of dissociated acid	Assumption
8	Freudlich-Steric factor model+Ka(T)	BET equation	Steric mass action	-Freudlich assumption -The equilibrium constant of lactic acid dissociation depend on temperature
9	BET-Steric factor model	BET equation	Steric mass action	-BET assumption -The equilibrium constant of lactic acid dissociation is assumed constant
10	BET-Steric factor model+Ka(T)	BET equation	Steric mass action	-BET assumption -The equilibrium constant of lactic acid dissociation depend on temperature
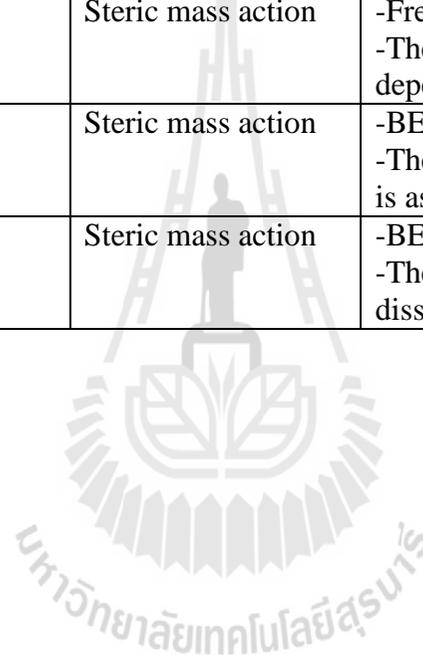
3.2.1 Physical Physical Adsorption Model

Langmuir-Langmuir Model

From chapter II, the model assumptions followed by Caetano et al. (2009). However, when the temperature was increased, the equilibrium constant of dissociated acid in liquid phase changes very little. Then, the equilibrium constant of dissociated acid in liquid phase assumes a constant.

Then Eq. (2.34) become,

$$Q_T = \frac{Q_{max}^{LH} K_{LH} C_T}{1 + \left(K_a / K_w\left(T\right)\right) \cdot 10^{-(14-pH)} + K_{LH} C_T} \\ + \frac{Q_{max}^{IE} K_{IE}\left(K_a / K_w\left(T\right)\right) \cdot C_T \cdot 10^{-(14-pH)}}{1 + \left(K_a / K_w\left(T\right)\right) \cdot 10^{-(14-pH)} \cdot \left(1 + K_{IE} C_T\right)} \tag{3.2}$$

The model describes the removal of lactic acid by the resin in the term of three unknown parameters ($K_{IE}, K_{LH}, Q_{max}^{LH}$) related to dissociated acid and undissociated acid adsorption.

Langmuir-langmuir model+Ka(T)

From chapter II, the model assumptions followed by Carmona et al. (2006).The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by Langmuir equation. The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by Langmuir equation. The equilibrium constant of dissociated acid in liquid phase depends on temperature.

Then Eq. (2.34) becomes,

$$Q_T = \frac{Q_{max}^{LH} K_{LH} C_T}{1 + \left(K_a(T)/K_w(T)\right) \cdot 10^{-(14-pH)} + K_{LH} C_T}$$
$$+ \frac{Q_{max}^{IE} K_{IE} \left(K_a(T)/K_w(T)\right) \cdot C_T \cdot 10^{-(14-pH)}}{1 + \left(K_a(T)/K_w(T)\right) \cdot 10^{-(14-pH)} \cdot \left(1 + K_{IE} C_T\right)} \quad (3.3)$$

The model describes the removal of lactic acid by the resin in the term of three unknown parameters (K_{IE} , K_{LH} , Q_{max}^{LH}) related to dissociated acid and undissociated acid adsorption.

3.2.2 Physical Chemical Adsorption Model

Freundlich-selectivity model

From chapter II, the model assumptions followed by Kanazawa et al. (2004). The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by the Freundlich equation. The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by selectivity coefficient. The equilibrium constant of dissociated acid in liquid phase assumes a constant.

The model equation is obtained:

$$
\begin{aligned}
Q_T = k\left[\frac{C_T C_{H^+}}{K_a + C_{H^+}}\right]^{1/n} \\[2ex]
+ \left[\frac{S_{Cl^-}^{L^-}}{2(W/V)}\right]\left[\frac{K_a C_T}{K_a + C_{H^+}}\right]\left[-1 + \sqrt{1 + \frac{4(W/V)Q_{max}^{IE}}{\left(S_{Cl^-}^{L^-} \cdot \left[\frac{K_a C_T}{K_a + C_{H^+}}\right]\right)}}\right]
\end{aligned}
\tag{3.4}
$$

The model describes the removal of lactic acid by the resin in the term of

three unknown parameters (k, n, $S_{Cl^-}^{L^-}$) related to dissociated acid and undissociated

acid adsorption.

Freundlich-selectivity model+Ka(T)

From chapter II, the model assumptions followed by Kanazawa et al.

(2004). The uptake of lactic acid into the resin beads takes place due to undissociated

acid adsorption can be correlated by the Freundlich equation. The adsorption of lactic

acid on the resin beads take place due to the dissociated acid adsorption can be

expressed by selectivity coefficient. The equilibrium constant of dissociated acid

depends on temperature.

The model equation is obtained:

$$Q_T = k\left[\frac{C_T C_{H^+}}{K_a(T) + C_{H^+}}\right]^{1/n}$$

$$+ \left[\frac{S^{L^-}_{Cl^-}}{2(W/V)}\right]\left[\frac{K_a(T)C_T}{K_a(T) + C_{H^+}}\right]\left[-1 + \sqrt{1 + \frac{4(W/V)Q^{IE}_{max}}{\left(S^{L^-}_{Cl^-} \cdot \left[\frac{K_a(T)C_T}{K_a(T) + C_{H^+}}\right]\right)}}\right] \quad (3.5)$$

The model describes the removal of lactic acid by the resin in the term of

three unknown parameters (k, n, $S^{L^-}_{Cl^-}$) related to dissociated acid and undissociated

acid adsorption.

BET-selectivity model

The uptake of lactic acid into the resin beads takes place due to
undissociated acid adsorption can be correlated by the BET equation.

$$Q_{LH} = Q^{LH}_{max}\left[\frac{CC_{LH}}{(C_S - C_{LH})\left(1 + (C-1)\left(\frac{C_{LH}}{C_S}\right)\right)}\right] \quad (3.6)$$

where C is the parameter constant in BET equation.

The adsorption of lactic acid on the resin beads take place due to the
dissociated acid adsorption can be expressed by selectivity coefficient. The
equilibrium constant of dissociated acid in liquid phase assumes a constant.

Then Eq. (2.41) becomes,

$$Q_{L^-} = \left[\frac{S^{L^-}_{Cl^-}}{2(W/V)}\right]\left[\frac{K_aC_T}{K_a+C_{H^+}}\right]\left[-1+\sqrt{1+\frac{4(W/V)Q^{IE}_{max}}{\left(S^{L^-}_{Cl^-}\cdot\left[\frac{K_aC_T}{K_a+C_{H^+}}\right]\right)}}\right] \quad (3.7)$$

The model equation is obtained:

$$Q_T = Q^{LH}_{max}\left[\frac{C\left(\dfrac{C_TC_{H^+}}{K_a+C_{H^+}}\right)}{\left(C_s-\left(\dfrac{C_TC_{H^+}}{K_a+C_{H^+}}\right)\right)\left(1+\left(\dfrac{C-1}{C_s}\right)\left(\dfrac{C_TC_{H^+}}{K_a+C_{H^+}}\right)\right)}\right]$$
$$+\left[\frac{S^{L^-}_{Cl^-}}{2(W/V)}\right]\left[\frac{K_aC_T}{K_a+C_{H^+}}\right]\left[-1+\sqrt{1+\frac{4(W/V)Q^{IE}_{max}}{\left(S^{L^-}_{Cl^-}\cdot\left[\frac{K_aC_T}{K_a+C_{H^+}}\right]\right)}}\right] \quad (3.8)$$

The model describes the removal of lactic acid by resin in the term of

three unknown parameters (Q^{LH}_{max}, C, $S^{L^-}_{Cl^-}$) related to dissociated acid and

undissociated acid adsorption.

BET-selectivity model+Ka(T)

The uptake of lactic acid into the resin beads takes place due to

undissociated acid adsorption can be correlated by the BET equation. The adsorption

of lactic acid on the resin beads take place due to the dissociated acid adsorption can

be expressed by selectivity coefficient. The equilibrium constant of dissociated acid depends on temperature.

The model equation is obtained:

$$Q_T = Q_{max}^{LH}\left[\dfrac{C\left(\dfrac{C_T C_{H^+}}{K_a(T)+C_{H^+}}\right)}{\left(C_s - \left(\dfrac{C_T C_{H^+}}{K_a(T)+C_{H^+}}\right)\right)\left(1+\left(\dfrac{C-1}{C_s}\right)\left(\dfrac{C_T C_{H^+}}{K_a(T)+C_{H^+}}\right)\right)}\right]$$

$$+\left[\dfrac{S_{Cl^-}^{L^-}}{2(W/V)}\right]\left[\dfrac{K_a(T)C_T}{K_a(T)+C_{H^+}}\right]\left[-1+\sqrt{1+\dfrac{4(W/V)Q_{max}^{IE}}{\left(S_{Cl^-}^{L^-}\cdot\left[\dfrac{K_a(T)C_T}{K_a(T)+C_{H^+}}\right]\right)}}\right]$$

(3.9)

The model describes the removal of lactic acid by resin in the term of three unknown parameters (Q_{max}^{LH}, C, $S_{Cl^-}^{L^-}$) related to dissociated acid and undissociated acid adsorption.

Freundlich-steric factor model

The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by Freundlich equation. The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by the steric mass action (SMA). The equilibrium constant of dissociated acid in liquid phase assumes a constant.

The steric mass action (SMA) can be obtained by

$$K_{ij} = \left(\frac{Q_i}{C_i}\right)^{\nu_j} \left(\frac{Q_j}{C_j}\right)^{\nu_i} ; i = 2, 3, ..., n \tag{3.10}$$

Each molecule may sterically shield some counterions on the adsorptive surface. Electroneutrality requires that:

$$Q_{max}^{IE} = Q_j + \sum_{i=2}^{n} (\nu_i + \sigma_i)Q_i \tag{3.11}$$

Where σ_i is the steric factor

Assumptions: 1) $\nu_{Cl^-} = 1$

        2) i=2 (i is lactate ion: L^-)

The equilibrium constant of the reaction from Eq. (3.9) may be written:

$$K_{LCl} = \left(\frac{Q_{L^-}}{C_{L^-}}\right)\left(\frac{C_{Cl^-}}{Q_{Cl^-}}\right)^{\nu_{L^-}} \tag{3.12}$$

Where ν_{L^-} is the characteristic charge of lactate ion.

    ν_{Cl^-} is the characteristic charge of chloride ion ($\nu_{Cl^-} = 1$).

Electroneutrality requires that:

$$Q_{max}^{IE} = Q_{Cl^-} + (\nu_{L^-} + \sigma_{L^-})Q_{L^-} \tag{3.13}$$

Where Q_{max}^{IE} is the maximum concentration of ion in the solid phase (mol/kg dry resin), σ_{L^-} is the steric factor of lactate ion.

Then Eq. (3.11) become

$$K_{LCl} = \left(\frac{Q_{L^-}}{C_{L^-}}\right)\left(\frac{C_{Cl^-}}{Q_{max}^{IE} - (v_{L^-} + \sigma_{L^-})Q_{L^-}}\right)^{v_{L^-}} \tag{3.14}$$

The steric factor can be calculated by $\dfrac{\sigma_1(unknow)}{\sigma_2(known)} = \dfrac{q_{uniquac1}}{q_{uniquac2}}$

Where the external surface area of Uniquac of lactate ion is 3.151. The external surface area of Uniquac of chymotrypsin is 700.2723 (Joao et al., 2004), The steric factor of chymotrypsin is 7.43 (Stuart, 2004). Then, the steric factor of lactate ion is 0.033432609.

$$Q_{L^-} = \frac{-C_{L^-} K_{LCl}(v_{L^-} + \sigma_{L^-})}{2(v_{L^-} + \sigma_{L^-})(W/V)} + \frac{\sqrt{\left[C_{L^-} K_{LCl}(v_{L^-} + \sigma_{L^-})\right]^2 + 4(W/V)\left(C_{L^-} - Q_{max}^{IE} K_{LCl}(v_{L^-} + \sigma_{L^-})\right)}}{2(v_{L^-} + \sigma_{L^-})(W/V)} \tag{3.15}$$

Defined

$$P = C_{L^-} K_{LCl}(v_{L^-} + \sigma_{L^-}) \tag{3.16}$$

$$Q_{L^-} = \frac{-P + \sqrt{P^2 + 4(W/V)PQ_{max}^{IE}}}{2(v_{L^-} + \sigma_{L^-})(W/V)} \qquad (3.17)$$

The model equation is obtained:

$$Q_T = k\left[\frac{C_T C_{H^+}}{K_a + C_{H^+}}\right]^{1/n} + \frac{-P + \sqrt{P^2 + 4(W/V)PQ_{max}^{IE}}}{2(v_{L^-} + \sigma_{L^-})(W/V)} \qquad (3.18)$$

The model describes the removal of lactic acid by resin in term of four unknown parameters (k, n, K_{LCl}, Q_{max}^{IE}) related to dissociated acid and undissociated acid adsorption.

Freundlich-steric factor model+Ka(T)

The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by Freundlich equation. The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by the steric mass action (SMA). The equilibrium constant of dissociated acid depends on temperature.

The model equation is obtained:

$$Q_T = k\left[\frac{C_T C_{H^+}}{K_a(T) + C_{H^+}}\right]^{1/n} + \frac{-P + \sqrt{P^2 + 4(W/V)PQ_{max}^{IE}}}{2(v_{L^-} + \sigma_{L^-})(W/V)} \qquad (3.19)$$

The model describes the removal of lactic acid by resin in term of four unknown parameters (k, n, K_{LCl}, Q_{max}^{IE}) related to dissociated acid and undissociated acid adsorption.

BET-steric factor model

The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by BET equation. The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by the steric mass action (SMA). The equilibrium constant of dissociated acid in liquid phase assumes a constant.

The model equation is obtained:

$$Q_T = Q_{max}^{LH} \left[\frac{C\left(\dfrac{C_T C_{H^+}}{K_a + C_{H^+}} \right)}{\left(C_s - \left(\dfrac{C_T C_{H^+}}{K_a + C_{H^+}} \right) \right)\left(1 + \left(\dfrac{C-1}{C_s} \right)\left(\dfrac{C_T C_{H^+}}{K_a + C_{H^+}} \right) \right)} \right]$$
$$+ \frac{-P + \sqrt{P^2 + 4(W/V)PQ_{max}^{IE}}}{2(v_{L^-} + \sigma_{L^-})(W/V)} \qquad (3.20)$$

The model describes the removal of lactic acid by resin in term of four unknown parameters (Q_{max}^{LH}, C, K_{LCl}, Q_{max}^{IE}) related to dissociated acid and undissociated acid adsorption.

BET-steric factor model+Ka(T)

The uptake of lactic acid into the resin beads takes place due to undissociated acid adsorption can be correlated by BET equation. The adsorption of lactic acid on the resin beads take place due to the dissociated acid adsorption can be expressed by the steric mass action (SMA). The equilibrium constant of dissociated acid depends on temperature.

The model equation is obtained:

$$Q_T = Q_{max}^{LH} \left[\frac{C\left(\dfrac{C_T C_{H^+}}{K_a(T) + C_{H^+}} \right)}{\left(C_s - \left(\dfrac{C_T C_{H^+}}{K_a(T) + C_{H^+}} \right) \right) \left(1 + \left(\dfrac{C-1}{C_s} \right) \left(\dfrac{C_T C_{H^+}}{K_a(T) + C_{H^+}} \right) \right)} \right] \tag{3.21}$$
$$+ \frac{-P + \sqrt{P^2 + 4(W/V)PQ_{max}^{IE}}}{2(v_{L^-} + \sigma_{L^-})(W/V)}$$

The model describes the removal of lactic acid by resin in term of four unknown parameters (Q_{max}^{LH}, C, K_{LCl}, Q_{max}^{IE}) related to dissociated acid and undissociated acid adsorption.

