การดูดซับสาร 1,3-โพรเพนไดออล จากสารละลายสังเคราะห์โดยใช้พอลิเมอร์เรซินเป็นตัวดูดซับ

นางสาววลัยภรณ์ เหลือรักษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2551

ADSORPTION OF 1,3-PROPANEDIOL FROM SYNTHETIC MIXTURE USING POLYMERIC RESIN AS ADSORBENTS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2008

Thesis Title	ADSORPTION OF 1,3-PROPANEDIOL FROM SYNTHETIC MIXTURE USING POLYMERIC RESIN AS ADSORBENTS
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ปัจจุบันมีการผลิตไบโอดีเซลเพิ่มขึ้น ดังนั้นการเปลี่ยนกลีเซอรอลที่เป็นผลพลอยได้จากการผลิตไบโอดีเซลให้เป็นผลิตภัณฑ์ที่มีมูลค่ามากขึ้น จึงเป็นงานวิจัยที่ได้รับความสนใจ สาร1,3-โพรเพนไดออลซึ่งเป็นสารตั้งต้นการผลิตโพลิเอสเตอร์ถือเป็นผลิตภัณฑ์หนึ่งที่สำคัญชนิดหนึ่งที่สามารถผลิตได้จากกลีเซอรอล โดยกระบวนการผลิตทางชีวภาพถือเป็นวิธีที่นิยมมากกว่าเนื่องจากมีความปลอดภัยต่อสิ่งแวดล้อมมากกว่าวิธีทางเคมี การแยก1,3-โพรเพนไดออลออกจากน้ำหมักนั้น จำเป็นต้องใช้กระบวนการที่มีค่าการแยกที่ดีและง่ายต่อการดำเนินการ โดยวัตถุประสงค์ของงานวิจัยนี้จึงมุ่งเน้นไปที่กระบวนการดูดซับ1,3-โพรเพนไดออลจากสารละลายน้ำหมักสังเคราะห์ด้วยโพลิเมอร์เรซินที่ไม่มีประจุ (พอลิเมอร์ชอบน้ำ XAD-7 และ พอลิเมอร์ไม่ชอบน้ำ XAD-16) จากการทดสอบหาไอโซเทอมการดูดซับที่สมดุลของ1,3-โพรเพนไดออลบนเรซินทั้งสองชนิดในระบบสององค์ประกอบ พบว่าค่าการดูดซับของ1,3-โพรเพนไดออลจะเพิ่มขึ้นเมื่อความเข้มข้นเริ่มต้นของ1,3-โพรเพนไดออลเพิ่มขึ้น โดยมีค่าการดูดซับสูงสุดที่ความเข้มข้นเริ่มต้น 160 กรัมต่อลิตร และการดูดซับสมดุลที่ 303 K สามาถอธิบายได้ดีด้วยแบบจำลองฟรุนดลิชและ XAD-7 มีค่าคงที่ของแบบจำลองสูงกว่าค่าคงที่ของ XAD-16 สำหรับในระบบสามองค์ประกอบที่มีกลีเซอรอลอยู่ในสารละลายด้วยจะช่วยส่งเสริมค่าการดูดซับของสาร1,3-โพรเพนไดออลบน XAD-16 ที่ 160 กรัมต่อลิตร อย่างไรก็ตาม XAD-16 ดูดซับกลีเซอรอลในปริมาณมาก จึงทำให้ค่าการเลือกต่ำและไม่เหมาะสมต่อการดูดซับสาร1,3-โพรเพนไดออล นอกจากนี้งานวิจัยนี้ยังพบอีกว่าในระบบหลายองค์ประกอบที่มีกรดอะซิติกและกรดบิวทิริกอยู่ในสารละลายจะช่วยส่งเสริมทั้งค่าการดูดซับและค่าการเลือกของสาร1,3-โพรเพนไดออลของเรซินทั้งสองชนิด และจากการศึกษาการคายซับด้วยสารละลายเอทานอลในน้ำ พบว่าการคายซับเพิ่มขึ้นเมื่อสัดส่วนขอเอทานอลเพิ่มขึ้น และเนื่องจากสัดส่วนมวลของ1,3-โพรเพนไดออลในสารละลายที่ถูกชะจาก XAD-7 (0.321) สูงกว่า XAD-16 (0.294) ขณะที่สัดส่วนมวลของกรดบิวทิริกในสารละลายที่ถูกชะจาก XAD-7 (0.087) น้อยกว่า XAD-16 (0.131) XAD-7 จึงเหมาะสมกับกระบวนการดูซับของ1,3-โพรเพนไดออลมากกว่า โดยให้ค่าการดูดซับ (1335.7 มิลลิกรัมต่อกรัม), ค่าการเลือก (4.46)

ภาควิชา.......วิศวกรรมเคมี....... ลายมือชื่อนิสิต..
สาขาวิชา.......วิศวกรรมเคมี....... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..............................
ปีการศึกษา 2551.......... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม..............................

4970556021 : MAJOR CHEMICAL ENGINEERING

KEY WORD: ADSORPTION / 1,3-PROPANEDIOL / GLYCEROL / POLYMERIC RESIN / ADSORPTION ISOTHERM

WALAIPORN LUERRUK: ADSORPTION OF 1,3-PROPANEDIOL FROM SYNTHETIC MIXTURE USING POLYMERIC RESIN AS ADSORBENTS. THESIS PRINCIPAL ADVISOR: ASSOC. PROF. CHIRAKARN MUANGNAPOH, Dr. Ing., THESIS COADVISOR: ASST. PROF. ARTIWAN SHOTIPRUK, Ph.D., 111 pp.

Nowadays, the production of biodiesel has been increased. The conversion of glycerol derived from biodiesel production into high value product has therefore become a big challenge. As a precursor for polyester production, 1,3-propanediol (1,3-PDO) is one of the most interesting high value chemicals produced from glycerol. Its production can be achieved either by a chemical or biological process, however the environmental friendly biological process is more preferable. For the separation of 1,3-PDO from fermentation broth, high separation factor and easy operation are the key issues, and this study therefore focuses on investigation of adsorption of 1,3-PDO in model mixture of fermentation broth onto non-ionic polymeric resins (hydrophilic XAD-7 and hydrophobic XAD-16). First, the adsorption equilibrium isotherm of 1,3-PDO on both XAD-7 and XAD-16 resins in binary system (303 K) were investigated. The results indicated that the amount of 1,3-PDO adsorbed increased with the increase in initial concentration of 1,3-PDO. In this study, the maximum adsorption was achieved at the initial concentration of 1,3-PDO at 160 g/L. The Freundlich type model gave a reasonable fit to the experimental adsorption isotherms for both resins, and the parametric constants for adsorption on XAD-7 were much higher than that for XAD-16. In the tertiary system, the presence of glycerol promoted 1,3-PDO adsorption for XAD-16 at 160 g/L initial concentration of 1,3-PDO. However, XAD-16 also adsorbed higher amount of glycerol caused lower the selectivity. In multiple component system, the presence of acetic acid and butyric acid in aqueous solution promoted 1,3-PDO adsorption and selectivity for both resins. In addition, the study of desorption with ethanol solution showed that the desorption yield increased with increasing the ethanol content. The mass fraction of 1,3-PDO in desorbed solution from XAD-7 (0.321) was higher than that for XAD-16 (0.294) while the mass fraction of butyric acid in desorbed solution of XAD-7 (0.087) was lower than that XAD-16 resin (0.131). Based on these results, XAD-7 was concluded to be appropriate, giving higher amount of 1,3-PDO adsorbed (1335.7 mg/g) and higher selectivity (4.46) compared to the adsorbs obtained by XAD-16 resins.

Department: Chemical Engineering Student's signature:……………………………..

Field of study: Chemical Engineering Principal Advisor's signature:…………………

Academic year: 2008 Co-advisor's signature:………………………..

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Associate Professor Chirakarn Muangnapoh, Dr. Ing. and Co-Advisor Artiwan Shotipruk, Ph.D. for their enthusiastic guidance, constructive suggestions and constant encouragement throughout the course of this study and the preparation of write-up.

Also, the author would like to gratefully thank to Associate Professor Sarawut Rimdusit, Ph.D, Associate Professor Seeroong Prichanont, Ph.D, and Phatthanont Prasitchoke, Ph.D. for serving as chairman and member of the thesis committee, respectively.

Special thanks to Associate Professor Deacha Chatsiriwech, Ph.D. for kindly give any constructive suggestions in my work. His comments are important and have added a great deal of quality to this work.

My sincere thank also go to Mrs. Sunun Rangseekansong for her kind assistance in analytical work and sincere thanks are made to all members of the Biochemical Engineering Research Laboratory for their any assistance.

Gratefulness is also felt for financial support for this research from the PTT Chemical Public Company Limited, the Graduate School and Department of Chemical Engineering Chulalongkorn University.

Furthermore, she wishes to convey her most sincere gratitude to her family who has always been the source of her inspiration.

Finally, many thanks go to her friends and all those who encouraged her over the year of his study.

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CHAPTER I

INTRODUCTION

1.1 Rationale

Crude glycerol is a principal by-product of biodiesel production by the transesterification of vegetable oils. For each 100 g of vegetable oils, about 10 g of glycerol would be produced. Since the production of biodiesel has been increasing tremendously from 1999 to 2007, the substantial amount of glycerol have been generated accordingly. The crude glycerol derived from biodiesel production can be used as an important industrial feedstock (food and cosmetic). Nowadays conversion of glycerol into high value products is a big challenge. One of the most important specialty chemical is 1,3-propanediol, which can be formulated into composites, adhesives, laminates, powder and UV-cured coating, novel aliphatic polyester, co-polyester, solvent, anti-freeze, and other end uses. There are currently two processes for chemical synthesis of 1,3-propandiol (e.g., acrolein hydration and hydrogenation). Both of these processes produce toxic intermediates and require a reduction step under high hydrogen pressure. Recently, several patents were filed describing a biological process for the conversion of glycerol to 1,3-propanediol using microorganism such as *Klebsiella pneumoniae, Citobacter frundii, Enterobacter agglomerans,* and *Clostridium butyricum*. Some advantages of the fermentative route include lower raw material cost and environmentally friendly process. However the biological route poses the problem of impurities such as organic acid, salts, glycerol, and other compounds, which are difficult to separate. Particularly, the high boiling point and hydrophilicity of 1,3-propanediol, economic separation of 1,3-propanediol from these contaminants by standard means is difficult.

Several processes have been investigated to purify 1,3-propanediol but they still have serious limitations. One standard technique to purify the 1,3-propanediol includes evaporation of the process stream followed by distillation, both of which reflect on the cost of the final product purified. Malinowski (2000) proposed a liquid-liquid extraction process with organic solvents to extract the 1,3-propanediol from dilute aqueous solutions. However this purification process requires the handling of large quantities of solvents since the distribution coefficient and separation efficiency of 1,3-propanediol is too low. Hao et al. (2005) reported the 1,3-propanediol purification process based on the reactive extraction, using aldehydes as both for reactant and extraction solvent. These procedures however involve the conversion of 1,3-propanediol to dioxane, and then back to 1,3-propanediol, thus are too complicated to achieve satisfactory yield. Li et al. (2001) used a zeolite membrane for separation 1,3-propanediol from glycerol and glucose by pervaporation, which still had some drawbacks such as low flux and selectivity. In addition, the operation of such system was difficult due to high pressure demand. Up until now, the separation of 1,3-propanediol have been focused to achieve better separation value and easy operation. Alternative to the methods mentioned above, adsorption is considered an interesting process as it is easy to operate and has low maintenance cost, while several adsorbents are available for use.

Several researches were conducted on the separation 1,3-propanediol from fermentation broth by adsorption process. Roturier et al. (2002) used polystyrene sulfonate, which is a strong cation exchange resin as an adsorbent. The resin consists of lanthanum lead iron zinc and aluminum, and water was used as an eluent. However, this method gives low yield of 1,3-propanediol. Hilaly et al. (2002) used polystyrene sulfonate which is strong cation exchange resin in the form of sodium and calcium, operated using simulate moving bed (SMB) technology. The model mixture of 1,3-propanediol was prepared, and was passed through adsorbent, using water as an eluent. This process was found to give slightly higher yield of 1,3-propanediol. In addition to ion-exchange resins, various types of zeolite have been used (Li et al., 2001, Corbin et al., 2003). Li et al. (2001) employed X-type, Y-type, and Na-ZSM-5 zeolite membrane in pervaporation, and Na-ZSM-5 was found to have the highest efficiency. Corbin et al. (2003) investigated the use of H-ZSM-5 as adsorbent through which a mimic solution of 1,3-propanediol was passed, followed by elution with the mixture of water and ethanol. However, the yield of 1,3-propanediol was relatively low because zeolite has small pore size, making it difficult for the solution to flow through zeolite pore.

Despite the non-ionic characteristics of 1,3-PDO, most of the adsorbents thus far studied were ionic adsorbents. It is therefore the objective of this study to examine the use of non-ionic polymeric adsorbents for the adsorption of 1,3-PDO from aqueous solution, in which the polymeric resins with moderate pore sizes such as hydrophilic Amberlite XAD-7 and hydrophobic XAD-16 were chosen for investigation. The experiments were conducted using synthetic mixture of fermentation broth to determine the behavior of1,3-PDO adsorption in binary (1,3-PDO, water), tertiary (1,3-PDO, water, and glycerol), and multiple component (1,3-PDO, water, glycerol, butyric acid, acetic acid) systems. In addition, the effect of pH of the solution on 1,3-PDO adsorption on the two resins was investigated. Moreover, desorption of each of the adsorbed components were investigated to determine the suitability of the adsorbents and optimal desorption conditions.

1.2 Objectives

1.2.1 To investigate adsorption and desorption behaviors of 1,3-PDO in binary, tertiary, and multiple component systems onto non-ionic polymeric resins.

1.2.2 To investigate the suitability of polymeric adsorbents for separating 1,3-PDO from synthetic mixture of fermentation broth.

1.3 Working scopes

1.3.1 Selection of polymeric adsorbents for separating 1,3-propanediol from model mixture of fermentation.

1.3.2 Experimental investigation of adsorption isotherm (303 K) involving the following variables.

- Type of adsorbent (Amberlite XAD-16 and XAD-7)
- Type of adsorbate (binary, tertiary, and multiple components)
- pH of solution (3, 5, 7)

1.3.3 Calculation of Adsorption performance in terms of

- Maximum adsorption capacity of 1,3-PDO
- Selectivity of adsorbents

1.3.4 Determination of desorption behavior with ethanol/water solution at

- Different concentrations of eluent (ratio of ethanol/water at 50, 60, \ 70, 80 % (v/v))

1.4 Expected benefits

To investigate the suitability of using polymeric resins and determine the suitable adsorption and desorption conditions for 1,3-propadiol adsorption from synthetic model mixture of fermentation broth.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 1,3-propanediol and its applications (Zeng et al., 2002)

As a bifunctional organic molecule 1,3-propanediol (1,3-PDO) or trimethylene glycol is a clear colorless viscous non-ionic liquid under normal conditions. It can be formulated into a variety of industrial products including composites, adhesives, laminates, powder and UV-cured coating, moldings, solvent, anti-freeze and other end uses.

Of particular importance, 1,3-PDO is an economical source for the production of poly(trimethylene terephthalate) (PTT). This copolyester is a condensation product of 1,3-PDO and terephtthalate acid. It has excellent properties such as good resilience, stain resistance, low static generation, principally used in the manufacture of carpet and textile fibers but are also finding applications as engineering thermoplastic, films and coatings. Plastics based on this monomer exhibit better product properties and higher light stability than those produced by 1,2-propanediol, butanediol or ethylene glycol.

2.2 Chemical process for 1,3-propanediol

The process uses the conventional preparation method starting from acrolein which is obtained by catalytic oxidation of propylene. Acrolein is hydrated at moderate temperature and pressure to 3-hydroxypropionaldehyde which, in a second reaction, is hydrogenated to 1,3-PDO over rubidium catalyst under high pressure (90 bar). The other process starts from ethylene oxide, which is prepared by oxidation of ethylene. Ethylene oxide is transformed with synthesis gas in a hydroformylation process to 3-hydroxypropanal as well, but for this reaction, very high pressure (150 bar) is required.

2.3 Microbial formation of 1,3-propanediol

The biological production of 1,3-PDO from glycerol was demonstrated for several bacterial strains, e.g., *Lactobacillus brevis* and *buchnerii*, *Bacillus wellchii*, *Citrobacter freundii*, *Klebsiella pneumoniae*, *Clostridium pastteurianum*, and *Clostridium butyricum*. The biosynthesis of 1,3-PDO under anaerobiosis take place via the following biochemical reaction: one portion of glycerol is oxidized to dihydroxyacetone by an NAD-dependent glycerol dehydrogenase, whereas the rest of the glycerol is dehydrated to 3-hydroxypropionaldehyde by a vitamin B12-dependent dehydratase. The production of the dehydration reaction, 3-hydroxypropionaldehyde (3-HPA), is reduced in 1.3-propanediol by an NAD-dependent oxidoreductase as shown in Figure 2-1. In this case, the final acceptor of the electrons is the 3-HPA.

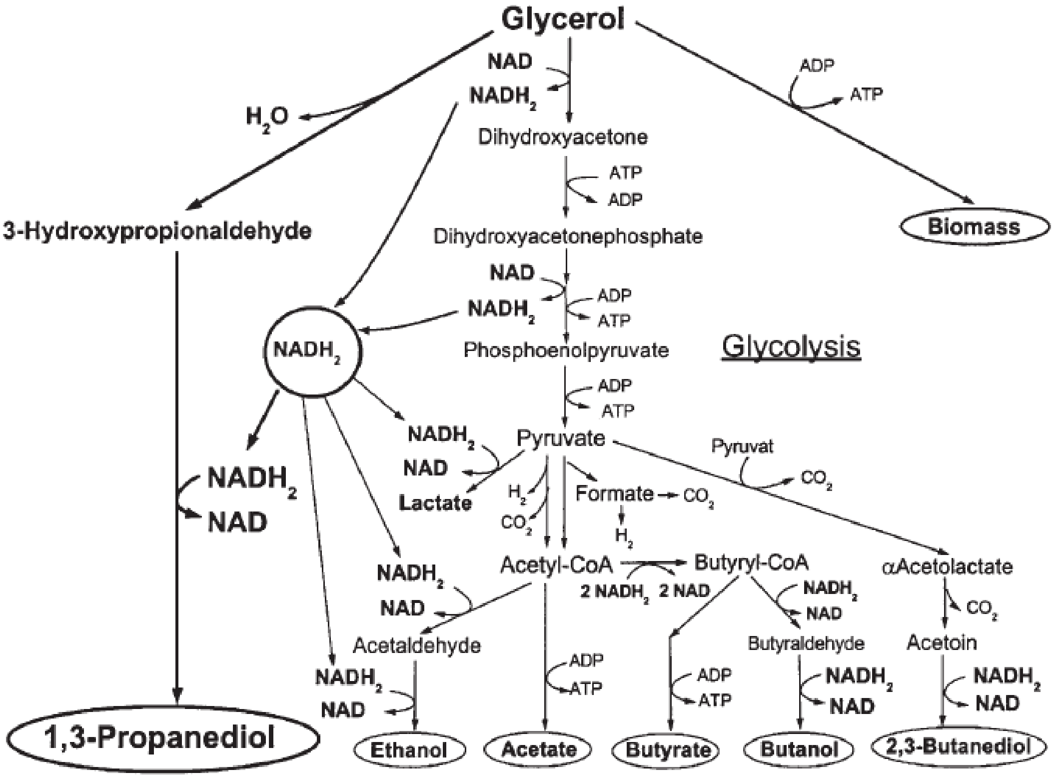


Figure 2-1 Metabolic pathways of glycerol metabolism (Zeng et al., 2002)

The yield of 1,3-PDO depends on the combination and stoichiometry of the reductive and oxidative pathways. It has been shown that the combination of 1,3-PDO generation with acetic acid as the sole by-product of the oxidative pathway results in the maximum yield of 1,3-PDO. For this combination, the fermentation equations can be written as:

$$\begin{array}{l} CH_2OH\text{-}CHOH\text{-}CH_2OH + H2O \text{ ---- } > CH_3COOH + CO_2 + H_2 + 4[H] \\ 2CH_20H\text{-}CHOH\text{-}CH_2OH + 4H \text{ ---- } > 2CH_2OH\text{-}CH_2\text{-}CH_2OH + 2H20 \\ \hline 3CH_2OH\text{-}CHOH\text{-}CH_2OH \text{ ---- } > CH_3COOH + CO_2 + H_2 + 2CH_20H\text{-}CH_2\text{-}CH_2OH \\ \qquad\qquad\qquad\qquad\qquad\qquad + H_2O \end{array}$$

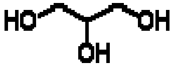
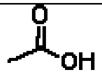
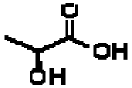
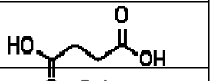
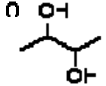
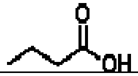
2.4 Property of 1,3-propanediol and by-products (Boonsongsawat et al**.,** 2007)

For separation of 1,3-PDO from the fermentation broth, it is important to know the properties of the product and other existing by-products. The by-products resulted from the fermentation are listed in Table 2-1, and their general characteristics of 1,3-propanediol and these by-products are Summarized in Table 2-2.

Table 2-1 By-products of fermentation (Boonsongsawat et al**.,** 2007)

Microorganisms	**By-product of 1,3-propanediol fermentation**	
Klebsiella Pneumoniae	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Citrobacter freundii	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Enterobacter agglomerans	Acetic acid, Ethanol, Lactic acid, Succinic acid, and 2,3-Butanediol	CO_2, H_2
Clostridium butyricum	Acetic acid, Butyric acid	CO_2, H_2
Clostridium pasteurianum	Acetic acid, Butanol	CO_2, H_2
Clostridium acetobutylicum	Acetic acid, Butyric acid	CO_2, H_2

Table 2-2 Properties of 1,3-propanediol and by-products (Boonsongsawat et al**.,** 2007)

Name	Synonyms	Molecular Formula	Molecular Weight	Melting point (°C)	Boiling point (°C)	Density (g/cm3)	Solubility in water	Structure
1,3-propanediol	1,3 propylene glycol	$C_3H_8O_2$	76.09	-32 °C	214 °C	1.052	100g/l	
Glycerol	Propane-1,2,3-triol	$C_3H_8O_3$	92.09	18°C	290°C	1.216	>500 g/l	
Acetic acid	Ethanoic acid	$C_2H_4O_2$	60.05	16 °C	117 °C	1.048	miscible	
Ethanol	Ethyl Alcohol	C_2H_6O	46.0688	-114.1 °C	78.3 °C	0.789	slightly soluble	
Lactic acid	2-Hydroxy propanoic acid	C3H6O3	90.07	53 °C	122 °C	1.05	miscible	
Succinic acid	Butanedioic acid	$C_4H_6O_4$	118.08	185 °C	235 °C	1.552	80g/l	
2,3-butanediol	2,3-Butylene glycol	$C_4H_{10}O_2$	90.12	19 °C	180 °C	1.01	miscible	
Butyric acid	n-Butyric acid	$C_4H_8O_2$	88.1	-7 °C	162°C	0.96	miscible	
Butanol	n-Butyl alcohol	$C_4H_{10}O$	74.12	-89.5 °C	117.6 °C	0.81	80 g/l	
Carbon dioxide	-	CO_2	44.01	-57 °C	-78 °C	1.98	-	-
Hydrogen	-	H_2	2	-259.14°C	-252.87°C	0.089	-	-

2.5 Literature reviews

The bioconversion of glycerol has been known for almost 120 years. Unpurified glycerol, in particular from biodiesel plants, has been shown to be an excellent fermentation substrate for 1,3-propanediol production (Zeng et al., 2002). Barbirato et al., (1998) compared the production of 1,3-PDO from industrial glycerol sources and demonstrated the feasibility of the microbial fermentation technology. Recently, several patents were filed describing an environmentally friendly biological process for the conversion of glycerol to 1,3-PDO using microorganism such as *Klebsiella pneumoniae, Citobacter frundii, Enterobacter agglomerans, Clostridium butyricum.* Among those microorganisms, *Clostridium butyricum* leads to 1,3-PDO as a major component, two acids (butyrate and acetate) as by-products and gaseous products, CO_2 and H_2. For suitable extraction-purification of the 1,3-PDO from fermentation broths, organic compound composition and proportion are key data and one can speculate that 1,3-PDO extraction would be easier if fewer organic compounds are present. *Clostridium butyricum* fits well with this demand. Moreover, Reimann et al., (1997) suggested that the productivity of 1,3-PDO from glycerol by *Clostridium butyricum* could be further improved by a factor of four in a continuous fermentation with cell recycling, in comparison to the continuous culture without cell recycling. In their study, cell recycling was achieved by filtration using hollow-fiber modules made from polysulphone. Its performance was checked at a retention ratio of 5, dilution rates between 0.2 h^{-1} and 1.0 h^{-1} and glycerol input concentrations of 32 g l^{-1} and 56 g l^{-1}. The optimum 1,3-PDO concentration of 26.5 g l^{-1} (for 56 g l^{-1} glycerol) was maintained up to dilution rate of 0.5 h^{-1} and the concentration decrease while the productivity was the highest at 0.7 h^{-1}.

Seraphim et al., (2000) investigated the cell growth of *Clostridium butyricum* and the formation of the major metabolites of the strain (1,3-PDO, acetate and butyrate), as well as the inhibitory effects of 1,3-PDO in batch and binary-stage continuous cultures. The first stage presented high 1,3-PDO volumetric productivity, whereas the second stage (with a lower dilution rate) served to further increase the final product concentration. High 1,3-PDO concentrations were achieved (41-46 g l^{-1}), with a maximum volumetric productivity of 3.4 g l^{-1} h^{-1}. A cell concentration decrease was reported between the second and the first fermentor.

In general, during fermentation, organic acids are produced which lowers the pH and inhibits the growth of bacillus, thus potassium hydroxide is added to keep the pH at 7.0. As a result, organic acid salts are formed and when employing vacuum evaporation to concentrate actual 1,3-PDO fermentation broth, the existence of salts makes the operating temperature rise and the on-off concentration ratio of 1,3-PDO less than 30%, requiring at least twice as much energy to achieve the required concentration ratio of 1,3-PDO. To solve these problems, a number of means are proposed, and one of which is suggested by Gong et al., (2004), who proposed the desalination of 1,3-PDO fermentation broth by electrodialysis and then followed by vacuum distillation.

