STUDY ON THE EFFECT OF PROCESSING PARAMETERS IN THE ADSORPTION OF XYLSOE FROM GLUCOSE-XYLOSE MIXTURE

LING YEU SHIN

Thesis submitted in partial fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering (Biotechnology)

Faculty of Chemical & Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

JUNE 2013

©LING YEU SHIN (2013)

ABSTRACT

Mixtures of sugars can be obtained from many sources. It primarily comprises glucose and xylose. Xylose is highly demand in industry and expensive sugar. It can used to produce xylitol and bioethanol. However, in the presence of the glucose, xylose cannot be converted into bioethanol efficiently. Since the structures of glucose and xylose have small differences, thus, the separation of these monosaccharides is necessary. The aimed of this research is to separate the glucose and xylose by using five different resins through the adsorption process. The resins included resins which include Amberlite IR 120, Lewatit Monoplus SP 112, Diaion PK 228, Lewatit Monoplus TP 214, and Lewatit CNP 105. In this project, the static method was performed. The glucose-xylose mixture was shaken in the incubator shaker at 160 rpm for 12 hours. In this research, different parameters were conducted, including 20 to 60 °C reaction temperature and different initial concentration of glucose and xylose. The efficiency of the resins was examined. The supernatant was collected and determined by using Anthrone Reaction method. Based on the results, all the resins that used were not suitable to separate the glucose and xylose. Moreover, it was found that an increase in the initial concentration and reaction temperature lead to an increase in the adsorption capacity. Desorption was recommended to be consider in the research.

ABSTRAK

Campuran gula boleh diperolehi daripada pelbagai sumber. Ia terutamanya terdiri daripada glukosa dan xylosa. Xylosa sangat menuntut dalam industri dan merupakan gula yang sangat mahal. Xylosa boleh digunakan untuk menghasilkan Xylitol dan bioetanol. Walau bagaimanapun, xylosa tidak boleh ditukar kepada bioetanol cekap dengan kehadiran glukosa. Sejak struktur glukosa dan xylosa mempunyai perbezaan yang kecil, oleh itu, pemisahan ini monosakarida adalah diperlukan. Kajian ini adalah untuk memisahkan glukosa dan xylosa dengan menggunakan lima resin yang berbeza melalui proses penjerapan. Lima resin termasuk Amberlite IR 120, Lewatit Monoplus SP 112, Diaion PK 228, Lewatit Monoplus TP 214, dan Lewatit CNP 105. Dalam projek ini, kaedah statik dilakukan. Campuran glukosa dan xylosa digegarkan dalam inkubator penggoncang pada 160 rpm selama 12 jam. Dalam kajian ini, parameter yang berbeza telah dijalankan, termasuk 20 hingga 60 °C suhu tindak balas dan kepekatan awal yang berbeza glukosa dan xylosa. Kecekapan damar yang diperiksa. Supernatan tersebut dikumpulkan dan ditentukan dengan menggunakan kaedah Reaksi Anthrone. Berdasarkan keputusan, semua resin yang digunakan tidak sesuai untuk memisahkan glukosa dan xylosa. Selain itu, ia telah mendapati bahawa peningkatan dalam kepekatan awal dan suhu tindak balas membawa kepada peningkatan dalam kapasiti penjerapan. Desorpsi telah dicadangkan untuk dipertimbangkan dalam kajian.

TABLE OF CONTENTS

SI	JPERV	/ISC	OR'S DECLARATION	IV
S	rudei	NT'S	S DECLARATION	V
D	edicati	on		VI
A	CKNO	WL	EDGEMENT	VII
A	BSTRA	ACT		VIII
A	BSTRA	4K		IX
T	ABLE	OF (CONTENTS	X
L	ST OF	FIC	JURES	XII
L	ST OF	TA TA	BLES	XIII
L	ST OF	SY	MBOLS	XIV
L	ST OF	AB	BREVIATIONS	XV
1			DUCTION	
	1.1	Bac	kground of Study	1
	1.2	Pro	olem Statements	2
	1.3	Obj	ectives	2
	1.4	Sco	pe of this research	2
	1.5	Mai	n contribution of this work	2
	1.6	Org	anisation of this thesis	
2	ד דיד	U	ATURE REVIEW	
Ζ	2.1			
	2.1		rview	
		2	ose Overview	
	2.3		cose Overview	
	2.4	Sep	aration methods	ð
	2.4.	1	Membrane	8
	2.4.	2	Chromatography	10
	2.4.	3	Adsorption	11
			3.1 Adsorption Theory and Concept	
		2.4	3.2 Adsorption Phenomena	11
		2.4.	3.3 Factor Influencing the Adsorption Process	12
	2.4.	4	Ion Exchange Resin	14
		2.4.	4.1 Anion Exchange Resin	15
		2.4.	4.2 Cation Exchange Resin	15
	2.5	Lew	vatit Monoplus TP 214	16
	2.6		atit Monoplus SP 112	
	2.7	Lew	atit CNP 105	18
	2.8	Am	berlite IR 120	18
	2.9	Dia	ion PK228	20
	2.10	Α	nalysis Method	21
	2.10	2.1	High Performance Liquid Chromatography	21
	2.10		Dinitrosalicyclic acid Method	
	2.10		Anthrone Reaction	
3			RIALS AND METHODS	
5	3.1		prview	
	3.2		erimental Design	
	3.3	-	micals and Reagents	
	3.4		ipments	