3.3   Numerical Methods

The total of lactic acid concentration in solid phase is solved by method of lsqnonlin in MATLAB.

```
┌─────────────────────────────────────────────┐
│      Main function of nonlinear least-squares │
│                                               │
│      Exam: x=lsqnonlin(@myfun,x0)             │
└─────────────────────────────────────────────┘
                      ⇓
┌─────────────────────────────────────────────┐
│           Function F = myfun(x)               │
│                                               │
│           F=………..                             │
└─────────────────────────────────────────────┘
                      ⇓
┌─────────────────────────────────────────────┐
│           Input initial guess x0              │
│                                               │
└─────────────────────────────────────────────┘
                      ⇓
┌─────────────────────────────────────────────┐
│    The objective function to be minimized is  │
│          given by the following:              │
│                                               │
│      E = Σ (Y_{i,exp} − Y_{i,th})²            │
└─────────────────────────────────────────────┘
                      ⇓
┌─────────────────────────────────────────────┐
│      Output shown x, Exitflag, resnorm        │
│                                               │
└─────────────────────────────────────────────┘
```

$$E = \sum_{i=1}^{n} (Y_{i,exp} - Y_{i,th})^2$$
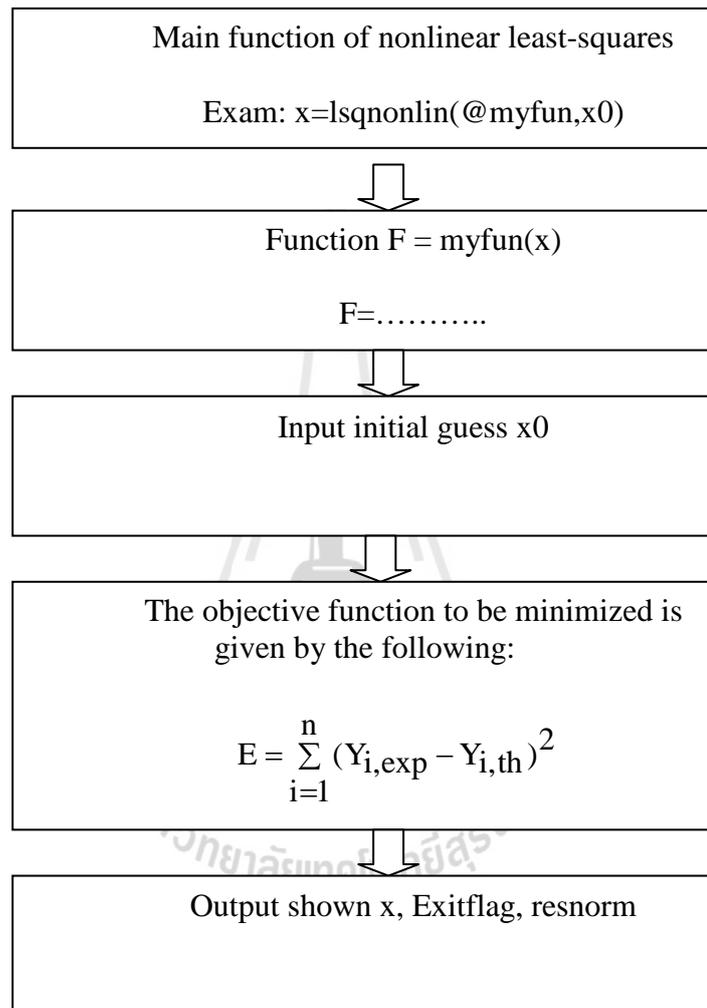
Figure 3.2 Process scheme for modeling.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Experimental results

4.1.1 Adsorption isotherm

The adsorption isotherm at pH 2 which is lower than pKa of lactic acid and those at pH 4 and 5 which is higher than pKa of lactic acid are obtained. Figure 4.1 shows the adsorption isotherms of lactic acid at 25 ˚C and pH 2, 4 and 5 as a function of lactic acid concentration. Figure 4.2 shows the adsorption isotherms of lactic acid at 40 ˚C and pH 2, 4 and 5 as a function of lactic acid concentration. As can be observed in Figure 4.1 and Figure 4.2, the adsorption of lactic acid is higher than the maximum capacity of 4.7 mol/kg dry resin at pH 4.85 for Amberlite IRA 96 reported by Moldes et al. (2003). Furthermore, the solid liquid adsorption isotherm is clearly an S curve.
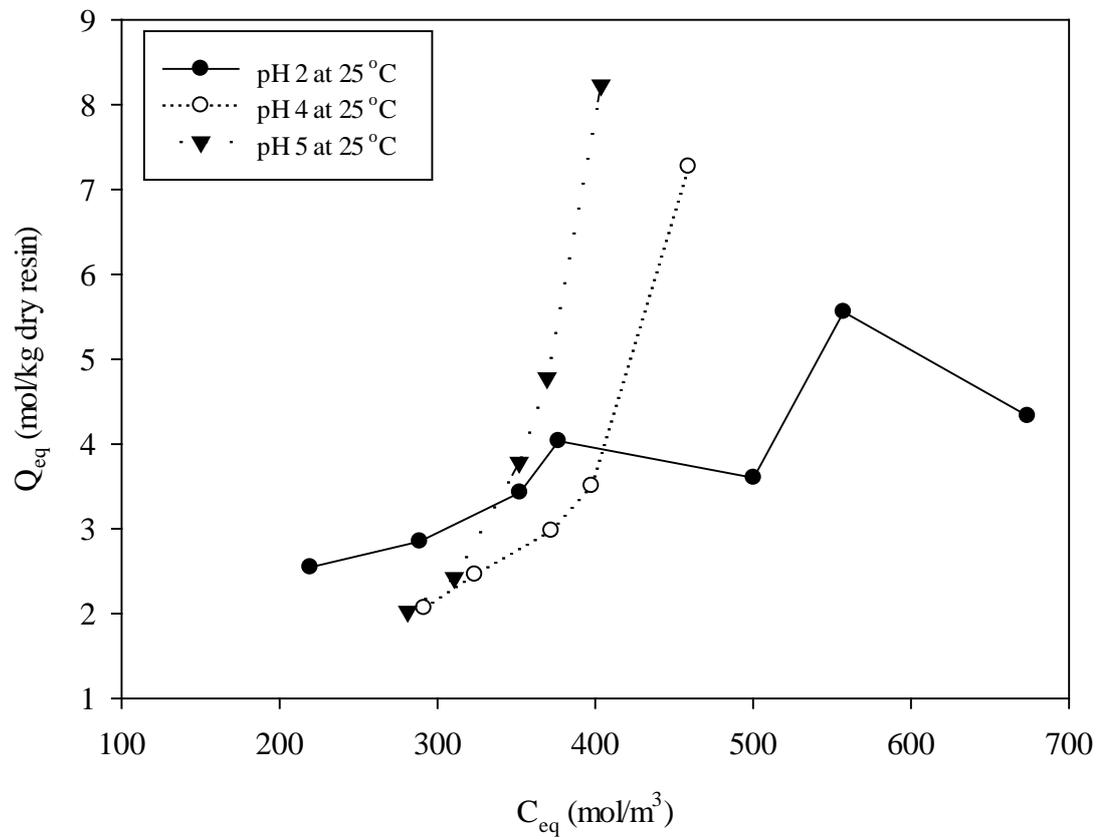
Figure 4.1 The adsorption isotherm of lactic acid on Amberlite IRA 96 at 25 ˚C.
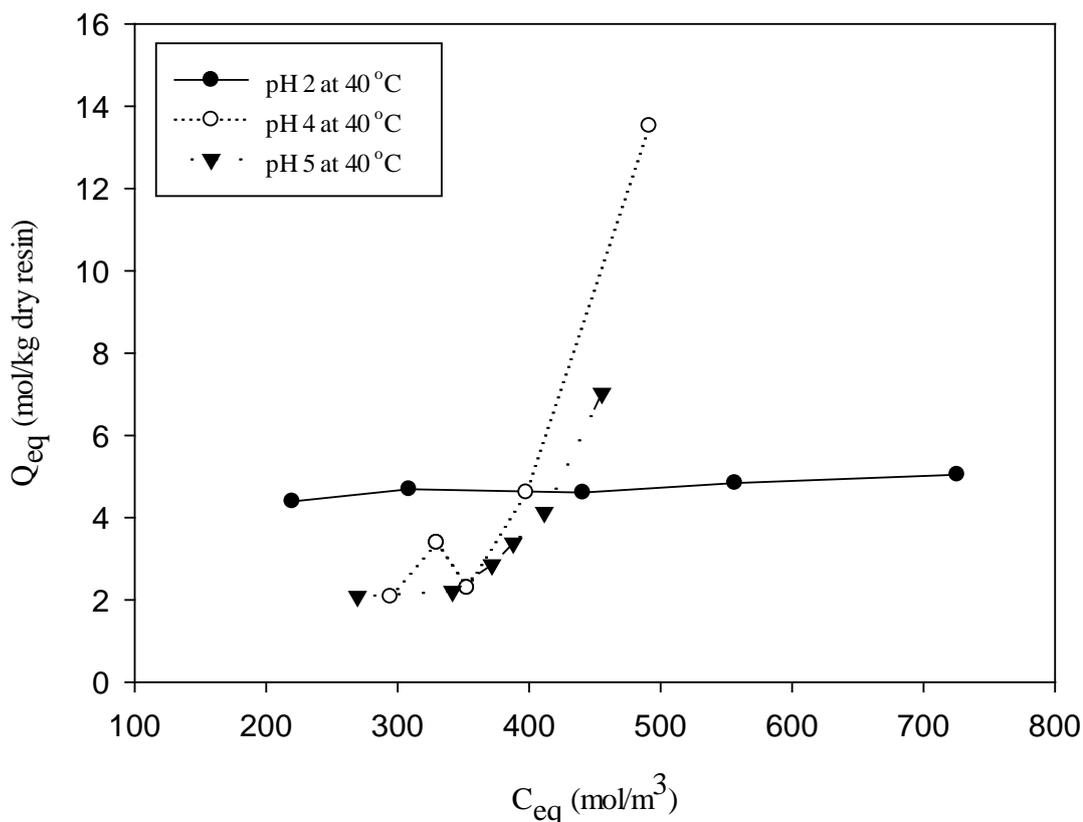
Figure 4.2 The adsorption isotherm of lactic acid on Amberlite IRA 96 at 40 ˚C.

4.1.2 Effect of pH

As shown in Figure 4.1 and Figure 4.2, the amount of lactic acid adsorbed at pH 4 and pH 5 is higher than that adsorbed at pH 2 because of the higher ion concentrations from the dissociated acid at pH 4 and 5. It quite agrees with the observation reported by Cao et al. (2002). Since the pH 5 is further from the pKa of lactic acid than the pH 4, the concentration of dissociated one at pH 5 is higher than that at pH 4. Therefore, the amount of lactic acid adsorbed at pH 5 and 25 ˚C is higher than the amount of lactic acid adsorbed at pH 4 and 25 ˚C as shown in Figure 4.1. However, the amount of lactic acid adsorbed at pH 5 and 40 ˚C is quite the same as the amount of lactic acid adsorbed at pH 4 at 40 ˚C because the pKa of lactic acid

increases with increasing temperature so the difference in pKa of lactic acid at pH 4 and pH 5 is less at this temperature. In addition, since the adsorption of lactic acid on Amberlite is exothermic, the effect of pH would be minimized at the higher temperature.

4.1.3 Effect of temperature

Figure 4.3 show the effect of temperature on the adsorption isotherm of lactic acid. From these figures, it is clearly observed that the amount of adsorbed lactic acid depends on temperature. Because of the dependence of dissociation constant of lactic acid on temperature, there is the undissociated acid adsorption (molecular adsorption) and dissociated acid adsorption (ion adsorption) occurred on the adsorption isotherm. The molecular adsorption is a result of physical adsorption and the ion adsorption is a result of chemical adsorption.

The equilibrium constant dependency on temperature was derived from Van't Hoff equation. The heat of adsorption of lactic acid was 29 ± 17 kJ/mol which is reported by Isam et al. (2005). In this thesis, the heat of adsorption of lactic acid at pH 2 was calculated as 10.8 kJ/mol. The heat of adsorption of lactic acid at pH 4 was calculated as 14.2 kJ/mol. The heat of adsorption of lactic acid at pH 5 was calculated as 36.7 kJ/mol.

The adsorption of lactic acid on ion exchange is an exothermic process because the heat of adsorption of lactic acid is negative as reported by Isam et al. (2005). Therefore the amount of lactic acid adsorbed decreases with increasing temperature, as indicated by Van't Hoff equation (Duong D.Do., 1998). The effect of temperature due to the chemical adsorption is higher than that due to the physical

adsorption because of the larger heat of adsorption for the chemical adsorption (Yu LTU et al., 2009).

The amount of dissociated lactic acid is low at pH 2 which is lower than pKa of lactic acid, and, thus, the molecular adsorption process is the predominant one. At higher concentration of lactic acid at pH 2, the amount of adsorption of lactic acid does not change significantly when the temperature change as shown in Figure 4.3(a) because the heat of adsorption for physical adsorption is smaller.
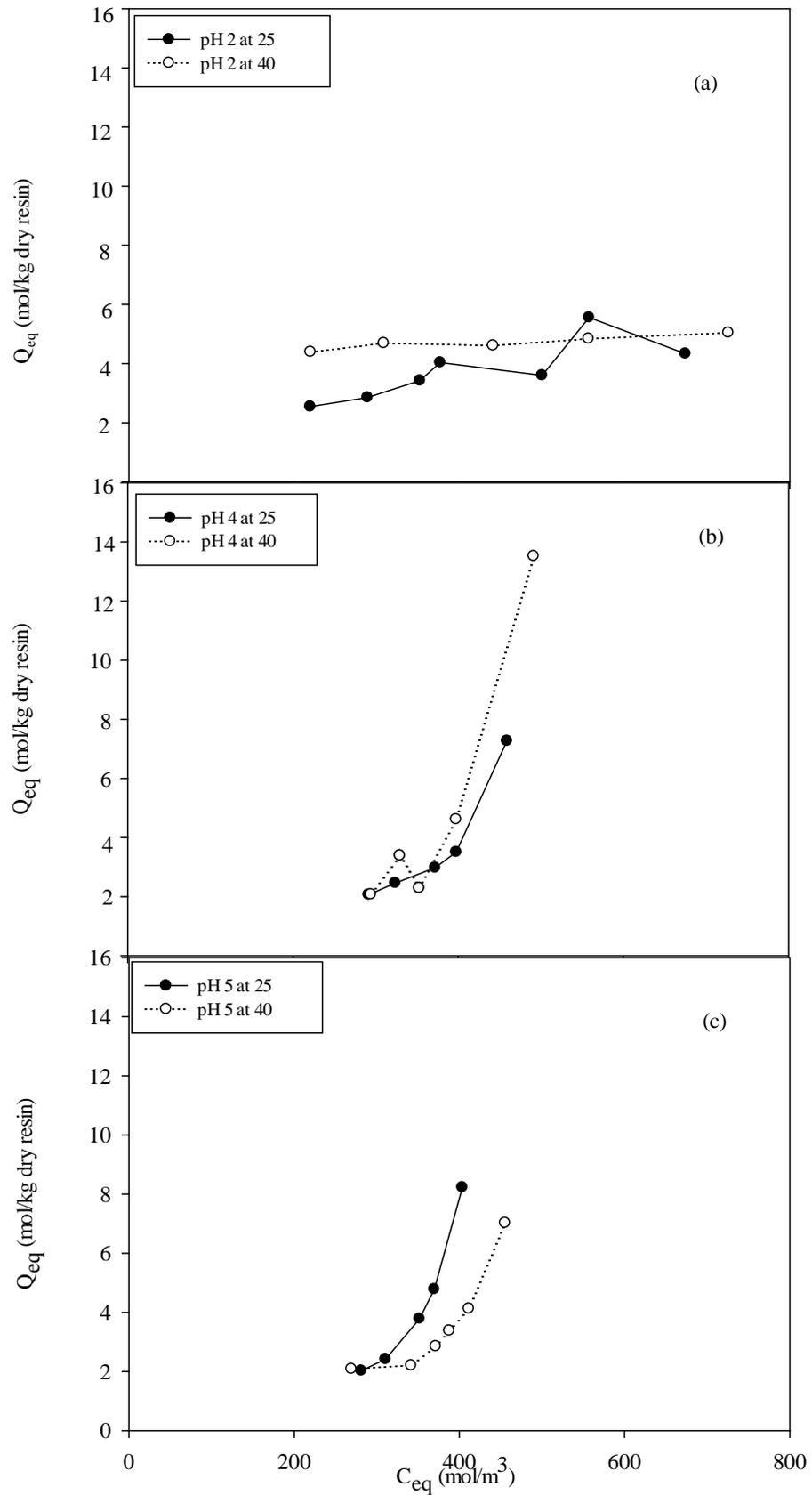
Figure 4.3 The adsorption isotherm of lactic acid on Amberlite IRA 96.

However, at lower concentration of lactic acid at pH 2, the amount of lactic acid adsorbed at 40 ˚C is higher than the amount of lactic acid adsorbed at 25 ˚C because there are the effects of heat of adsorption and the heat of dissociation of lactic acid occurred. Nevertheless the amount of adsorbed lactic acid is low. Since the molecular adsorption is the predominant one at pH 2, the heat of adsorption for physical adsorption is smaller and the heat of dissociation of lactic acid is negative (Ren Jie, 2010), the amount of dissociated lactic acid decreases with increasing temperature. As a result the molecular adsorption of pH 2 at 40 ˚C is higher than the molecular adsorption at 25 ˚C as shown in Figure 4.3(a).

The amount of dissociated lactic acid is high at pH 4 and 5 which is higher than pKa of lactic acid, and, thus, the mechanism for lactic acid adsorption at pH 4 and pH 5 were mainly the chemical adsorption rather than the physical adsorption. Moreover, the effect of temperature on adsorption isotherm is greater because the heat of adsorption by chemical adsorption is high (Yu LTU et al., 2009). As can be observed in Figure 4.3(c), the amount of adsorption of lactic acid of pH 5 at 25 ˚C is higher than the amount of adsorption of lactic acid of pH 5 at 40 ˚C. Therefore the amount of lactic acid adsorbed is different when the temperature changes. However, the amount of adsorption of lactic acid at pH 4 does not change significantly when the temperature change as shown in Figure 4.3(b) because pH 4 is slightly higher than pKa of lactic acid then the mechanism for lactic acid adsorption at pH 4 were the chemical adsorption slightly rather than the physical adsorption.