The downstream purification of 1,3-PDO can be proceeded with various other methods. The conventional process is by evaporation and distillation, which give high yield and purity for recovery 1,3-PDO (Ames., 2002). However these processes are difficult due to characteristics of 1,3-propanediol such as strong hydrophilic and low volatility in aqueous solutions, and thus the processes are neither economical nor suitable. Alternatively, liquid-liquid extraction of aqueous 1,3-PDO was investigated by Malinowski et al., (1999) who reported that aldehydes are the most suitable solvents, which gives high distribution coefficient and selectivity. However, the distribution of 1,3-PDO was disclosed as not good enough to make simple extraction efficient. Subsequently, Malinowski et al., (2000) proposed a technique to recover 1,3-PDO form fermentation broth by first converting it into a substance without hydroxyl groups (dioxane), which can be easily extracted by organic solvent such as toluene, o-xylene, and ethylbenzene. He found that the dioxane extraction yield was 91-92%, the overall conversion of 1,3-propanediol was 98%, and recovery of dioxane into the organic solvent was 75%. In a subsequent study by Hao et al., (2005). The improved recovery of 1,3-PDO was demonstrated by employing reactive extraction using aldehyde as both reactant and extractant. Three aldehydes: propionaldehyde, butyraldehyde, or isobutyraldehyde were tested in this study. First the excess amount of adehydes was added to the fermentation broth to form substituted 1,3-dioxane, which was then extracted from the aqueous phase into the aldehyde phase. Compared with using different solvent as extractant, this method reduces the step to separate acetals from aldehyde. In addition, because the aldehyde concentration in the aqueous phase remained at a high level while that of acetal remains at the low level, the conversion rate of 1,3-PDO could be enhanced. In this study, the recovery rates of

1,3-PDO were found to be 65%, 85%, and 87% for propionaldehyde, butyraldehyde, and isobutyraldehyde, respectively. In addition, the reaction equilibrium constants of isobutyraldehyde and the mass distribution coefficients of its substituted 1,3-dioxanes achieved were found to be the highest. Although the acetalization reaction gave rather high yield, conversion with hydrolysis reaction of acetals back to 1,3-PDO was needed, and the solvents must be separated by distillation. Such procedures were too complicated to achieve satisfactory yield of 1,3-PDO. Recently, Kim et al., (2006) studied a novel isolation and purification method for producing 1,3-propanediol with high purity and high yield from mixture containing 1,3-PDO, 1,2-propanediol, glycerol, glucose. Their method consisted of phase separation to remove glucose and glycerol from the mixture and then followed by chromatography for the purification of 1,3-propanediol from its mixture with 1,2-propanediol. The optimal feed concentration in the phase separation step was reported to be 40 g/L on the basis of 1,3-PDO when their solvent was ethyl acetate. In the chromatographic separation, a column packed with silica resin was used. The elution condition was attained by using ethyl acetate/methanol (98/2, v/v) as a mobile phase in an isocratic mode. Their study showed that the over all purity and yield of 1,3-PDO were 98% and 82% in the purification process, respectively.

Li et al., (2001) investigated separation process for 1,3-PDO from glycerol and glucose using a ZSM-5 zeolite membrane by pervaporation. Such membrane operation have advantages over a packed bed in that its operation is continuous and it does not require an additional separating agent such as ethanol used for a packed bed, which means that the distillation step can be eliminated. In their results, it was found that 1,3-PDO/glycerol selectivity decreased over the temperature range 308-328 K, whereas the 1,3-PDO/glucose selectivity increased for the same range. In addition, they showed that the presence of glycerol inhibited glucose permeation and thus increased the 1,3-PDO/glucose selectivity. Furthermore, the presence of glucose was found to decrease the total flux but increased the 1,3-PDO/glycerol selectivity. Despite the advantages of ZSM-5 zeolite membrane pervaporation over the packed bed, the technique carries some drawbacks such as low flux and selectivity.

Alternatively, Roturier et al., (2002) proposed the purification of 1,3-PDO form fermentation medium by chromatography using a strong acidic cation exchange resin of the polystyrene sulfonic acid type crosslinked with divinylbenzene, consisting of lanthanum, lead, zinc, iron, and aluminum with water as eluent. The maximum yield, which in the first fraction of elution was 31.9% when using resin as lanthanum and 47% when usin1,3-PDO and the other compounds involved. At the same time, Hilaly et al., (2002) studied a method of recovering 1,3-PDO from fermentation broth by ion exchange resins and utilized simulated moving bed technology, which is a convenient and efficient method of chromatographic separation of fermentation broth. In this method, ionic components were rejected due to ionic repulsion. The non-ionic components entered the pores of the stationary phase and, therefore, eluted from the column later than other ionic components. The purity of 88.1% and the recovery of 1,3-PDO was 86.7% where achieved in a column containing 100 ml of a cation exchange resin (CS11GC350). The SMB experiments were carried out wherein 12 column, were loaded with 300 ml of cation resin (CS11GC350). The purity of 89.4% and the recovery of 99.5% were achieved. Despite the high purity and yield, SMB technology was too complicated to be applied in large scale. Selective sorbents have been interested for 1,3-PDO separation. Corbin et al., (2003) proposed a separation process of 1,3-PDO, glycerol, or a mixture of 1,3-PDO and glycerol from a biological mixture using a molecular sieve. The zeolite H-ZSM-5 (Si/Al=140) was used for batch 1,3-PDO removal from the cell-free fermentation and ethanol/water mixture was used as an eluent. Moreover, the yield of 1,3-PDO was increased by increasing the concentration of ethanol, which indicated the desirability of performing the elution of 1,3-PDO by an ethanol-rich mixture. The total recovery of 1,3-PDO product was found to be as high as 94.7%.

Of all the processes, the Adsorption process makes use of relatively simple equipment and allows relatively easy maintenance. The size of the units which can vary from laboratory scale to commercial scale and can range in flow rates from as little as a few milliliters to many thousands of gallons per hour. The reviews of the studies in the adsorption process are summarized in table 2-3 to 2-6. Most of the processes employed involved either ion exchange resin or molecular sieve adsorbent. It is therefore the main purpose of this work to determine an alternative adsorption process for separation of 1,3-PDO using polymeric adsorbents.

Table 2-3 Review of adsorption for separation of 1,3-propanediol by molecular sieve.

Author	Corbin et al., September 29, 2000. US Patent No. 6603048.
Separation process	Based on adsorption/desorption (zeolite packed column)
Liquid composition	Fermentation broth provided inoculums of *E.coli* capable of producing 1,3-propanediol from glucose was added to fermentor
	● Using ISPR technique ● Remove cellular by passing cross-flow filtration unit ● Contact mixture with ***first zeolite*** packed column (zeolite selective 1,3-propanediol and glycerol) ● Desorbent with ethanol: water, collecting1,3-propanediol and glycerol and repeating step ● Contact mixture with ***second zeolite*** packed column (zeolite selective 1,3-propanediol and glycerol) ● Desorbent with ethanol: water, collecting1,3-propanediol or glycerol and repeating step
Adsorbent	Zeolite MFI (H-ZSM-5 (Si/AI= 140)) selected on the basis its selectivity to 1,3-propanediol
Elution	Ethanol: water, C.sub1 - C.sub4 alcohol: water
	1.) Yield of 1,3-propanediol was increase by increasing the concentration of ethanol 2.) Total recovery will be high as 94.7% 3.) Desorption at room temperature 4.) ISPR technique increase production rate to the highest rate of entire run

Advantage	1. Easily to distillation 2. Process is clean and satisfies the environmental protection standard
	3. Process consumes less energy
Disadvantage	1. Low yield. 2.Requirment of dewatering step for high purity of 99%

Table 2-4 Review of adsorption for separation of 1,3-propanediol by ion exchange resin.

Author	Hilaly et al., March 15, 2001. US patent No. 6479716
Separation process	Ion exchange chromatography (simulated moving bed apparatus and technique)
Liquid composition	Fermentation broth (1-50% 1,3-propanediol) and mimic fermentation broth (5-24% 1,3-propanediol)
Methods	a.) Contact liquid composition comprising 1,3-propanediol with cation exchange resin b.) Adding solvent and eluting fraction C.) Recovering 1,3-propanediol by distillation step *Chromatographic separation to reject salt, sugars and other materials* ● Ionic component are rejected due to ionic repulsion ● Non-ionic component enter the pores of the stationary phase ● Elute from a column later than the ionic component (the chemical nature of PDO is non-ionic) ● The fermentation by-product and sugar elute earlier than 1,3-prapanediol because of difference in molecular properties ● The first fraction (impurity salts, sugar, other by-product) can be recycle back to fermentation ● The second fraction (mainly 1,3-propanediol) *Simulated moving bed (SMB)* ● Multiple column containing ion exchange resins are connected in series ● Fluid flow counter current movement of resins ● Apparatus consist of three zone (adsorption zone, enrichment zone, elution zone)

	● Step time 2-20 min ● Flow rate of resin 33.3 ml/min, eluent 32.5mL/min, product 17.3 ml/min, waste 22.5 ml/min and feed 7.3 ml/min (column 300mL and ambient temperature)
Adsorbent	Cation resin (polystyrene sulfonate strong cation exchange resin) size 100-500 micron and 200-350 micron
Elution	Water
Product fraction	At least 50% 1,3-propanediol,75%, 85%
Result	By varying the number of effluent fraction, the purity of 1,3-propamediol in the product fraction can be varied from at least 50% to greater than 90%
Advantage	1. Process is clean and satisfies the environmental protection standard (no organic solvent used) 2. Process consumes less energy
Disadvantage	1. Low yield 2. Requirement of dewatering step for high purity of 99%

Table 2-5 Review of adsorption for separation of 1,3-propanediol by ion exchange resin.

Author	Roturiea et al., August 6, 2002. US Patent No. 6428992
Separation process	Chromatography
Liquid composition	Fermentation broth provided recombinant microorganism of the *E.coli* contain some glucose
Methods	**First step** remove cellular debris and protein and the effect of desalination ○ Microfiltration membrane porosity 0.1 micron ○ Clarified aqueous solution through a column charcoal and demineralize it on a strong cation resin and on anion resin **Second step** separation step ○ Passing the clarified aqueous solution over a cation exchange resin ○ Carried out batch- wise or continuous process ○ Remove all the 1,3-propanediol fermentation coproduct in the first fraction eluted enabling 1,3-propanediol to emerge in the last chromatographic fraction
Adsorbent	Strong acidic exchange resin of the polystyrene sulfonic acid type crosslinked with lead 4%, preferably at least 7%, of divinylbenzene (cation such as lanthanum, lead, iron, zinc, aluminum)
Elution	Water
	Using cation resin was **lanthanum** (65^{o}C, water flow rate 3 ml/min) 1.) 30 ml containing 2.0 g/L of 1,3-propanediol (yield of 31.9%) 2.) 30 ml a mixture containing 0.8 g/L glycerol and 2.7 g/L 1,3-propanediol (yield of 57.9%)

	3.) 30 ml containing 0.5 g/L of glycerol (yield of 31.9%)
	Using cation resin was **lead** (65°C, water flow rate 3 ml/min) 1.) 48 ml containing 3.0 g/L of 1,3-propanediol (yield of 47%) 2.) 54 ml a mixture containing 0.7 g/L glycerol and 1.4 g/L 1,3-propanediol (yield of 37.5%) 3.) 70 ml containing 0.5 g/L of glycerol (yield of 11%)
Advantage	1. Process is clean and satisfies the environmental protection standard (no organic solvent used) 2. Process consumes less energy
Disadvantage	1. Low yield. 2. Requirement of dewatering step for high purity of 99%

Table 2-6 Review of adsorption for separation of 1,3-propanediol.

Author	Wilkins et al., January 23, 2007. US patent No. 7166460
Separation process	Chromatographic removal of target molecule using ISPR technique
Liquid composition	Fermentation broth US patent 5686276
Methods	● Remove cell from broth by cross-flow filtration or centrifugation ● Remove other component from cell-free broth by second stage cross-flow filtration ● Remove water from cell-free solution (distillation, reverse osmosis, vapor recompression or evaporation) ● Target molecule separation via passage through a chromatographic medium and eluent ● Recovering target molecule from *first fraction* (distillation) ● Recovering eluent from second fraction of cell-free and target molecule-free solution ● Adding water removed from cell-free to the cell-free and target molecule-free for return to the biofermentation ● Return cell-free and target molecule-free from any of step to biofermentation
Adsorbent	adsorbent : activated carbon, zeolite, polymeric neutral resins, and immobilized complexation materials
Elution	water removal, non-aqueous eluent such as short chain alcohols, ethanol, or acetone (used alone or combination with water)
Advantage	1. Lowers costs for isolating target molecules from a biofermentation broth 2. Improves the productivity of biofermentation by removing interfering target molecule 3. Relatively simple equipment and easy maintenance.
Disadvantage	1. Requirement of dewatering step for high purity.

2.6 Adsorption (D.M. Ruthven, 1984).

Adsorption is brought about by the interactions between the solid and the molecules in the fluid phase. Two kinds of force are involved, which give rise to physical adsorption (physisorption) or chemisorption. Physisorption are the same as those responsible for the condensation of vapor and the deviations from ideal gas behavior, whereas chemisorption interactions are essentially those responsible for the formation of chemical compounds.

The most important distinguishing features may be summarized as follows:

1. Physisorption is general phenomenon with a relative low degree of specificity, whereas chemisorption is dependent on the reactivity of the adsorbent and adsorptive.

2. Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to monolayer. At high relative pressures, physisorption generally occurs as a monolayer.

3. A physisorbed molecule keeps its identity and on desorption returns to the fluid phase in its original form. If a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption.

4. The energy of chemisorption is the same order of magnitude as the energy change in a comparable chemical reaction. Physisorption is always exothermic, but the energy involved is generally not much larger than the energy of condensation of the adsorptive. However, it is appreciably enhanced when physisorption takes place in very narrow pores.

5. The activation energy is involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain thermodynamic equilibrium. Physisorption systems generally attain equilibrium fairly rapidly, but equilibration may be slow if the transport process is rate determining.

2.6.1 Adsorption isotherm

2.6.1.1 Classification of adsorption isotherms in solid-vapor system (M. Drew, 1946)

The five isotherms to be considered are shown schematically in Figure 2-2. The type I isotherm, usually termed the Langmuir type, is characterized by a fairly rapid initial rise in the amount of gas adsorbed with increasing gas pressure until some limiting value is reached. That limiting value is usually identified with the attainment of a complete monolayer coverage. Such an isotherm would be expected, for example, in chemisorption, where the system is limited to a monolayer. It may also be found for systems in which there is a strong nonspecific attractive interaction between the adsorbate and adsorbent, but weak attraction between the adsorbate molecules themselves. Such isotherms may also be encountered in systems in which the solid has a very fine microporous structure.

Type II isotherms are typical of physical adsorption on nonporous solid. In contrast to type I, the adsorbate molecules in these cases also have relatively strong mutual interactions, which lead to the tendency for multilayer formation. The initial rapidly rising part of the isotherm corresponds to the equivalent type I adsorption. Point *B* on the curve is identified with complete monolayer coverage. Multilayer formation then begins which may lead to surface condensation. Type II isotherms are sometimes encountered for microporous solids, in which case point *B* would correspond to both completion of monolayer coverage and filling of the micropores by capillary condensation. The rest of the curve would then correspond to normal multilayer formation.

Type III and V isotherms are relatively rare and correspond to systems in which the interaction between adsorbate molecules is stronger than that between adsorbate and adsorbent. In these cases, the uptake of gas molecules is initially slow until surface coverage is sufficient so that interactions between adsorbed and free molecules begins to dominate the process. One might say that the process are autocatalytic in terms of the adsorption process.

Type IV isotherm are obviously similar to type II and usually correspond to systems involving capillary condensation in porous solids. In this case, however, once the pores have become filled, further adsorption to form multilayer does not occur and the terminating plateau region results. This would indicate a relatively weak interaction between the adsorbate molecules. While more complex isotherm classifications are available, they generally represent combinations and extensions of the five basics types described above.

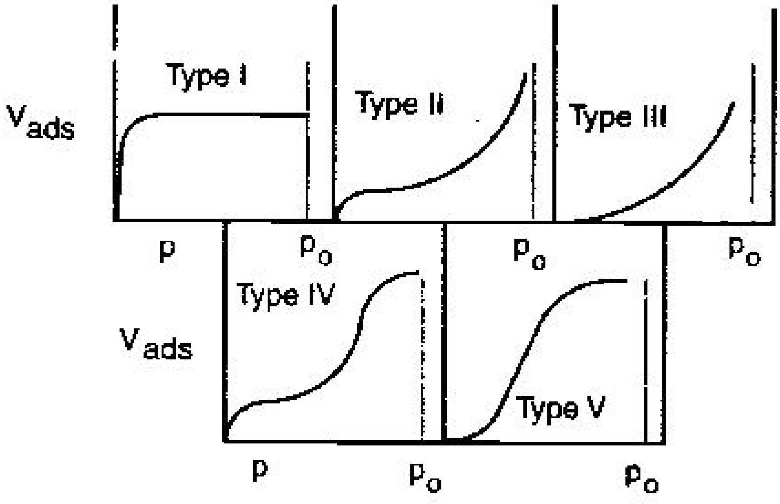


Figure 2-2. Adsorption isotherms are generally divided into five main types depending on the degree of adsorption (monolayer or multilayer), the mechanism of adsorption (physical or chemisorption), the nature of the adsorbent surface (porous or nonporous), and the relative strengths of adsorbate-adsorbent interactions. (M. Drew, 1946)

2.6.1.2 The Langmuir isotherm

Because of its simplicity and wide utility, the Langmuir isotherm has found wide applicability in a number of useful situations. Like many such “classic” approaches, it has its fundamental weaknesses, but its utility generally outweighs its shortcomings. The Langmuir isotherm model is based on the assumptions that adsorption is restricted to monolayer coverage, that adsorption is localized (i.e., that specific adsorption sites exist ant interactions are between the sites and a specific molecule), and that the heat of adsorption is independent of the amount of material adsorbed. The Langmuir approach is based on a molecular kinetic model of the adsorption-desorption process in which the rate of adsorption (rate constant k_A) is assumed to be proportional to the partial pressure of the adsorbate (p) and the number of unoccupied adsorption sites ($N-n$), where N is the total number of adsorption sites on the surface and n is the number of occupies sites, and the rate of adsorption (rate constant k_D) is proportional to n.

At equilibrium, the rates of adsorption and desorption will be equal so that

$$k_A p(N-n) = k_D n \tag{2-1}$$

Ignoring entropy effects, the equilibrium constant for the process will be $K_{eq} = k_A / k_D$, so that

$$K_{eq} = \frac{n}{p(N-n)} = \exp\frac{-\Delta H^\circ}{RT} \tag{2-2}$$

where ΔH° is the heat of adsorption per mole at temperature T and standard pressure P_{st}.

The fraction of the adsorption sites occupied at a given time, q, is given by

$$q = \frac{n}{N} \tag{2-3}$$

so that equation (2-2) can be written

$$q = \frac{K_{eq} p}{1 + K_{eq} p} \tag{2-4}$$

or

$$q = \frac{p}{p + K_{eq}^{-1}} = \frac{p}{p = P_{st}\exp(\Delta H^\circ)/R} \tag{2-5}$$

A useful characteristic of the Langmuir isotherm is that it can be rearranged to the linearized form

$$n^{-1} = N^{-1} + (K_{eq} N p)^{-1} \tag{2-6}$$

so that a plot of n^{-1} versus p^{-1} should be linear and yield values of K_{eq} and N from the slope and intercept. If the plot is not linear, then the Langmuir model does not fit the adsorption process in question.

The assumptions accompanying the derivation of the Langmuir isotherm mentioned above are rather rigorous. Although those conditions are almost never met in practice, the ability of the model to accurately express a significant amount of adsorption data in a mathematically simple and accessible way makes it invaluable as a basis for adsorption studies.

2.6.2.3 The Freundlich adsorption isotherm

It is often found that the simple Langmuir isotherm does not adequately describe adsorption systems of theoretical and practical interest. Another classic isotherm that has found application in describing adsorption, especially at moderate pressures, is the so-called Freundlich adsorption isotherm

$$V = kp^{1/a} \tag{2-7}$$

Where V is the volume of adsorbed gas and k and a are constants, a usually being greater than 1. Equation (2-7) can be linearized by taking the logarithm of each side to give

$$\ln V = \ln k + \frac{1}{a \ln p} \tag{2-8}$$

Obviously, a plot of In V versus In p should give a straight line. Although originally derived empirically, the Freundlich equation can also be derived theoretically using a model in which it is assumed that the heat of adsorption is not constant but varies exponentially with the extent of surface coverage, a condition that is probably closer than the Langmuir assumption in most cases.

2.6.2 Quantification of solute adsorption

The conventional method for determining the above quantities in a given system is by way of the adsorption isotherm, using the basic concepts already introduced. The basic quantitative equation describing the adsorption of one component of a tertiary solution onto a solid substrate can be written as

$$\frac{n_0 \Delta x_1}{m} = n_1 \sigma x_2 - n_2 \sigma x_1 \tag{2-9}$$

where n_0 is the total number of models of solution before adsorption, $x_{1,0}$ the mole fraction of the adsorbing component 2 in solution before adsorption, x_1 and x_2 the mole fractions of components 1 and 2 at adsorption equilibrium $(\Delta x_1 = x_{1,0} - x_1)$, m the mass of solid adsorbent present, in grams, and n_1 and n_2 the number of moles of components 1 and 2 adsorbed per gram of solid at equilibrium.

2.6.3 Adsorption at solid-liquid interfaces

Interactions between solid surfaces and solution are of fundamental importance in many biological systems (joint lubrication and movement, implant rejection, etc), as well as in mechanics (lubrication and adhesion), in agriculture (soil wetting and conditioning and pesticide application), in communications (ink and pigment dispersions), in electronics (microcircuit fabrication), in energy production (secondary and tertiary oil recovery techniques), in foods (starch-water interactions in bakery dough), and in paint production and application (latex polymer and pigment dispersion stabilization).

With so many applications in theory and in practice, a good basic understanding of adsorption phenomena at solid-liquid interfaces can be of great importance to both the theoretician and the practitioner. As was the case for solid-vapor adsorption, the proper interpretation of experimental observations will almost always require a sound conceptual idea of the processes (possibly) involved, even though a specific model may not exactly describe the results.

2.6.3.1 Adsorption isotherms in solid-liquid systems

The experimental evaluation of adsorption from solution at solid-liquid interface usually involves the measurement of changes in the concentration of the solute in the solution after adsorption has occurred. The usual method for evaluating the adsorption mechanism is through the adsorption isotherm. The important factors to be considered are (1) the nature of the interaction(s) between the adsorbate and the adsorbent, (2) the rate of adsorption, (3) the shape of the adsorption isotherm and the significance of plateaus, points of inflection, and so on, (4) the extent of adsorption (i.e., monolayer or multilayer formation), (5) the interaction of solvent with the solid surface (salvation effects), (6) the orientation of the adsorbed molecules at the interface, and (7) the effect of environmental factors such as temperature, solvent composition, and pH on these factors.

Just as in the case of solid-vapor adsorption, interactions between the adsorbent and adsorbate may fall into two categories: relatively weak and reversible physical adsorption, and stronger and sometimes irreversible specific adsorption or chemisorption. Because of the varied possibilities of adsorption mechanisms, a variety of isotherm shapes have been determined experimentally. Although most are found to fall into two main categories, a satisfying theory of adsorption must encompass the complete range of forms. A general classification of isotherms with various shapes that have been justified theoretically is shown in Figure 2-3. The classification system give four fundamental isotherm shapes based on the form of the isotherm at low concentrations: the subgroups are then determined by their behavior at higher concentrations.

The L-class (Langmuir) isotherm is the most common and is identified by having its initial region (L1) concave to the concentration axis. As the concentration of adsorbate increases, the isotherm may reach a plateau (L2), followed by a section convex to the concentration axis (L3). If the L3 region attains a second plateau, the region is designated L4. This family of isotherms can be compared to types I, II, and IV for solid-vapor adsorption shown in Figure 2-2.

In the S class of isotherms, the initial slope is convex to the concentration axis (S1) and is often broken by a point of inflection leading to the characteristic S shape (S2). Further concentration increases may then parallel those of the L class (see types III and V, Fig. 9.7). The H or high-affinity class of isotherm occurs as a result of very strong adsorption at low adsorbate concentrations. The result is that the isotherm appears to have a positive intercept on the ordinate. Higher concentrations lead to similar changes to those found in the L and S classes.

The final type of isotherm is the C class. Such systems exhibit an initial linear portion of the isotherm, indicating a constant partitioning of the adsorbate between the solution and the solid. Such isotherms are not found for homogeneous solid surface but occur in systems in which the solid is microporous. The classification system has proved very useful in providing information about the mechanism of adsorption.

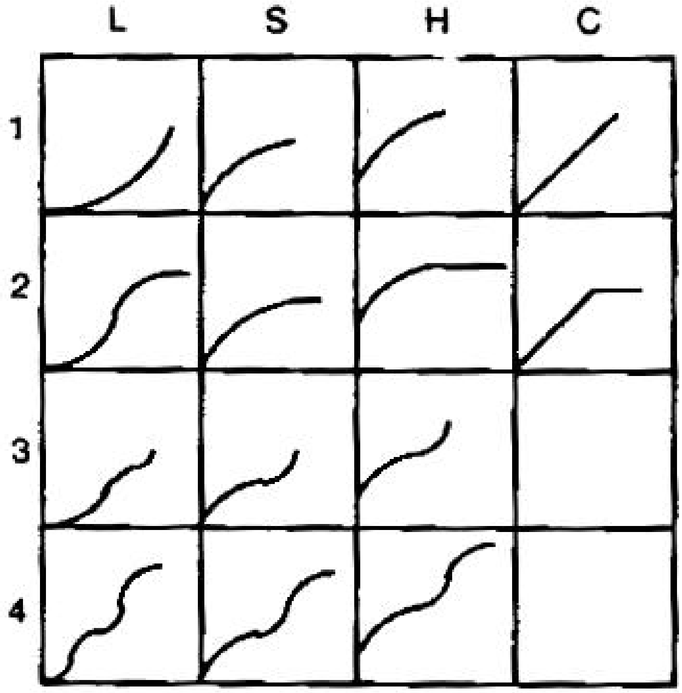


Figure 2-3 Various isotherm shapes are encountered in adsorption from solution. The more common shapes are illustrated here. (M. Drew, 1946)

2.7 Adsorbent (R. T. Yang, 2003)

For many separation processes, the separation is caused by a mass separating agent. The mass separating agent for adsorption is adsorbent, or sorbent. Consequently, the performance of any adsorptive separation or purification process is directly by the quality of the sorbent. The adsorptive separation is achieved by one of three mechanisms: steric, kinetic or equilibrium effect. The steric effect derives from the molecular sieving properties of zeolites and molecular sieves. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences diffusion rate of different molecules. A large majority of processes operate through the equilibrium adsorption of mixture and hence are called equilibrium separation processes.