	3.5	Experiment Procedures	
	3.5	.1 Glucose and Xylose Preparation	
	3.5		
	3.5	.3 Determination of Adsorbed Amount	
	3.5	.4 Preparation of Anthrone reagent	
	3.6	Data Collection	
	3.6	.1 Obtaining Data	
	3.6	.2 Analyzing Data	
4	RE	SULTS AND DISCUSSION	
	4.1	Overview	
	4.2	Glucose Standard Curve	
	4.3	Efficiency of the Resin	
	4.4	The Effect of Temperature	
	4.5	The Effect of Initial Concentration	
5	CC	NCLUSIONS AND RECOMMENDATIONS	
	5.1	Conclusions	
	5.2	Recommendations	
R	EFRE	NCES	
A	PPEN	DICES	

LIST OF FIGURES

Figure 2-1: Metabolic steps of D-Xylose by Lachke (2002)	6
Figure 2-2: Structure of D-Xylose	6
Figure 2-3: Structure of D-Glucose	8
Figure 2-4: Classification of membrane processes	9
Figure 2-5: Chemical Structure of SilprImCl 1	.1
Figure 2-6: Schematic representation of an IER bead by Zaganiaris (2009)1	5
Figure 2-7: Structure of thiourea1	6
Figure 2-8: Structure of sulfonic acid1	7
Figure 2-9: Bed Expansion of Amberlite IR 120 1	9
Figure 2-10: Pressure drop of Amberlite IR 120 2	20
Figure 2-11: Chemical structure of Diaion PK 228 2	20
Figure 2-12: Principles of Anthrone Reaction	:3
Figure 3-1: The flow chart of the experimental design	25
Figure 4-1: Glucose Standard Curve	0
Figure 4-2: Final Glucose Concentration against Temperature for all five resins when the initial glucose concentration is 0.45 g/L	5
Figure 4-3: Final Glucose Concentration against Temperature for all five resins when the initial glucose concentration is 0.90 g/L	6
Figure 4-4: Final Glucose Concentration against Temperature for all five resins when the initial glucose concentration is 1.35 g/L	6
Figure 4-5: The Percentage of Unadsorbed Glucose against Initial Xylose Concentratio at 40 °C	
Figure A-1: Preparation of glucose standard curve5	5
Figure A-2: 0.5 g of resins were placed into the centrifugal tube	5
Figure A-3: Glucose and xylsoe mixture was added	6
Figure A-4: Centrifuge tubes were hermetically sealed and fixed in a horizontal positio	
Figure A-5: Analyzing the sample with Anthrone reagent (Diaion PK 228)	7
Figure A-6: Analyzing the sample with Anthrone reagent (Lewatit Monoplus SP 112)5	7
Figure A-7: Analyzing the sample with Anthrone reagent (Amberlite IR 120)	