4.2   Modeling of Lactic Acid Adsorption

4.2.1 Physical-Physical Adsorption Model

As can be observed in Figure 4.4, Langmuir- Langmuir model correlates the adsorption isotherm at pH 2 adequately because, at pH lower than pKa of lactic acid, lactic acid in solution appears mainly as the undissociated form; thus, the amount of lactic acid adsorbed by physical adsorption process is higher than the amount of lactic acid adsorbed by chemical adsorption. Consequently, Langmuir-Langmuir model, which is all based on physical interaction, is good for correlating the adsorption isotherm of lactic acid in this region. The average absolute deviation (AAD) is ranging from 0.0154 to 0.1063 and the correlated isotherms were almost agreed with experimental data. The values of the parameters obtained by fitting the experimental data are shown in Table 4.1 to Table 4.2.
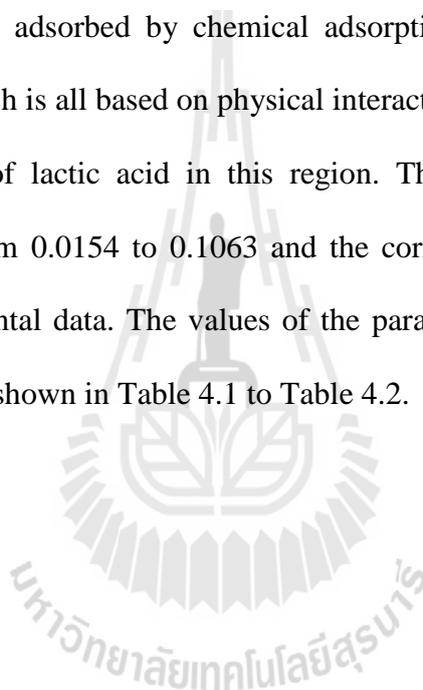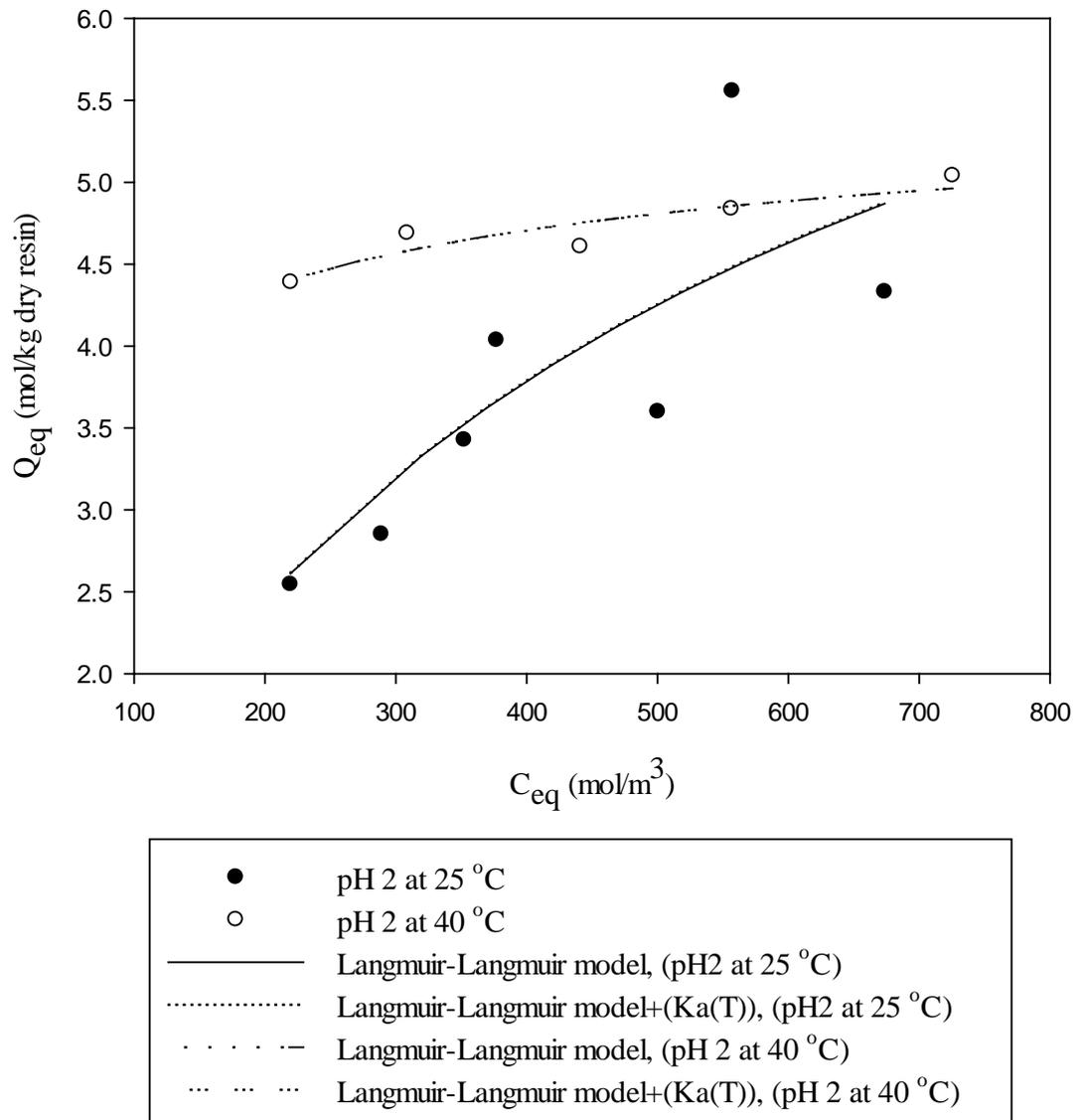
Figure 4.4 The correlated and experimental results at pH 2.

Table 4.1 The value parameter of Langmuir- Langmuir model (Ka constant)

Adsorption	Undissociated acid (Q_{LH})		Dissociated acid (Q_{L^-})			
Langmuir Langmuir model	Langmuir		Langmuir			
Langmuir Langmuir model	Temp	X				
pH	Temp	K_{IE}	Q_{max}^{LH}		K_{LH}	%AAD
2	25	2.10×10^{-3}	1.52×10^{-1}		7.16×10^{0}	10.63
4	25	1.29×10^{-4}	1.20×10^{-3}		1.82×10^{2}	33.38
5	25	1.20×10^{-3}	3.09×10^{-4}		1.63×10^{2}	43.53
2	40	5.83×10^{-2}	3.65×10^{-1}		4.40×10^{0}	1.54
4	40	1.83×10^{-4}	2.60×10^{-3}		1.22×10^{2}	75.86
5	40	5.85×10^{-4}	1.87×10^{-5}		1.01×10^{2}	27.33

Table 4.2 The value parameter of Langmuir- Langmuir model (Langmuir- Langmuir model+(Ka(T))

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})			
Langmuir Langmuir model (Ka)	Langmuir	Langmuir			
Langmuir Langmuir model (Ka)	Temp	X			
pH	Temp	K_{IE}	Q_{max}^{LH}	K_{LH}	%AAD
2	25	2.10×10^{-3}	1.91×10^{-1}	7.17×10^{0}	10.74
4	25	4.10×10^{-3}	1.70×10^{-3}	8.30×10^{0}	36.54
5	25	5.70×10^{-3}	1.30×10^{-3}	2.87×10^{1}	42.21
2	40	5.95×10^{-2}	5.74×10^{-1}	4.34×10^{0}	1.54
4	40	3.46×10^{3}	9.40×10^{-3}	4.59×10^{0}	79.21
5	40	2.84×10^{-2}	2.70×10^{-3}	4.51×10^{0}	34.77

As can be observed in Figure 4.5 to Figure 4.6, the Langmuir-Langmuir model cannot adequately correlate the adsorption isotherm at pH 4 and pH 5 where pH is higher than pKa of lactic acid since lactic acid normally appears in solution in dissociated form and the lactic acid is therefore mainly adsorbed by chemical adsorption.

●	pH 4 at 25 $^{\circ}$C
○	pH 4 at 40 $^{\circ}$C
———	Langmuir-Langmuir model, (pH 4 at 25 $^{\circ}$C)
·············	Langmuir-Langmuir model+(Ka(T)), (pH 4 at 25 $^{\circ}$C)
· · · · ––	Langmuir-Langmuir model, (pH 4 at 40 $^{\circ}$C)
··· ··· ···	Langmuir-Langmuir model+(Ka(T)), (pH 4 at 40 $^{\circ}$C)
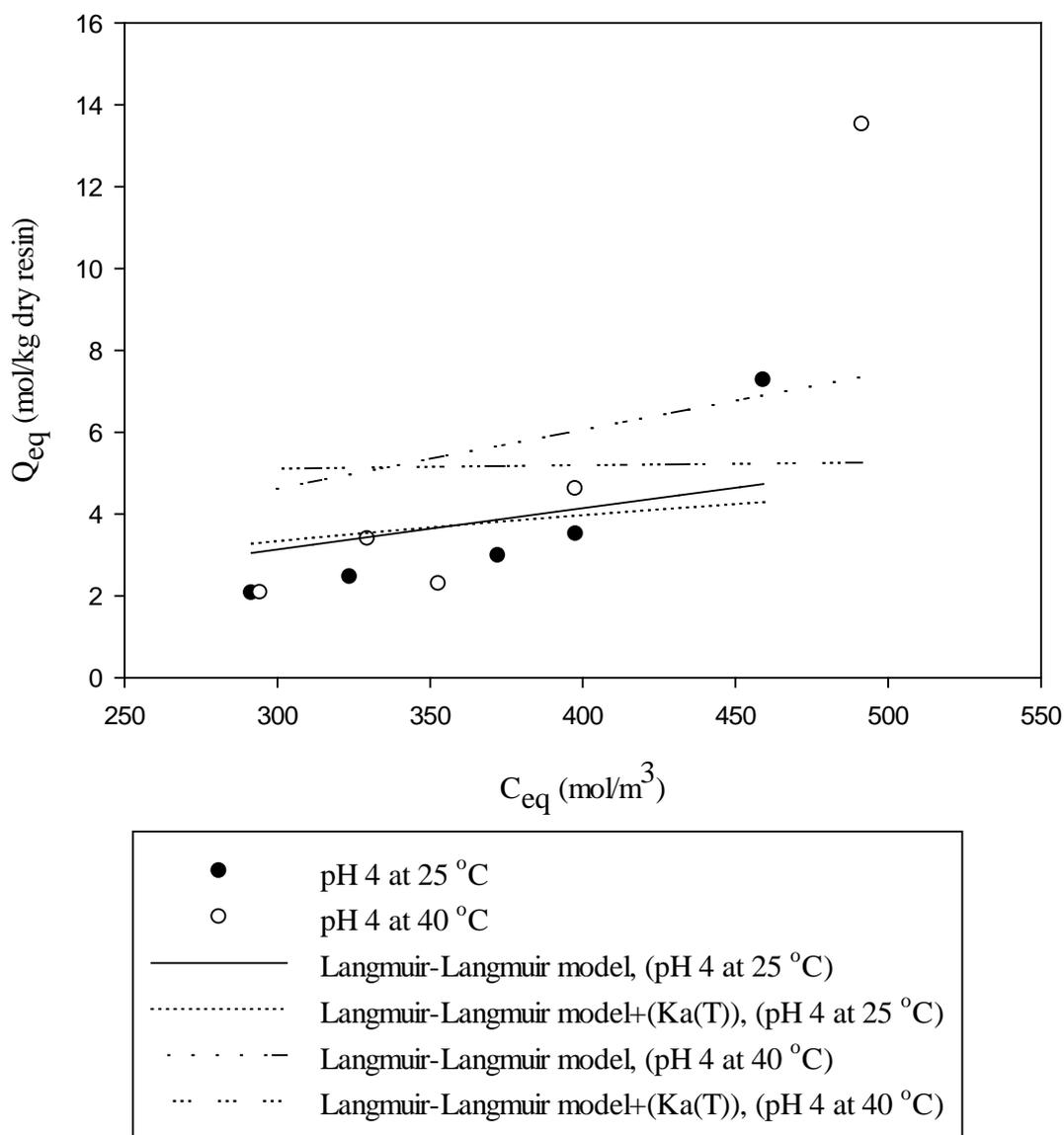
Figure 4.5 The correlated and experimental results at pH 4.
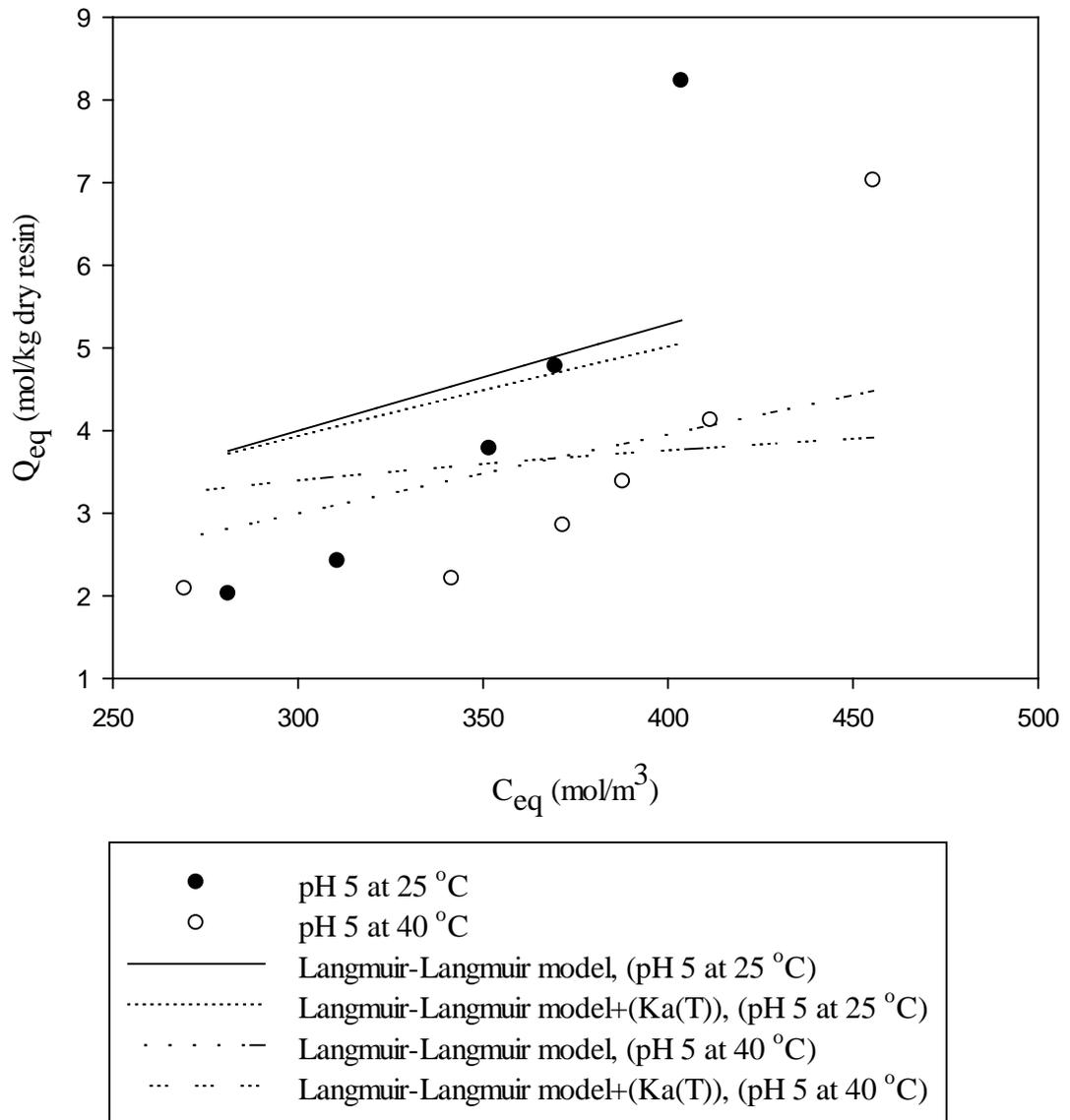
Figure 4.6 The correlated and experimental results at pH 5.

As a result, Langmuir-Langmuir model, which is all based on physical interaction, is not good for correlation adsorption isotherm when pH is higher than pKa. The average absolute deviation (AAD) is ranging from 0.2733 to 0.7586 which is too high and it is concluded that Langmuir-Langmuir cannot be used to correlate

the adsorption isotherm when pH is higher than pKa. The values of the parameters obtained by fitting the experimental data are shown in Table 4.1 to Table 4.2.

The effect of temperature dependent on Ka to Langmuir- Langmuir model was studied by Langmuir- Langmuir model+(Ka(T)). Evidently, the result of correlation of adsorption isotherm by Langmuir- Langmuir model+(Ka(T)) is similar to the Langmuir- Langmuir model as depicted in Figure 4.4 to Figure 4.6. As can be observed in Table 4.3, the effect of temperature dependent on Ka to %AAD is very low such as the average absolute deviation (AAD) of pH 2 at 25 °C for Langmuir-Langmuir model+ (Ka(T)) and Langmuir-Langmuir model is 0.1074 and 0.1063, respectively. Therefore, it is concluded that there is no need to consider the dependence of temperature on dissociation constant when the adsorption of lactic acid on ion exchange is correlated.