For equilibrium separation, the starting point for sorbent design/selection is to examine the fundamental properties of the targeted molecule that is to be adsorbed (compare with other molecule in the mixture): polarizability, magnetic susceptibility, permanent dipole moment and quadrupole moment. Sorbent design/selection is a complex problem, because the process for which the sorbent is used needs to be considered at the same time.

2.7.1 Fundamental factors for designing adsorbent

Selection or synthesis of adsorbents for a target adsorbate molecule is based on the adsorption isotherm. With the availability of high-speed computing, it is now possible to calculate the adsorption isotherms based on: (1) interaction potentials and (2) structure/geometry of the adsorbent. Let us begin with a review of the basic forces between the adsorbent and adsorbate, paying particular attention to adsorbent design.

2.7.1.1 Effect of adsorbate properties on adsorption: polarizability (α), dipole moment (μ) and quadrupole moment (Q)

For a given sorbent, the sorbate-sorbent interaction potential depends on the properties of the sorbate. Among the five different types of interactions, the nonspecific interactions, $Ø_D$ and $Ø_R$, are nonelectrostatic. The most important property that determines these interactions (and also $Ø_{Ind}$) is the polarizability, α. On a surface without charge, such as graphite, $Ø_{Ind} = 0$. The value of α generally increases with molecular weigh because more electrons are available for polarization. From the expressions for $Ø_D$, $Ø_R$ and $Ø_{Ind}$, it is seen that these energies are nearly proportional to α. The dispersion energy also increases with the magnetic susceptibility, χ, but not as strongly as α.

2.7.2. Polymeric resin

A broad range of synthetic, non-ionic polymers are available for used as sorbents, ion exchanges and chromatographic column packings. The technology of the designing and building porosity into polymers was accomplished in the late 1950’s and early 1960’s. These macroporous molecules are termed macroreticular polymers. Building porosity can be accomplished by emulsion polymerization of the monomers in the presence of a solvent which dissolves the monomer but which is a poor swelling agent for the polymer. Although macroreticular polymers of acrylates and methacrylates are available, most commercial macroreticular polymers are based on styrene crosslinked by divinylbenzene (DVB). Over the years, these styrene/DVB copolymers have been produced with a wide range of porosities and macropore sizes.

The macroporous polymeric resins can be further reacted to attach functional group to the benzene rings to generate functionalities for ion exchange. The resulting polymers are ion exchange resins. For example, polystyrene can be sulfonated by sulfuric acid resulting in an –SO3-H+ group attached to the benzene ring, and the proton can be easily exchanged with other cations. Likewise, attaching ammonium or amine groups results in anion exchange resins. These polymeric resins and the functional groups results are illustrated in Figure 2-4.

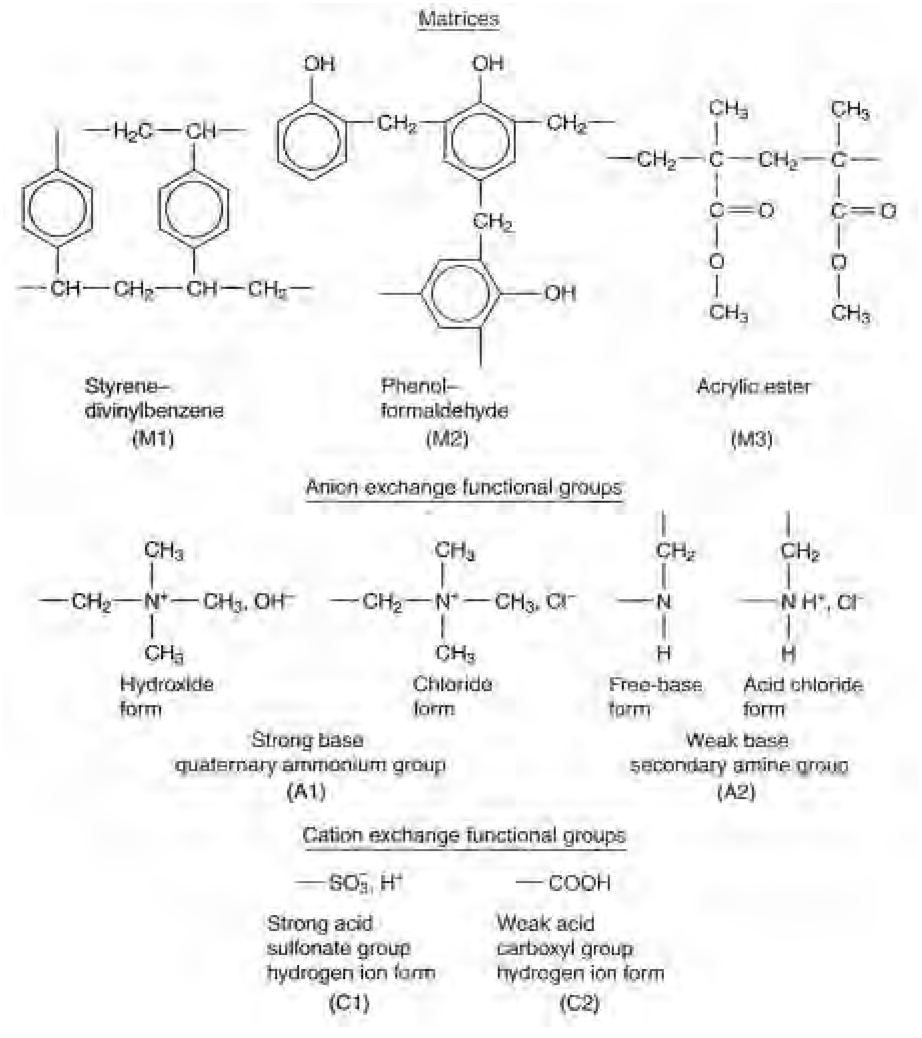


Figure 2-4 Polymeric resins and functional groups that are attached to the benzene ring of matrix. Most commercial are based on Styrene/DVB. (R. T. Yang, 2003).

The general properties of some representative commercial resins are given in table 2-7**.** The average pore size given by the manufacturers are not very meaningful because of the bi-modal pore distribution.

Table 2-7 Typical polymeric adsorbent (R. T. Yang, 2003)

Resin Name	Chemical Nature	BET Surface Area (m2/g)	Nominal Avg. Pore Diameter (A)	Hydrophobicity
XAD-2	PS/DVB	300	90	Yes
XAD-4	PS/DVB	725	40	Yes
XAD-7	Acrylic ester	450	90	No
XUS-43493	PS/high DVB	1125	35	No
Dowex Optipore	PS/DVB/tert. Amine	800	50	No
XE-563	Carbonaceous	550	38	No
XE-572	Carbonaceous	1100	30	No

The surface of the resins is highly aromatic. Sizable fractions of the surfaces are benzene ring. For this reason, the unfunctionalized polymeric resins are hydrophobic. The ion exchange resin are, however, not hydrophobic. The hydrophobic resins need to be pretreated to become wetted prior to use in water treatment. The pretreatment involves immersion in water soluble solvent, such as acetone or methanol, to displace air from the pore, followed by displacement of the solvent by water or aqueous solution. The aromatic surface of the resins makes them excellent sorbents for removal of organic compounds from aqueous solution, particularly those with low solubilities.

Ease in regeneration is a major practical advantage for the resins. Regeneration can be achieved with nonaqueous solvent and aqueous solution of acids, bases or salts. The non aqueous solvent can also be regenerated for re-use, and the adsorbates may be recovered if desired. The major use for polymeric resin is water treatment. Commercial applications include removal of halogen organic compounds, phenol and pesticides from water, decolorization of effluents and dye wastes, removal of VOCs from air, and bioseparations.

CHAPTER III

MATERIALS AND METHODS

The experimental and analysis techniques are described in this chapter. First, the chemical reagents and experimental apparatus are described. Then, the research procedures for the preparation of adsorbent as well as the experimental procedures for the investigation of adsorption 1,3-PDO behaviors of XAD-7 and XAD-16 are provided for adsorption in binary, tertiary, and multiple component systems. In addition, the desorption of 1,3-PDO form both resins adsorbed were investigated. Lastly, the analysis procedures for the determination of the 1,3-PDO and other components are described.

3.1 Chemical reagents and apparatus.

3.1.1 Chemical reagents.

Adsorbents:

- Amberlite XAD-16 (Rohm and Haas, 1982) is rigid, non-ionic, crosslinked macroreticular copolymer of styrene and divinylbenzene, with high surface area and aromatic nature of its surface.
- Amberlite XAD-7 (Rohm and Haas, 1982) is a non-ionic aliphatic acrylic polymer. Its adsorptive properties were derived from its macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), high surface area and aliphatic nature of its surface. It is characterized as a hydrophilic adsorbent having somewhat hydrophobic structure compared with XAD-16. The properties of these adsorbents are presented in Table 3-1:

Table 3-1 Properties of polymeric resins

Properties	XAD-16	XAD-7
Characteristic	Non-polar or hydrophobicity with styrenic adsorbent	Polarity or hydrophilicity with acrylic adsorbent
Moisture holding capacity	62 to 70%	61 to 69%
Dipole moment	0.4 debye	1.83 debye
Specific gravity	1.015 to 1.025	1.06 to 1.08
Particle size		
Harmonic mean size	0.56-0.71 mm	0.56-0.71 mm
Surface area	> 800 m^2/g	> 380 m^2/g
Porosity	> 0.55 ml/ml	> 0.50 ml/ml
Suggested operating conditions		
pH rang	0-14	0-14
Maximum temperature limit	150°C	80 to 100°C

Reagents :

Number	Reagent	Reagent Type
1	1,3-Propanediol 98% ($C_3H_6O_2$)	Analytical Reagent Grade
2	Glycerol ($C_3H_8O_3$)	Analytical Reagent Grade
3	Acetic acid (CH_2COOH)	Analytical Reagent Grade
4	Butyric acid (C_3H_7COOH)	Analytical Reagent Grade
5	Ethanol (C_2H_5OH)	Analytical Reagent Grade
6	Sodium hydroxide (NaOH)	Analytical Reagent Grade

3.1.2 Apparatus:

Number	Apparatus	Brand : Series
1	Weigh Balance	Mettler Toledo : AB204
2	Incubator Shaker	New Brunswick scienctific : innova^{TM} 4330
3	pH meter	Shindengen : ISFET KS723
4	Conductivity meter	inoLab Cond Level 2 : 01370049

3.2 Experimental procedures

3.2.1 Preparation and pretreatment of resins

In the final manufacturing process, the resins are usually imbibed with salts to retard bacterial growth. Therefore, the salts must be washed from resins prior to use. To validate the method of the pretreatment of Amberlite XAD-16 and XAD-7 to ensure complete salts removal. Therefore, beads of the examined resins () were washed initially with distilled water four times to displace salt (Na_2CO_3). The complete salts removal was confirmed by measuring the conductivity of wash water. The detailed of resins preparation are shown in appendix A.

3.2.2 Adsorption of 1,3-PDO

In this experiment, the 1,3-PDO adsorption behavior by both resins were determined in binary, tertiary, and multiple component systems to investigate the adsorption capacity of 1,3-PDO and adsorptive selectivity of 1,3-PDO. The proportion of initial concentrations of solutes in synthetic mixture employed here were the same as the experimental concentrations in fermentation broth: 44 g/L of 1,3-PDO, 0.2 g/L of glycerol, 0.7 g/L of acetic acid, and 6 g/L of butyric acid, respectively (Pullsirisombat, 2007). All of the experiments were performed at 303 K, and the procedures are described below.

3.2.2.1 Adsorption isotherms in binary component system

The purpose of this experiment is to investigate the adsorption isotherm (at 303 K) of 1,3-PDO on XAD-16 and XAD-7. The experiment was carried out in a batch system in which blotted dried beads (approximately 0.5 g dry weight) were introduced into a series of 150 ml conical flasks containing 30 ml aqueous solution of 1,3-PDO at known initial concentrations(C_0), ranging between 10 and 200 g/L. The flasks were then completely sealed and placed in an incubator shaker which was operated at 150 rpm for 48 h. This was found to be sufficient to reach the system equilibration. The equilibrium concentrations of 1,3-PDO remained in the solutions were measured using HPLC, from which the amount of 1,3-PDO adsorbed can be calculated. The amount of adsorbate adsorbed onto the adsorbent (q_e, g/g) was calculated by Eq.3-1:

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{3-1}$$

where *V* is the volume of solution (L), C_e is equilibrium concentration (g/L), W is the weight of dry resin (g).

3.2.2.2 Adsorption of 1,3-PDO in tertiary system.

For investigating the amount of 1,3-PDO adsorbed in the presence of glycerol in aqueous solution, the experiment was carried out in a similar fashion as described previously for binary system, but in an aqueous system with glycerol addition. For the tertiary mixture, glycerol was added into the solution at a fixed proportion with the amount of 1,3-PDO in the solution. The initial glycerol concentrations tested in this experiment ranged between 0.364 and 0.727 g/L of the solution for the tertiary mixtures whose 1,3-PDO concentrations ranged between 80 and 160 g/L. This proportion of glycerol was used according to the experimental glycerol concentration in actual fermentation broth (Pullsirisombat, 2007). The equilibrium concentration of each component the solutions was measured using HPLC, which allow the amount of the component adsorbed and the adsorption selectivity to be calculated. The amount of adsorbate adsorbed onto the adsorbent (q_e, g/g) was calculated by Eq.3-1, and the equilibrium selectivity ($\alpha_{1,2}$) was determined from the following equation:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \tag{3-2}$$

where x_1, x_2 are the mole fraction of 1,3-PDO and glycerol on the adsorbent surface, whereas y_1, y_2 are the corresponding mole fractions in the liquid phase.

3.3.2.3 Adsorption of 1,3-PDO in multiple component system.

The fermentative production of 1,3-PDO typically resulted in a production of acid by-products such as acetic acid and butyric acid, which caused the pH of the broth to decrease. Not only does this pH change caused the inhibition of growth and product formation during the fermentation process, but it could also have an effect on the adsorption behavior of 1,3-PDO on the two polymeric resins. In this study, adsorption in the multiple component system containing 1,3-PDO, glycerol, butyric and acetic acids was investigated at 303 K, in which the effect of pH on the adsorption of each component was determined at 3, 5, and 7. The concentrations and the proportional of the components in the synthetic mixtures prepared for this study mimicked that in the fermentation broth, and the pH was adjusted by using NaOH solution. The amount of each component adsorbed can be determined by Eq 3-1 and the selectivity of 1,3-PDO was determined by Eq. 3-2, in which x_2 in this case is the sum of the mole fractions of glycerol, acetic acid, and butyric acid on the adsorbent, whereas y_2 are the corresponding mole fractions in the liquid phase.

The summary of the initial concentrations of the 1,3-PDO and other components, pH, and of the adsorption mixtures for different systems investigated in this study are given in Table 3-2.

Table 3-2 Initial concentrations of solutes in aqueous solutions.

System	Solutes	Initial Concentration (g/L)					pH
Binary component	1,3-PDO	10, 20, 30, 40, 60, 80, 100, 120, 140, 160, 200					5
Tertiary component	1,3-PDO	80	100	120	140	160	5
	Glycerol	0.364	0.455	0.546	0.636	0.727	
Multiple component	1,3-PDO	80	100	120	140	160	3, 5, and 7
	Glycerol	0.364	0.455	0.546	0.636	0.727	
	Acetic acid	1.273	1.591	1.909	2.227	2.546	
	Butyric acid	10.909	13.636	16.364	19.091	21.818	

3.2.3 Desorption of 1,3-PDO with ethanol/water solution

The desorption behavior was determined for the adsorbed resins obtained from adsorption in binary, tertiary, and multiple system. For each system, the conditions employed for adsorption was 160 g/L initial concentration of PDO, at pH5, and at ? K and the suitable ratio of ethanol/water elution solution was determined. The adsorption conditions and initial concentrations different components in the binary, tertiary, and multiple component system employed for the desorption experiments are summarized in Table 3-3. Desorption was carried out by placing 0.5 g of adsorbed resins in a flask containing 30 ml ethanol/water mixture (ethanol/water ratio of 50, 60, 70 and 80% (v/v)). The flask was completely sealed and shaken at the rotation speed of 150 rpm, and the temperature was controlled at 303 K. After 48 h, the equilibrium concentrations were reached and were measured using HPLC to determine the amount of desorbed species. The percent desorption yield, $\%y$, was calculated by Eq.3-3:

$$\%y = \frac{W_{desorbed}}{W_{adsorbed}} \times 100 \tag{3-3}$$

where $W_{adsorbed}$ is weight of 1,3-PDO originally adsorbed on the resins, and $W_{desorbed}$ is the weight of 1,3-PDO desorbed from resins.

Table 3-3 Parameter in 1,3-PDO desorption with ethanol/water solutions.

System	**Solutes**	**Initial Concentration (g/L)**	**pH**	**Ethanol/water ratio %(v/v)**
Binary component	1,3-PDO	160	5	50:50, 60:40, 70:30, and 80:20
Tertiary component	1,3-PDO Glycerol	160 0.727		
Multiple component	1,3-PDO Glycerol Acetic acid Butyric acid	160 0.727 2.546 21.818		

3.3 HPLC Analysis

The concentrations of the solutes in aqueous solutions were measured using HPLC with the Lichrocart-C18 analytic column (250 mm x 4 mm I.D.). The analysis was carried out at room temperature with the isocratic mode in which 5% MeOH used as a mobile phase was passed through the system at a constant flow rate of 0.5 ml/min. The injection volume used was 20 µL and the column effluent was monitored by an RI detector.

CHAPTER IV

RESULTS AND DISCUSSIONS

The present study is concerned with adsorption of 1,3-PDO on both hydrophilic XAD-7 and hydrophobic XAD-16 resins and the elution of the adsorbed product in binary, tertiary, and multiple systems. This chapter is divided into five parts. The first part presents the investigation of 1,3-PDO adsorption isotherm in binary component system. The second part involves the determination of 1,3-PDO adsorbed in a tertiary system. The third part aims to provide the best condition for adsorption of 1,3-PDO in multiple components system. The fourth part examines the desorption of 1,3-PDO and other species from both resins. Finally, the last part involves the comparison of the adsorption and desorption behavior of 1,3-PDO onto both resins and suggests the suitable resin and proper conditions for 1,3-PDO adsorption.

4.1 Binary component system

4.1.1 Effect of initial concentration on 1,3-PDO adsorption

The amounts of 1,3-PDO adsorbed on XAD-7 and XAD-16 resins, q (mg adsorbate per g adsorbent), at different initial 1,3-PDO concentration (10-200 g/L) are shown in Figure 4-1. The amounts of 1,3-PDO adsorbed were calculated using Eq. (3-1). At low initial 1,3-PDO concentration (10-30 g/L), 1,3-PDO seemed to prefer to be in the solution, giving low adsorption ability (Boonsongsawat et al**.,** 2007). However, 1,3-PDO adsorption on both polymeric adsorbents became more favorable when the initial concentration of the adsorbate was increased from 40-160 g/L. Beyond 160 g/L (160-200 g/L), there is no significant change in the amount of adsorbed 1,3-PDO. This plateau represents saturation of the active sites available on the resins for interaction with 1,3-PDO in aqueous solution. Maximum experimental adsorption capacity of 1,3-PDO at 160 g/L onto XAD-7 and XAD-16 was 835.96 and 584.61 mg of 1,3-PDO/ g dry resin respectively. These results show that the XAD-7 resin was suitable for 1,3-PDO adsorption from aqueous media. Moreover, the maximum experimental adsorption capacity of 1,3-PDO onto XAD-7 and XAD-16 resins in this study were higher than H-ZSM-5 zeolite adsorbent at batch condition (Corbin et al., 2000), which gave a capacity of 91.3 mg 1,3-PDO/ g zeolite. This is due to preferential adsorption of 1,3-PDO with non-ionic resin, on the basis that "like attracts like" (Rohm and Hass Company, 2002). From these results, the suitable initial concentration for 1,3-PDO adsorption is at 160 g/L, which gave the highest amount of 1,3-PDO adsorbed on both resins.

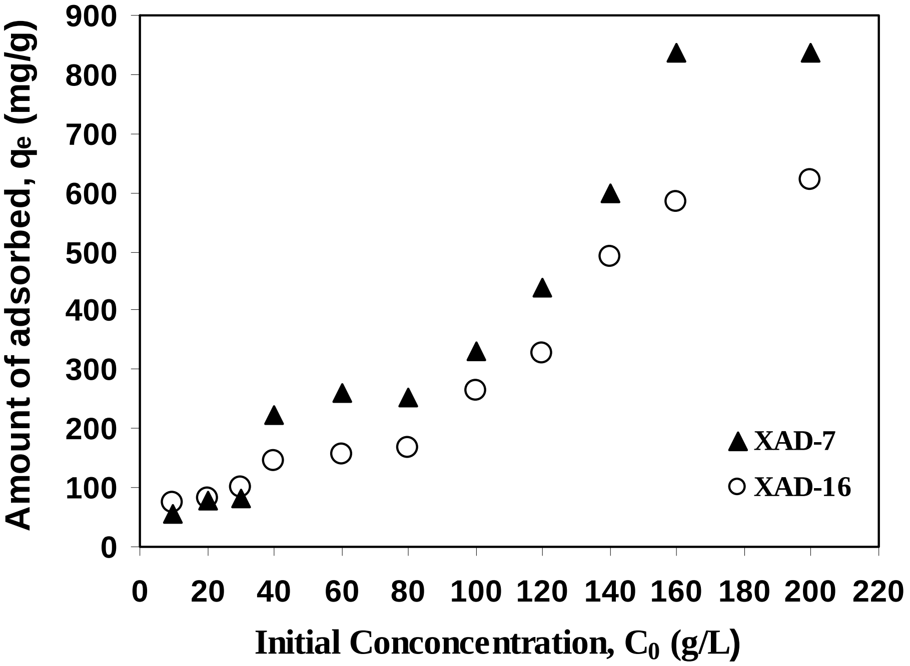


Figure 4-1 Adsorption of 1,3-propanediol onto XAD-7 and XAD-16 resins versus initial concentrations at pH 5, 303 K, and 48 hours.

4.1.2 Adsorption isotherm

The adsorption isotherm of 1,3-PDO on XAD-7 and XAD-16 resins are shown in Figure 4-2 to 4-3. The results illustrate that the adsorption isotherms exist as those of type II isotherm, which is typical of physisorption on microporous solid. It corresponds to both completion of monolayer coverage and filling of the micropores by capillary condensation. The plateau part of the curve (160-200 g/L) would then correspond to normal multilayer formation (Myers, 1946).

The different characteristics of isotherms observed for the XAD-7 and XAD-16 resins can be ascribed to the different hydrophobicities of the two types of resins. Van der waals force is normally dominant force for the adsorption from the aqueous phase onto a hydrophobic adsorbent. However, the electrostatic attraction has been important for molecules with certain functional groups. Therefore, the dominant factor for adsorption of 1,3-PDO onto XAD-16 resin is van der waals force while that on the XAD-7 resin may be the cooperation of hydrophobic interaction and electrostatic attraction (Yang et al., 2007).

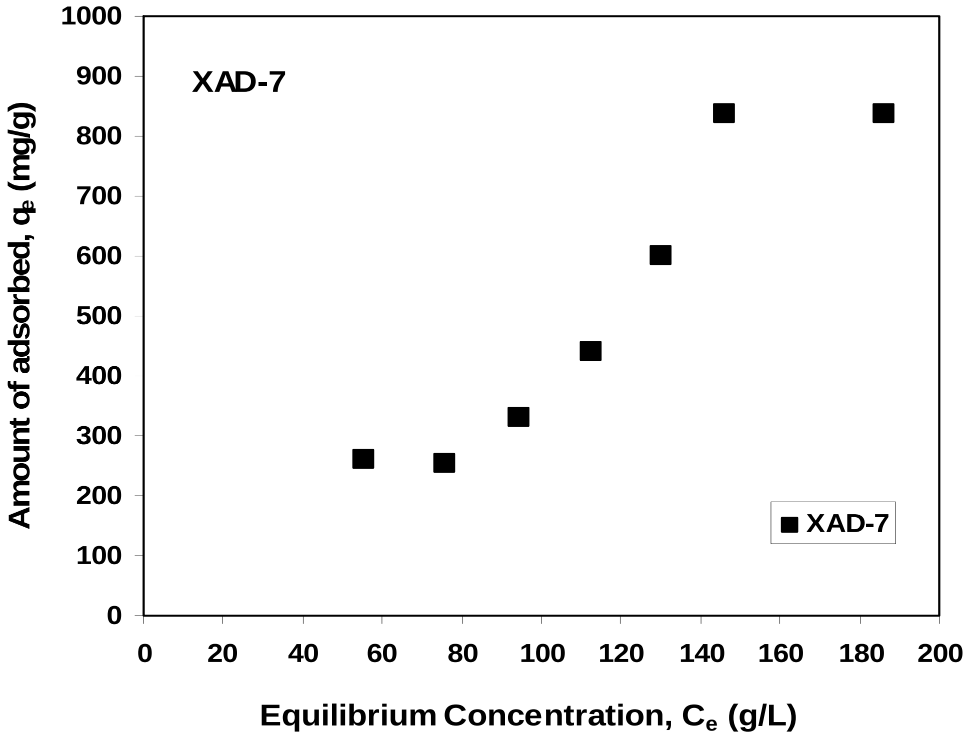


Figure 4-2 1,3-PDO equilibrium adsorption isotherm on XAD-7 resin in binary component system at pH 5, 303 K, and 48 hours..