LIST OF TABLES

Table 2-1: Properties of Xylose (Valsange et al., 2012)	5
Table 2-2: Properties of Glucose	8
Table 2-3: Properties of Lewatit Monoplus TP 214	. 17
Table 2-4: Properties of Lewatit Monoplus SP 112	. 18
Table 2-5: Properties of Lewatit CNP 105	. 18
Table 2-6: Properties of Amberlite IR 120	. 19
Table 2-7: Properties of Diaion PK 228	. 21
Table 3-1: Chemical and reagents used in the study	. 26
Table 3-2: List of equipments used in the study	. 26
Table 4-1: Glucose Standard Curve	. 29
Table 4-2: The initial concentration of the glucose and xylose	. 31
Table 4-3: Percentage of adsorbed glucose in Amberlite IR 120 at 20 °C	. 31
Table 4-4: Percentage of adsorbed glucose in Lewatit Monoplus SP112 at 20 $^{\circ}C$. 31
Table 4-5: Percentage of adsorbed glucose in Diaion PK228 at 20 $^{\circ}C$. 32
Table 4-6: Percentage of adsorbed glucose in Lewatit Monoplus TP214 at 20 °C	. 32
Table 4-7: Percentage of adsorbed glucose in Lewatit CNP105 at 20 °C	. 32
Table 4-8: Experimental result for the initial glucose concentration in 0.45 g/L	. 34
Table 4-9: Experimental result for the initial glucose concentration in 0.90 g/L	. 34
Table 4-10: Experimental result for the initial glucose concentration in 1.35 g/L	. 35
Table 4-11: The initial concentration of the xylose and glucose in each reaction	. 39
Table 4-12: Amberlite IR 120 resin in different initial concentration at 40 °C	. 39
Table 4-13: Lewatit Monoplus SP112 resin in different initial concentration at 40 $^{\circ}$ C	. 39
Table 4-14: Diaion PK228 resin in different initial concentration at 40 $^{\circ}C$. 40
Table 4-15: Lewatit Monoplus TP214 resin in different initial concentration at 40 $^{\circ}$ C	. 40
Table 4-16: Lewatit CNP105 resin in different initial concentration at 40 $^{\circ}$ C	. 40
Table 4-17: Percentage of Unadsorbed Glucose in Amberlite IR 120 at 40 $^{\circ}C$. 42
Table 4-18: Percentage of Unadsorbed Glucose in Lewatit Monoplus SP112 at 40 $^{\circ}$ C	42
Table 4-19: Percentage of Unadsorbed Glucose in Diaion PK228 at 40 $^{\circ}$ C	. 43
Table 4-20: Percentage of Unadsorbed Glucose in Lewatit Monoplus TP214 at 40 $^{\circ}$ C	243
Table 4-21: Percentage of Unadsorbed Glucose in Lewatit CNP105 at 40 $^{\circ}\mathrm{C}$.43
Table 4-22: Percentage of Unadsorbed Glucose at 20 $^{\circ}\!\mathrm{C}$.45
Table 4-23: Percentage of Unadsorbed Glucose at 60 $^{\circ}\mathrm{C}$. 45

LIST OF SYMBOLS

%	Percentage
${}^{\mathcal{C}}$	Degree Celcius
3	Porosity
g	Grams
g/L	Grams per liter
g/mL	Grams per mililter
hr	hours
meq/mL	Milliequivalents per milliliter
m^2/g	Meter Squared per gram
m/h	Meter per hours
mL	Milliliter
mm Hg	Millimeters of Mercury
nm	Nanometer
rpm	Rotation per minute
μL	Microliter
μm	Micrometer

Greek

$C_{0,g}$	Initial glucose concentration
$C_{A,g}$	Concentration of adsorbed glucose
$C_{un,g}$	Concentration of unadsorbed glucose
V _{dry}	Volume of dry membrane
V _{wet}	Volume of the swollen membrane

LIST OF ABBREVIATIONS

- DNS
- 3,5-dinitrosalicyclic acid High Performance Liquid Chromatography Ion exchange resins Optical density HPLC
- IER
- OD

1 INTRODUCTION

1.1 Background of Study

Xylose is a natural sugar that can found from the wood. It is commonly called wood sugar. Glucose is the most important simple sugar in the human metabolism. It is also known as dextrose. It is one of the primary molecules that serve as the energy sources for the animals and plants.

Xylose can be used to produce bioethanol. Bioethanol is a form of renewable energy that can be used as a biofuel or gasoline additive and it can be produced by the fermentation, mostly from agricultural feedstocks such as sugarcane, corn and other carbon-based sources. According to Bi *et al.* (2010), the enzymatic hydrolysis products of xylan and cellulose, which are the main polysaccharides found in these plants cell walls are xylose and glucose. However, in the presence of the glucose, xylose cannot be converted into bioethanol efficiently in industrial quantities.

In addition, xylose is the raw material to produce xylitol by catalytic hydrogenation or microbial conversion (Emodi, 1978). Xylitol is a high value sweetener for both the food industry and biomedical field. It is a sugar substitute for the treatment of diabetes and has many positive affects in the digestive process (Winkelhausen *et al.*, 1998). Recently, one kilogram of xylose cost RM 1012.50. Since the structures of glucose and xylose have small differences, thus, the separation of these monosaccharides is necessary.

There are many methods that can be used to separate the glucose and xylose. In this research, adsorption process by using the ion exchange resins (IER) was used to separate the glucose and xylose. It comprises a part of the separation technologies. IER have been used to separate the sugar in the food industry (Zaganiaris, 2009). In the adsorption process, the resin is not performing as a real ion exchanger. It is merely acting as an adsorbent (Saari *et al.*, 2010). Five different cation exchange resins which include Lewatit Monoplus TP 214, Lewatit Monoplus SP 112, Lewatit CNP 105, Amberlite IR 120 and Diaion PK 228 were used to determine the separation efficiency of the resin in the glucose-xylose mixture.