Table 4.3 The percent average absolute deviation (%AAD) of Physical Physical

Adsorption Model

pH	Temp	%AAD of physical physical model	
		Langmuir-Langmuir model	Langmuir-Langmuir model+(Ka(T))
2	25	10.63	10.74
2	40	1.54	1.54
4	25	33.38	36.54
4	40	75.86	79.21
5	25	43.53	42.21
5	40	27.33	34.77

4.2.2 Physical-Chemical Adsorption Model

The physical and chemical adsorptions model is used in this work due to the fact that Langmuir-Langmuir model cannot explain the adsorption when pH is higher than pKa as discussed previously probably because both chemical and physical adsorptions occurred in this pH range.

It is found that Freundlich-steric factor model and BET-steric factor model can be used to correlate adsorption isotherm at pH 2, pH 4 and pH 5. This is because of their assumption and the advantage of more parameter contained in the model, which increases the capacity of correlation. However, BET-steric factor model cannot usually be used to correlate the adsorption isotherm because of its assumption that does not include the effect of interaction among adsorbed molecule but it has been included in the Freundlich-steric factor model (Courtney et al., 2012) then Freundlich-steric factor model can correlate adsorption isotherm at pH 4 and pH 5 as can be observed in Figure 4.7 to Figure 4.10.
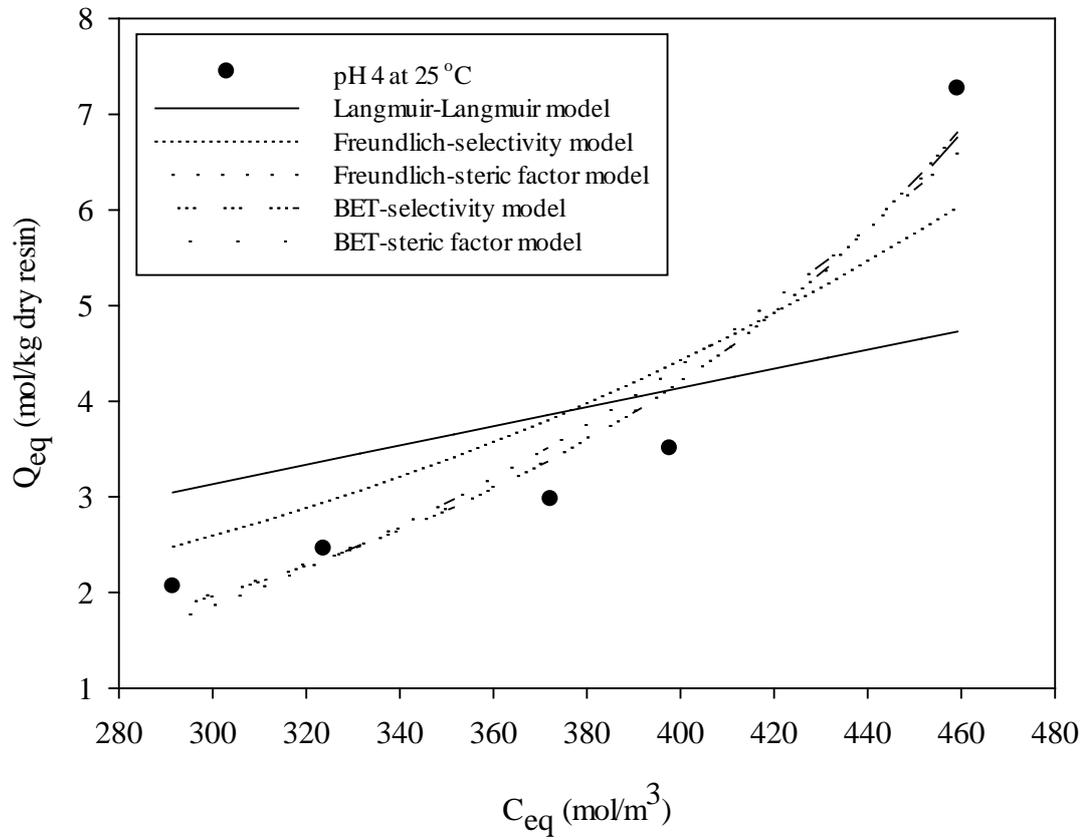
Figure 4.7 The correlated and experimental results at pH 4 and 25 °C .
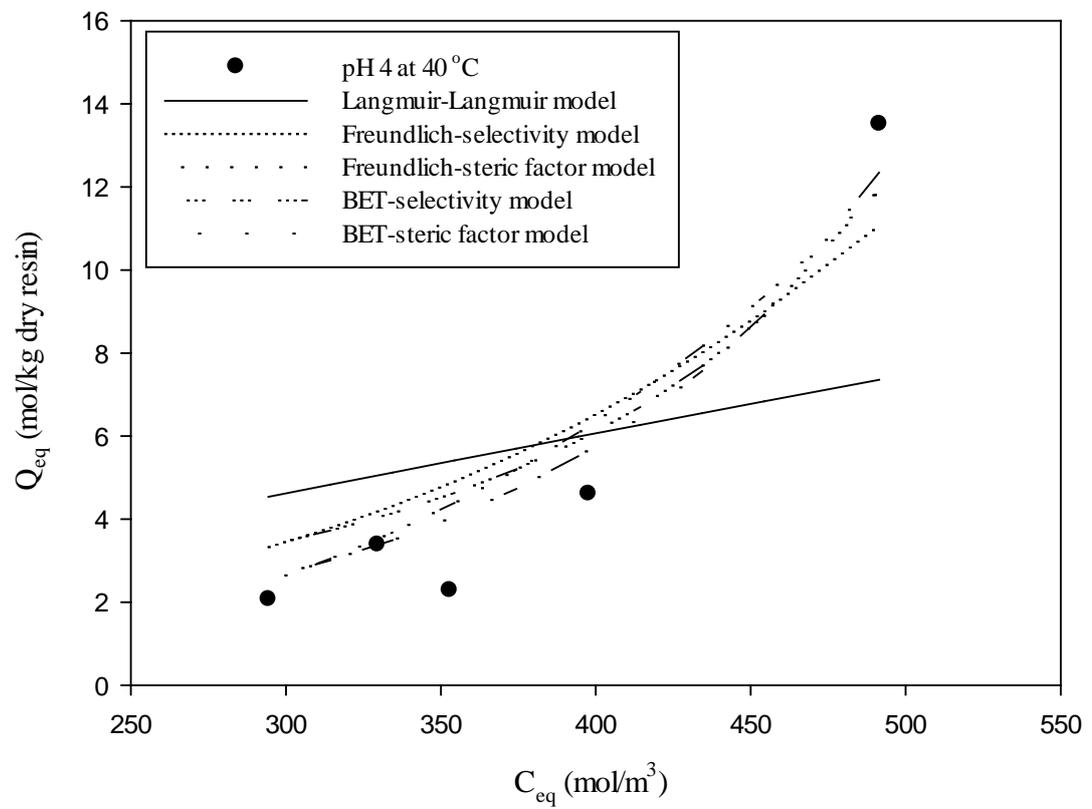
Figure 4.8 The correlated and experimental results at pH 4 and 40 °C.
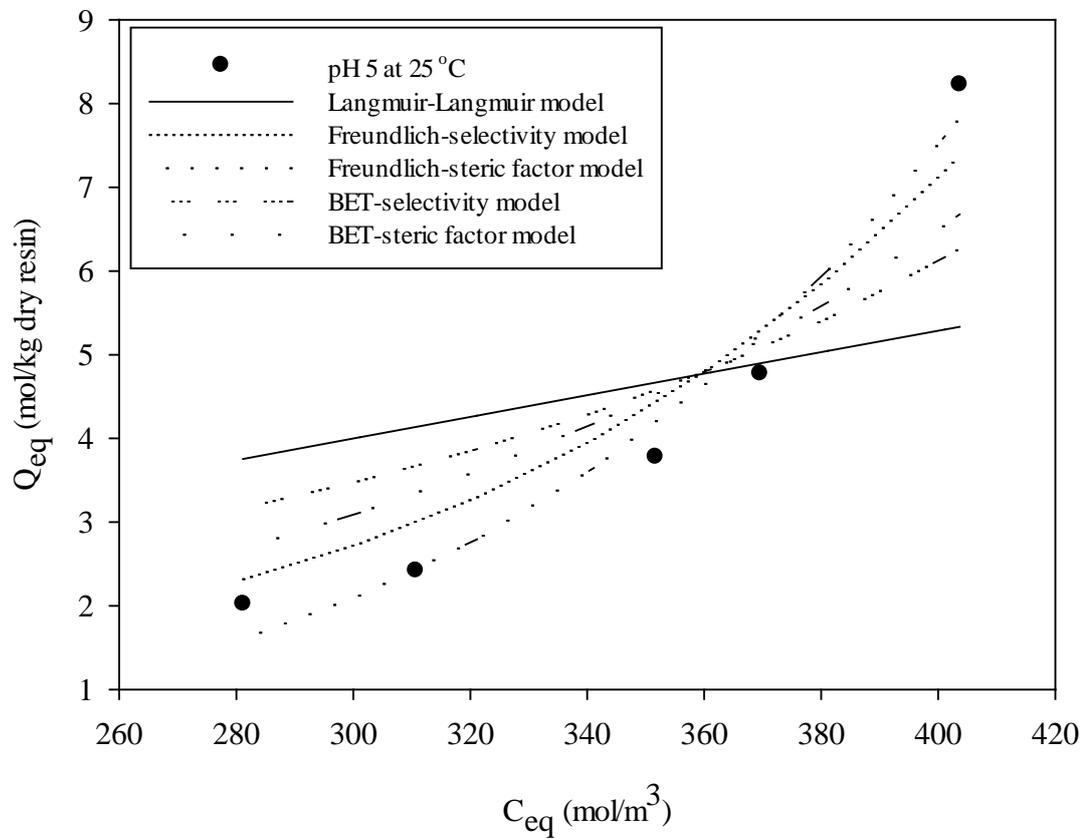
Figure 4.9 The correlated and experimental results at pH 5 and 25 °C .
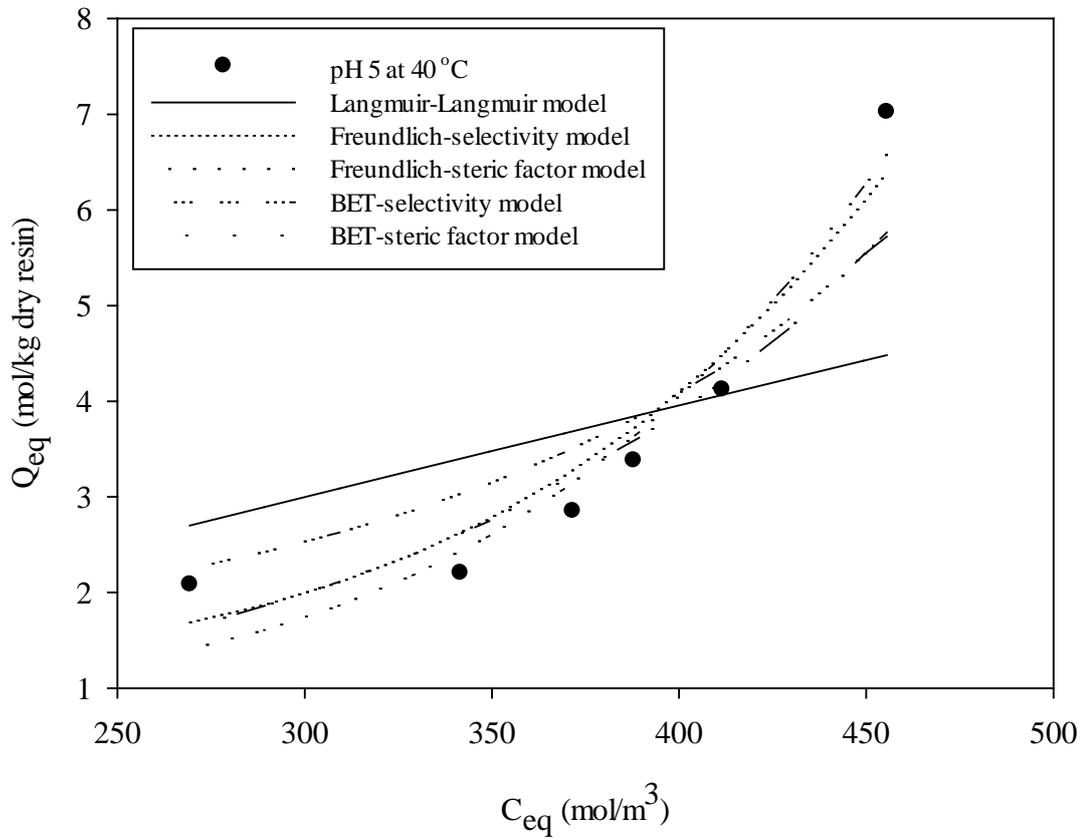
Figure 4.10 The correlated and experimental results at pH 5 and $40\,^\circ\text{C}$.

In other models, the Freundlich-selectivity model and BET-selectivity model was used to correlate adsorption isotherm at pH 2, pH 4 and pH 5. However, there is limit of the maximum capacity parameter in the model. As a result Freundlich-selectivity model and BET-selectivity model cannot correlate adsorption isotherm because the maximum capacity parameter of model is limited as correlated in Figure 4.7 to Figure 4.12.

Besides, the physical and chemical adsorptions model can correlate the adsorption isotherm at pH 2 which is lower than pKa of lactic acid. As can be observed in Figure 4.11 to Figure 4.12, the adsorption isotherm can correlate by Freundlich-steric factor model.

Freundlich-steric factor model can correlate the adsorption isotherm of lactic acid at pH 2, 4 and 5. For the Freundich equation, the constant k is an approximate indicator of adsorption capacity. While n is a function of the strength of adsorption in the adsorption process. The value of n is above one it indicates a molecular adsorption. However, the value of n is below one it indicates ion adsorption and molecular adsorption (Dada et al., 2012). The parameter n of Freundlich-steric factor model show in Table 4.6. At pH 2, the value of n is above one it indicates molecular adsorption at pH 2. At pH 4 and 5, the value of n is below one it indicates ions adsorption and molecular adsorption at pH 4 and 5.
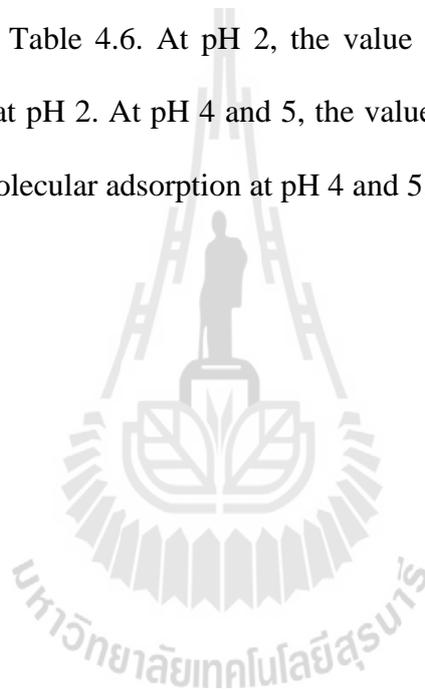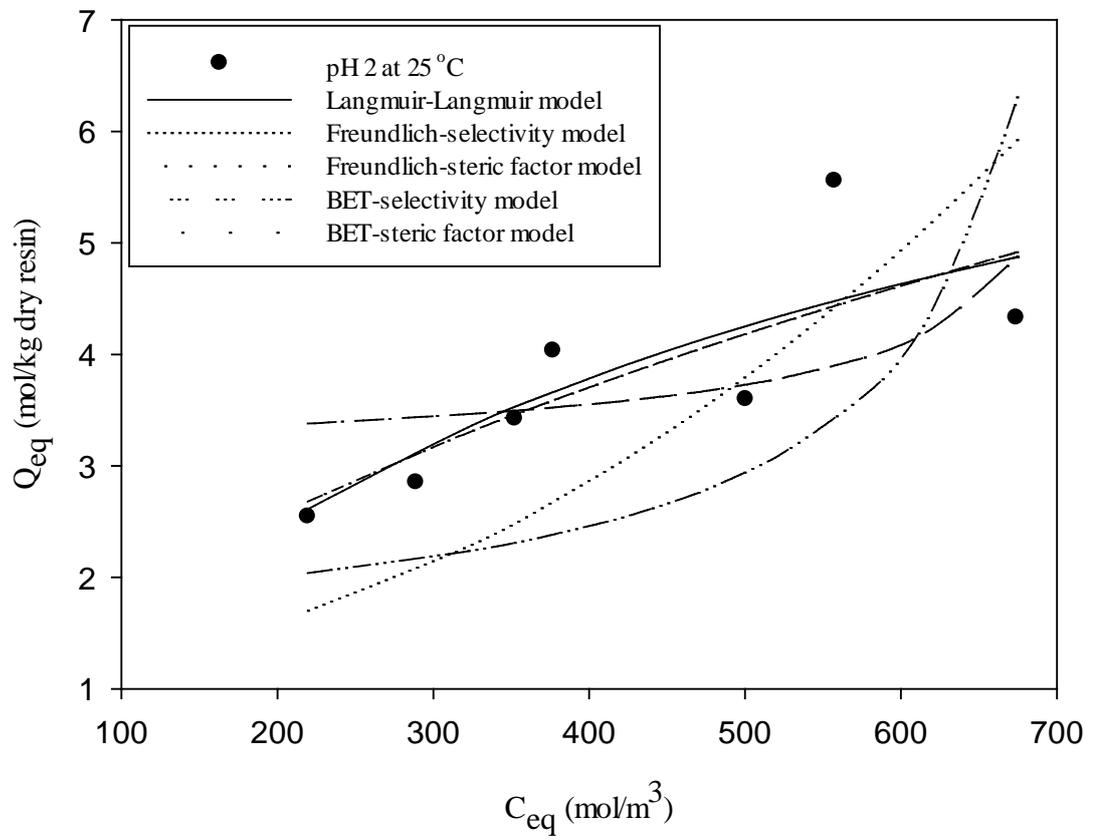
Figure 4.11 The correlated and experimental results at pH 2 and 25 °C.
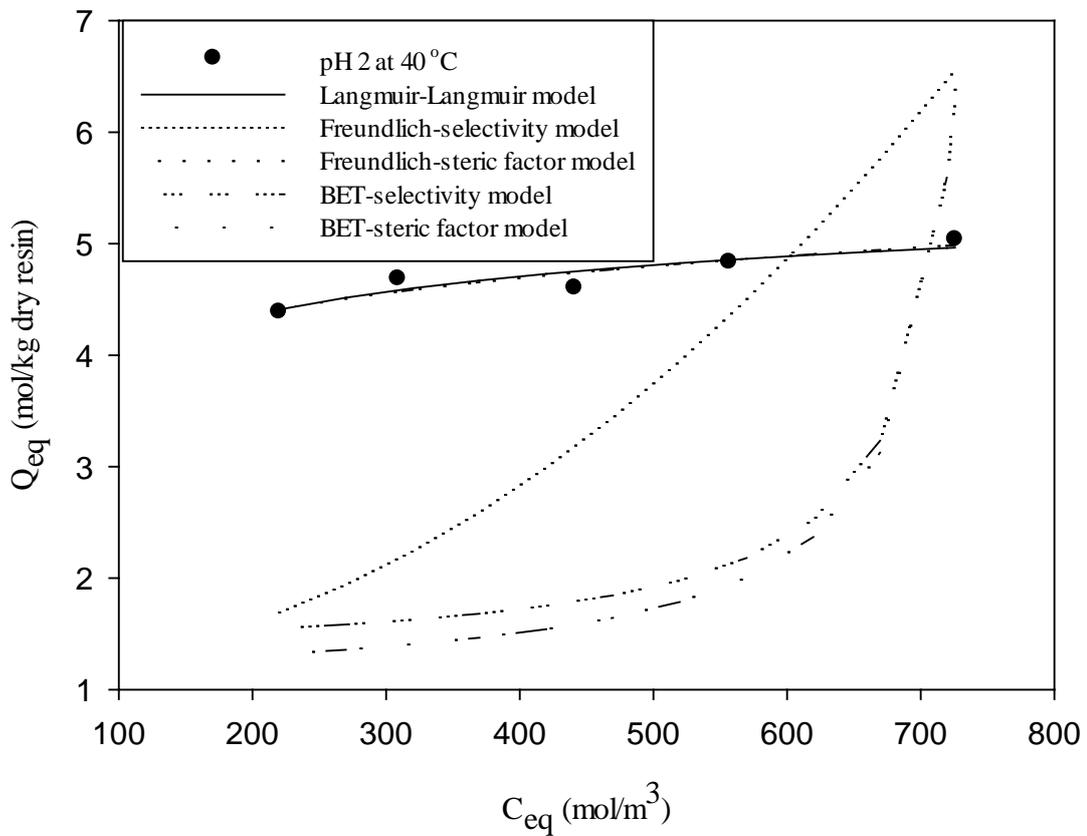
Figure 4.12 The correlated and experimental results at pH 2 and 40 °C.