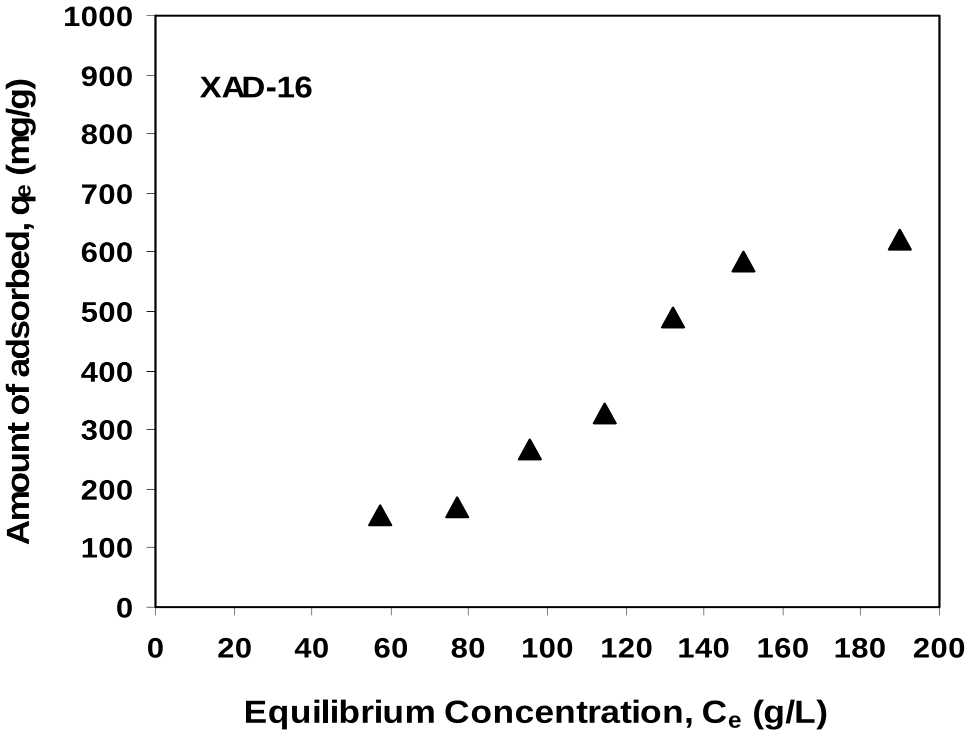


Figure 4-3 1,3-PDO equilibrium adsorption isotherm on XAD-16 resin in binary component system at pH 5, 303 K, and 48 hours.

4.1.3 Model fitting

The equilibrium adsorption data were analyzed using Langmuir and Freundlich equation. The Langmuir equation can be written in the following form:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{4-1}$$

$$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \tag{4-2}$$

where K_L and a_L are the Langmuir constants.

The empirical Freundlich equation is given below by Eq (4-3)

$$q_e = K_F C_e^{1/n} \tag{4-3}$$

$$\log q_e = \log K_F + 1/n \log C_e \tag{4-4}$$

where K_F and n are the Freundlich constants. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively.

The linear plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ and log q_e versus log C_e for the Langmuir and Freundlich isotherm models are shown in Figure 4-4 to 4-5, respectively. The Langmuir and Freundlich constants are determined from the intercept and the slope of the plot and are presented in Table 5.2.1-5.2.2.

In order to quantitatively compare the applicability the parameters of the two models, a normalized standard deviation, Δq, are calculated

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum((q_{t\exp} - q_{tcal})/q_{t\exp})^2}{n-1}} \tag{4-5}$$

where n is the number of data points; $q_{t\ exp}$ the experimental values; and $q_{t\ cal}$ the calculated values by models.

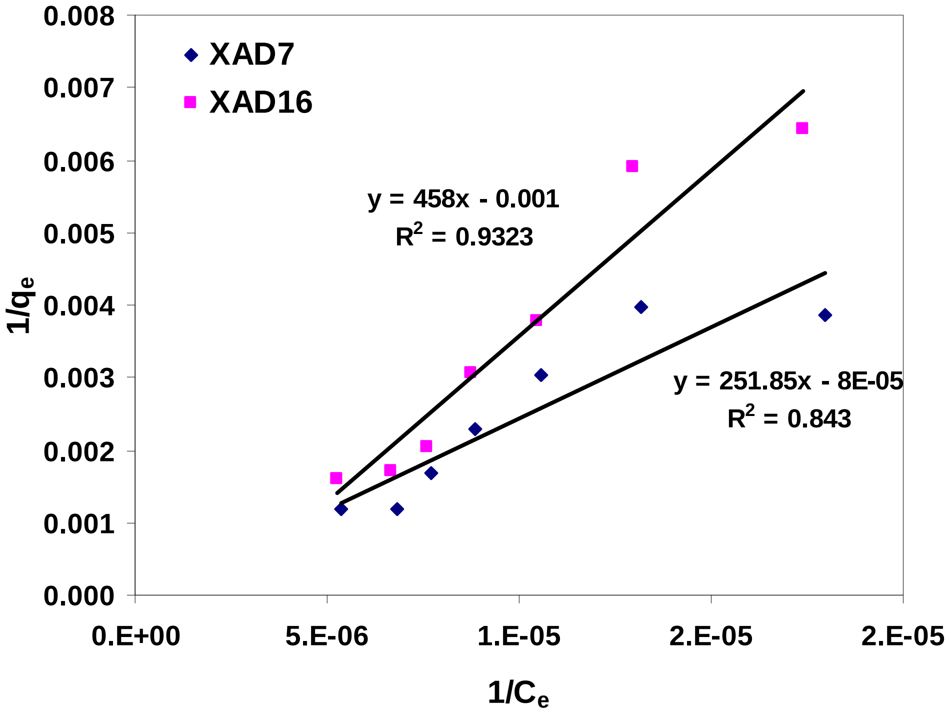


Figure 4-4 The linear plot of experimental equilibrium data by Langmuir model of XAD-7 and XAD-16 resins.

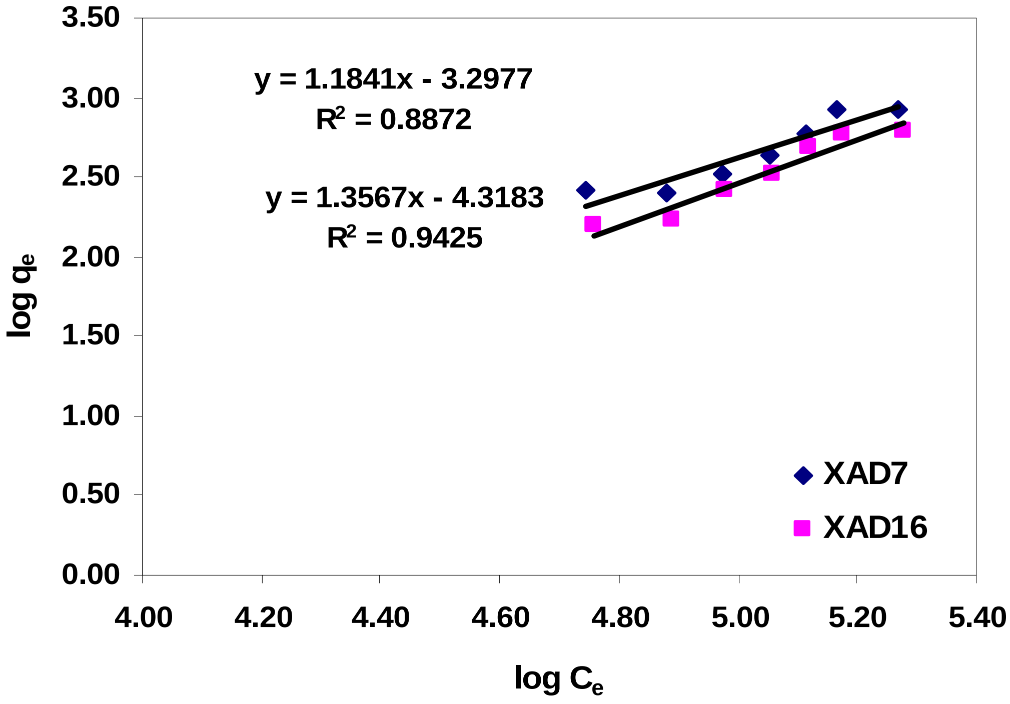


Figure 4-5 The linear plot of experimental equilibrium data by Freundlich model of XAD-7 and XAD-16 resins.

Table 4-1 Fitting parameters of models

Langmuir model				
Adsorbents	k_L (mg/g)	a_L (L/mg)	R^2	Δq (%)
XAD-7	-12500	-3.176E-07	0.8430	4.531
XAD-16	-1000	-2.183E-06	0.9323	3.044
Freundlich model				
Adsorbents	k_F (mg/g)	n (L/g)	R^2	Δq (%)
XAD-7	5.038E-05	0.8445	0.8872	3.743
XAD-16	4.800E-05	0.7371	0.9425	2.087

The fitting parameters of Langmuir and Freundlich models were determined graphically by linear regression (shown in Table 4-1). From figure 4-6 to 4-7, it can be seen that the adsorption data for 1,3-PDO onto these two polymeric adsorbents are similar. It is quite obvious that the Freundlich model is better fitted than Langmuir model for the entire isotherm, as supported by the lowest mean relative deviation value (Δq) (Table 4-1). The value of K_F and n of 1,3-PDO adsorbed on XAD-7 are much higher than those on XAD-16, in which higher K_F means that XAD-7 has higher adsorption capacity, while n is related to magnitude of the adsorption driving force. Therefore, the XAD-7 is more suitable for 1,3-PDO adsorption than XAD-16. All correlation coefficient R^2 for the XAD-16 is larger than 0.932 and those for the XAD-7 resin is less than 0.887. These results indicate that the adsorption mechanism of 1,3-PDO on XAD-7 and XAD-16 resin may be different (Yang et al.,2007).

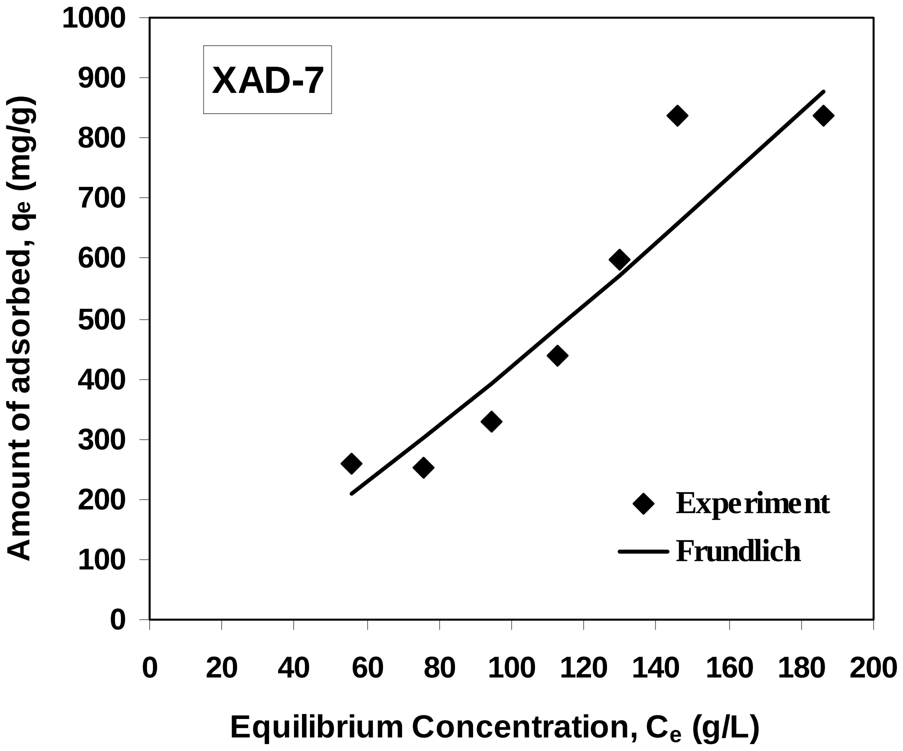


Figure 4-6 Experimental data and Freundlich model for 1,3-PDO adsorption isotherm on XAD-7 at pH 5, 303 K, and 48 hours.

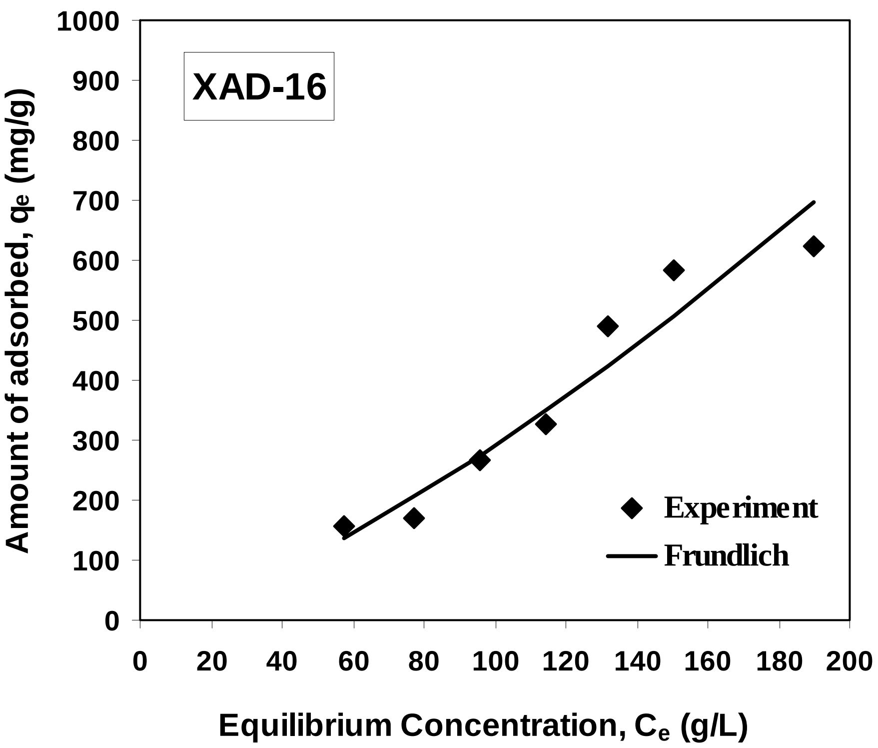


Figure 4-7 Experimental data and Freundlich model for 1,3-PDO adsorption isotherm with XAD-16 resin at pH 5, 303 K, and 48 hours.

4.2 Tertiary components system

In the fermentation process in practice, a small amount of glycerol remained unconverted. In this experiment, the effect of the presence of glycerol on the adsorption behavior was determined in the tertiary component system. Here, the aqueous solution resembling fermentation broth was used for the experiment.

4.2.1 Adsorption isotherm of 1,3-PDO and glycerol

The individual isotherm of 1,3-PDO and glycerol adsorption with XAD-7 and XAD-16 resins are shown in Figure 4-8 to 4-9. The amount of adsorption of 1,3-PDO and glycerol onto both resin increased when the initial 1,3-PDO and glycerol concentrations were increased. Figure 4-8 illustrates that the amount of 1,3-PDO adsorbed onto XAD-7 resin (726.68 mg/g) was slightly lower than XAD-16 (770.04 mg/g). On a contrary, the amount of glycerol adsorbed onto XAD-16 resin (10.41 mg/g) was higher than the XAD-7 resin (2.21mg/g). This results indicated that, although, the XAD-16 resin has higher amount of 1,3-PDO adsorbed than XAD-7 resin, the XAD-16 also adsorbed higher amount of glycerol, giving lower 1,3-PDO selectivity (discussed in the following section). For this reason, it can be concluded that XAD-7 is still more appropriate than XAD-16 for 1,3-PDO adsorption.

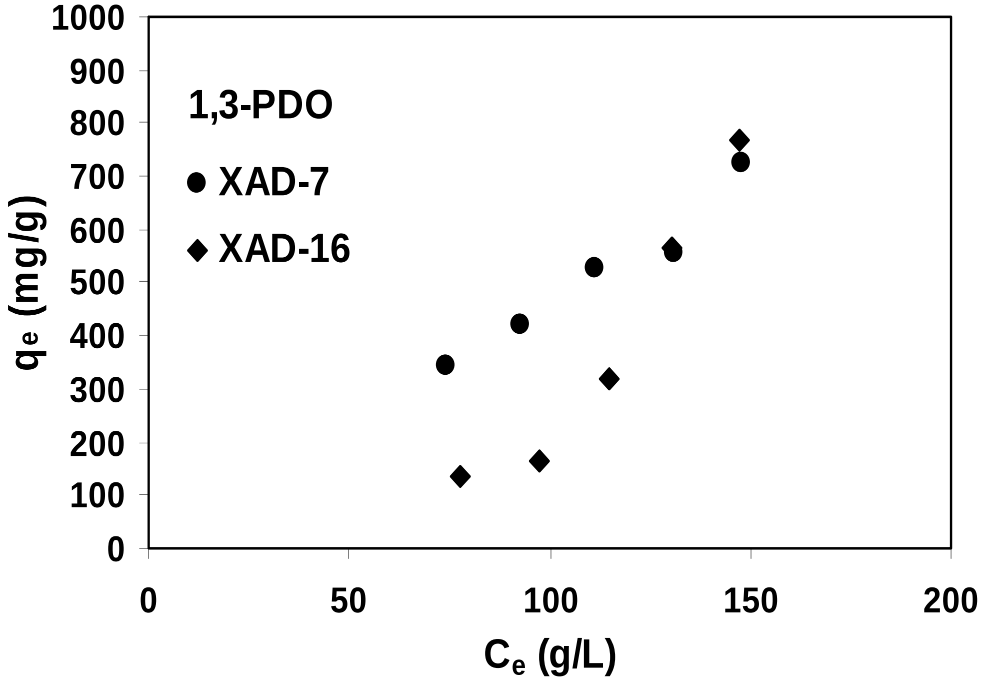


Figure 4-8 The 1,3-PDO equilibrium adsorption isotherm with XAD-7 and XAD-16 resin in tertiary component system at pH 5, 303 K, and 48 hours.

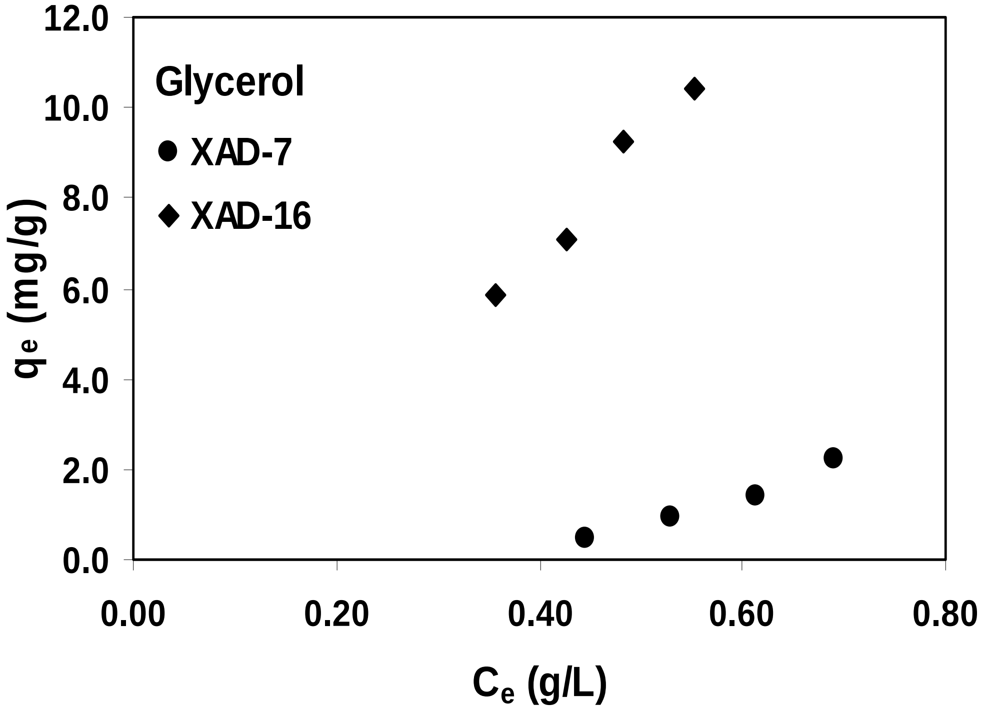


Figure 4-9 The glycerol equilibrium adsorption isotherm with XAD-7 and XAD-16 resin in tertiary component system at pH 5, 303 K, and 48 hours.

4.2.2 Adsorptive selectivity

The selectivity, $\alpha_{1,2}$, is defined as the ratio of the two components of the adsorbed phase over the ratio of the same two components in the unadsorbed phase at equilibrium conditions. The1,3-PDO over glycerol (1,3-PDO/glycerol) selectivity of both resin were calculated using Eq (4-6) in the following form:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \tag{4-6}$$

where subscript 1 and 2 are 1,3-PDO and glycerol and then x_1, x_2 are the mole fractions of the two components on the adsorbent surface, whereas y_1, y_2 are the corresponding mole fractions in the aqueous phase. The 1,3-PDO/glycerol selectivity of both resins were shown in Table 4-2.

The 1,3-PDO/glycerol selectivity, $\alpha_{1,2}$, of XAD-7 resin, is in the range of 1.53-7.49, whereas the selectivity of XAD-16 resin is less than 1.0. This would indicate that the glycerol is preferentially adsorbed so an adsorbed phase richer in glycerol (Kulprathipanja, 1988), implying that XAD-7 is more favorable in adsorption of 1,3-PDO. In general, the higher the selectivity, the easier the separation is to perform. Higher selectivity and adsorption capability permit a smaller amount of adsorbent to be used.

On the other hand, XAD-16 resin shows the preference of glycerol adsorption. Although glycerol (M.W. = 92, 3 hydroxyls) is expected to be more soluble in water than 1,3-PDO (M.W. = 76, 2 hydroxyls), as a result of higher number of hydroxyl group, and the thermodynamic stability of glycerol-water interactions would thus be expected to be higher, however the experimental results shows that was glycerol was more easily adsorbed onto XAD-16 than 1,3-PDO. This could be explained by values for heat of adsorption of the two compound on XAD-16 (20-30 kJ/mol for 1,3-PDO, and ~10 kJ/mol for glycerol) (Yang, 2003), thus confirming the experimental results.

In case of XAD-7, although the higher polarity glycerol compared with 1,3-PDO (due to higher number of hydroxyl group) and the significantly higher polarizability compared with 1,3-PDO, might suggest stronger interaction between glycerol and the XAD-7 surface, the higher selectivity of 1,3-PDO/glycerol by XAD-7 resin, on the other hand, could be explained by the higher thermodynamic stability of the glycerol-water interactions, compared with the interaction between glycerol and resin surface.

Table 4-2 1,3-PDO/glycerol selectivity of both resins.

	Selectivity of 1,3-PDO/glycerol	
Initial concentration (g/L)	**XAD-7**	**XAD-16**
80	7.49	0.11
100	4.12	0.10
120	2.71	0.17
140	1.83	0.23
160	1.53	0.28

4.2.3 Effect of glycerol on 1,3-PDO adsorption

The amount of 1,3-PDO adsorbed onto both resins in binary and tertiary system were compared in order to investigate the effect of glycerol on 1,3-PDO adsorption. Figure 4-10 to 4-11 illustrate the adsorption isotherm of 1,3-PDO in binary and tertiary component in aqueous solution onto both resins. Interestingly, 1,3-PDO equilibrium adsorption on XAD-7 resin in tertiary system shows a significant increase in the adsorption capacity of 1,3-PDO in the range of 80-140 g/L 1,3-PDO initial concentrations, while in the concentration range of 140-160 g/L, the adsorption decreased. The higher of 1,3-PDO adsorption in tertiary system at low concentration could be caused by the reduction of 1,3-PDO-water interaction caused by the presence of glycerol The different 1,3-PDO adsorption behavior was observed for XAD-16 resin, which decreased in the range of 80-120 g/L while increased between 140-160 g/L. At high concentration, the lower of 1,3-PDO adsorption in tertiary than binary system could be resulted by the hindrance of 1,3-PDO adsorption site by glycerol. On XAD-16 on the other hand, at low concentration the 1,3-PDO adsorption in tertiary did not differ significantly from the binary system, but drastically increased when the initial 1,3-PDO concentration increased. From the above results, it can be concluded that the presence of glycerol could either enhance 1,3-PDO adsorption by the reduction of 1,3-PDO-water by glycerol or hinder the adsorption by interfering the 1,3-PDO- surface interactions. Nevertheless, the reason for the differences in 1,3-PDO adsorption onto the resins and the preferability glycerol on polymeric resins is rather complex. Furthermore, the precise role-played by the polar group, the aromatic center is uncertain (Yang et al., 2007). From the above results however, it can be observed that the glycerol affected to reduce the amount of 1,3-PDO adsorbed onto XAD-7 resin and enhance 1,3-PDO adsorption onto XAD-16 resin at high concentration.

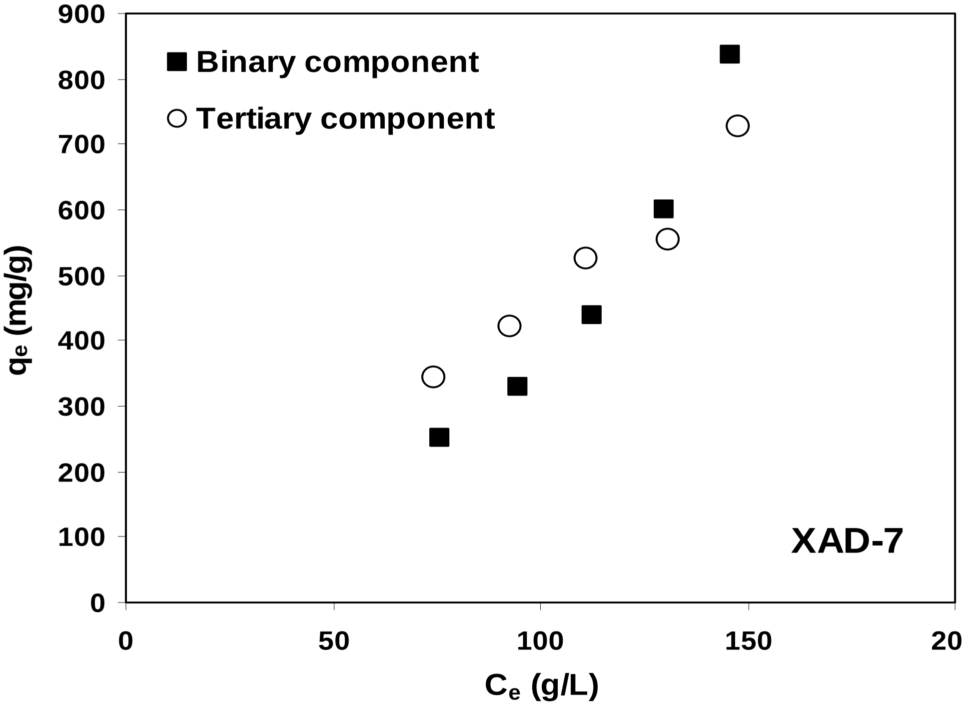


Figure 4-10 Comparison of the experimental binary equilibrium adsorption data with tertiary equilibrium adsorption data of 1,3-PDO onto XAD-7 resin at pH 5, 303 K, and 48 hours.