1.2 Problem Statements

Xylose is highly demand in the industry and expensive sugar. It is relatively expensive by about \$7/kg (Leathers, 2003) comparatively with other natural sweeteners. Xylose can be used to produce xylitol. Xylitol is one of the most expensive sweeteners and has a specific health claims in the world market. It is suitable for diabetes, and strongly recommended for oral health (Makinen, 2000). However, the chemical process that used to produce xylitol is expensive because of high temperature and pressure required for hydrogenation of xylose. Moreover, extensive steps for separation and purification of xylose add to the cost. Thus, it is very important to obtain the pure xylose which can reduce the cost of the production (Sreenivas *et al.*, 2006).

According to Lachke (2002), xylose can be further process into bioethanol by a few yeasts. However, in the presence of the glucose, xylose cannot be converted into bioethanol efficiently. Hence, the separation of these monosaccharides is necessary.

1.3 Objectives

The purpose of this research is to investigate the processing parameters affecting the adsorption process to separate the glucose and xylose using five different resins.

1.4 Scope of this research

In order to achieve the objective, the following scopes have been identified:

- i. To investigate the reaction temperature in the adsorption process
- ii. To investigate the initial concentration of the glucose-xylose mixture in the adsorption process

1.5 Main contribution of this work

Xylose has a potential in a future because from the xylose, many valuable product can be produce. By obtaining the pure xylose, it can be used for further fermentation to produce xylitol and bioethanol. Xylitol is a high value product. The demand on xylitol is high because it can make it as a sweetener which is useful in the food industry and biomedical sector. In the food industry, xylitol is widely used as a sugar substitute and it can make it as "sugar-free" chewing gums, mints, and other candies. As a medicine, xylitol has a big potential in preventing dental caries and ear infections in young children. The xylose is strongly recommended to the obese and diabetic patients due to its insulin-independent metabolism (Mussatto and Teixeira, 2010).

Furthernore, bioethanol is known as renewable resources and as an alternative potential of fuel. Bioethanol has the same function with the crude oil like petrol. However, bioethanol has a lower cost and lower price than the petrol. The economic impact of conversion of xylose to bioethanol, the maximum potential reduction in the price is estimated to be \$0.42 per gallon from a base case price of \$1.65 (Hinman *et al.*, 1989).

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the xylose and glucose overview. A summary of the previous experimental work on the separation of the sugar are presented. This chapter also provides a brief discussion of the adsorption process method. A brief discussion on the factors that affect the adsorption process is provided. A general description on the ion exchange resins is presented. Different analysis method that had been used by the previous studied also provided. The characteristics of the resins that used in this research are given.

Chapter 3 gives a review of the research design in terms of chemicals and reagents, equipments selection and procedures. The data collection in terms of obtaining and analyzing data are presented.

Chapter 4 is focused on the results and discussion after run the experiment. The efficiency of the resin, the effect of the temperature and the effect of the initial concentration are focused. Different figures and tables are shown. All the results must be supported by the reasons. The discussions are based on the agreement with the earlier work.

Chapter 5 draws together a summary of the thesis and outlines the recommendations that can contribute to the research's improvement in the future.

2 LITERATURE REVIEW

2.1 Overview

This literature about the xylose is presented in section 2.2. It covers the overview of the xylose and its physical properties. The overview of the glucose and its physical properties are described in section 2.3. The conventional methods for the separation process of the glucose and xylose are described in section 2.4. It comprises all the published works on the methods of separation of monosaccharides which include membrane, chromatography and adsorption process. Based on these published works, the adsorption process by utilising the ion exchange resin was selected as the method for glucose and xylose separation. Hence, this section includes the details on adsorption theory and concept and phenomena. Furthermore, factors that influence the adsorption process are also discussed. The properties of all the five resins include Lewatit Monoplus TP 214, Lewatit Monoplus SP 112, Lewatit CNP 105, Amberlite IR 120 and Diaion PK 228 are presented in senction 2.5 to 2.9. Finally, different analysis methods are presented in section 2.10.

2.2 Xylose Overview

Xylose is the second most abundant sugar in plant biomass. It is a natural sugar which can be isolated from the wood. It can be found in the embryos of the most edible plants. Xylose was first isolated from wood by Koch in 1881 (Valsange *et al.*, 2012). It is classified as a monosaccharide that contains five carbon atoms, which is known as aldopentoses. It is white coloured sugar amorphous and water soluble.