The comparison of Freundlich-steric factor model which is physical-chemical adsorption model and Langmuir-Langmuir model which is physical-physical adsorption model at pH 2, there are the AAD values in Freundlich-steric factor model that is similar to the AAD values in Langmuir-Langmuir model such as the AAD values of pH 2 at 25 °C for Freundlich-steric factor model and Langmuir-Langmuir model is 0.1088 and 0.1063, respectively, and the AAD values of pH 2 at 40 °C for Freundlich-steric factor model and Langmuir-Langmuir model is 0.0147 and 0.0154, respectively. The values of the parameters obtained by fitting the experimental data are shown in Table 4.4 to Table 4.7.

Table 4.4 The value parameter of Freundlich-selectivity model (Ka constant)

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})			
Freundlich selectivity model	Freundlich	Selectivity coefficient			
Freundlich selectivity model	Temp	X			
pH	Temp	k	n	$S_{Cl^-}^{L^-}$	%AAD
2	25	1.07×10^{-5}	5.00×10^{-1}	1.98×10^{5}	26.33
4	25	1.00×10^{-6}	3.42×10^{-1}	9.70×10^{3}	21.93
5	25	1.00×10^{-6}	2.11×10^{-1}	1.01×10^{3}	15.13
2	40	1.05×10^{-5}	5.00×10^{-1}	3.29×10^{5}	37.29
4	40	1.13×10^{-6}	3.33×10^{-1}	1.69×10^{4}	50.59
5	40	1.01×10^{-6}	2.22×10^{-1}	3.23×10^{4}	13.37

Table 4.5 The value parameter of BET-selectivity model (Ka constant)

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})			
BET selectivity model	BET	Selectivity coefficient			
BET selectivity model	Temp	X			
pH	Temp	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	%AAD
2	25	1.75×10^5	5.97×10^{-1}	2.10×10^5	31.52
2	40	4.30×10^5	2.48×10^{-1}	3.68×10^5	54.54
4	25	2.59×10^{-2}	7.18×10^1	5.91×10^{-6}	10.66
4	40	1.40×10^{-3}	1.51×10^3	1.44×10^5	44.67
5	25	3.00×10^{-3}	7.10×10^2	7.00×10^4	31.78
5	40	2.40×10^{-3}	5.19×10^2	3.51×10^3	17.38

Table 4.6 The value parameter of Freundlich-steric factor model (Ka constant)

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})				
Freundlich steric factor model	Freundlich	The steric mass action				
Freundlich steric factor model	Temp	X				
pH	Temp	k	n	K_{LCl}	Q_{max}^{IE}	%AAD
2	25	1.46×10^{-1}	1.85×10^{0}	2.11×10^{5}	1.00×10^{-6}	10.88
4	25	1.00×10^{-6}	3.35×10^{-1}	4.88×10^{5}	6.85×10^{-4}	14.68
5	25	1.02×10^{-6}	2.09×10^{-1}	4.88×10^{5}	2.82×10^{-1}	9.06
2	40	2.55×10^{0}	9.80×10^{0}	2.11×10^{5}	1.00×10^{-5}	1.47
4	40	1.00×10^{-6}	3.27×10^{-1}	4.88×10^{5}	1.00×10^{-2}	31.99
5	40	1.00×10^{-6}	2.20×10^{-1}	4.88×10^{5}	9.11×10^{-1}	12.48

Table 4.7 The value parameter of BET-steric factor model (Ka constant)

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})				
BET steric factor model	BET	The steric mass action				
BET steric factor model	Temp	X				
pH	Temp	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	%AAD
2	25	1.00×10^6	6.47×10^{-1}	5.00×10^2	1.00×10^0	35.63
4	25	4.98×10^{-2}	3.84×10^1	1.00×10^{-6}	1.00×10^0	10.58
5	25	6.40×10^{-2}	4.69×10^1	1.00×10^{-6}	1.00×10^0	23.30
2	40	1.00×10^6	2.64×10^{-1}	5.00×10^2	1.00×10^0	58.58
4	40	3.57×10^{-2}	7.24×10^1	1.00×10^{-6}	1.00×10^0	26.35
5	40	2.02×10^{-1}	9.87×10^0	9.76×10^{-6}	1.00×10^2	13.36

The effect of temperature dependent on Ka to the each model as can be observed in Figure 4.13 to Figure 4.18, the correlation of adsorption isotherm by Freundlich-steric factor model+(Ka(T)) and BET-steric factor model+(Ka(T)) are similar to the result correlated from the Freundlich-steric factor model and BET-steric factor model. Furthermore, the correlation of adsorption isotherm by Freundlich-selectivity model+(Ka(T)) and BET-selectivity model+(Ka(T)) are similar to the result correlated from the Freundlich- selectivity model and BET- selectivity model. The values of the parameters obtained by fitting the experimental data are shown in Table 4.8 to Table 4.11.
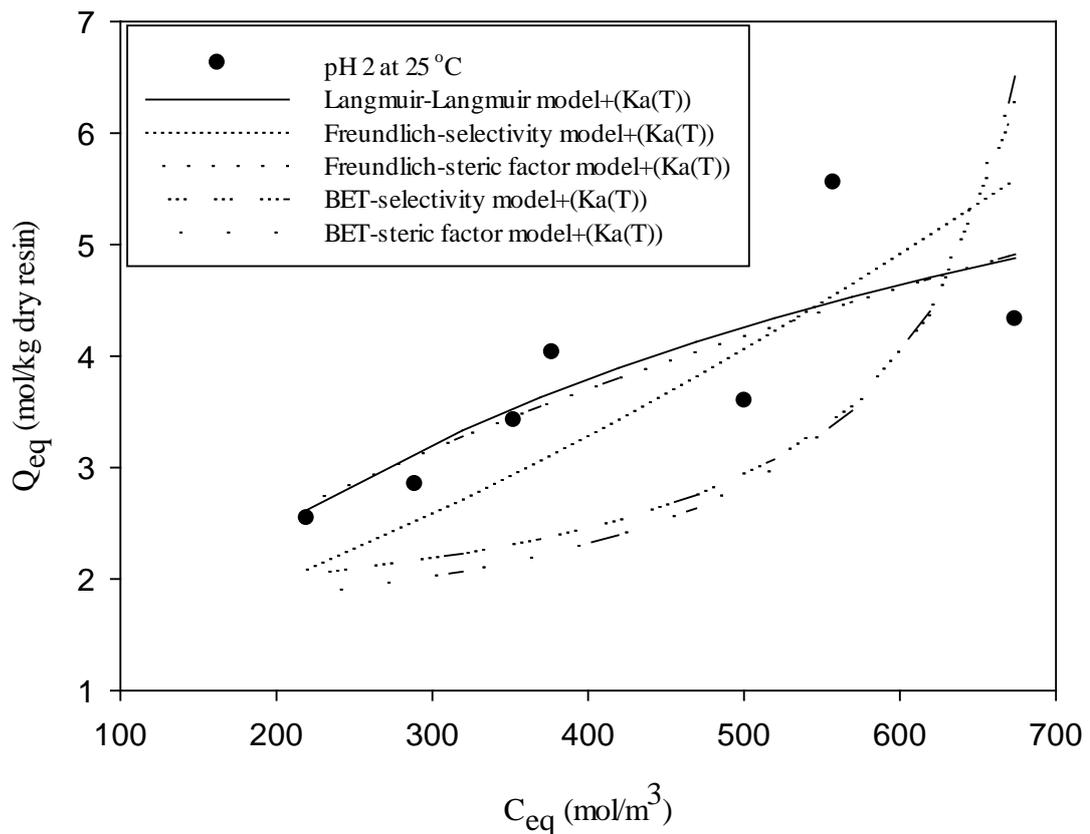
Figure 4.13 The correlated and experimental results at pH 2 and 25 °C.
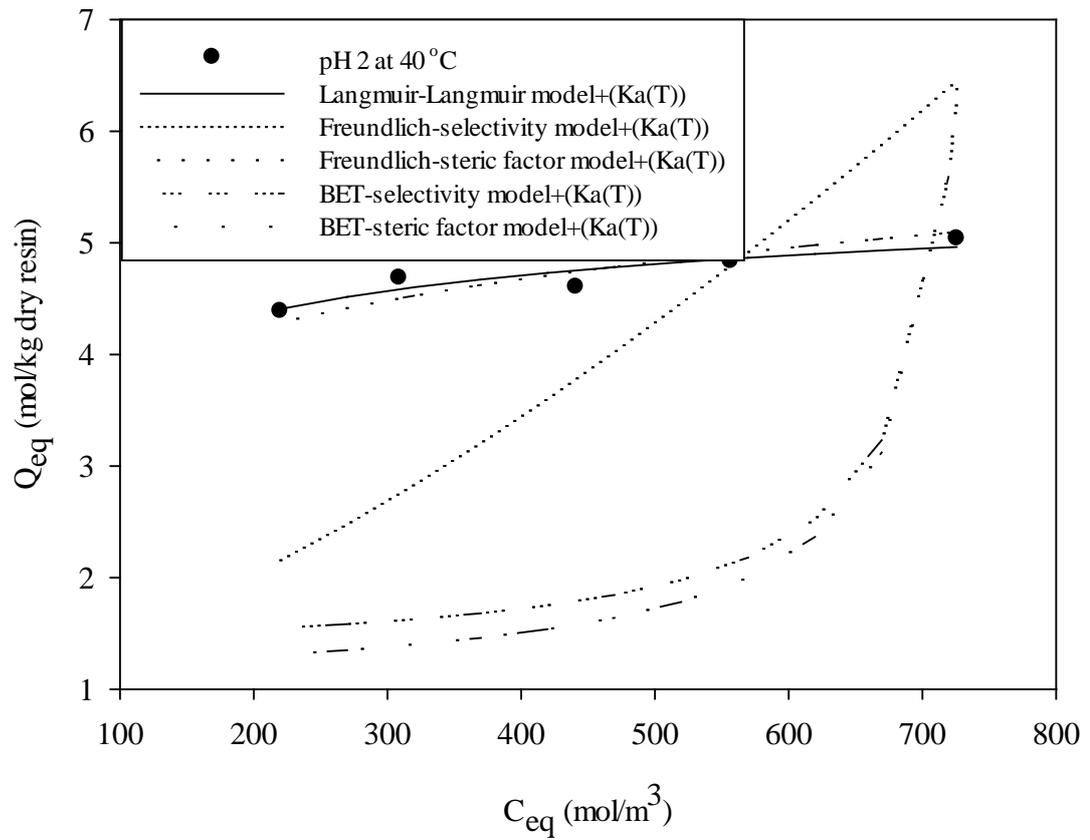
Figure 4.14 The correlated and experimental results at pH 2 and 40 °C.
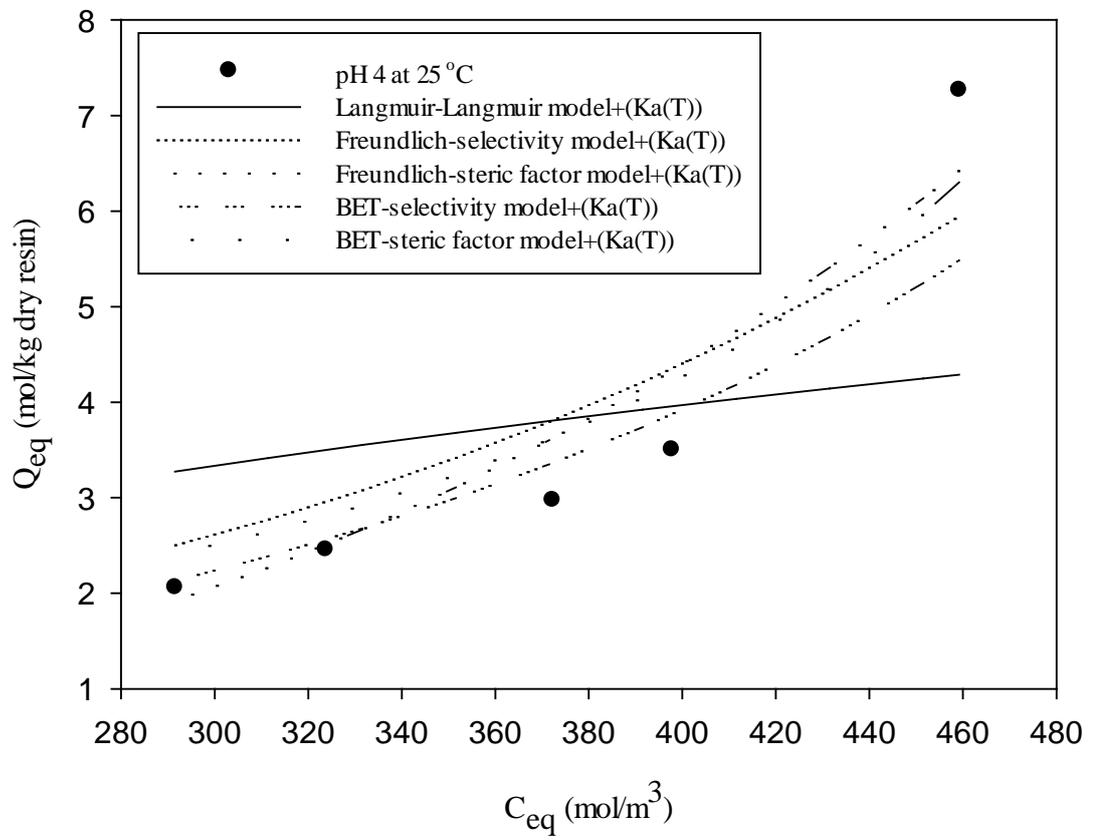
Figure 4.15 The correlated and experimental results at pH 4 and 25 °C .
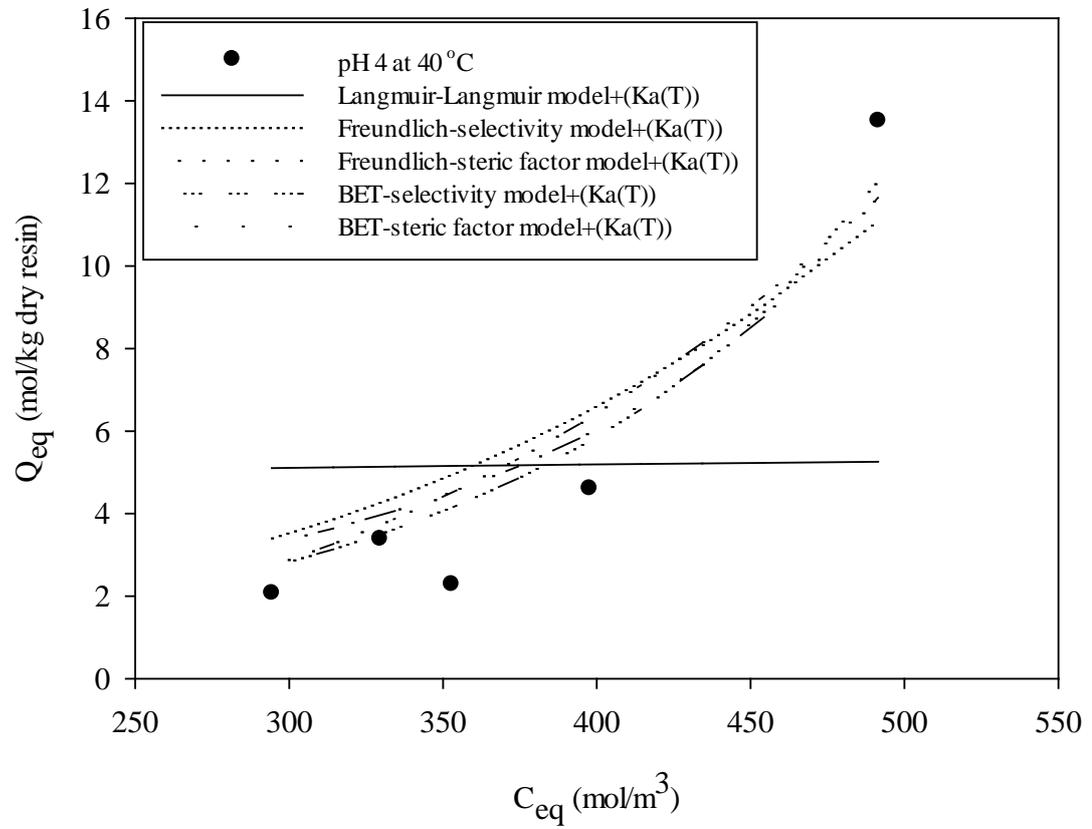
Figure 4.16 The correlated and experimental results at pH 4 and 40 °C.
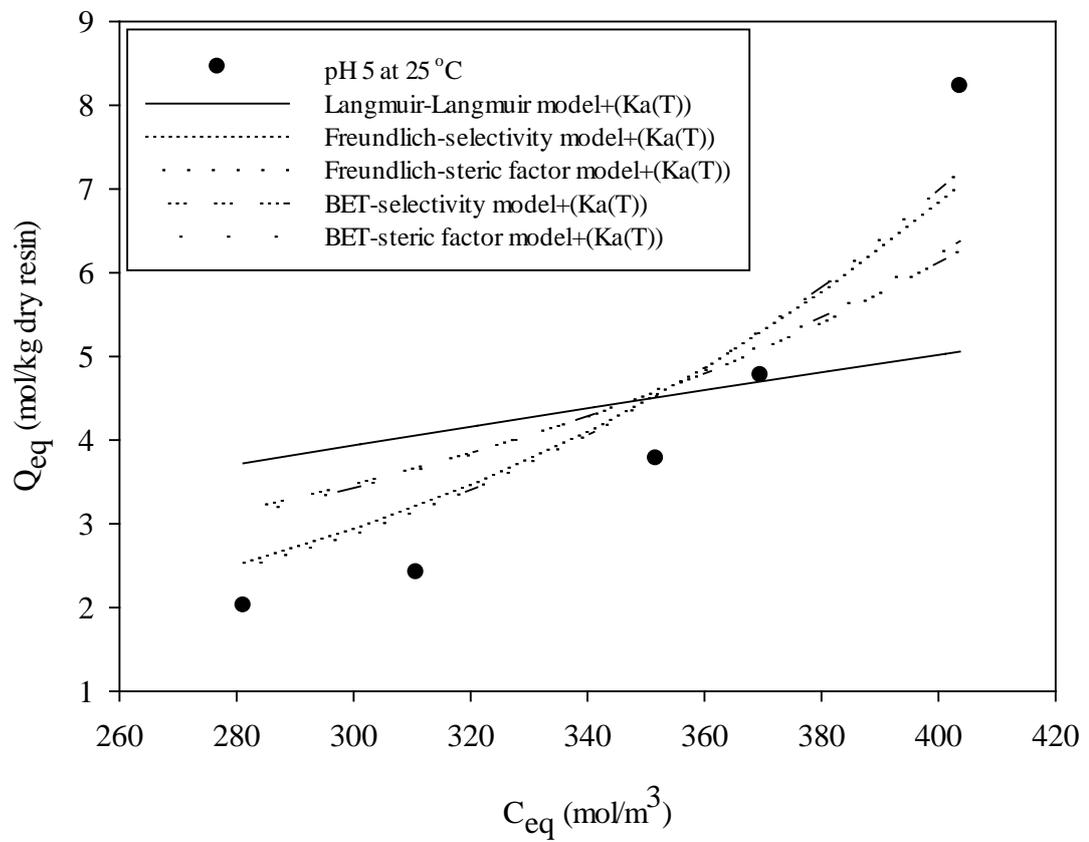
Figure 4.17 The correlated and experimental results at pH 5 and 25 °C.
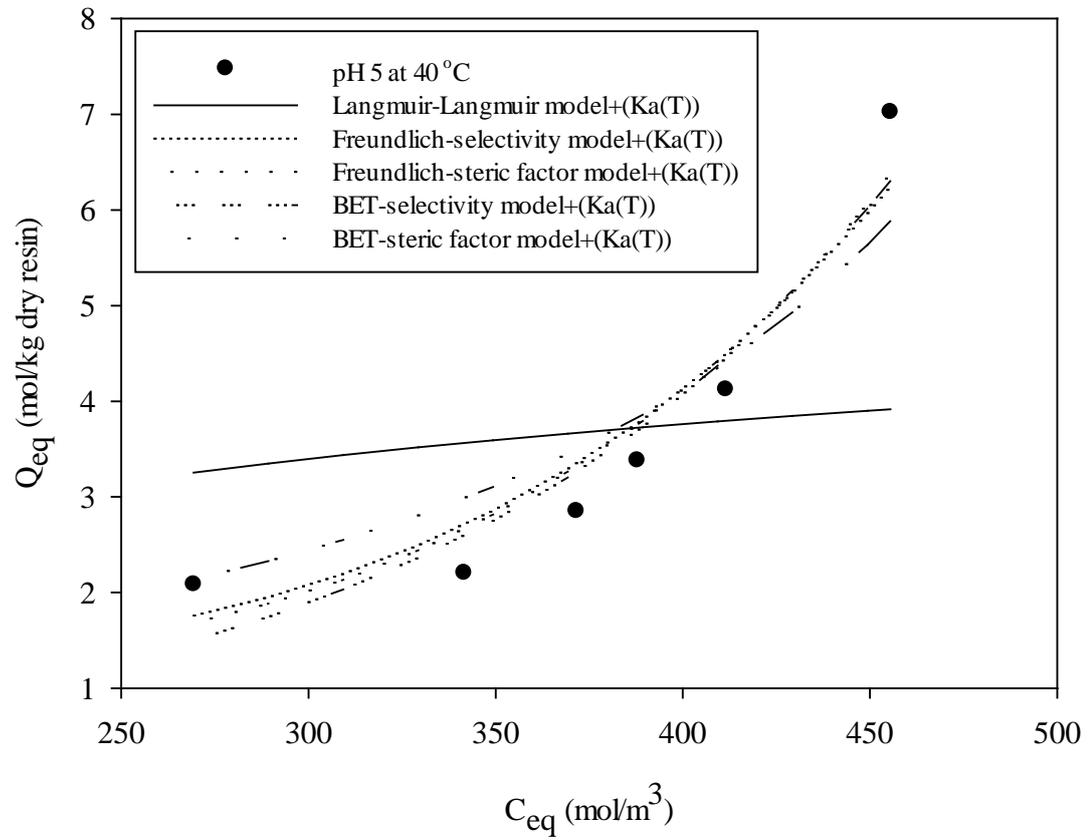
Figure 4.18 The correlated and experimental results at pH 5 and 40 °C .