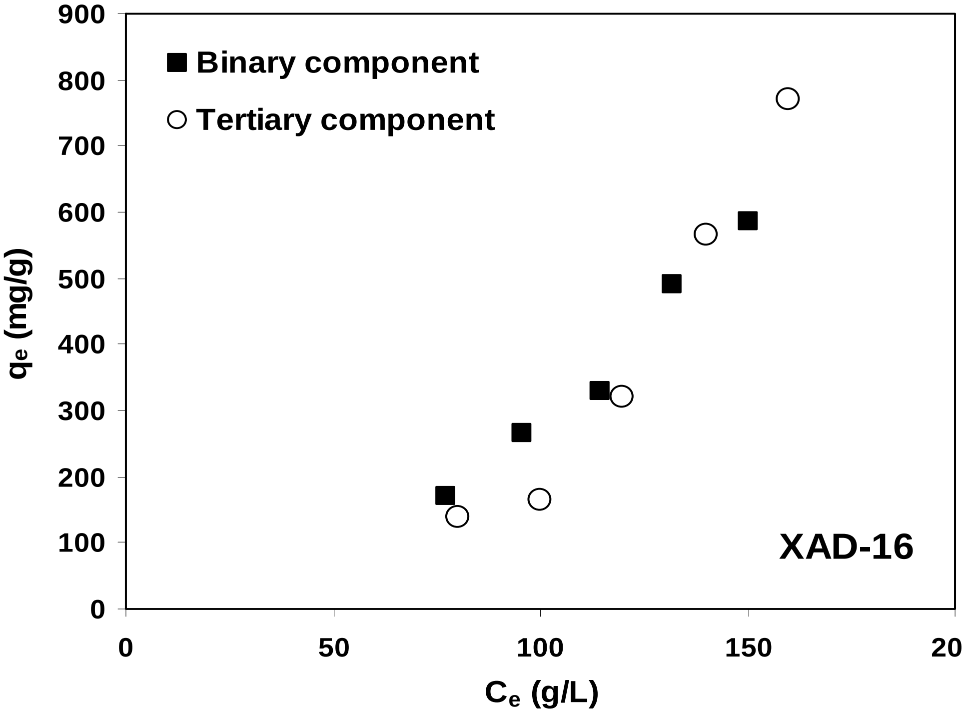


Figure 4-11 Comparison of the experimental binary equilibrium adsorption data with tertiary equilibrium adsorption data of 1,3-PDO onto XAD-16 resin at pH 5, 303 K, and 48 hours.

4.3 Multiple components system

From previous experiments, the presence of glycerol in solution was found to affect 1,3-PDO adsorption. In this section, the model mixture imitating fermentation broth was applied to investigate the effects of other components on 1,3-PDO adsorption. These components include glycerol, acetic acid, and butyric acid. Furthermore, the pHs of aqueous solution were also studied to find the suitable condition for 1,3-PDO adsorption on both resins such multiple component system.

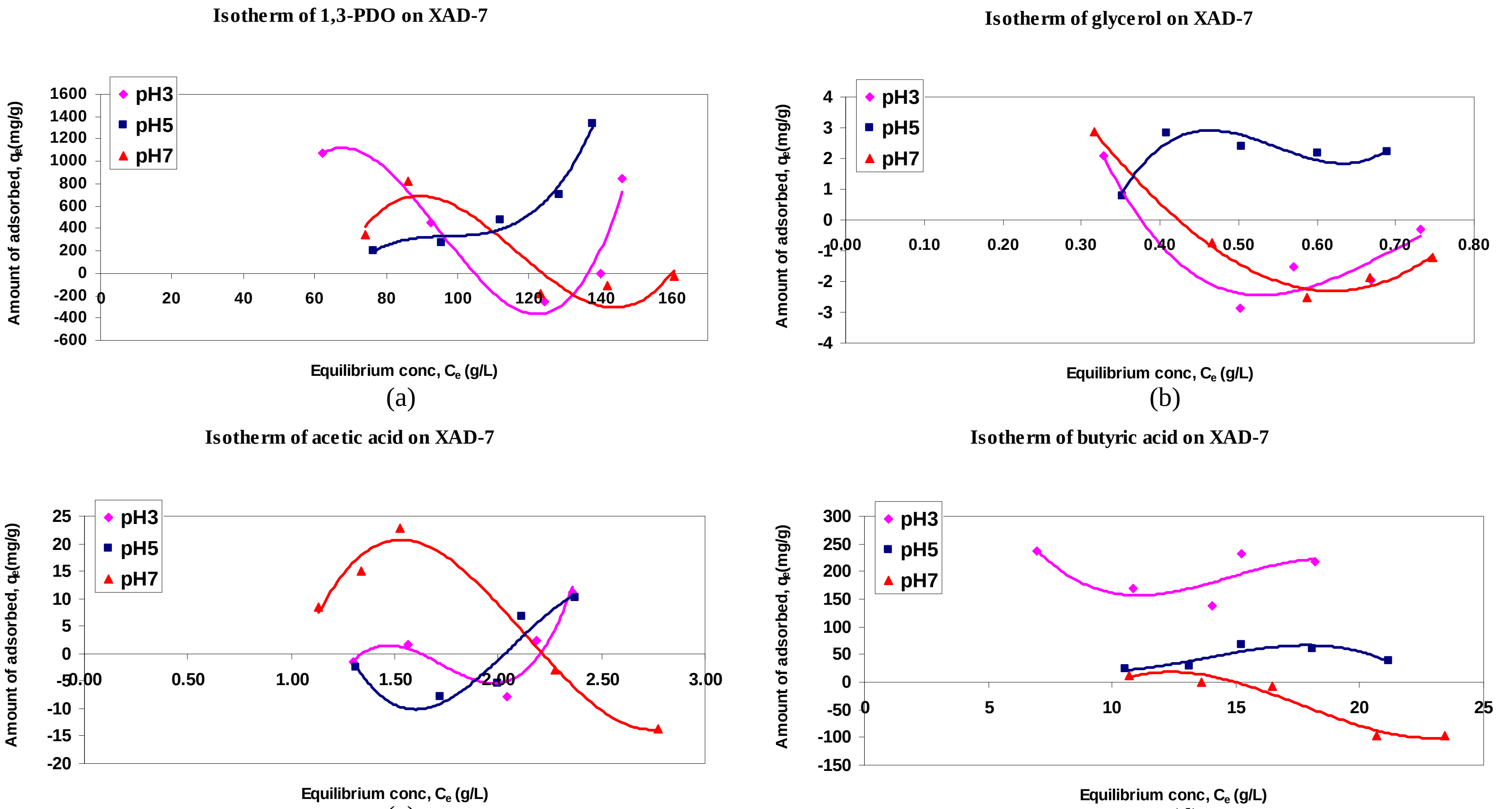
4.3.1 Effect of pH on adsorption

The purpose of this experiment is to provide the suitable pH for 1,3-PDO adsorption from aqueous solution. The pHs of the solution in this experiment were adjusted to 3, 5, and 7 by using NaOH solution.

Figure 4-12 to 4-13 show the individual isotherms of each component in aqueous solution on both resins at pH 3, 5 and 7. The results show that, both resins show both the *positive* and *negative* values of the amount of adsorbate adsorbed in some range of the concentrations of the individual component. The “Positive” adsorption of component 1 would mean that, at equilibrium, the component is present on the adsorbed layer in greater proportion than in the bulk liquid, while the “Negative” adsorption of component 1 means preferential adsorption of component 2 (Kipling, 1965). So, in Figure 4-12 to 4-13, the negative value of the amount of 1,3-PDO adsorbed thus means resins have preferential adsorption of other components.

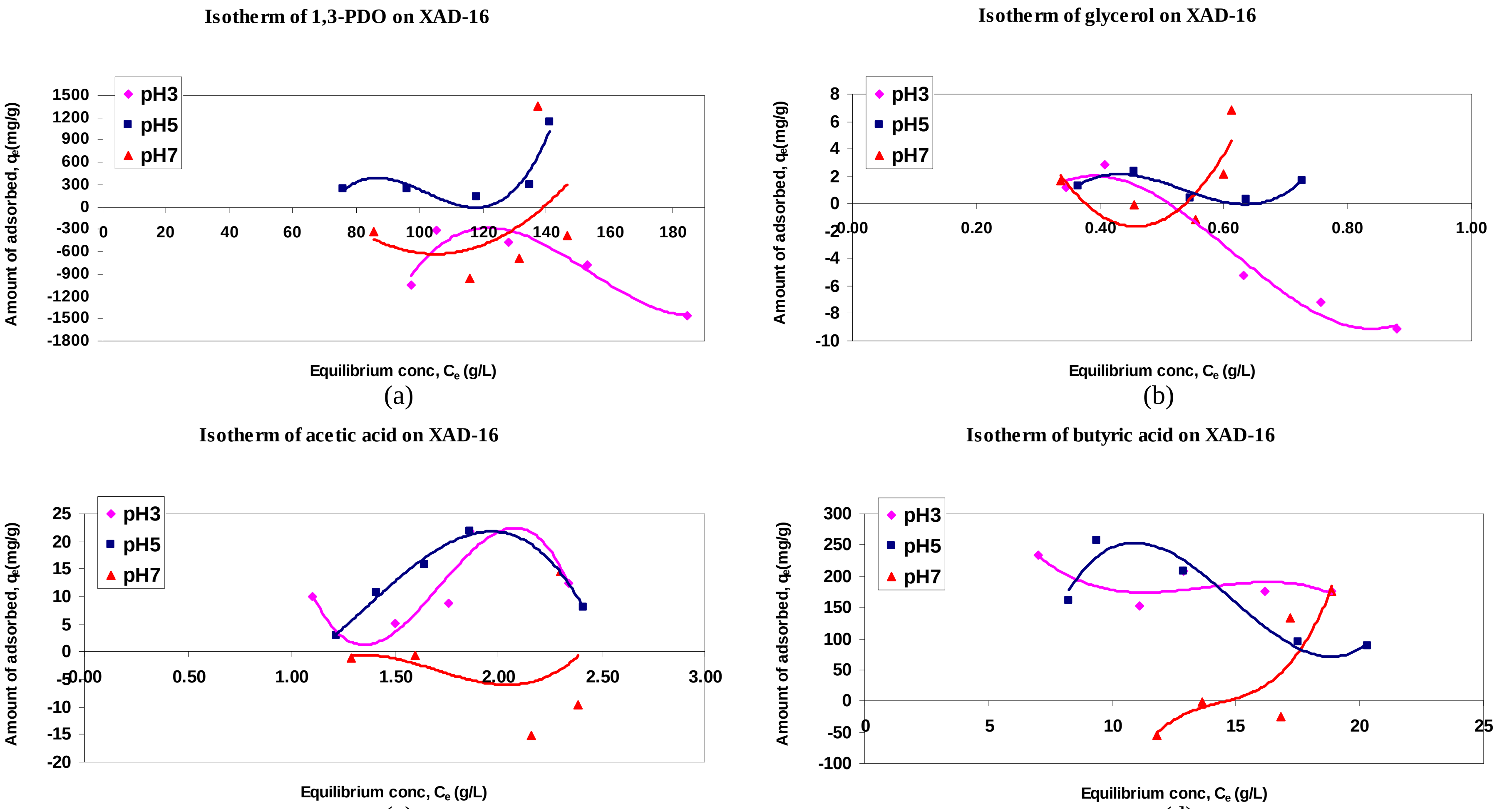
Figure 4-12 to 4-13 illustrate the amount of 1,3-PDO and other component in aqueous solution adsorbed onto two resins at pH 3, 5, and 7. The results of 1,3-PDO adsorption (Figure 4-12a and 4-13 a) on both resins at pH 5 show positive adsorption in all range of concentrations, and increased when 1,3-PDO concentrations increased to the maximum value at 160 g/L. It is concluded that pH 5 is the most suitable pH condition for 1,3-PDO. The maximum adsorption at pH 5 was due to the appropriate surface charge of resin causing interaction potential between solute and the surface of resin. In part of butyric acid adsorption (Figure 4-12 d and Figure 4-13 d), the amounts of butyric acid adsorbed on both resins at low pH were higher than at higher pHs. Especially at pH 3, a net charge on the solid surface was induced, making it more favorable for adsorption of electrolyte solutes (such as acetic acid and butyric acid) than the non-electrolyte solutes (such as 1,3-PDO and glycerol). On the other hand, the reduction of butyric acid adsorbed at high pH solution indicated smaller net charge on the resin surface. For the acetic adsorption on both resins at different pH, the results show similar behavior with butyric acid, except for the adsorption of acetic cid on XAD-7. This could be resulted from the experimental errors caused by the small quantity of acetic acid used.

From these results, it can be conclude that the change of pHs would affect to the 1,3-PDO and other component adsorption in multiple system. In addition, at pH 5, the 1,3-PDO adsorption ability of XAD-7 is higher than XAD-16 while XAD-16 showed higher butyric acid adsorption than XAD-7 which is not suitable to apply in our system.



(a) (b) (c) (d)

Figure 4-12 Individual isotherm of each of component in aqueous solution with XAD-7 resin at pH 3, 5, and 7 in multiple component system.



(a)

(b)

(c)

(d)

Figure 4-13 Individual isotherm of each of component in aqueous solution with XAD-16 resin at pH 3, 5, and 7 in multiple component system.

4.3.2Adsorption isotherm and adsorptive selectivity of 1,3-PDO

To determine the suitability of the two resins, the amount of 1,3-PDO adsorbed and 1,3-PDO selectivity in multiple component system were considered at pH 5, which was found previously to be the most appropriate pH for adsorption.

The comparison of individual isotherm of each component between XAD-7 and XAD-16 resin are shown in Figure 4-14. The selectivity of 1,3-PDO over other components in aqueous solution was calculated using Eq (4-6) in the following form:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \tag{4-6}$$

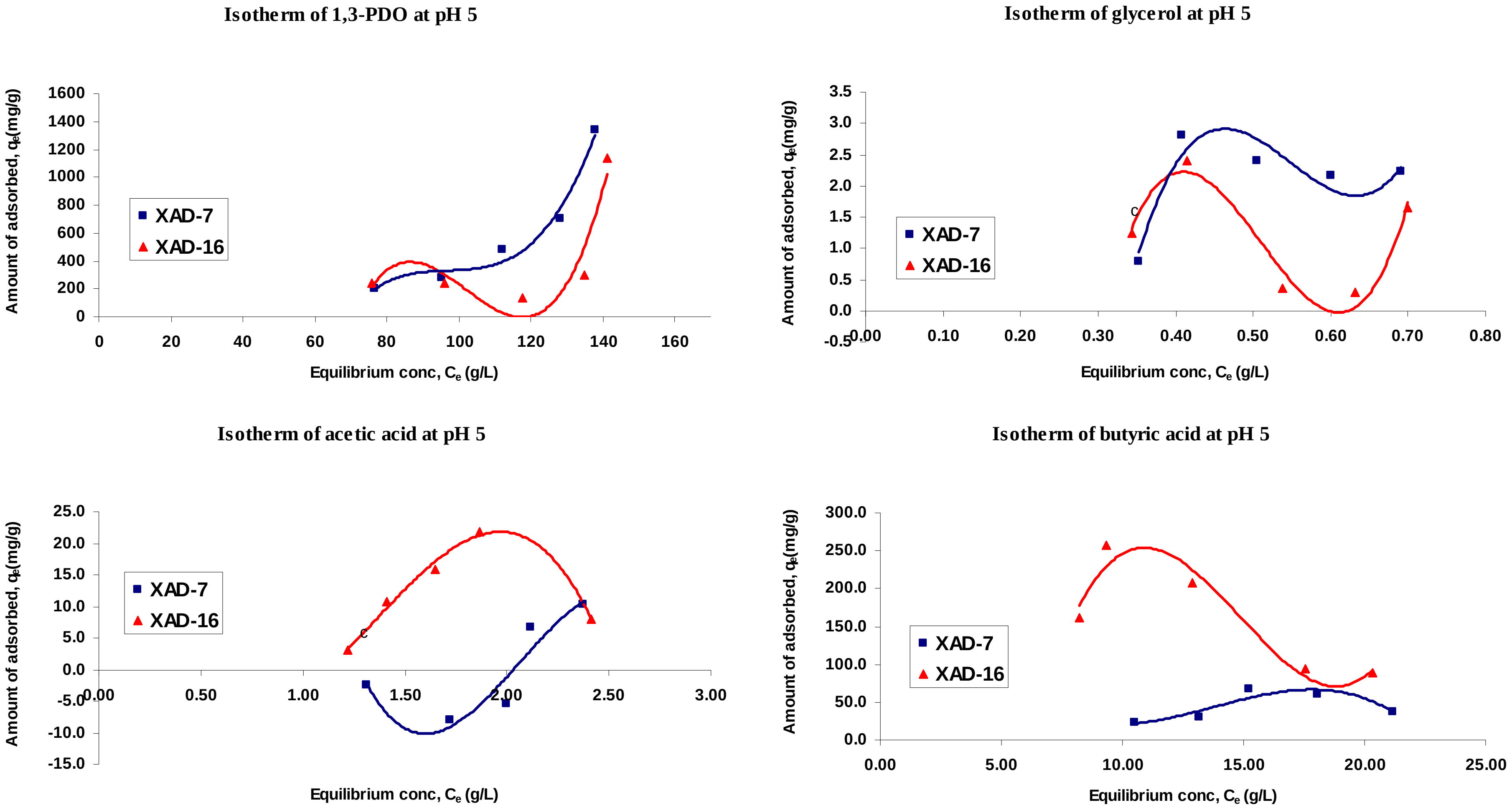
where subscript 1 represented 1,3-PDO and the subscript 2 represented all other components (glycerol, acetic and butyric acid), x_1 and x_2 are the mole fractions of components on the adsorbent surface, while y_1 and y_2 are the corresponding mole fractions in the aqueous phase. The 1,3-PDO selectivity of both resins were shown in Table 4-3.

From Figure 4-15, the amount of 1,3-PDO adsorbed on both resins increased with an increase in the initial concentration of 1,3-PDO. Interestingly, at 160 g/L of initial concentration of 1,3-PDO and in the presence of acids, the amount of 1,3-PDO adsorbed on both resins drastically increased (i.e. 1335.7 mg/g for XAD-7, and 1136.3 mg/g for XAD-16 resin), compared with adsorption in tertiary system. Moreover, the amount of other components adsorbed on XAD-16 resin was higher than the XAD-7, especially the butyric acid, in which approximately 250 mg/g was adsorbed. This result indicated that XAD-7 gave higher 1,3-PDO adsorption than XAD-16. Whereas, the XAD-16 adsorbed higher amount of other components, thus making it unsuitable for 1,3-PDO adsorption.

In comparing 1,3-PDO selectivity ($\alpha_{1,2}$) of 1,3-PDO on XAD-7 and XAD-16, XAD-7 resin was found to give larger $\alpha_{1,2}$ than 1.0 and the highest selectivity was 4.46 at 160 g/L, while the $\alpha_{1,2}$ of XAD-16 resin was lower. At 80-140 g/L, the $\alpha_{1,2}$ of XAD-16 was less than 1.0 and the highest value was 1.93 at 160 g/L. This result would indicate that XAD-7 was more favorable for adsorption of 1,3-PDO than XAD-16.

Table 4-3 1,3-PDO selectivity of both resins in multiple component system.

	Selectivity of 1,3-PDO/other component	
Initial concentration (g/L)	**XAD-7**	**XAD-16**
80	1.41	0.20
100	1.45	0.11
120	1.15	0.08
140	1.88	0.37
160	4.46	1.93



Isotherm of 1,3-PDO at pH 5

Isotherm of glycerol at pH 5

Isotherm of acetic acid at pH 5

Isotherm of butyric acid at pH 5

Figure 4-14 Comparison of the individual isotherm of each component in aqueous solution for XAD-7 and XAD-16 in multiple component system at pH 5, and 303K.

4.3.3 Effect of acid on 1,3-PDO adsorption onto both resins in multiple component system

The adsorption isotherm of 1,3-PDO in binary, tertiary, and multiple component system onto both resins are compared in Figure 4-15 to 4-16. In the high concentration range of 1,3-PDO (140-160 g/L), acid additions caused higher amount of 1,3-PDO adsorbed onto both XAD-7 and XAD-16 resin in multiple system, compared with those in the binary and tertiary system. The high content of acid additions reflects the reduction of water volume in the solution and also reduce the 1,3-PDO-water interaction. Therefore, the 1,3-PDO can be more easily bind and adsorbed on the surface resin.

In case of XAD-16, 1,3-PDO adsorption in binary, tertiary and multiple component system at whole range of concentrations seem to be fluctuation when acids were added in the solution.

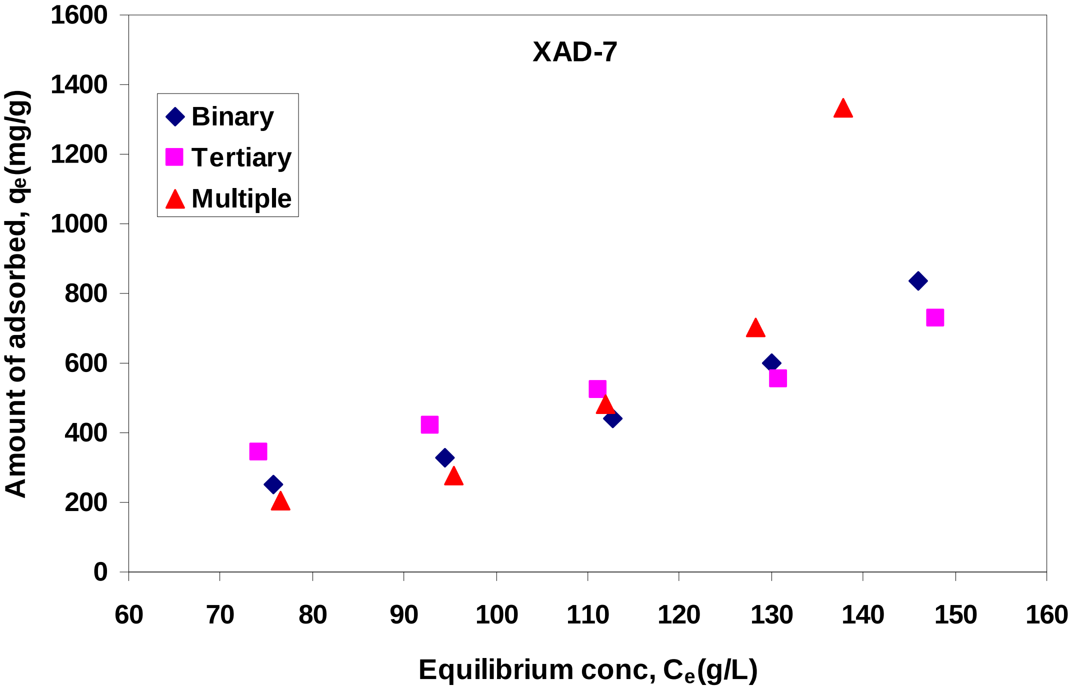


Figure 4-15 Comparison of the experimental equilibrium adsorption data of 1,3-PDO onto XAD-7 resin between binary, tertiary, and multiple system at pH 5, 303 K, and 48 hours..

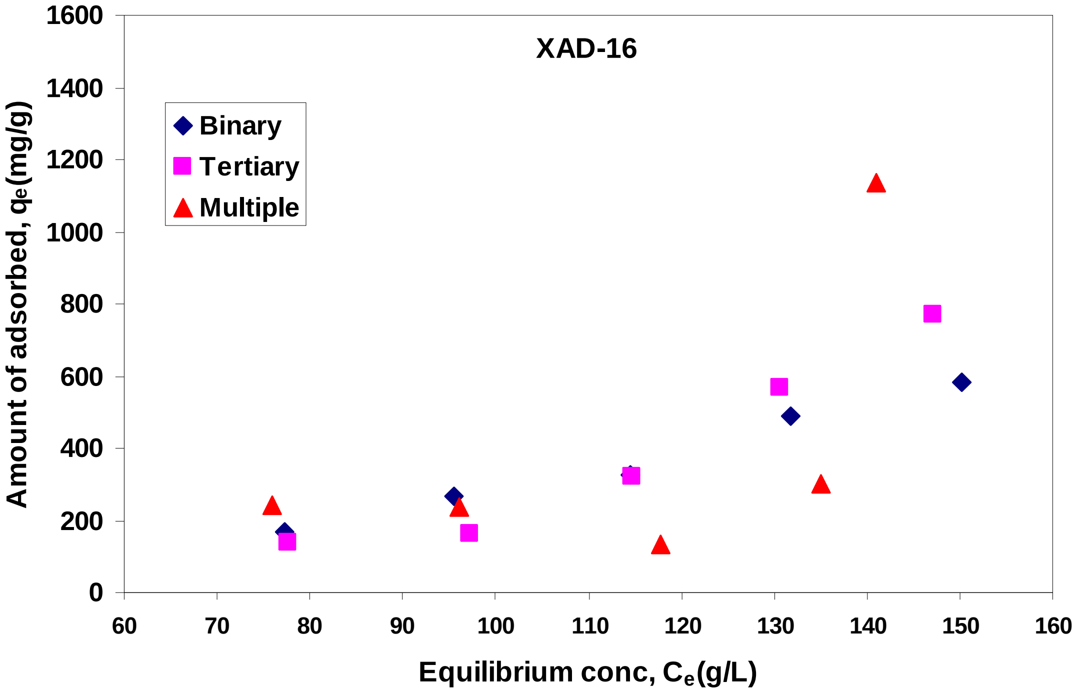


Figure 4-16 Comparison of the experimental equilibrium adsorption data of 1,3-PDO onto XAD-16 resin between binary, tertiary, and multiple system at pH 5, 303 K, and 48 hours..

4.4 Desorption of 1,3-PDO

In general, the structures and properties of both solute and resins significantly impact the solute uptake. The high adsorption potential and affinity of the resin matrix for the solute may render solutes elution from resins very difficult. It is worthwhile to investigate the desorption behavior of the 1,3-PDO from these two resins which will impact to the possibility of resin reuse.

In this part, 1,3-PDO adsorbed resins were investigated in order to determine the ability of 1,3-PDO desorption in binary, tertiary, and multiple component system. The results shown in Figure 4-17 indicated that the existence of other components adsorbed onto resins (as in tertiary and multiple component system) caused the reduction in the desorption yield of 1,3-PDO. This may be related to the interfering effect of other components on the hydrophobic interaction and electrostatic attraction of the resins. In addition, the results in Figure 4-17 also shows the influence of ethanol concentration on the desorption yield of 1,3-PDO from the XAD-7 and XAD-16 resins, which increased when the ethanol content was increased. This indicated that ethanol could give rise to electrostatic attraction to the solute, enhancing the desorption yield from the resins. The desorption yield of 1,3-PDO for XAD-16 resin were generally higher than those for XAD-7 in binary and tertiary system, while in multiple system, XAD-16 shows the lowest desorption value. This can be explained that XAD-7 resin has high affinity for the 1,3-PDO adsorption, therefore 1,3-PDO elution from the resins seem to be very difficult.