Xylan is the major constituent of hemicelluloses and constitutes 20-40 % of total plant biomass (Ninawe and Kuhad, 2005). Hemicellulose is a linear and heterogeneous mixture of five different sugars consists of D-xylose, D-glucose, D-mannose, Dgalactose and L-arabinose. Hydrolysis of xylan is an important step to liberate valuable products, mainly xylose. The xylose can be used as substrate for production of a wide variety of compounds by chemical and biochemical processes. According to Lachke (2002), xylose can be further process into ethanol by a few yeasts. Ethanol is viewed as a potential fuel that is available from biomass. Xylitol is a high value product with a five carbon alcohol sugar (Barbosa *et al.*, 1988). It is produced by the fermentation of xylose. Xylitol has being widely used as a natural food sweetener, sugar substitute for diabetics and also act as a dental caries reducer (Mussatto and Teixeira, 2010). Xylose is also a versatile sugar compound and has many applications such as sugar source for non-nutritive agent in pharmaceutical industry, additive in colour photography and brightener in zinc electroplating (Murthy *et al.*, 2005).

Chemical formula	$C_5H_{10}O_5$
IUPAC name	D-Xylose
Chemical properties	Reducing sugar
Molar mass	150.13 g/mol
Density	$1.525 \text{ g/cm}^3 (20 \text{ C})$
Bulk density	450 kg/m^3
Melting point	144 – 145 ℃
Solubility	550 g/L (20 °C)
pH	6.0 − 6.5 (100 g/L, H ₂ O, 20 °C)
Storage temperature	Room temperature
Appearance	White crystals or powder
Stability	Stable. Incompatible with strong
	oxidizing agent.

Table 2-1: Properties of Xylose (Valsange et al., 2012)

The metabolic steps involved in the fermentation of D-Xylose are showed in the Figure 2.1. D-Xylose is isomerized to D-Xylulose by using the bacteria, *D-Xylose isomerase*. The *D-Xylose reductase* converts D-Xylose to xylitol. In the following step, xylitol is converted to D-Xylulose by *Xylitol dehydrogenase*. Phosphorylation of D-Xylulose is then catalyzed by D-xylulokinase. D-xylulokinase will form glyceraldehydes-3-phosphate and fructose-6-phosphate by epimerase, isomerase, transketolase and transaldolase.

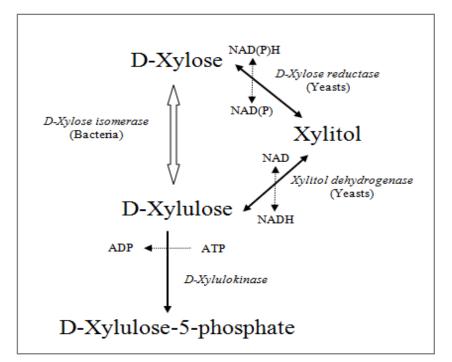


Figure 2-1: Metabolic steps of D-Xylose by Lachke (2002)

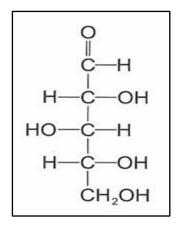


Figure 2-2: Structure of D-Xylose

2.3 Glucose Overview

Glucose is a simple monosaccharide and it is an essential energy source for the cells. It is the most common carbohydrate and known as aldohexose which contain six carbon atoms. The aldohexose sugars contains two isomers are known as glucose and only one of which (D-glucose) is biologically active. This form (D-glucose) is often referred to as dextrose (dextrose monohydrate). The mirror-image of the molecule, L-glucose, cannot be used by cells.

The transformation of foodstuffs to the glucose begins with the consumption of food. The food is dissolved and processed by the stomach acids, which turned the food into the simple sugar glucose. Once the food has been broken down into its basic components, the nutrients are absorbed through the lining of your intestines. As a result, the glucose is deposited directly into the bloodstream and is transferred throughout the body which helps to supply the energy to the body (Lutz, 2010). Glucose is stored in the liver as glycogen. Fat cells can also be converted to glucose when the body needs more energy (Albert *et al.*, 2009).

There are many applications of glucose. Plant cells used the glucose in the photosynthesis and it helps to store the energy. Besides that, glucose is widely used in the evolution, ecosystem and metabolism. It is because the glucose enables to form from the formaldehyde under antibiotic conditions; hence it may well have been available to primitive biochemical systems.

Glucose has wide application in the Maillard reaction, which is the reaction between the carbohydrates and amino acids. Maillard reaction is responsible for change in color, flavor and nutritive in food. Most of the research studies on the Maillard reaction have been done using simpler model systems (MacDougall, 2002). These model systems involve the reaction between a reducing sugar and amino acids. Yaylayan and Kaminsky (1998) used the glucose and glycine and Ames *et al.* (1997) used glucose and lysine in these model systems.