Table 4.8 The value parameter of Freundlich-selectivity model+(Ka(T))

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})			
Freundlich selectivity model (Ka)	Freundlich	Selectivity coefficient			
Freundlich selectivity model (Ka)	Temp	X			
pH	Temp	k	n	$S_{Cl^-}^{L^-}$	%AAD
2	25	4.06×10^{-4}	7.00×10^{-1}	5.04×10^{5}	18.22
4	25	1.00×10^{-6}	3.51×10^{-1}	4.22×10^{5}	22.31
5	25	3.21×10^{-6}	2.44×10^{-1}	8.25×10^{4}	20.43
2	40	4.37×10^{-4}	7.00×10^{-1}	4.93×10^{5}	27.85
4	40	1.00×10^{-6}	3.40×10^{-1}	4.78×10^{5}	52.74
5	40	1.00×10^{-6}	2.38×10^{-1}	4.12×10^{5}	14.59
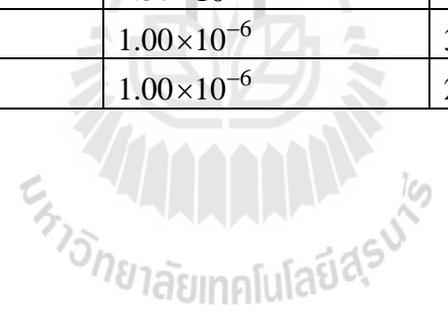
Table 4.9 The value parameter of BET-selectivity model+(Ka(T))

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})			
BET selectivity model (Ka)	BET	Selectivity coefficient			
BET selectivity model (Ka)	Temp	X			
pH	Temp	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	%AAD
2	25	2.26×10^5	5.97×10^{-1}	2.63×10^5	31.52
4	25	7.81×10^{-1}	3.99×10^0	5.58×10^{-4}	12.23
5	25	2.60×10^{-3}	8.19×10^2	1.26×10^5	31.75
2	40	4.37×10^5	2.48×10^{-1}	3.70×10^5	54.54
4	40	1.06×10^{-1}	2.66×10^1	1.00×10^{-6}	30.08
5	40	2.48×10^{-2}	7.26×10^1	1.00×10^{-6}	14.37

Table 4.10 The value parameter of Freundlich-steric factor model+(Ka(T))

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})				
Freundlich steric factor model (Ka)	Freundlich	The streic mass action				
Freundlich steric factor model (Ka)	Temp	X				
pH	Temp	k	n	K_{LCl}	Q_{max}^{IE}	%AAD
2	25	1.46×10^{-1}	1.85×10^{0}	2.11×10^{5}	1.00×10^{-6}	10.88
4	25	1.00×10^{-6}	3.45×10^{-1}	4.88×10^{5}	2.78×10^{-1}	13.11
5	25	1.00×10^{-6}	2.26×10^{-1}	4.88×10^{5}	1.32×10^{0}	18.82
2	40	1.97×10^{0}	6.93×10^{0}	2.11×10^{5}	1.00×10^{-5}	2.33
4	40	1.00×10^{-6}	3.37×10^{-1}	4.88×10^{5}	2.37×10^{-6}	37.74
5	40	1.00×10^{-6}	2.38×10^{-1}	4.88×10^{5}	1.15×10^{0}	14.44
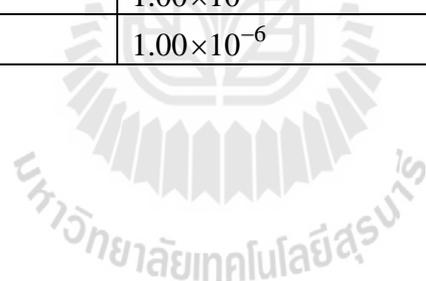
Table 4.11 The value parameter of BET-steric factor model+(Ka(T))

Adsorption	Undissociated acid (Q_{LH})	Dissociated acid (Q_{L^-})				
BET steric factor model (Ka)	BET	The steric mass action				
BET steric factor model (Ka)	Temp	X				
pH	Temp	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	%AAD
2	25	1.00×10^{6}	6.47×10^{-1}	5.00×10^{2}	1.00×10^{0}	35.69
4	25	2.74×10^{-2}	5.34×10^{1}	1.23×10^{5}	1.00×10^{0}	17.07
5	25	3.04×10^{-2}	7.72×10^{1}	1.20×10^{5}	1.00×10^{0}	30.85
2	40	1.00×10^{6}	2.64×10^{-1}	5.00×10^{2}	1.00×10^{0}	58.66
4	40	6.30×10^{-2}	3.71×10^{1}	1.23×10^{5}	1.00×10^{0}	42.85
5	40	4.18×10^{-2}	3.40×10^{1}	1.32×10^{5}	1.00×10^{0}	16.10

As can be observed in Table 4.12, the effect of temperature dependent on Ka to %AAD is very low. Therefore, it is concluded that the dependence of temperature on dissociation constant of lactic acid can be neglected for a correlation of lactic acid adsorption isotherm on ion exchange resin.

Summarizing, the Freundlich-steric factor model is relatively adequate for correlation of adsorption isotherm of lactic acid on Amberlite IRA-96 at all range of pH investigated while Langmuir-Langmuir model is only applicable at pH 2 where the pH is lower than pKa of lactic acid. Furthermore, the resin Amberite IRA-96 could be used to separate lactic acid from liquid phase, due to the high removal capacity observed at high pH, which is higher than the maximum capacity.
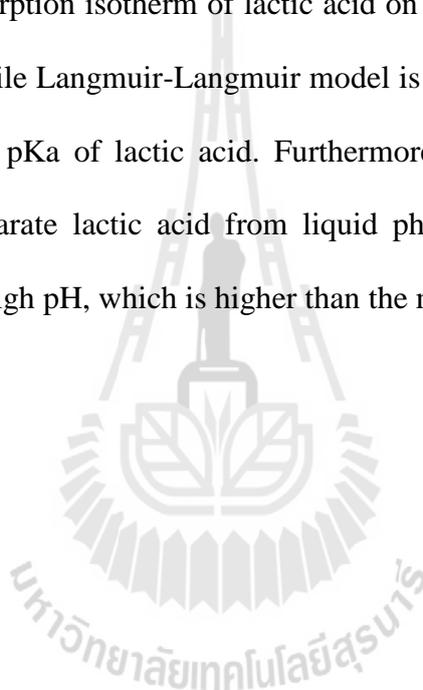
Table 4.12 the percent average absolute deviation (%AAD) of Physical Chemical Adsorption Model

pH	Temp	%AAD of physical Chemical model							
		Freundlich-selectivity model	Freundlich-selectivity model+(Ka(T))	BET-selectivity model	BET-selectivity model+(Ka(T))	Freundlich-steric factor model	Freundlich-steric factor model+(Ka(T))	BET-steric factor model	BET-steric factor model+(Ka(T))
2	25	26.33	18.22	31.52	31.52	10.88	10.88	35.63	35.69
2	40	37.29	27.85	54.54	54.54	1.47	2.33	58.58	58.66
4	25	21.93	22.31	10.66	12.23	14.68	13.11	10.58	17.07
4	40	50.59	52.74	44.67	30.08	31.99	37.74	26.35	42.85
5	25	15.13	20.43	31.78	31.75	9.06	18.82	23.30	30.85
5	40	13.37	14.59	17.38	14.37	12.48	14.44	13.36	16.10

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

In this thesis, the equilibrium adsorption data of lactic acid on ion exchange Amberlite IRA-96 anion exchange resin was investigated and represented in the form of adsorption isotherm. Based on these isotherms, the model for description of complex composition in equilibrium of ion exchange in solution was studied. The effect of pH and temperature of the solution was also considered.

5.1   Adsorption Isotherm

The solid liquid adsorption isotherm is clearly a S curve. The amount of lactic acid adsorbed decreases with increasing temperature. Therefore, the adsorption of lactic acid is an exothermic process. The amount of lactic acid adsorbed at pH 4 and pH 5 is higher than that adsorbed at pH 2. The amount of lactic acid adsorbed clearly depends on temperature. The effect of temperature on the adsorption isotherm is high at pH 5. As a result, the amount of adsorption of lactic acid of pH5 at 25 ˚C is higher than the amount of adsorption of lactic acid of pH5 at 40 ˚C.

5.2   Modeling

The adsorption of lactic acid is higher than the maximum capacity of resin in free form reported in the literature. Both physical and chemical adsorption model is used in modeling due to that the both mechanisms occurred in the process. The model

formulation comprises the non-linear equations. The model is solved and fitted numerically with lsqnonlin in Matlab. The Langmuir- Langmuir model, which is based on physical interaction, is good for correlation adsorption isotherm at pH 2 which is lower than pKa of lactic acid. The Freundlich-steric factor model, which is combining between physical and chemical interaction, is good for correlation adsorption isotherm in pH 2, 4 and 5 which is both lower and higher than pKa of lactic acid.