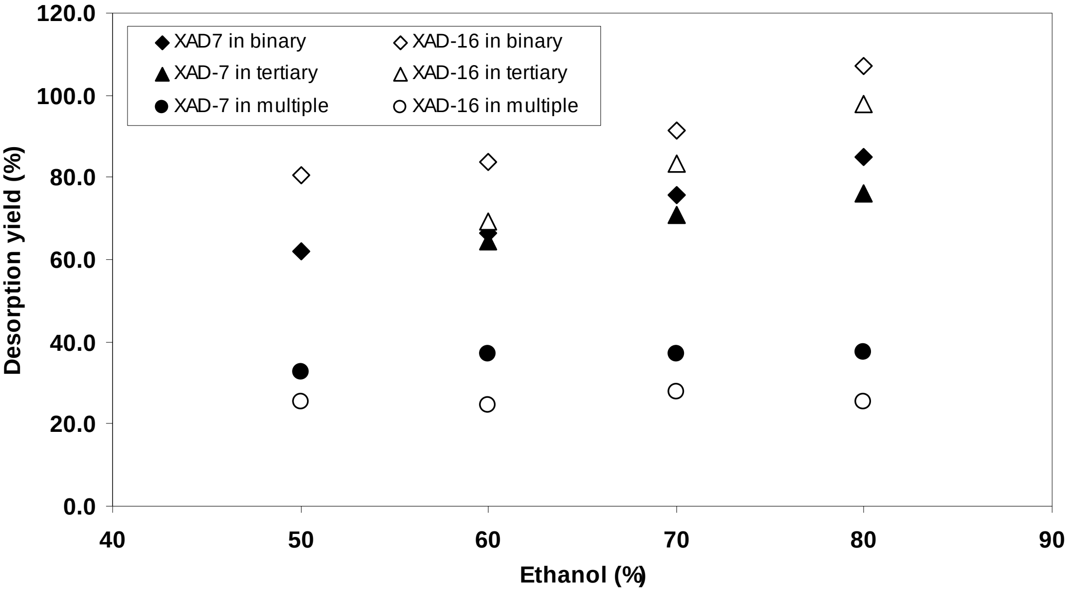


Figure 4-17 Desorption of 1,3-PDO adsorbed on both resins in binary, tertiary, and multiple system at various contents of ethanol at pH 5, 303 K, and 48 hours.

4.5 Selection of resin for 1,3-PDO adsorption

The prior art has also recognized that certain characteristics of adsorbents are highly desirable, if not absolutely necessary, to the successful operation of a selective adsorption process. Such characteristics are equally important to this process. Among such characteristics are: (1) amount of adsorbed for some volume(adsorptive capacity), q_e (mg adsorbate per g adsorbent); (2) the selective adsorption of and extract component with respect to a raffinate component; and (3) sufficient mass of the extract component desorbed from the adsorbent. The characteristics of resin mention above would reduce the amount of adsorbent needed to separate the interested component.

In this part, the amount of 1,3-PDO adsorbed, 1,3-PDO selectivity, and ability of 1,3-PDO desorbed were compared for the two resins. From previous result, the maximum amount of 1,3-PDO adsorbed at 160 g/L onto XAD-7 was 1335.7 mg/g higher than XAD-16 was 1136.3 mg/g, while the amounts of other components adsorbed on XAD-16 were higher than XAD-7 (shown in Figure 4-18). In addition, the 1,3-PDO selectivity of XAD-7 was found previously to be higher than XAD-16, both in tertiary and multiple system. Here, the desorption of 1,3-PDO and other components from the two resins in multiple system were compared by determining mass fraction of each component in desorbed solution. Figure 4-19 shows the comparison of the mass of each component in desorbed solution from the two resins in multiple system with 80% v/v ethanol solution. Evidently, mass fraction of 1,3-PDO in desorbed solution from XAD-7 was higher than that from XAD-16 resin. In contrary, mass fraction of butyric acid in desorbed solution from XAD-7 was lower than that from XAD-16. From these result, it can be concluded that XAD-7 was a more appropriate adsorbent for 1,3-PDO adsorption.

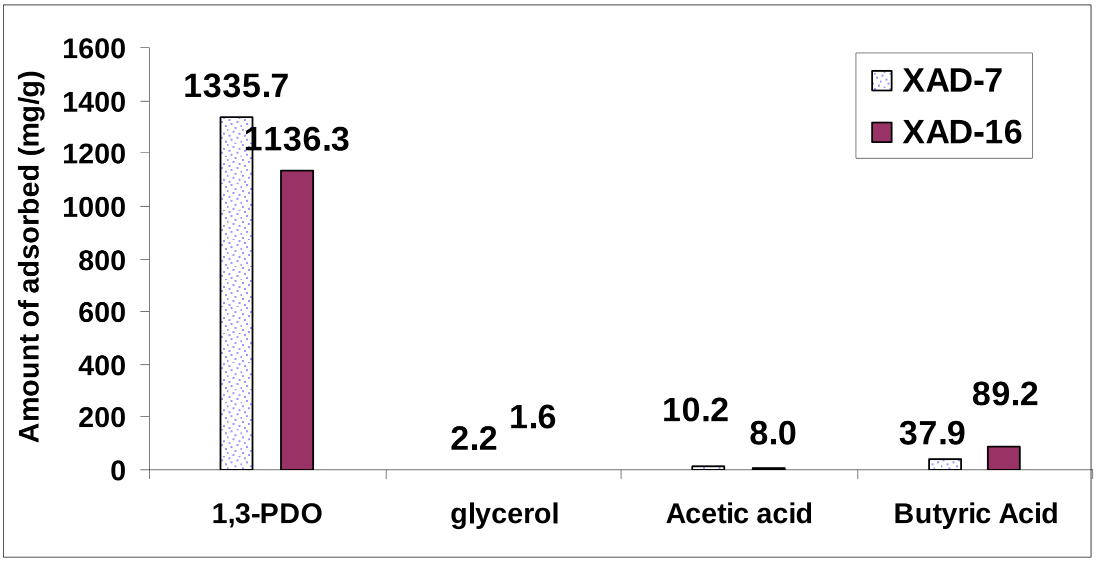


Figure 4-18 The comparison of solutes adsorbed on two resins in multiple system at 160 g/L initial concentration of 1,3-PDO at pH 5, 303 K, and 48 hours.

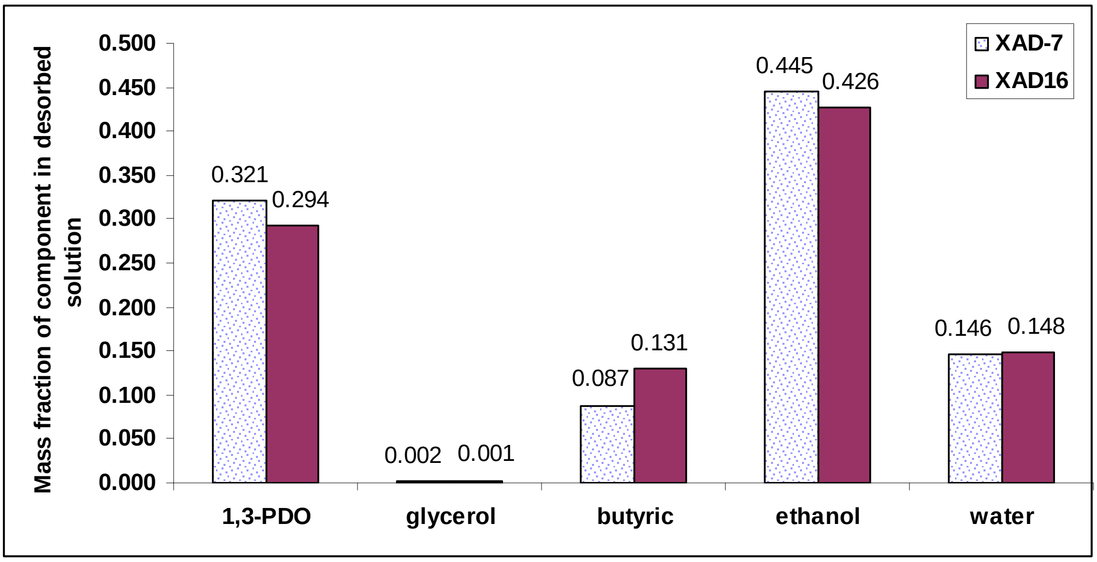


Figure 4-19 The comparison of mass fraction of each components adsorbed in desorbed solution of two resins in multiple system with 80% v/v ethanol solution at pH 5, 303 K, and 48 hours.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Amberlite XAD-7 and XAD-16 resin were proven to be good adsorbents for adsorption of biological derived 1,3-PDO in aqueous solution. In binary component system, the amount of 1,3-PDO adsorbed increased with an increase in initial concentration of 1,3-PDO, and the maximum adsorption was obtained at 160 g/L. The experimental adsorption data of 1,3-PDO from both resins were fitted well by Freundlich model and the parameter constants for XAD-7 were found to be much higher than those for XAD-16, indicating that XAD-7 was more favorable for 1,3-PDO adsorption.

The results in the tertiary and multiple system indicated that the suitable pH for 1,3-PDO adsorption at 303 K (30°C) is 5. Furthermore, the presence of other components in aqueous solution affect 1,3-PDO adsorption. In general, XAD-16 was found to more preferably adsorbs other components than XAD-7. In addition, the presence of acid in the system promoted 1,3-PDO adsorption in both resins. Considering the selectivity of 1,3-PDO on the resins, XAD-7 was more selective of 1,3-PDO adsorption than XAD-16, both in tertiary and multiple systems.

From the desorption experiment, it was shown that the desorption yield increased with increasing the ethanol content in the ethanol/water eluent. The mass fraction of 1,3-PDO in desorbed solution from XAD-7 was higher than that from XAD-16 due to higher adsorption and higher desorption yield of XAD-7. In contrary, mass fraction of butyric in the desorbed solution of XAD-7 (0.087) was lower than XAD-16 resin (0.131). In conclusion of this study, the adsorption of 1,3-PDO using polymeric resins is an alternative method for separation of 1,3-PDO from model solution of fermentation broth. With the higher amount of 1,3-PDO adsorbed (1335.7 mg/g), higher selectivity (4.46), and higher mass fraction of 1,3-PDO in desorbed solution (0.321), XAD-7 is concluded to be more preferable adsorbent for 1,3-PDO adsorption process.

5.2 Recommendations

1. Use fermentation broth instead of model solution in order to study the influence of actual components of the fermentation broth to the adsorption behavior.
2. Perform in a continuous process such as in a fixed bed adsorption column in order to study the capacity and the lifetime of adsorbent.

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APPENDICES

APPENDIX A

EXPERIMENTAL DATA

A-1 Preparation resins to ensure completely salts removal by measuring the conductivity of wash water

Table A-1.1 Conductivity data of wash water from salts removal of two resins.

Time (min)	Volume of wash water (L)	Conductivity (µS/cm)	
		XAD-7	XAD-16
20	1	930	1039
40	1	14.2	8.7
60	1	1.2	1.2
80	1	1.1	1.1

A-2 Resin dry weight

Table A-2 Data of weigh of resins was cleaned

No.	Resins	Weight of resin before clean (g)	Weight of resin after clean (g)	weight of salts into resins (g)
1	XAD-7	10.02	4.53	5.49
	XAD-16	10.11	4.15	5.96
2	XAD-7	20.00	9.14	10.86
	XAD-16	20.00	8.09	11.91

A-3 Standard calibration curve and equilibrium adsorption isotherm data of two resins in binary system

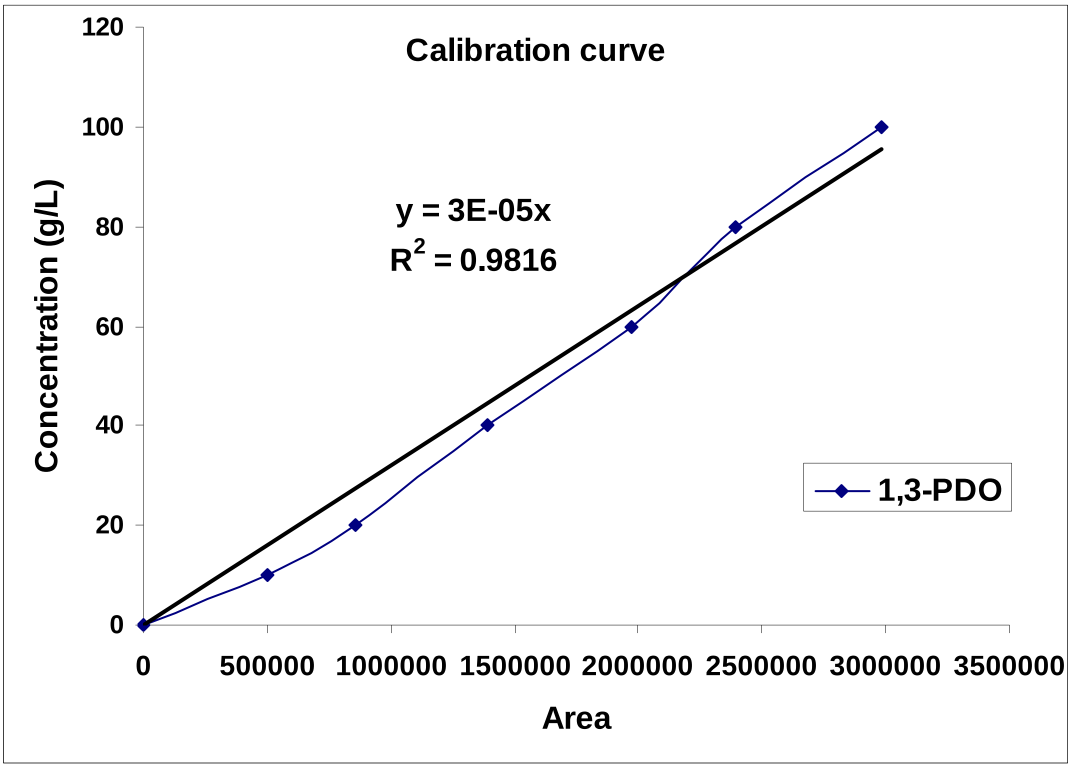

Figure A-3.1 Standard calibration curve of 1,3-PDO in binary system

Table A-3.1 Equilibrium adsorption isotherm data of 1,3-PDO on XAD-7

Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Amount of Adsorbed, q_e (mg/g)
10	9.0697	55.8180
20	18.7127	77.2380
30	28.6181	82.9140
40	36.2532	224.8080
60	55.6830	259.0200
80	75.7967	252.1980
100	94.5072	329.5680
120	112.6890	438.6600
140	130.0235	598.5900
160	146.0673	835.9620
200	186.0539	836.7660

Table A-3.2 Equilibrium adsorption isotherm data of 1,3-PDO on XAD-16

Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
10	8.7894	72.6360
20	18.6147	83.1180
30	28.3338	99.9720
40	37.5900	144.6000
60	57.4080	155.5200
80	77.1806	169.1640
100	95.5761	265.4340
120	114.5328	328.0320
140	131.8291	490.2540
160	150.2565	584.6100
200	189.6351	621.8926

Table A-3.3 The linearized of equilibrium isotherm data for the Langmuir and Freundlich isotherm model of XAD-7

Langmuir Model			**Freundlich Model**		
$1/C_e$	**$1/q_e$**	**Amount of Adsorbed, q_e (mg/g)**	**Log C_e**	**Log q_e**	**Amount of Adsorbed, q_e (mg/g)**
1.10E-04	1.79E-02	36.1164	3.9576	1.7468	24.4689
5.34E-05	1.29E-02	74.7454	4.2721	1.8878	57.6868
3.49E-05	1.21E-02	114.6742	4.4566	1.9186	95.4013
2.76E-05	4.45E-03	145.6249	4.5593	2.3518	126.2325
1.80E-05	3.86E-03	225.0774	4.7457	2.4133	209.8289
1.32E-05	3.97E-03	308.3852	4.8797	2.4017	302.3107
1.06E-05	3.03E-03	386.8665	4.9755	2.5179	392.5642
8.87E-06	2.28E-03	464.0570	5.0519	2.6421	483.5018
7.69E-06	1.67E-03	538.5163	5.1140	2.7771	572.7703
6.85E-06	1.20E-03	608.1978	5.1646	2.9222	657.3794
5.37E-06	1.20E-03	785.1528	5.2696	2.9226	875.4908

Table A-3.4 The linearized of equilibrium isotherm data for the Langmuir and Freundlich isotherm model of XAD-16

Langmuir Model			Freundlich Model		
$1/C_e$	**$1/q_e$**	**Amount of Adsorbed, q_e (mg/g)**	**Log C_e**	**Log q_e**	**Amount of Adsorbed, q_e (mg/g)**
1.14E-04	1.38E-02	19.5663	3.9440	1.8612	10.7732
5.37E-05	1.20E-02	42.3652	4.2699	1.9197	29.8181
3.53E-05	1.00E-02	65.9436	4.4523	1.9999	52.7232
2.66E-05	6.92E-03	89.4124	4.5751	2.1602	77.3672
1.74E-05	6.43E-03	143.3074	4.7590	2.1918	137.4194
1.30E-05	5.91E-03	202.6691	4.8875	2.2283	205.3187
1.05E-05	3.77E-03	263.7126	4.9803	2.4240	274.3993
8.73E-06	3.05E-03	333.4594	5.0589	2.5159	350.7445
7.59E-06	2.04E-03	404.1703	5.1200	2.6904	424.4808
6.66E-06	1.71E-03	488.2504	5.1768	2.7669	506.9284
5.27E-06	1.61E-03	706.6283	5.2779	2.7937	695.1621

A-4 Standard calibration curve and equilibrium quilibrium adsorption isotherm data of two resins in tertiary system

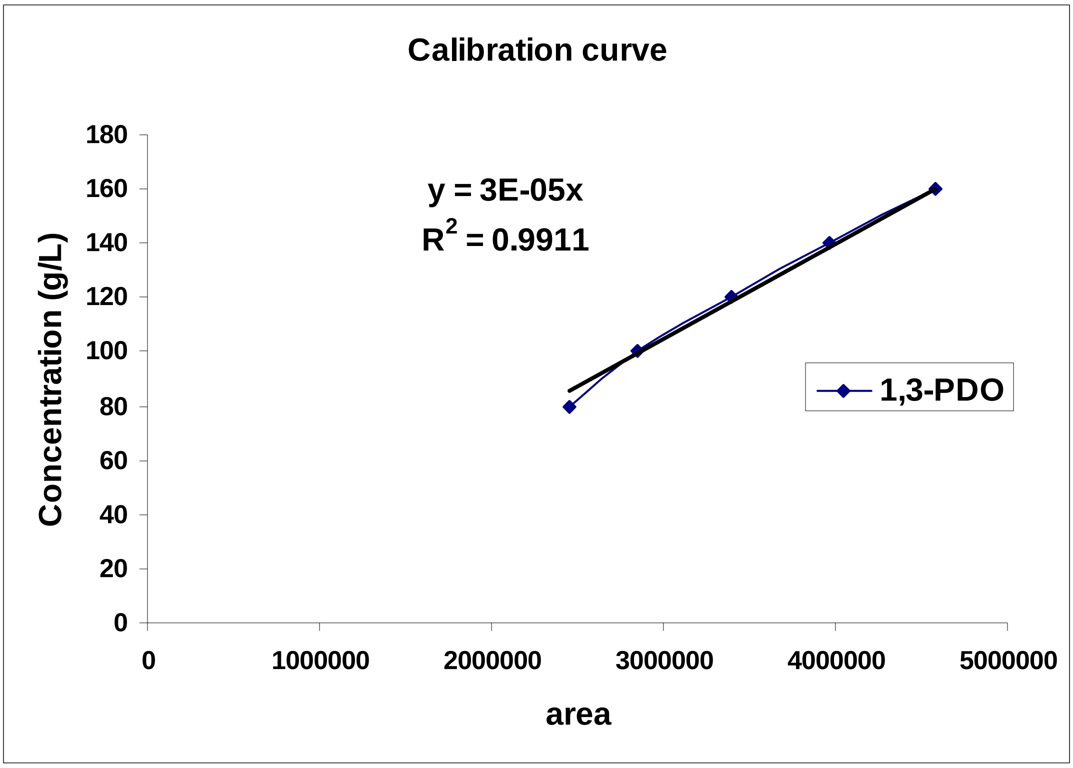

Figure A-4.1 Standard calibration curve of 1,3-PDO in tertiary system

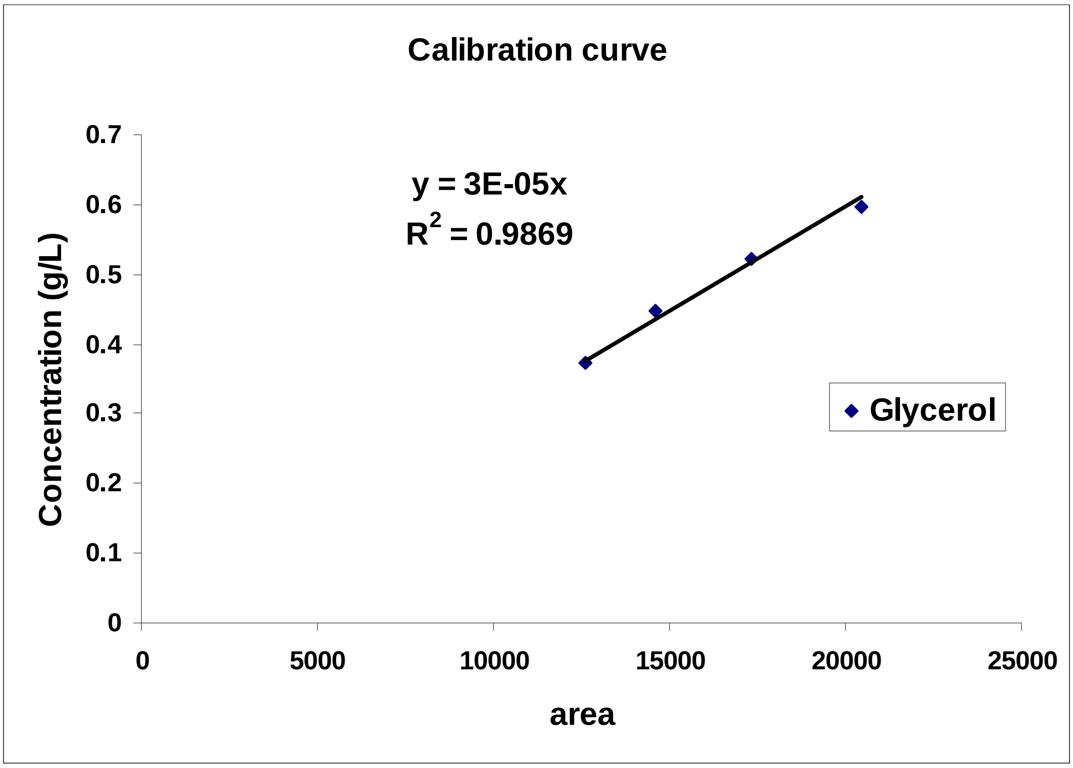

Figure A-4.2 Standard calibration curve of glycerol in tertiary system

Table A-4.1 Equilibrium adsorption isotherm data of 1,3-PDO on two resins.

1,3-PDO	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	74.2789	343.266
100	92.9686	421.884
120	111.2548	524.712
140	130.7696	553.824
160	147.8886	726.684
1,3-PDO	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	77.7152	137.088
100	97.2512	164.928
120	114.6764	319.416
140	130.5609	566.346
160	147.1659	770.046

Table A-4.2 Equilibrium adsorption isotherm data of glycerol on two resins.