Table 2-2: Properties of Glucose

Chemical formula	$C_{6}H_{12}O_{6}$
IUPAC name	D-Glucose
Chemical properties	Weak reducing sugar
Molar mass	180.16 g/mol
Density	$1.54 \text{ g/cm}^3 (20 ^{\circ}\text{C})$
Melting point	146 – 152 °C
Solubility	910 g/L (20 °C)
Appearance	White crystalline powder
Stability	Stable. Combustible. Substances to be
	avoided include strong oxidizing agent.

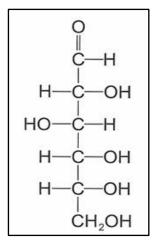


Figure 2-3: Structure of D-Glucose

2.4 Separation methods

There are different method that can be used to separate the glucose and xylose. Based on these published works, many methods have been used in the separation of xylose and glucose.

2.4.1 Membrane

Membranes are widely used to separate solute molecules based on their size. A membrane is a thin semi-permeable barrier which can be used for the particle-liquid separation, particle-solute separation, solute-solvent separation and solute-solute separation. It can serve as a molecular sieve to separate the solute molecules of different molecular size. Most of the membranes are made from polymers and ceramic membranes (Shuler & Kargi, 2002).

Ghosh (2006) mentioned that the membrane can be classified into four types: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Microfiltration is normally used to separate the fine particles from the solutions by surface filtration. Ultrafiltration membranes retain the macromolecules while it allows the smaller molecule to pass through. Nanofiltration membranes retain larger molecules such as hormones, sugars and peptides and allowing salts and other small molecules to pass through. Reverse osmosis membranes only allow water to go through but retain all dissolved species present in the feed. In this membrane, the water travels from the lower solute concentration side to the higher solute concentration side of the membrane.

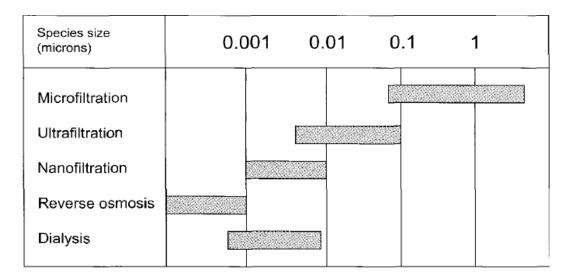


Figure 2-4: Classification of membrane processes

According to Avramescu *et al.* (2003) and Saiful *et al.* (2006), the membrane porosity was measured with porosity, ε (%), which can be defined as:

$$arepsilon = rac{V_{wet} - V_{dry}}{V_{wet}} imes 100\%$$

where V_{dry} and V_{wet} are, respectively, the volume of the dry membrane and the volume of the swollen membrane after 24 hr of immersion in a water bath at room temperature. Before weighing the wet membrane, surface water was removed by dry padding the membrane with the filter paper. The volume of dry membrane was calculated as the ration between the weight of dried membrane and the polymer density. Sjöman *et al.* (2007) investigated the separation of xylose from glucose by nanofiltration from concentrated monosaccharides solution at 50 $^{\circ}$ C and the pressure were from 2 to 40 bar. Xylose and glucose retentions are depend on the effective filtration pressure and thus on the total permeate flux. Higher glucose retentions are due to larger size of the glucose molecule. From the results that obtained, higher xylose separation from glucose is achieved with a high feed concentration at high pressure. High xylose concentrations in the feed showed higher total permeate fluxes and higher xylose retentions at 30 bar. On the other hand, a high glucose concentration in the feed enhances xylose permeation and reduces total permeate flux at the same applied pressure. By using the nanofiltration, the solution pH, filtration temperature and pressure might change the membrane structure which will affect the separation process.

2.4.2 Chromatography

Ghosh (2006) explained that the chromatography is a solute fractionation technique which relies on the dynamic distribution of molecules to be separated between a stationary phase and a mobile phase. Mobile phase flow through the stationary phase and carry the components of the mixture. Typically a column is packed with adsorbent particles, which may be solid, a porous solid, a gel, or a liquid phase immobilized in or on a solid. Different solutes in the mixture interact differently with the adsorbent material or stationary phase (Shuler & Kargi, 2002). For the molecules that have the strong interaction with the stationary phase will come out lately from the column while the molecules that have the weak interaction with the stationary phase will come early from the column.

Previous study used the ion-exchange chromatography to separate the xylose and glucose. In the ion-exchange chromatography, silica-based NH₂ columns are most widely applied in small scale to separate the sugar mixtures. However, by increasing the water proportion, silica-based NH₂ columns will be gradually damaged. Bi *et al.* (2010) proposed that the silica-based ionic liquid can overcome the weakness of the columns and increase the separation efficiency. The ionic liquid-modified silica particles were packed into a stainless steel column and operated at 25 °C. SilprImCl has been proved to be the best of the silica-based ionic liquid stationary phase and the mixture of acetonitrile and water was suitable to use as a mobile phase (Bi *et al.*, 2010).