5.3   Recommendations

In this thesis, the adsorption isotherm of lactic acid was modeled and the lactic acid concentration and the amount of lactic acid adsorption were investigated. The purification by ion exchange is interest to reduce the costs of lactic acid purification. The future research should focus in ion-exchange simulated moving bed.

Although the effect of temperature dependent on Ka is well known, however it has little or no net effect in the model. Therefore, the effect of temperature dependent on Ka would be able to be neglected for further development of the model.

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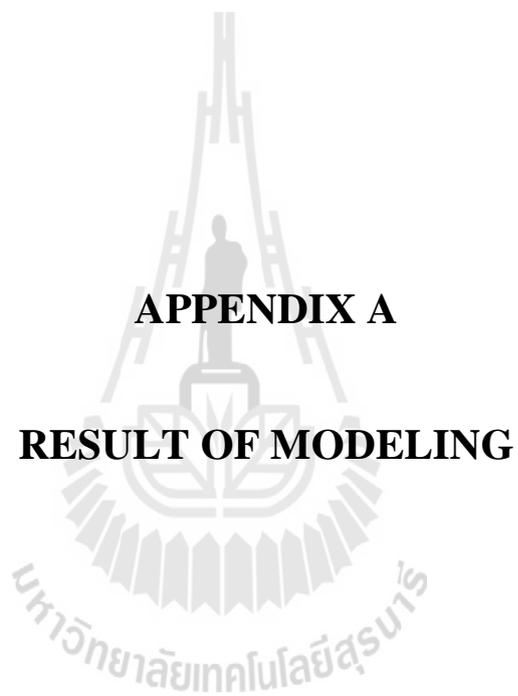
APPENDIX A

RESULT OF MODELING

APPENDIX A1 The value parameter of physical-physical model

APPENDIX A1.1 The value parameter of Langmuir-Langmuir model (Ka constant)

C_T	Q_T	K_{LH}	K_{IE}	Q_{max}^{LH}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	2.10×10^{-3}	1.52×10^{-1}	7.16×10^{0}	0.3722	2.2389	2.6111
288.8003	2.8514				0.4462	2.6820	3.1282
352.1506	3.4260				0.5030	3.0222	3.5252
376.8722	4.0356				0.5229	3.1413	3.6642
500.3136	3.6008				0.6075	3.6465	4.2540
557.2509	5.5584				0.6398	3.8392	4.4789
673.8105	4.3320				0.6960	4.1743	4.8703
pH2Temp40							
219.7472	4.3905	5.83×10^{-2}	3.65×10^{-1}	4.40×10^{0}	0.3289	4.0807	4.4096
308.5428	4.6894				0.4158	4.1679	4.5837
440.9319	4.6085				0.5173	4.2352	4.7524
556.5116	4.8383				0.5866	4.2685	4.8551
725.7144	5.0411				0.6660	4.2986	4.9646
pH4Temp25							
291.5324	2.0638	1.29×10^{-4}	1.20×10^{-3}	1.82×10^{2}	0.2018	2.8447	3.0465
323.7074	2.4600				0.2200	3.1532	3.3732
372.2495	2.9767				0.2462	3.6166	3.8628
397.7235	3.5055				0.2594	3.8588	4.1183
459.1514	7.2709				0.2898	4.4402	4.7301

APPENDIX A1.1 The value parameter of Langmuir-Langmuir model (Ka constant) (Continued)

C_T	Q_T	K_{LH}	K_{IE}	Q_{max}^{LH}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40							
294.3466	2.0731	1.83×10^{-4}	2.6×10^{-3}	1.22×10^2	0.2368	4.2972	4.5340
352.7350	2.2901				0.2731	5.1138	5.3869
329.5165	3.3897				0.2590	4.7904	5.0494
397.6313	4.6129				0.2992	5.7340	6.0332
491.4559	13.5243				0.3493	7.0090	7.3583
pH5Temp25							
281.1475	2.0232	1.20×10^{-3}	3.09×10^{-4}	1.63×10^2	0.0898	3.6640	3.7539
310.6630	2.4204				0.0985	4.0392	4.1377
351.6829	3.7799				0.1103	4.5576	4.6679
369.5635	4.7798				0.1153	4.7826	4.8979
403.6729	8.2309				0.1249	5.2099	5.3348
pH5Temp40							
269.3176	2.0850	5.85×10^{-4}	1.87×10^{-5}	1.01×10^2	0.0050	2.6942	2.6992
341.5866	2.2065				0.0063	3.3928	3.3991
371.5928	2.8530				0.0068	3.6800	3.6868
387.8541	3.3814				0.0071	3.8349	3.8420
411.5258	4.1254				0.0076	4.0595	4.0671
455.4748	7.0256				0.0084	4.4738	4.4822

APPENDIX A1.2 The value parameter of Langmuir- Langmuir model+(Ka(T))

C_T	Q_T	K_{LH}	K_{IE}	Q_{max}^{LH}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	2.10×10^{-3}	1.91×10^{-1}	7.17×10^{0}	0.3712	2.2460	2.6173
288.8003	2.8514				0.4451	2.6900	3.1352
352.1506	3.4260				0.5019	3.0308	3.5327
376.8722	4.0356				0.5218	3.1502	3.6720
500.3136	3.6008				0.6064	3.6561	4.2625
557.2509	5.5584				0.6386	3.8489	4.4876
673.8105	4.3320				0.6949	4.1844	4.8793
pH2Temp40							
219.7472	4.3905	5.95×10^{-2}	5.74×10^{-1}	4.34×10^{0}	0.3734	4.0345	4.4080
308.5428	4.6894				0.4658	4.1190	4.5848
440.9319	4.6085				0.5706	4.1841	4.7547
556.5116	4.8383				0.6404	4.2164	4.8568
725.7144	5.0411				0.7185	4.2455	4.9640
pH4Temp25							
291.5324	2.0638	4.10×10^{-3}	1.70×10^{-3}	8.30×10^{0}	0.2459	3.0274	3.2733
323.7074	2.4600				0.2670	3.2315	3.4985
372.2495	2.9767				0.2971	3.5112	3.8083
397.7235	3.5055				0.3122	3.6459	3.9581
459.1514	7.2709				0.3464	3.9418	4.2882

APPENDIX A1.2 The value parameter of Langmuir- Langmuir model+(Ka(T)) (Continued)

C_T	Q_T	K_{LH}	K_{IE}	Q_{max}^{LH}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40							
294.3466	2.0731	3.46×10^3	9.40×10^{-3}	4.59×10^0	0.5072	4.5921	5.0993
352.7350	2.2901				0.5608	4.5921	5.1529
329.5165	3.3897				0.5405	4.5921	5.1326
397.6313	4.6129				0.5966	4.5921	5.1887
491.4559	13.5243				0.6600	4.5921	5.2521
pH5Temp25							
281.1475	2.0232	5.70×10^{-3}	1.30×10^{-3}	2.87×10^1	0.3009	3.4209	3.7217
310.6630	2.4204				0.3239	3.7332	4.0572
351.6829	3.7799				0.3541	4.1548	4.5088
369.5635	4.7798				0.3666	4.3341	4.7007
403.6729	8.2309				0.3894	4.6690	5.0584
pH5Temp40							
269.3176	2.0850	2.84×10^{-2}	2.70×10^{-3}	4.51×10^0	0.4352	2.8184	3.2535
341.5866	2.2065				0.5030	3.0615	3.5645
371.5928	2.8530				0.5278	3.1431	3.6709
387.8541	3.3814				0.5405	3.1836	3.7241
411.5258	4.1254				0.5581	3.2385	3.7966
455.4748	7.0256				0.5885	3.3292	3.9176

APPENDIX A2 The value parameter of physical-chemical model

APPENDIX A2.1 The value parameter of Freundlich-selectivity model (Ka constant)

C_T	Q_T	k	n	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	1.07×10^{-5}	5.00×10^{-1}	1.98×10^5	1.1999	0.4998	1.6998
288.8003	2.8514				1.2000	0.8660	2.0660
352.1506	3.4260				1.2000	1.2876	2.4876
376.8722	4.0356				1.1999	1.4748	2.6747
500.3136	3.6008				1.2000	2.5991	3.7991
557.2509	5.5584				1.2000	3.2243	4.4243
673.8105	4.3320				1.2000	4.7143	5.9142
pH2Temp40							
219.7472	4.3905	1.05×10^{-5}	5.00×10^{-1}	3.29×10^5	1.1999	0.4913	1.6913
308.5428	4.6894				1.2000	0.9687	2.1686
440.9319	4.6085				1.2000	1.9783	3.1782
556.5116	4.8383				1.2000	3.1513	4.3513
725.7144	5.0411				1.2000	5.3589	6.5588
pH4Temp25							
291.5324	2.0638	1.00×10^{-6}	3.42×10^{-1}	9.70×10^3	1.2000	1.2799	2.4799
323.7074	2.4600				1.2000	1.7384	2.9384
372.2495	2.9767				1.2000	2.6159	3.8159

APPENDIX A2.1 The value parameter of Freundlich-selectivity model (Ka constant) (Continued)

C_T	Q_T	k	n	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp25							
397.7235	3.5055				1.2000	3.1747	4.3747
459.1514	7.2709				1.2000	4.8322	6.0322
pH4Temp40							
294.3466	2.0731	1.13×10^{-6}	3.34×10^{-1}	1.69×10^{4}	1.2000	2.1227	3.3227
352.7350	2.2901				1.2000	3.6526	4.8526
329.5165	3.3897				1.2000	2.9779	4.1779
397.6313	4.6129				1.2000	5.2320	6.4320
491.4559	13.5243				1.2000	9.8770	11.0769
pH5Temp25							
281.1475	2.0232	1.00×10^{-6}	2.11×10^{-1}	1.01×10^{3}	1.1999	1.1170	2.3169
310.6630	2.4204				1.1999	1.7912	2.9911
351.6829	3.7799				1.1999	3.2206	4.4204
369.5635	4.7798				1.1998	4.0721	5.2719
403.6729	8.2309				1.1997	6.1827	7.3824
pH5Temp40							
269.3176	2.0850	1.01×10^{-6}	2.22×10^{-1}	3.23×10^{4}	1.2000	0.4858	1.6858
341.5866	2.2065				1.2000	1.4186	2.6186
371.5928	2.8530				1.2000	2.0736	3.2736
387.8541	3.3814				1.2000	2.5153	3.7153
411.5258	4.1254				1.2000	3.2855	4.4854
455.4748	7.0256				1.2000	5.1913	6.3913

APPENDIX A2.2 The value parameter of Freundlich-selectivity model+(Ka(T))

C_T	Q_T	k	n	$S^{L^-}_{Cl^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	4.06×10^{-4}	7.00×10^{-1}	5.04×10^{5}	1.2000	0.8836	2.0835
288.8003	2.8514				1.2000	1.3084	2.5084
352.1506	3.4260				1.2000	1.7369	2.9369
376.8722	4.0356				1.2000	1.9137	3.1137
500.3136	3.6008				1.2000	2.8685	4.0685
557.2509	5.5584				1.2000	3.3460	4.5460
673.8105	4.3320				1.2000	4.3890	5.5890
pH2Temp40							
219.7472	4.3905	4.37×10^{-4}	7.00×10^{-1}	4.93×10^{5}	1.1999	0.9536	2.1535
308.5428	4.6894				1.2000	1.5485	2.7485
440.9319	4.6085				1.2000	2.5789	3.7788
556.5116	4.8383				1.2000	3.5963	4.7963
725.7144	5.0411				1.2000	5.2549	6.4549
pH4Temp25							
291.5324	2.0638	1.00×10^{-6}	3.51×10^{-1}	4.22×10^{5}	1.2000	1.3005	2.5005
323.7074	2.4600				1.2000	1.7527	2.9527
372.2495	2.9767				1.2000	2.6102	3.8102
397.7235	3.5055				1.2000	3.1523	4.3523
459.1514	7.2709				1.2000	4.7472	5.9472

APPENDIX A2.2 The value parameter of Freundlich-selectivity model+(Ka(T)) (Continued)

C_T	Q_T	k	n	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40							
294.3466	2.0731	1.00×10^{-6}	3.40×10^{-1}	4.78×10^{5}	1.2000	2.1930	3.3930
352.7350	2.2901				1.2000	3.7329	4.9329
329.5165	3.3897				1.2000	3.0558	4.2558
397.6313	4.6129				1.2000	5.3088	6.5088
491.4559	13.5243				1.2000	9.8955	11.0955
pH5Temp25							
281.1475	2.0232	3.21×10^{-6}	2.44×10^{-1}	8.25×10^{4}	1.2000	1.3322	2.5322
310.6630	2.4204				1.2000	2.0046	3.2046
351.6829	3.7799				1.2000	3.3305	4.5305
369.5635	4.7798				1.2000	4.0801	5.2801
403.6729	8.2309				1.2000	5.8561	7.0561
pH5Temp40							
269.3176	2.0850	1.00×10^{-4}	2.38×10^{-1}	4.12×10^{5}	1.2000	0.5569	1.7569
341.5866	2.2065				1.2000	1.5095	2.7095
371.5928	2.8530				1.2000	2.1489	3.3489
387.8541	3.3814				1.2000	2.5718	3.7718
411.5258	4.1254				1.2000	3.2973	4.4973
455.4748	7.0256				1.2000	5.0466	6.2466

APPENDIX A2.3 The value parameter of BET-selectivity model (Ka constant)

C_T	Q_T	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	1.75×10^5	5.97×10^{-1}	2.10×10^5	1.1999	0.8383	2.0383
288.8003	2.8514				1.2000	0.9611	2.1610
352.1506	3.4260				1.2000	1.1094	2.3093
376.8722	4.0356				1.2000	1.1804	2.3804
500.3136	3.6008				1.2000	1.7356	2.9356
557.2509	5.5584				1.2000	2.2165	3.4164
673.8105	4.3320				1.2000	5.1206	6.3206
pH2Temp40							
219.7472	4.3905	4.30×10^5	2.48×10^{-1}	3.68×10^5	1.1999	0.3479	1.5479
308.5428	4.6894				1.2000	0.4160	1.6159
440.9319	4.6085				1.2000	0.5871	1.7870
556.5116	4.8383				1.2000	0.9160	2.1160
725.7144	5.0411				1.2000	5.0988	6.2988
pH4Temp25							
291.5324	2.0638	1.46×10^{-1}	1.85×10^0	2.50×10^{-3}	0.1551	0.2474	0.4024
323.7074	2.4600				0.1500	0.3115	0.4615
372.2495	2.9767				0.1465	0.4402	0.5867
397.7235	3.5055				0.1400	0.5291	0.6690
459.1514	7.2709				0.1061	0.8383	0.9444

APPENDIX A2.3 The value parameter of BET-selectivity model (Ka constant) (Continued)

C_T	Q_T	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40							
294.3466	2.0731	1.46×10^{-1}	1.85×10^{0}	3.30×10^{-3}	0.1767	0.2526	0.4293
352.7350	2.2901				0.1835	0.3832	0.5667
329.5165	3.3897				0.1483	0.3248	0.4731
397.6313	4.6129				0.1402	0.5290	0.6692
491.4559	13.5243				0.0930	1.0855	1.1785
pH5Temp25							
281.1475	2.0232	1.46×10^{-1}	1.85×10^{0}	2.50×10^{-3}	0.1916	0.2293	0.4209
310.6630	2.4204				0.1847	0.2836	0.4684
351.6829	3.7799				0.1593	0.3798	0.5391
369.5635	4.7798				0.1461	0.4316	0.5777
403.6729	8.2309				0.1179	0.5522	0.6701
pH5Temp40							
269.3176	2.0850	1.46×10^{-1}	1.85×10^{0}	2.20×10^{-3}	0.1747	0.2103	0.3850
341.5866	2.2065				0.1899	0.3535	0.5434
371.5928	2.8530				0.1754	0.4379	0.6133
387.8541	3.3814				0.1654	0.4922	0.6576
411.5258	4.1254				0.1550	0.5849	0.7399
455.4748	7.0256				0.1266	0.8143	0.9409

APPENDIX A2.4 The value parameter of BET-selectivity model+(Ka(T))

C_T	Q_T	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25							
219.4046	2.5452	2.26×10^5	5.97×10^{-1}	2.63×10^5	1.1999	0.8383	2.0383
288.8003	2.8514				1.2000	0.9611	2.1610
352.1506	3.4260				1.2000	1.1094	2.3093
376.8722	4.0356				1.2000	1.1804	2.3804
500.3136	3.6008				1.2000	1.7356	2.9356
557.2509	5.5584				1.2000	2.2165	3.4164
673.8105	4.3320				1.2000	5.1206	6.3206
pH2Temp40							
219.7472	4.3905	4.37×10^5	2.48×10^{-1}	3.70×10^5	1.1999	0.3479	1.5479
308.5428	4.6894				1.1999	0.4160	1.6159
440.9319	4.6085				1.2000	0.5871	1.7870
556.5116	4.8383				1.2000	0.9160	2.1160
725.7144	5.0411				1.2000	5.0988	6.2987
pH4Temp25							
291.5324	2.0638	7.81×10^{-1}	3.99×10^0	5.58×10^{-4}	0.0722	2.1040	2.1762
323.7074	2.4600				0.0698	2.5330	2.6027
372.2495	2.9767				0.0681	3.3260	3.3941
397.7235	3.5055				0.0649	3.8331	3.8980
459.1514	7.2709				0.0488	5.4286	5.4774

APPENDIX A2.4 The value parameter of BET-selectivity model+(Ka(T)) (Continued)