Glycerol	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636		
0.4545	0.4463	0.492
0.5445	0.5292	0.918
0.6364	0.6127	1.422
0.7273	0.6904	2.214
Glycerol	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636		
0.4545	0.3565	5.88
0.5445	0.426	7.11
0.6364	0.482	9.264
0.7273	0.5537	10.416

A-5 Standard calibration curve and equilibrium quilibrium adsorption isotherm data of two resins in multiple system

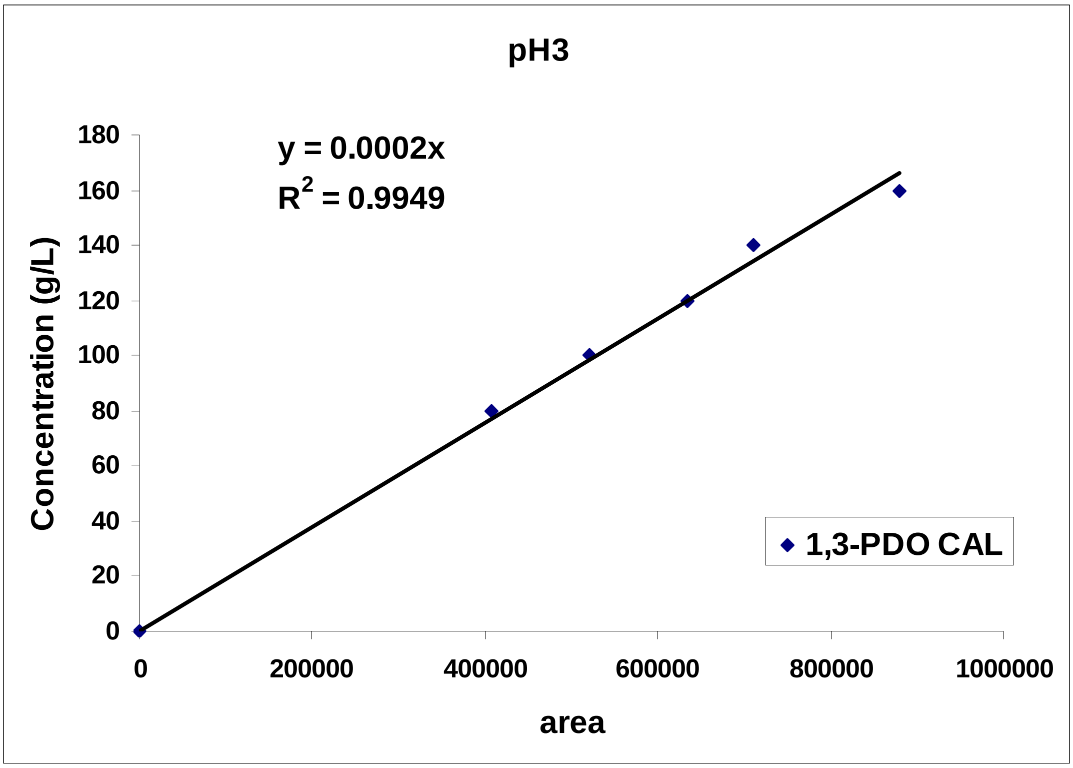

Figure A-5.1 Standard calibration curve of 1,3-PDO in mutiple system at pH 3

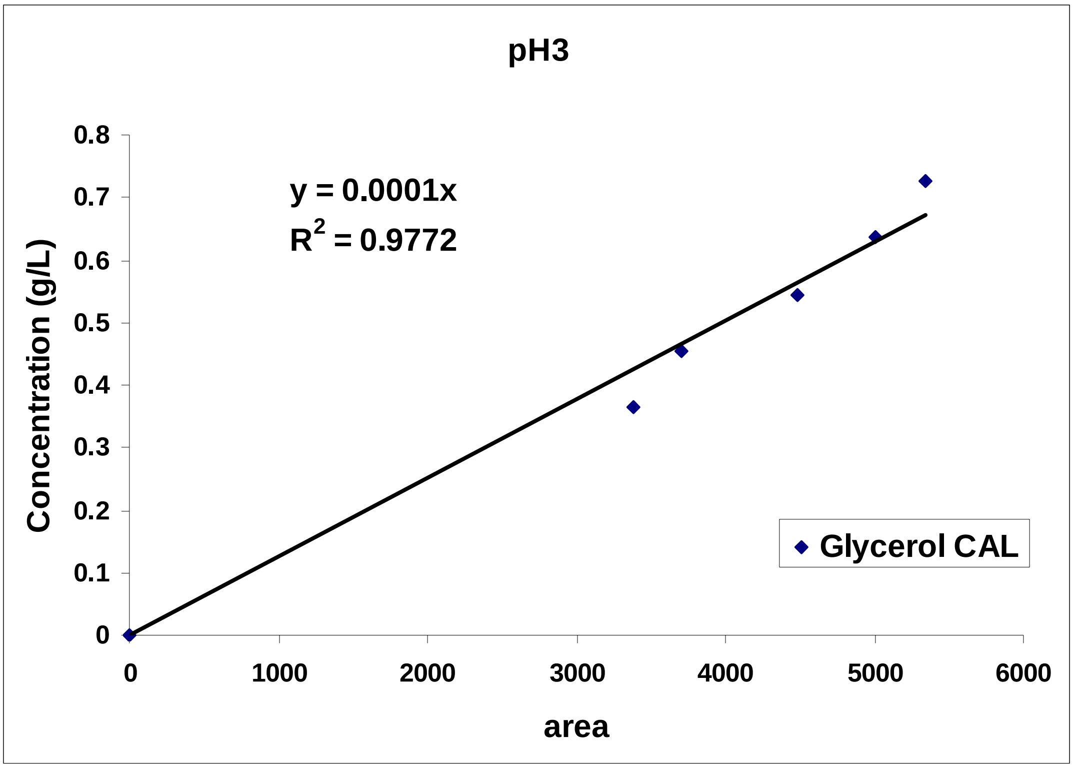

Figure A-5.2 Standard calibration curve of glycerol in mutiple system at pH 3

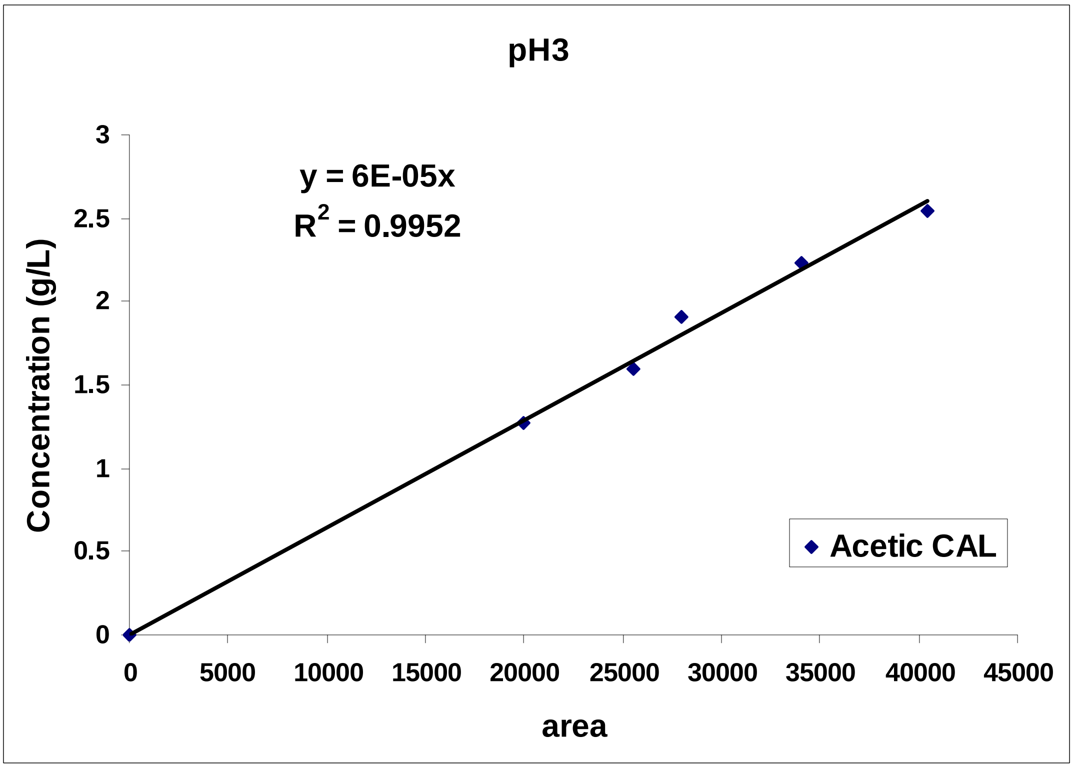

Figure A-5.3 Standard calibration curve of acetic acid in mutiple system at pH 3

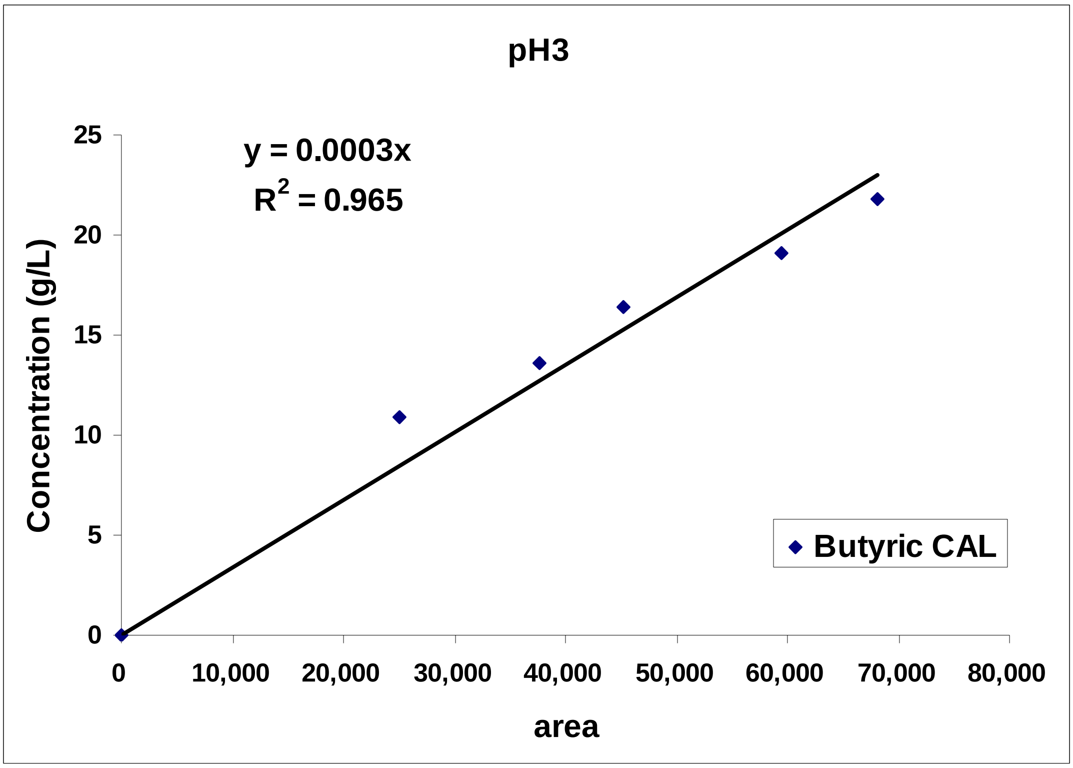

Figure A-5.2 Standard calibration curve of butyric acid in mutiple system at pH 3

Table A-5.4 Equilibrium adsorption isotherm data of butyric acid on two resins at pH 3.

1,3-PDO	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	62.0793	1075.242
100	92.426	454.44
120	124.2253	-253.518
140	139.9426	3.444
160	145.9425	843.45
1,3-PDO	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	97.5188	-1051.128
100	105.2854	-317.124
120	127.8688	-472.128
140	152.8867	-773.202
160	184.3608	-1461.648

Table A-5.2 Equilibrium adsorption isotherm data of glycerol on two resins at pH 3.

Glycerol	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3285	2.106
0.4545	0.5024	-2.874
0.5445	0.5696	-1.506
0.6364	0.6688	-1.944
0.7273	0.7325	-0.312
Glycerol	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3444	1.152
0.4545	0.4067	2.868
0.5445	0.6314	-5.214
0.6364	0.7566	-7.212
0.7273	0.8789	-9.096

Table A-5.3 Equilibrium adsorption isotherm data of acetic acid on two resins at pH 3.

Acetic	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.29952	-1.6092
1.5909	1.5632	1.662
1.9091	2.0404	-7.878
2.2273	2.1865	2.448
2.5455	2.3593	11.172
Acetic	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.1061	9.996
1.5909	1.5036	5.238
1.9091	1.7635	8.736
2.2273	1.8642	21.786
2.5455	2.3397	12.348

Table A-5.4 Equilibrium adsorption isotherm data of butyric acid on two resins at pH 3.

Butyric **Initial concentration, C_0 (g/L)**	**XAD-7** **Equilibrium concentration, C_e (g/L)**	 **Amount of Adsorbed, q_e (mg/g)**
10.9091	6.9473	237.708
13.6364	10.8264	168.6
16.3636	14.0623	138.078
19.0909	15.2144	232.59
21.8182	18.1907	217.65
Butyric **Initial concentration, C_0 (g/L)**	**XAD-16** **Equilibrium concentration, C_e (g/L)**	 **Amount of Adsorbed, q_e (mg/g)**
10.9091	6.9985	234.636
13.6364	11.0889	152.85
16.3636	12.8975	207.966
19.0909	16.1645	175.584
21.8182	18.8788	176.364

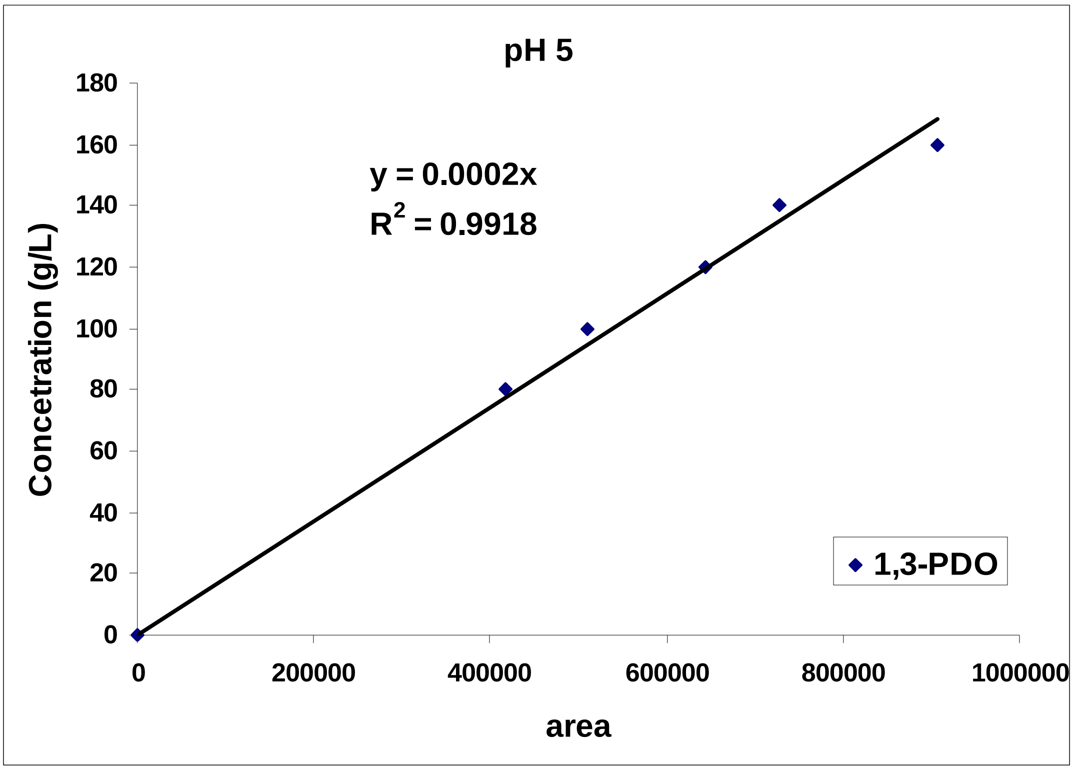

Figure A-5.2 Standard calibration curve of 1,3-PDO in mutiple system at pH 5

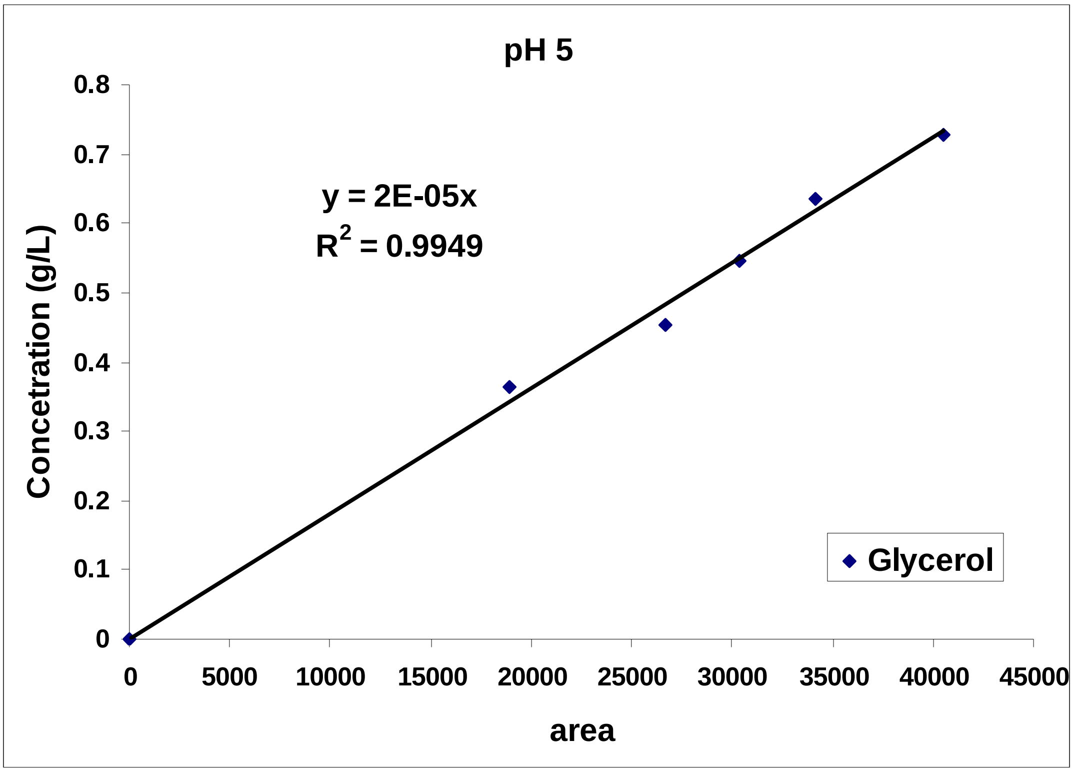

Figure A-5.2 Standard calibration curve of glycerol in mutiple system at pH 5

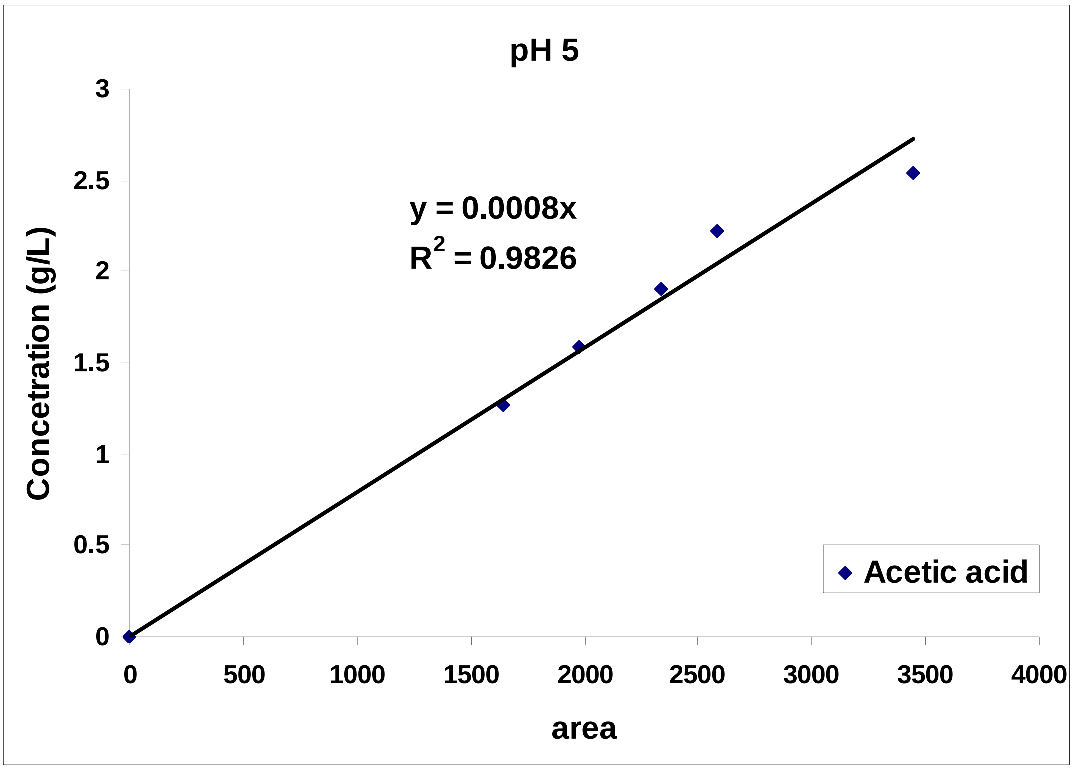

Figure A-5.2 Standard calibration curve of Acetic acid in mutiple system at pH 5

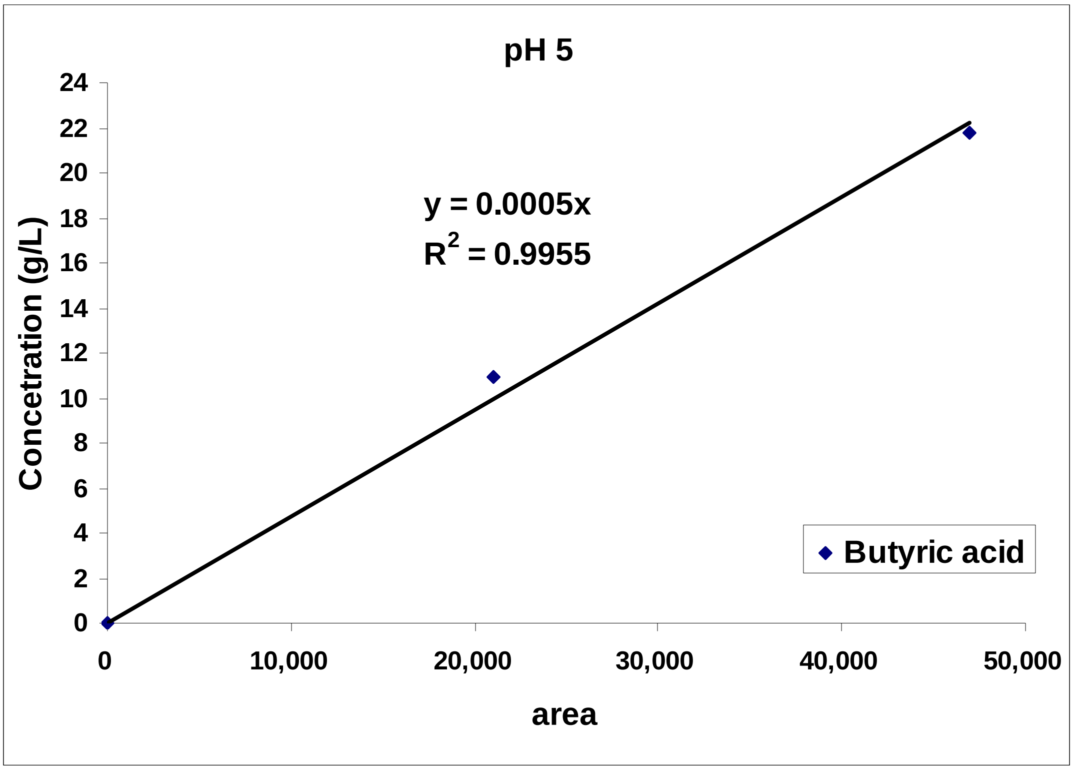

Figure A-5.2 Standard calibration curve of butyric acid in mutiple system at pH 5

Table A-5.5 Equilibrium adsorption isotherm data of 1,3-PDO on two resins at pH 5.

1,3-PDO	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	76.5702	205.7850
100	95.359	278.4315
120	111.9676	481.9405
140	128.3284	700.2911
160	137.7382	1335.7068
1,3-PDO	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
80	75.9965	240.2051
100	96.0089	239.4604
120	117.8099	131.4051
140	134.9701	301.7915
160	141.0620	1136.2788

Table A-5.6 Equilibrium adsorption isotherm data of glycerol on two resins at pH 5.

Glycerol **Initial concentration, C_0 (g/L)**	**XAD-7**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3529	0.7960
0.4545	0.4077	2.8056
0.5445	0.5045	2.4000
0.6364	0.6002	2.1697
0.7273	0.6900	2.2335
Glycerol **Initial concentration, C_0 (g/L)**	**XAD-16**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3429	1.2390
0.4545	0.4145	2.3949
0.5445	0.5383	0.3682
0.6364	0.6314	0.2941
0.7273	0.6998	1.6447

Table A-5.7 Equilibrium adsorption isotherm data of acetic acid on two resins at pH 5.

Acetic **Initial concentration, C_0 (g/L)**	**XAD-7**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.3145	-2.5097
1.5909	1.7222	-7.8819
1.9091	1.9980	-5.334
2.2273	2.1167	6.6360
2.5455	2.3749	10.2322
Acetic **Initial concentration, C_0 (g/L)**	**XAD-16**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.2223	3.0210
1.5909	1.4119	10.7349
1.9091	1.6451	15.8391
2.2273	1.8642	21.7860
2.5455	2.4126	7.9731

Table A-5.8 Equilibrium adsorption isotherm data of butyric acid on two resins at pH 5.