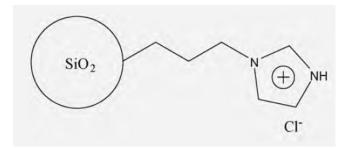


Figure 2-5: Chemical Structure of SilprImCl

2.4.3 Adsorption

2.4.3.1 Adsorption Theory and Concept

Adsorption has been used as a physical-chemical process for many years; however the process has just developed to a stage over the last four decades where it is now a major industrial separation technique (Harker *et al.*, 2002). It is gaining wider acceptance for large-scale separation from liquids due to low energy consumption when compared to other operations such as evaporation and distillation. Adsorption is a surface phenomenon which refers to the penetration of substances into the porous structure within solid material. Substances present in the liquid are adsorbed on the solid surface if the concentration of the substances in the solid-liquid boundary region is higher than in the bulk of the liquid.

Ghosh (2006) stated that adsorption can be used to separate a molecule from a complex mixture of molecules, or simply to separate a solute from its solvent. This can be achieved by contacting the solvent with the solid material which is also known as the adsorbent. The molecule that binds on the adsorbent is referred to as the adsorbate. The bonding between the adsorbate and the solvent must be broken before the new force form between the adsorbate and the adsorbent.

2.4.3.2 Adsorption Phenomena

Since adsorption phenomenon are operative in most natural physical, chemical, and biological environmental systems, the use of adsorbents by employing solids such as activated carbon and synthetic resins are used widely in industrial applications. According to Weber (1985), four principal types of adsorption are ion exchange adsorption, physical adsorption, chemical adsorption and specific adsorption.

Ion exchange adsorption takes places because of the electrostatic interaction between the molecule and the adsorbent. A cation exchange adsorbent brings negative charge and it can bind the molecule with positive charge. On the other hand, an anion exchange adsorbent is positively charges and can bind negatively charged molecules (Ghosh, 2006).

Physical adsorption or physisorption is mainly caused by the Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Since the forces are weak, the adsorption may be easily reversed (Harker *et al.*, 2002). Moreover, the physical adsorption serves to concentrate the molecules of substances at a surface. Smith (1981) clarified that physical adsorption is not highly independent on the irregularities in the nature of the surface, but it is usually directly proportional to the amount of the surface. Weber (1972) mentioned that the extent of adsorption is related to certain properties of the adsorbate relative to the solution phase, notably those of surface tension and solubility. Thus adsorbents are characterized by surface properties such as surface area and polarity.

Chemical adsorption which is also known as chemisorption involves a reaction between the adsorbate molecule and the surface of the adsorbent results in the exchange or sharing of the electrons, or possibly molecules forming atoms or radicals. Chemical adsorption involves forces much stronger than physical adsorption. The forces involved are valence forces of the same kind as those occurring between atoms in molecules (McCabe *et al.*, 1993).

Specific adsorption is the attachment of an adsorbate molecule at the functional group on the surface of the adsorbent. This adsorption will not result in the adsorbate transformation. Weber (1985) clarified that the net dispersion, chemisorptive, electrostatic and functional group interactions are used to define an adsorbent for a specific adsorbate.

2.4.3.3 Factor Influencing the Adsorption Process

According to Bi *et al.* (2010), temperature has a strong effect on the adsorption process. The temperature of the solution will bring two major effects on adsorption. The first effect is the rate of adsorption will increase at higher temperature due to the higher rate of diffusion of adsorbate molecules through the solution to the adsorbent.

Another effect is the temperature influence toward the solubility. Carabasa *et al.* (1998) mentioned that the solubility and adsorption are inversely related, as the temperature affects the solubility, it will also affect the adsorption. When the temperature increase, the adsorption efficiency increase as well where the viscosity of the solution will decrease which is favourable for the external transfer and diffusion of the adsorbate within the adsorbent.

Lei *et al.* (2010) investigated the adsorption behaviour of glucose, xylose, and arabinose on five different cation exchange resins at 25 $^{\circ}$ C at 160 rpm for about 12 hours. Bi *et al.* (2010) studied the separation of xylose and glucose on different silica-confined ionic liquid stationary phase at different temperature ranging from 25 $^{\circ}$ C to 45 $^{\circ}$ C. From the results, it was found that 25 $^{\circ}$ C was the most suitable temperature for the separation of xylose and glucose.

According to previous studies, almost all the uptake of the adsorbate increases with the increase of an initial concentration. The initial concentration provides an important driving force to overcome all the mass transfer resistances (Tewari *et al.*, 2005). Therefore, a higher initial concentration of xylose will enhance the adsorption process.