C_T	Q_T	C	Q_{max}^{LH}	$S_{Cl^-}^{L^-}$	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40							
294.3466	2.0731	1.06×10^{-1}	26.64×10^{0}	1.00×10^{-6}	0.0031	2.7066	2.7098
352.7350	2.2901				0.0033	4.1378	4.1410
329.5165	3.3897				0.0026	3.4960	3.4986
397.6313	4.6129				0.0024	5.7543	5.7567
491.4559	13.5243				0.0016	12.0546	12.0562
pH5Temp25							
281.1475	2.0232	2.60×10^{-3}	818.89×10^{0}	1.26×10^{5}	1.2000	1.9654	3.1654
310.6630	2.4204				1.2000	2.4639	3.6639
351.6829	3.7799				1.2000	3.3722	4.5722
369.5635	4.7798				1.2000	3.8724	5.0724
403.6729	8.2309				1.2000	5.0691	6.2691
pH5Temp40							
269.3176	2.0850	2.48×10^{-2}	72.57×10^{0}	1.00×10^{-6}	0.0040	1.4982	1.5021
341.5866	2.2065				0.0044	2.5914	2.5958
371.5928	2.8530				0.0040	3.2571	3.2611
387.8541	3.3814				0.0038	3.6934	3.6971
411.5258	4.1254				0.0035	4.4500	4.4535
455.4748	7.0256				0.0028	6.3870	6.3899

APPENDIX A2.5 The value parameter of Freundlich-steric factor model (Ka constant)

C_T	Q_T	k	n	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	QTcal
pH2Temp25								
219.4046	2.5452	1.46×10^{-1}	1.85×10^{0}	2.11×10^{5}	1.00×10^{-6}	9.68×10^{-7}	2.6787	2.6787
288.8003	2.8514					9.68×10^{-7}	3.1081	3.1081
352.1506	3.4260					9.68×10^{-7}	3.4600	3.4600
376.8722	4.0356					9.68×10^{-7}	3.5894	3.5894
500.3136	3.6008					9.68×10^{-7}	4.1839	4.1839
557.2509	5.5584					9.68×10^{-7}	4.4351	4.4351
673.8105	4.3320					9.68×10^{-7}	4.9150	4.9150
pH2Temp40								
219.7472	4.3905	2.55×10^{0}	9.80×10^{0}	2.11×10^{5}	1.00×10^{-5}	9.68×10^{-6}	4.4151	4.4151
308.5428	4.6894					9.68×10^{-6}	4.5707	4.5707
440.9319	4.6085					9.68×10^{-6}	4.7402	4.7402
556.5116	4.8383					9.68×10^{-6}	4.8541	4.8541
725.7144	5.0411					9.68×10^{-6}	4.9873	4.9873
pH4Temp25								
291.5324	2.0638	1.00×10^{-6}	3.35×10^{-1}	4.88×10^{5}	6.85×10^{-4}	6.63×10^{-4}	1.7011	1.7017
323.7074	2.4600					6.63×10^{-4}	2.3248	2.3255
372.2495	2.9767					6.63×10^{-4}	3.5275	3.5282
397.7235	3.5055					6.63×10^{-4}	4.2978	4.2985

APPENDIX A2.5 The value parameter of Freundlich-steric factor model (Ka constant) (Continued)

C_T	Q_T	k	n	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	QTcal
459.1514	7.2709					$6.63{\times}10^{-4}$	6.5974	6.5981
pH4Temp40								
294.3466	2.0731	$1.00{\times}10^{-6}$	$3.27{\times}10^{-1}$	$4.80{\times}10^{5}$	$1.00{\times}10^{-2}$	$9.68{\times}10^{-3}$	2.4824	2.4921
352.7350	2.2901					$9.68{\times}10^{-3}$	4.3161	4.3257
329.5165	3.3897					$9.68{\times}10^{-3}$	3.5051	3.5148
397.6313	4.6129					$9.68{\times}10^{-3}$	6.2248	6.2345
491.4559	13.5243					$9.68{\times}10^{-3}$	11.8942	11.9039
pH5Temp25								
281.1475	2.0232	$1.01{\times}10^{-6}$	$2.09{\times}10^{-1}$	$4.80{\times}10^{5}$	$2.86{\times}10^{-1}$	$2.77{\times}10^{-1}$	1.3335	1.6104
310.6630	2.4204					$2.77{\times}10^{-1}$	2.1506	2.4275
351.6829	3.7799					$2.77{\times}10^{-1}$	3.8942	4.1711
369.5635	4.7798					$2.77{\times}10^{-1}$	4.9378	5.2147
403.6729	8.2309					$2.77{\times}10^{-1}$	7.5351	7.8120
pH5Temp40								
269.3176	2.0850	$1.00{\times}10^{-6}$	$2.20{\times}10^{-1}$	$4.88{\times}10^{5}$	$9.11{\times}10^{-1}$	$8.81{\times}10^{-1}$	0.5248	1.4059
341.5866	2.2065					$8.81{\times}10^{-1}$	1.5442	2.4253
371.5928	2.8530					$8.81{\times}10^{-1}$	2.2632	3.1443
387.8541	3.3814					$8.81{\times}10^{-1}$	2.7490	3.6301
411.5258	4.1254					$8.81{\times}10^{-1}$	3.5974	4.4785
455.4748	7.0256					$8.81{\times}10^{-1}$	5.7024	6.5835

APPENDIX A2.6 The value parameter of Freundlich-steric factor model+(Ka(T)) (Ka(T))

C_T	Q_T	k	n	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	QTcal
pH2Temp25								
219.4046	2.5452	1.46×10^{-1}	1.85×10^{0}	2.11×10^{5}	1.00×10^{-6}	9.68×10^{-7}	2.6784	2.6784
288.8003	2.8514					9.68×10^{-7}	3.1078	3.1078
352.1506	3.4260					9.68×10^{-7}	3.4598	3.4598
376.8722	4.0356					9.68×10^{-7}	3.5892	3.5892
500.3136	3.6008					9.68×10^{-7}	4.1838	4.1838
557.2509	5.5584					9.68×10^{-7}	4.4350	4.4350
673.8105	4.3320					9.68×10^{-7}	4.9150	4.9150
pH2Temp40								
219.7472	4.3905	1.97×10^{0}	6.93×10^{0}	2.11×10^{5}	1.00×10^{-5}	9.68×10^{-6}	4.2899	4.2899
308.5428	4.6894					9.68×10^{-6}	4.5054	4.5054
440.9319	4.6085					9.68×10^{-6}	4.7438	4.7438
556.5116	4.8383					9.68×10^{-6}	4.9059	4.9059
725.7144	5.0411					9.68×10^{-6}	5.0976	5.0976
pH4Temp25								
291.5324	2.0638	1.00×10^{-6}	3.45×10^{-1}	4.88×10^{5}	2.78×10^{-1}	2.69×10^{-1}	1.6496	1.9188
323.7074	2.4600					2.69×10^{-1}	2.2347	2.5039
372.2495	2.9767					2.69×10^{-1}	3.3510	3.6202
397.7235	3.5055					2.69×10^{-1}	4.0601	4.3293

APPENDIX A2.6 The value parameter of Freundlich-steric factor model+(Ka(T)) (Ka(T)) (Continued)

C_T	Q_T	k	n	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	QTcal
459.1514	7.2709					2.69×10^{-1}	6.1575	6.4267
pH4Temp40								
294.3466	2.0731	1.00×10^{-6}	3.37×10^{-1}	4.88E+05	2.37×10^{-1}	2.29×10^{-1}	2.4972	2.7267
352.7350	2.2901					2.29×10^{-1}	4.2709	4.5004
329.5165	3.3897					2.29×10^{-1}	3.4900	3.7194
397.6313	4.6129					2.29×10^{-1}	6.0929	6.3224
491.4559	13.5243					2.29×10^{-1}	11.4202	11.6496
pH5Temp25								
281.1475	2.0232	1.00×10^{-6}	2.26×10^{-1}	4.88×10^5	1.32×10^0	1.27×10^0	1.1990	2.4722
310.6630	2.4204					1.27×10^0	1.8656	3.1388
351.6829	3.7799					1.27×10^0	3.2311	4.5043
369.5635	4.7798					1.27×10^0	4.0246	5.2978
403.6729	8.2309					1.27×10^0	5.9500	7.2232
pH5Temp40								
269.3176	2.0850	1.00×10^{-6}	2.38×10^{-1}	4.88×10^5	1.15×10^0	1.11×10^0	0.5705	1.6833
341.5866	2.2065					1.11×10^0	1.5488	2.6616
371.5928	2.8530					1.11×10^0	2.2061	3.3189
387.8541	3.3814					1.11×10^0	2.6411	3.7539
411.5258	4.1254					1.11×10^0	3.3876	4.5004
455.4748	7.0256					1.11×10^0	5.1886	6.3014

APPENDIX A2.7 The value parameter of BET-steric factor model (Ka constant)

C_T	Q_T	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25								
219.4046	2.5452	1.00×10^6	6.47×10^{-1}	5.00×10^2	1.00×10^0	0.9539	0.9082	1.8621
288.8003	2.8514					0.9559	1.0412	1.9971
352.1506	3.4260					0.9560	1.2019	2.1579
376.8722	4.0356					0.9549	1.2789	2.2338
500.3136	3.6008					0.9590	1.8804	2.8394
557.2509	5.5584					0.9557	2.4013	3.3570
673.8105	4.3320					0.9599	5.5476	6.5075
pH2Temp40								
219.7472	4.3905	1.00×10^6	2.64×10^{-1}	5.00×10^2	1.00×10^0	0.9444	0.3708	1.3152
308.5428	4.6894					0.9497	0.4433	1.3931
440.9319	4.6085					0.9552	0.6257	1.5809
556.5116	4.8383					0.9572	0.9763	1.9335
725.7144	5.0411					0.9593	5.4343	6.3936
pH4Temp25								
291.5324	2.0638	4.98×10^{-2}	3.84×10^1	1.00×10^{-6}	1.00×10^0	0.0030	1.8570	1.8599
323.7074	2.4600					0.0029	2.3616	2.3645
372.2495	2.9767					0.0028	3.3976	3.4004
397.7235	3.5055					0.0027	4.1277	4.1304
459.1514	7.2709					0.0020	6.7536	6.7556

APPENDIX A2.7 The value parameter of BET-steric factor model (Ka constant) (Continued)

C_T	Q_T	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH4Temp40								
294.3466	2.0731	3.57×10^{-2}	7.24×10^1	1.00×10^{-6}	1.00×10^0	0.0030	2.5823	2.5853
352.7350	2.2901					0.0031	4.0063	4.0094
329.5165	3.3897					0.0025	3.3638	3.3663
397.6313	4.6129					0.0023	5.6504	5.6527
491.4559	13.5243					0.0015	12.3428	12.3443
pH5Temp25								
281.1475	2.0232	6.40×10^{-2}	4.69×10^1	1.00×10^{-6}	1.00×10^0	0.0037	2.6740	2.6778
310.6630	2.4204					0.0036	3.3319	3.3355
351.6829	3.7799					0.0031	4.5155	4.5186
369.5635	4.7798					0.0028	5.1600	5.1628
403.6729	8.2309					0.0022	6.6835	6.6857
pH5Temp40								
269.3176	2.0850	2.02×10^{-1}	9.87×10^0	9.76×10^{-6}	1.00×10^2	0.1130	1.5143	1.6273
341.5866	2.2065					0.1237	2.5151	2.6388
371.5928	2.8530					0.1135	3.0972	3.2107
387.8541	3.3814					0.1065	3.4696	3.5761
411.5258	4.1254					0.0993	4.1004	4.1997
455.4748	7.0256					0.0801	5.6431	5.7232

APPENDIX A2.8 The value parameter of BET-steric factor model+(Ka(T))

C_T	Q_T	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	Q_{Tcal}
pH2Temp25								
219.4046	2.5452	1.00×10^6	6.47×10^{-1}	5.00×10^2	1.00×10^0	0.9504	0.9087	1.8591
288.8003	2.8514					0.9529	1.0418	1.9947
352.1506	3.4260					0.9531	1.2025	2.1556
376.8722	4.0356					0.9517	1.2795	2.2312
500.3136	3.6008					0.9568	1.8813	2.8381
557.2509	5.5584					0.9527	2.4026	3.3553
673.8105	4.3320					0.9579	5.5505	6.5084
pH2Temp40								
219.7472	4.3905	1.00×10^6	2.64×10^{-1}	5.00×10^2	1.00×10^0	0.9375	0.3709	1.3085
308.5428	4.6894					0.9444	0.4434	1.3878
440.9319	4.6085					0.9514	0.6258	1.5772
556.5116	4.8383					0.9541	0.9765	1.9306
725.7144	5.0411					0.9568	5.4353	6.3921
pH4Temp25								
291.5324	2.0638	2.74×10^{-2}	5.34×10^1	1.23×10^5	1.00×10^0	0.9676	1.4398	2.4074
323.7074	2.4600					0.9676	1.8357	2.8033
372.2495	2.9767					0.9676	2.6530	3.6206
397.7235	3.5055					0.9676	3.2321	4.1998
459.1514	7.2709					0.9676	5.3340	6.3016
pH4Temp40								
294.3466	2.0731	6.30×10^{-2}	3.71×10^1	1.23×10^5	1.00×10^0	0.9676	2.3009	3.2685

APPENDIX A2.8 The value parameter of BET-steric factor model+(Ka(T)) (Continued)

C_T	Q_T	C	Q_{max}^{LH}	K_{LCl}	Q_{max}^{IE}	Q_{L^-}	Q_{LH}	Q_{Tcal}
352.7350	2.2901					0.9676	3.5487	4.5163
pH4Temp40								
329.5165	3.3897					0.9676	2.9871	3.9547
397.6313	4.6129					0.9676	4.9766	5.9442
491.4559	13.5243					0.9676	10.6857	11.6533
pH5Temp25								
281.1475	2.0232	3.04×10^{-2}	7.72×10^{1}	1.20×10^{5}	1.00×10^{0}	0.9676	2.1294	3.0971
310.6630	2.4204					0.9676	2.6620	3.6297
351.6829	3.7799					0.9676	3.6268	4.5944
369.5635	4.7798					0.9676	4.1553	5.1229
403.6729	8.2309					0.9676	5.4125	6.3802
pH5Temp40								
269.3176	2.0850	4.18×10^{-2}	3.40×10^{1}	1.32×10^{5}	1.00×10^{0}	0.9676	1.1701	2.1378
341.5866	2.2065					0.9676	2.0153	2.9830
371.5928	2.8530					0.9676	2.5274	3.4950
387.8541	3.3814					0.9676	2.8621	3.8297
411.5258	4.1254					0.9676	3.4410	4.4086
455.4748	7.0256					0.9676	4.9150	5.8826
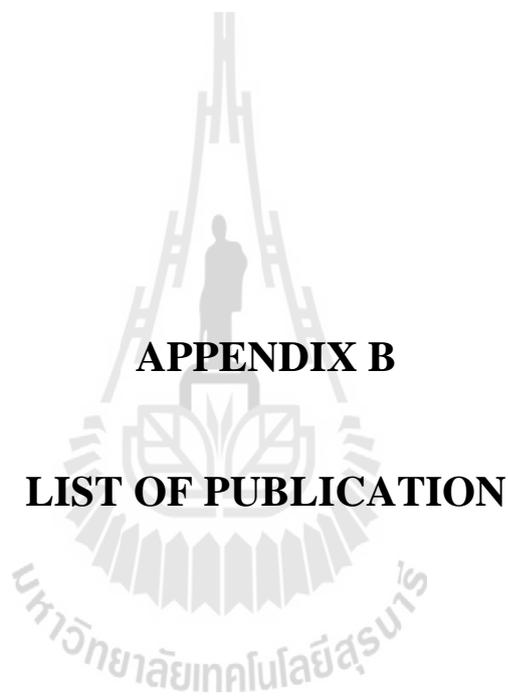
APPENDIX B

LIST OF PUBLICATION

List of Publication

Sodsai, W. and Sookkumnerd, T. (2013). Modeling of Lactic Acid Adsorption

    Isotherm by Anion Exchange Resin Amberlite IRA-96. **KMITL Science and**

    Technology Journal. 13(2): 82-86.

BIOGRAPHY

Miss Wanwisa Sodsai was born on Tuesday the 19th of April 1987, in Nimueng Sub-District, Mueng District, Nakhonratchasima Province of Thailand. She started her primary education at Marie Vithaya School, Nakhonratchasima Province of Thailand in 1994 where she completed her primary education 1999. Between 2000-2005, she studied at Suranaree Wittaya 2 High school, Nakhonratchasima Province of Thailand for her secondary education. Between 2006-2009, she studied at Suranaree University of Technology (SUT), Nakhonratchasima Province of Thailand for bachelor degree study. During her bachelor degree study, she participated in the Cooperative Education Program for four months in the field of chemical engineering at the thai paraxylene company limited with topic of Manual of Parex Unit for operator. She participated in the National Science and Technology Development Agency (MTEC) for two months in the field of the Young Scientist and Technology Programme: YSTP with topic of Development of High Porosity Ceramics and Anti-Bacteria Coating for Filter Application. She participated in the 24th SEA GAMES (2007) in the field of a transportation athlete in Sports Village. She participated in the 4th ASEAN GAMES (2008) in the field of a transportation athlete in Sports Village.

In 2010, She graduated with a bachelor degree in chemical engineering from SUT. After her graduation, she has received scholarship for a research assistant at SUT to study for the master degree in chemical engineering at sut since 2010.