Tumin *et al.* (2008) explained that higher initial concentrations lead to an increase in the affinity of the ions towards the active site of the adsorbent. It provided higher interaction between the adsorbate and adsorbent. Malkoc *et al.* (2006) supported that increased the initial concentration, the adsorbent offered a finite number of surface binding sites, and hence more adsorbate can bind to the adsorbent. It has also been observed that for all initial concentrations, the adsorption rates are initially rapid at the beginning of the adsorption process because of rapidly accessible active sites. As times goes by, these active sites become filled with the adsorbate and then the process reaches a much lower rate until it stops upon reaching equilibrium.

A study about the effect of initial concentration of chromium (VI) by *Mucor hiemalis* in the adsorption process by Tewari *et al.* (2005) indicates that the amount uptake of chromium (VI) increase significantly with increasing initial concentration. This result was expected due to the decrease in resistance to the uptake of solute from the solution with increasing solute concentration. Thus, the increase in driving force results in increasing the adsorption rate. Similar results were also obtained in the adsorption of

lead ions onto bael tree leaf powder which was used as an adsorbent by Kumar and Gayathri (2009). The adsorption capacities of all adsorbates increased with increasing initial concentrations.

The amount of adsorbent controls the adsorption process. An increase in the amount of the adsorbent used usually increased the adsorption. The effect of the adsorbent dosage in the adsorption of nickel onto the bael tree leaf powder was studied by Kumar and Kirthika (2009). In their study, they obtained that the adsorption of nickel increases rapidly with increase the amount of adsorbent due to greater availability of the surface area at higher concentration of the adsorbent. However, they also agreed that when the adsorbent dosage added until certain point, it did not cause any significant change in the adsorbent particles.

An investigation on the adsorption of lead from aqueous solution by activated carbon was conducted by Elaigwu *et al.* (2010). In their study, they concluded that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of metal ion adsorbed onto the surface of the adsorbent since there will be more sites for the adsorbate to be adsorbed. Therefore, competition for bonding sites between molecules of the adsorbate should decrease with increase in dosage of the adsorbent. Thus, it can be concluded that the number of available adsorption sites increases by increasing the amount of adsorbent and it will increase the adsorption rate (Al-Qaim, 2011).

2.4.4 Ion Exchange Resin

Ion exchange resins (IER) constitute a part of the separation technologies. IER consist of a polymeric matrix and a functional group with a mobile ion that enable to exchange the ions present in a solution. In general, IER are spherical but some are made in granular form. IER have numerous industrial applications such as separate the sugar in the food industry, removal of heavy metals and organics in the waste water treatment and processing of pharmaceuticals such as antibiotics and vitamins (Zaganiaris, 2009). Srikanth *et al.* (2010) explained that the resins used contain acidic groups, such as sulfonic and carboxylic for cation exchangers; or basic groups, such as quaternary ammonium group for anion exchangers. The IER are strong acid cation, weak acid cation, strong base anion and weak base anion exchangers. The advantages of using IER in the process include the low running costs, little energy is required, regenerant chemicals are cheap and the resins can last for many years (Rutherford, 2012). In adsorption, where ion-exchange resins are used, the resin is not performing as a real ion exchanger but is merely acting as an adsorbent (Saari *et al.*, 2010).

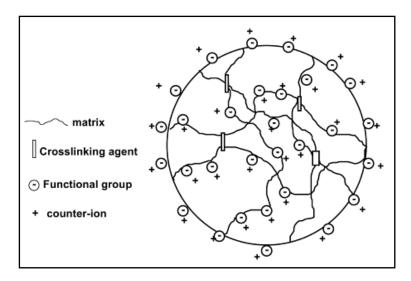


Figure 2-6: Schematic representation of an IER bead by Zaganiaris (2009)

2.4.4.1 Anion Exchange Resin

Strong base anion exchange resins have a styrene or acrylic skeleton. When the functional groups are adding to the strong base anion resins, it involves two steps: chloromethylation and amination. There are two chemicals that are generally used for the amination step, each producing a different type of resin with different chemical properties. Type I strong base anion resins are aminated with trimethylamine where Type II are animated with dimethyl-ethanolamine which are developed after Type I. Weak base anion exchange resins are the new type of the resins and they are still lacking large scale industrial applications (Saari, 2011). Heikkila *et al.* (2006) described that the anion exchange resins can be used to separate the fructose from glucose but the resins do not result in good xylose separation because xylose is overlapped by other sugars.

2.4.4.2 Cation Exchange Resin

Strong acid cation exchange resins have a styrene or acrylic skeleton. Most of the resin is a sulphonated polystyrene-divinylbenzene resin. The resin may also be cross-linked