Butyric **Initial concentration, C_0 (g/L)**	**XAD-7** **Equilibrium concentration, C_e (g/L)**	 **Amount of Adsorbed, q_e (mg/g)**
10.9091	10.5137	23.7240
13.6364	13.1427	29.6220
16.3636	15.2461	67.0500
19.0909	18.0785	60.7384
21.8182	21.1870	37.8719
Butyric **Initial concentration, C_0 (g/L)**	**XAD-16** **Equilibrium concentration, C_e (g/L)**	 **Amount of Adsorbed, q_e (mg/g)**
10.9091	8.2207	161.3019
13.6364	9.3532	256.9915
16.3636	12.8975	207.9660
19.0909	17.5284	93.7500
21.8182	20.3320	89.1720

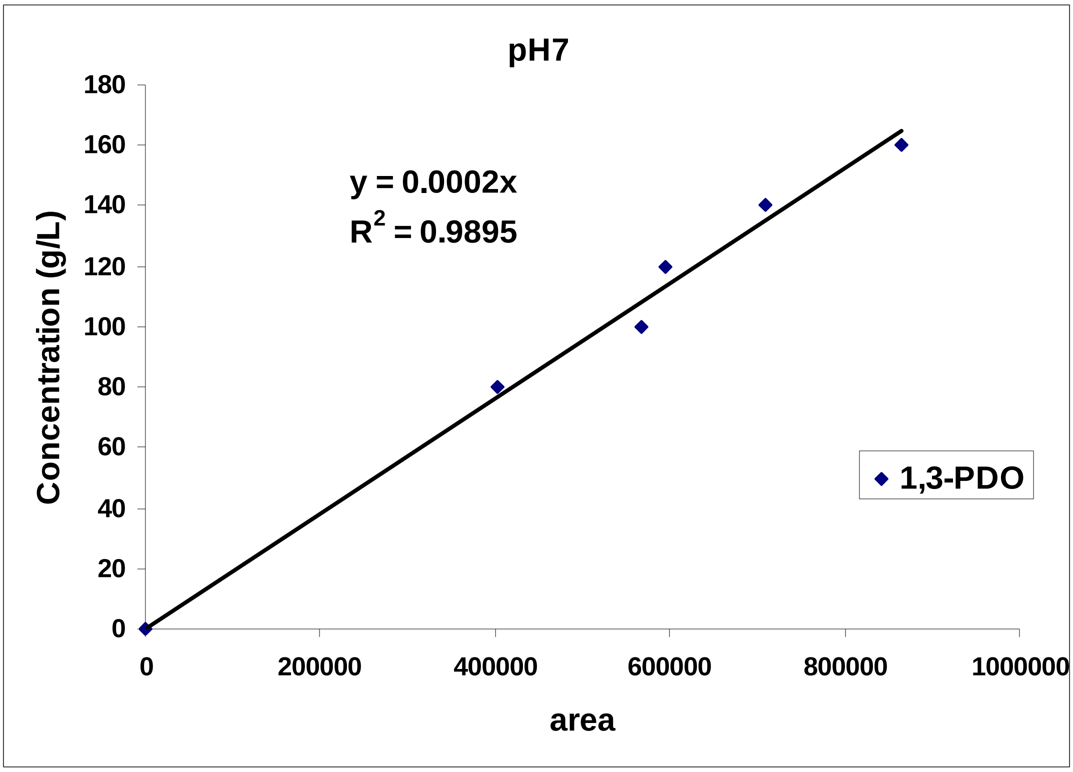

Figure A-5.2 Standard calibration curve of 1,3-PDO in mutiple system at pH 7

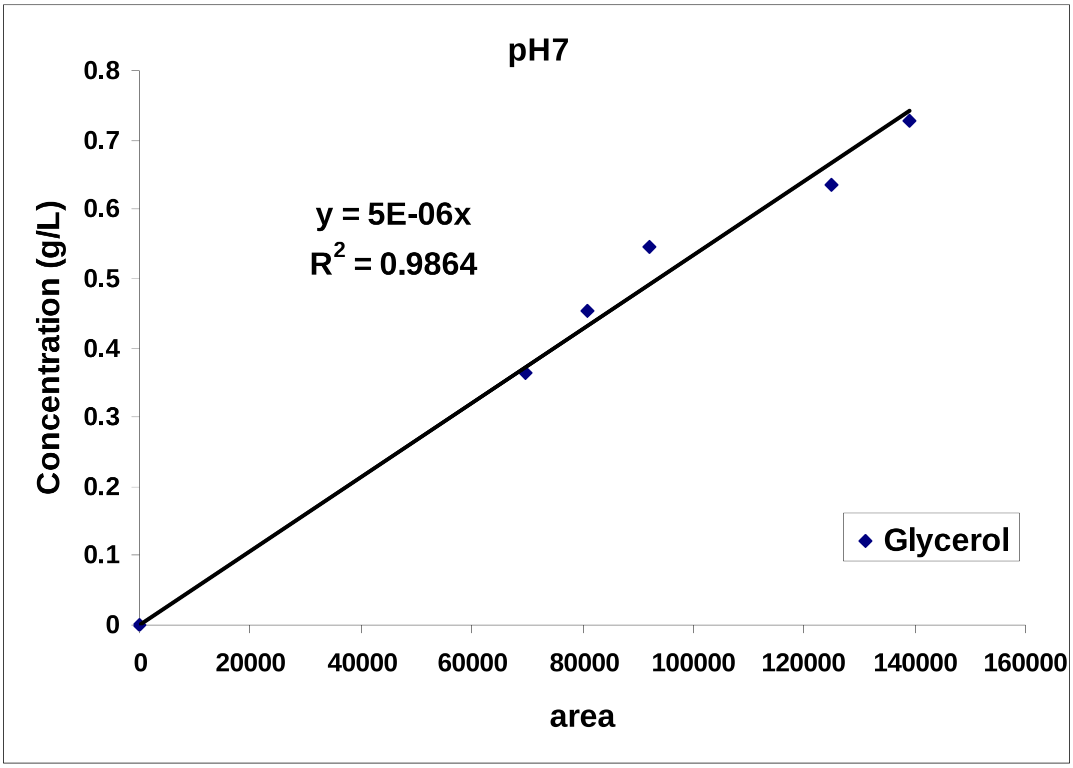

Figure A-5.2 Standard calibration curve of glycerol in mutiple system at pH 7

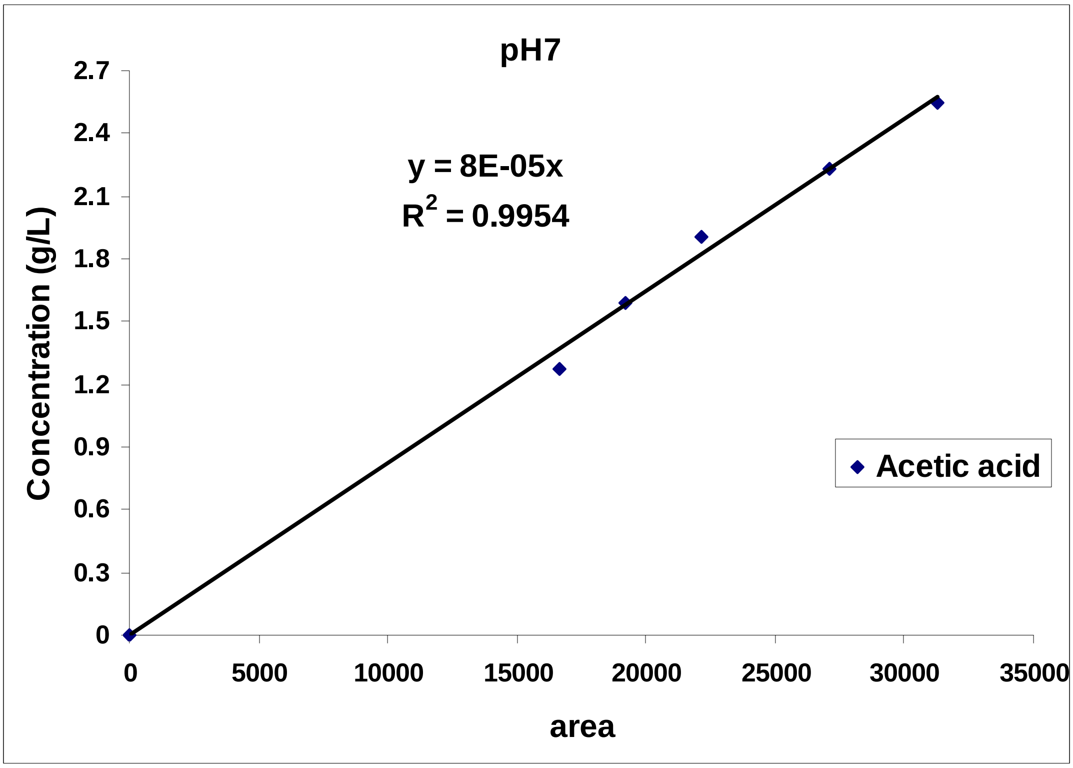

Figure A-5.2 Standard calibration curve of acetic acidl in mutiple system at pH 5

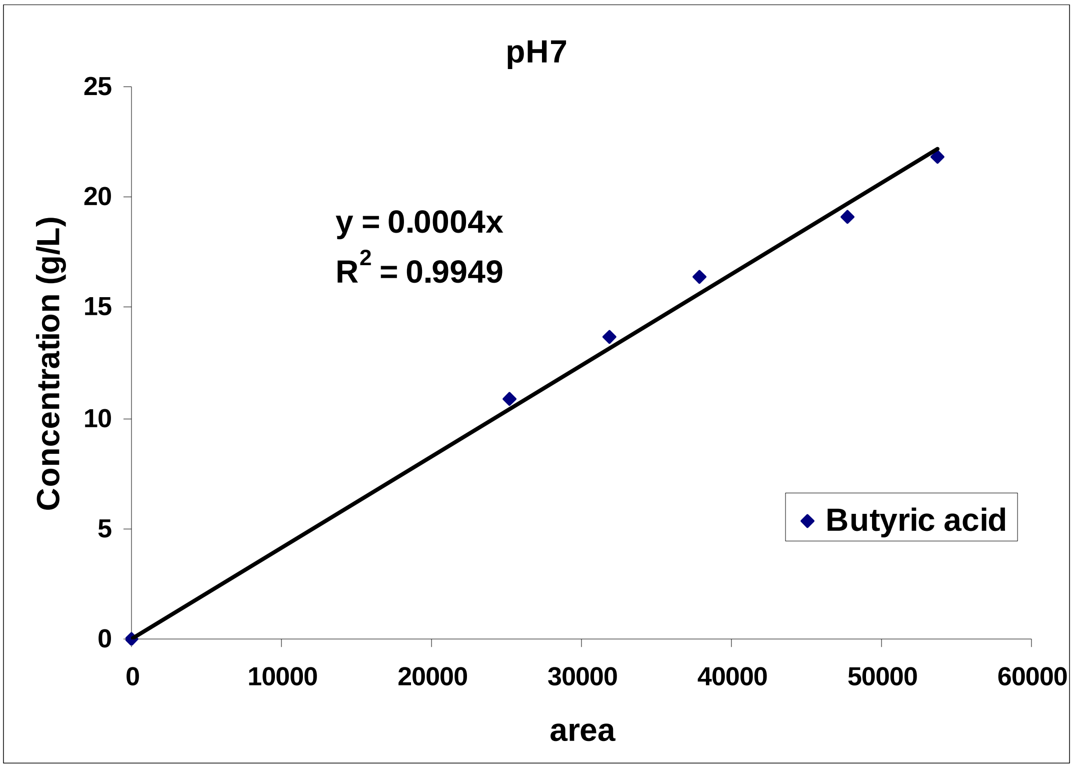

Figure A-5.2 Standard calibration curve of butyric acid in mutiple system at pH 7

Table A-5.9 Equilibrium adsorption isotherm data of 1,3-PDO on two resins at pH 7.

1,3-PDO Initial concentration, C_0 (g/L)	**XAD-7**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
80	74.2050	347.6669
100	86.3016	821.9026
120	123.1004	-186.0279
140	141.7791	-106.7462
160	160.4907	-29.4432
1,3-PDO Initial concentration, C_0 (g/L)	**XAD-16**	
	Equilibrium concentration, C_e (g/L)	**Amount of Adsorbed, q_e (mg/g)**
80	85.5718	-334.3139
100	115.9896	-959.3760
120	131.4394	-686.3688
140	146.4208	-385.2518
160	137.3842	1356.9434

Table A-5.10 Equilibrium adsorption isotherm data of glycerol on two resins at pH 7.

Glycerol	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3158	2.8644
0.4545	0.4671	-0.7592
0.5445	0.5868	-2.5404
0.6364	0.6672	-1.8808
0.7273	0.7476	-1.2211
Glycerol	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
0.3636	0.3363	1.6321
0.4545	0.4554	-0.0540
0.5445	0.5545	-1.1723
0.6364	0.6000	2.1840
0.7273	0.6130	6.8525

Table A-5.11 Equilibrium adsorption isotherm data of acetic acid on two resins at pH 7.

Acetic	**XAD-7**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.1330	8.3762
1.5909	1.3400	15.0496
1.9091	1.5275	22.8936
2.2273	2.2777	-3.0267
2.5455	2.7729	-13.6458
Acetic	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
1.2727	1.2930	-1.2234
1.5909	1.6009	-0.6000
1.9091	2.1637	-15.2784
2.2273	2.3886	-9.6827
2.5455	2.3026	14.5707

Table A-5.12 Equilibrium adsorption isotherm data of butyric acid on two resins at pH 7.

Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
10.9091	10.7078	12.0730
13.6364	13.6197	1.0014
16.3636	16.4699	-6.3780
19.0909	20.7009	-96.6000
21.8182	23.4339	-96.9444
Butyric	**XAD-16**	
Initial concentration, C_0 (g/L)	**Equilibrium concentration, C_e (g/L)**	**Amount of Adsorbed, q_e (mg/g)**
10.9091	11.8106	-54.0944
13.6364	13.6564	-1.2000
16.3636	16.7936	-25.8058
19.0909	17.2143	134.0000
21.8182	18.8809	176.2361

A-6 Adsorptive selectivity data of two resins in tertiary system

Table A-6.1 1,3-PDO/glycerol selectivity data of XAD-7 resins.

Total mole of sulutes in liquid phase (mol)	Total mole of sulutes on solid surface (mol)	Mole fraction of 1,3-PDO on solid surface	Mole fraction of glycerol on solid surface	Mole fraction of 1,3-PDO in liquid phase	Mole fraction of Glycerol in liquid phase	1,3-PDO selectivity
0.0294	0.0023	0.9994	0.0006	0.9952	0.0048	7.4919
0.0368	0.0028	0.9988	0.0012	0.9952	0.0048	4.1164
0.0441	0.0035	0.9983	0.0017	0.9953	0.0047	2.7188
0.0518	0.0036	0.9974	0.0026	0.9953	0.0047	1.8248
0.0586	0.0048	0.9970	0.0030	0.9954	0.0046	1.5323

Table A-6.1 1,3-PDO/glycerol selectivity data of XAD-16 resins.

Total mole of sulutes in liquid phase (mol)	Total mole of sulutes on solid surface (mol)	Mole fraction of 1,3-PDO on solid surface	Mole fraction of glycerol on solid surface	Mole fraction of 1,3-PDO in liquid phase	Mole fraction of Glycerol in liquid phase	1,3-PDO selectivity
0.0308	0.0009	0.9682	0.0318	0.9963	0.0037	0.1131
0.0385	0.0011	0.9656	0.0344	0.9963	0.0037	0.1028
0.0454	0.0021	0.9782	0.0218	0.9963	0.0037	0.1669
0.0517	0.0038	0.9839	0.0161	0.9963	0.0037	0.2257
0.0582	0.0051	0.9867	0.0133	0.9963	0.0037	0.2782

A-7 Adsorptive selectivity data of two resins in multiple system

Table A-7.1 1,3-PDO selectivity data of XAD-7 resins.

Total mole of sulutes in liquid phase (mol)	**Total mole of sulutes on solid surface (mol)**	**Mole fraction of 1,3-PDO on solid surface**	**Mole fraction of other on solid surface**	**Mole fraction of 1,3-PDO in liquid phase**	**Mole fraction of other in liquid phase**	**1,3-PDO selectivity**
1.1512	0.0497	0.9073	0.0927	0.8741	0.1259	1.4099
1.4353	0.0671	0.9089	0.0911	0.8731	0.1269	1.4497
1.6831	0.1187	0.8895	0.1105	0.8743	0.1257	1.1569
1.9332	0.1653	0.9281	0.0719	0.8724	0.1276	1.8883
2.0974	0.3030	0.9657	0.0343	0.8631	0.1369	4.4692

Table A-7.2 1,3-PDO selectivity data of XAD-16 resins.

Total mole of sulutes in liquid phase (mol)	**Total mole of sulutes on solid surface (mol)**	**Mole fraction of 1,3-PDO on solid surface**	**Mole fraction of other on solid surface**	**Mole fraction of 1,3-PDO in liquid phase**	**Mole fraction of other in liquid phase**	**1,3-PDO selectivity**
1.1160	0.0842	0.6250	0.3750	0.8949	0.1051	0.1956
1.3958	0.1045	0.5021	0.4979	0.9040	0.0960	0.1071
1.7277	0.0726	0.3967	0.6033	0.8961	0.1039	0.0762
2.0105	0.0899	0.7353	0.2647	0.8823	0.1177	0.3707
2.1321	0.2683	0.9278	0.0722	0.8695	0.1305	1.9293

A-8 Desorption of 1,3-PDO from adsorbed resin in binary system

Table A-8.1 desorption data of 1,3-PDO of XAD-7 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	160	151.3652	261.2796	14.29827508	161.6734	61.8775
60/40	160	151.2947	261.1580	15.3207	173.2340	66.3330
70/30	160	152.3871	232.4679	13.93828576	176.3458	75.8581
80/20	160	152.2577	232.2704	15.6016	197.3896	84.9827

Table A-8.2 desorption data of 1,3-PDO of XAD-16 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	160	154.1025	184.4515	12.92322784	148.7278	80.6325
60/40	160	153.8612	184.1627	13.4237	154.4880	83.8867
70/30	160	153.2572	202.2839	15.5067	184.5983	91.2570
80/20	160	153.6372	190.8835	16.1832	204.3995	107.0808

A-9 Desorption of 1,3-PDO from adsorbed resin in tertiary system

Table A-9.1 desorption data of 1,3-PDO of XAD-7 resin.

Ratio of ethanol/water, %(v/v)	**Initial concentration, C_0 (g/L)**	**Equilibrium concentration, C_e (g/L)**	**Mass of Adsorbed, MA (mg)**	**Equilibrium concentration, Ce (g/L)**	**Mass of Desorbed, MD (mg)**	**%Yield of Desorbed**
60/40	160	151.7467	247.5976	13.9046	159.8650	64.5665
70/30	160	151.1014	266.9594	15.8624	188.9350	70.7729
80/20	160	151.2392	262.8234	15.8270	200.1315	76.1467

Table A-9.2 desorption data of 1,3-PDO of XAD-16 resin.

Ratio of ethanol/water, %(v/v)	**Initial concentration, C_0 (g/L)**	**Equilibrium concentration, C_e (g/L)**	**Mass of Adsorbed, MA (mg)**	**Equilibrium concentration, Ce (g/L)**	**Mass of Desorbed, MD (mg)**	**%Yield of Desorbed**
60/40	160	152.6829	219.5117	13.2485	152.2764	69.3705
70/30	160	152.9427	211.7201	14.8136	176.3866	83.3112
80/20	160	152.7818	216.5451	16.7992	212.1843	97.9862

A-10 Desorption of 1,3-PDO from adsorbed resin in multiple system

Table A-10.1 desorption data of 1,3-PDO of XAD-7 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	160	139.9279	602.1641	13.4022	196.7822	32.6792
60/40	160	140.5905	582.2841	14.3658	214.5827	36.8519
70/30	160	141.2728	561.8172	14.4862	209.1949	37.2354
80/20	160	140.4282	587.1554	15.0952	220.6435	37.5784

Table A-10.2 desorption data of 1,3-PDO of XAD-16 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	160	132.5076	824.7713	14.2906	209.5740	25.4100
60/40	160	131.5921	852.2379	14.3696	209.0239	24.5265
70/30	160	132.4036	827.8926	15.4068	229.3767	27.7061
80/20	160	133.8052	785.8452	14.2352	198.4405	25.2519

Table A-10.3 desorption data of glycerol of XAD-7 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	0.7273	0.6377	2.6878	0.1018	1.4949	55.6168
60/40	0.7273	0.6307	2.8988	0.0843	1.2598	43.4578
70/30	0.7273	0.6591	2.0449	0.0721	1.0415	50.9301
80/20	0.7273	0.6730	1.6302	0.0724	1.0581	64.9046

Table A-10.4 desorption data of glycerol of XAD-16 resin.

Ratio of ethanol/water, %(v/v)	Initial concentration, C_0 (g/L)	Equilibrium concentration, C_e (g/L)	Mass of Adsorbed, MA (mg)	Equilibrium concentration, Ce (g/L)	Mass of Desorbed, MD (mg)	%Yield of Desorbed
50/50	0.7273	0.6516	2.2707	0.1080	1.5844	69.7745
60/40	0.7273	0.6600	2.0199	0.0913	1.3275	65.7224
70/30	0.7273	0.6204	3.2083	0.0639	0.9514	29.6545
80/20	0.7273	0.5737	4.6092	0.0699	0.9739	21.1283

Table A-10.5 desorption data of acetic acid of XAD-7 resin.

Ratio of ethanol/water, %(v/v)	**Initial concentration, C_0 (g/L)**	**Equilibrium concentration, C_e (g/L)**	**Mass of Adsorbed, MA (mg)**	**Equilibrium concentration, Ce (g/L)**	**Mass of Desorbed, MD (mg)**	**%Yield of Desorbed**
50/50	21.8182	18.4986	99.5883	3.9965	58.6796	58.9221
60/40	21.8182	17.4341	131.5223	4.2226	63.0736	47.9566
70/30	21.8182	16.6863	153.9570	4.7576	68.7042	44.6256
80/20	21.8182	16.9735	145.3415	4.1019	59.9561	41.2519

Table A-10.6 desorption data of acetic acid of XAD-16 resin.

Ratio of ethanol/water, %(v/v)	**Initial concentration, C_0 (g/L)**	**Equilibrium concentration, C_e (g/L)**	**Mass of Adsorbed, MA (mg)**	**Equilibrium concentration, Ce (g/L)**	**Mass of Desorbed, MD (mg)**	**%Yield of Desorbed**
50/50	21.8182	15.4714	190.4027	4.5897	67.3092	35.3509
60/40	21.8182	16.0100	174.2459	6.4371	93.6356	53.7376
70/30	21.8182	16.3485	164.0906	7.1162	105.9460	64.5656
80/20	21.8182	16.3485	164.0906	6.3519	88.5461	53.9617

Table A-10.7 Mass fraction of each of adsorbed solute in desorbed solution of two resins.

Ratio of ethanol (%v)	XAD-7				
	1,3-PDO	glycerol	butyric	ethanol	water
50	0.283	0.002	0.084	0.271	0.359
60	0.301	0.002	0.088	0.329	0.280
70	0.303	0.002	0.100	0.379	0.217
80	0.321	0.002	0.087	0.445	0.146

Ratio of ethanol (%v)	XAD-16				
	1,3-PDO	glycerol	butyric	ethanol	water
50	0.292	0.002	0.094	0.263	0.349
60	0.287	0.002	0.128	0.308	0.274
70	0.302	0.001	0.139	0.360	0.198
80	0.294	0.001	0.131	0.426	0.148

APPENDIX B

LIST OF PUBLICATION

The 12th Asian Pacific Confederation of Chemical Engineering Congress

(APPChE 12th)

4-6 August 2008, Dalian, China

Adsorption of 1,3-PDO from synthetic mixture using polymeric resin as adsorbents

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12th APCChE Congress **Vol. 5-123**
Aug 4~6,2008, Dalian,China

Adsorption of 1,3-propanediol from synthetic mixture using polymeric resin as adsorbents

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Abstract

The aim of this work was to separate 1,3-PDO from synthetic mixture using polymeric resins, Amberlite XAD-7 and XAD-16 resins. The equilibrium adsorption of 1,3-PDO onto two polymeric resins were investigated in single and binary systems. Experimental results of single component adsorption equilibrium indicated that the adsorption capacity (q) of 1,3-PDO at 160 g/L onto XAD-7 and XAD-16 was 835.96 and 584.61 mg 1,3-PDO/g dry resin, respectively. The equilibrium adsorption data were adequately characterized by Freundlich model. The value of $\boldsymbol{K_F}$ and n of 1,3-PDO adsorbed on XAD-7 are much higher than those on XAD-16. This result suggested that the XAD-7 is favorable for 1,3-PDO adsorption than XAD-16 resin. Moreover, the value of adsorption capacity of 1,3-PDO in single and binary components were compared at the same conditions. The results showed that the selectivity of 1,3-PDO from XAD-7 was approximately six times higher than XAD-16 but, interestingly, in binary components, the adsorption capacity of 1,3-PDO at 160 g/L onto XAD-16 was higher than XAD-7. However, the mass of adsorbed/desorbed 1,3-PDO from XAD-16 at 160 g/L was higher than XAD-7, which demonstrated that the adsorption of 1,3-PDO onto XAD-16 is favorable than XAD-7 in binary components. Furthermore, the investigation about desorption by ethanol/water mixture at 50% (v/v) indicated that the desorption yield from XAD-7 was 80.91% which was lower than the XAD-16 (85.13%). This was due to more favorable adsorption characteristic of XDA-7 resin than XAD-16 resin.

Keywords: Adsorption, 1,3-propanediol, glycerol, polymeric resin, adsorption isotherm.

1. Introduction

1,3-propandiol (1,3-PDO) is of interest as a feedstock for biodegradable polymer, especially for polyester production. 1,3-PDO can be produced via chemical and fermentation processes. In recent years, the crisis of petroleum resources have an impact on the price of petroleum based products, therefore, 1,3-PDO fermentation using glycerol(from biodiesel production) as substrate has been successfully revived since fermentation process is favorable for environmental protection, renewable and involving with cheap raw materials (1-4).

Regarding to 1,3-PDO separation from fermentation, several processes have been investigated but they still have serious limitations. Because 1,3-PDO has low volatility and strong hydrophilic characteristics in aqueous solutions, the recovery of 1,3-PDO from fermentation broth is difficult. Conventional distillation processes (5) applied to the separation of product from dilute aqueous solution requires a substantial energy input which accounts for high cost of the final product. Several other methods including a liquid-liquid extraction (6) and a phase separation method (7) have also been proposed, however, no appropriate extractant with a higher mass distribution coefficient has been found for the strong hydrophilic character of 1,3-PDO. Up until now, the separation of 1,3-PDO have been focused to achieve better separation value and easy operation. Since adsorption is easy to operate and has low maintenance cost, and several adsorbents are available for use. Therefore, it is interesting to use adsorption process for 1,3-PDO separation (8-11).

Since the selection of an adsorbent is one of the key factors for the success in the separation of 1,3-PDO from the aqueous solution. From our knowledge, only zeolite, activated carbon and ion exchange resins were used to separate 1,3-PDO. Therefore, it is interesting to apply non-ionic polymeric adsorbent in our research work. Thus, the aim of this study was to investigate non-ionic adsorbent for the separation of the non-ionic 1,3-PDO from aqueous fermentation mixture. The adsorbent should have both hydrophobicity and hydrophilicity which is a characteristics of 1,3-PDO, and the pore size of adsorbent should not be too small. Based on the above criteria, polymeric adsorbents are thus selected as an adsorbent in this study.

2. Materials and methods

2.1 Chemicals

The aqueous feed mixture was 1,3-PDO and glycerol, which corresponds to a typical composition in the fermentation broths from our laboratory. 98% 1,3-PDO and 99% glycerol were purchased from Acros Organic Co. and Ajax Finechem respectively.

The resins used in experiments were Amberlite XAD-7 (Rohm and Haas, 1982) and Amberlite XAD-16 (Rohm and Haas, 1982). Amberlite XAD-7 is a non-ionic aliphatic acrylic polymer, which derives its adsorptive properties from its macroreticular structure (containing both a continuous polymer phase and a continuous pore phase), high surface area and aliphatic nature of its surface. Amberlite XAD-16 (Rohm and Haas, 1982) is rigid, non-ionic, crosslinked macroreticular copolymer of styrene and divinylbenzene, with high surface area and aromatic nature of its surface.

2.2 Equilibrium adsorption experiments

Adsorption experiments were carried out at 303 K. The wet beads of resin (approximately 0.5 g dry weight) was introduced into a series of 150 ml conical flasks containing 30 ml aqueous solution with known concentrations. Firstly, the single component equilibrium adsorption was determined using the initial concentrations (C_0) of 1,3-PDO solution from 60 to 200 g/L. Secondly, binary component equilibrium adsorption and selectivity were investigated using the initial concentration of 1,3-PDO from 80 to 160 g/L and initial concentration of glycerol from 0.36 to 0.73 g/L. The flask were then completely sealed and placed in an incubator shaker with shaking speed of 150 rpm for 48 h, which was sufficient for system equilibration. Each of equilibrium concentrations of the solutions were measured using HPLC.

2.3 Elution

To determine the amount of 1,3-PDO eluted for the adsorption of 1,3-PDO onto the XAD-7 and XAD-16 resins, 30 ml of 160 g/L 1,3-PDO solution were introduced into a series of 150 ml conical flasks and then shaken with 0.5 g resin at 48 h. The amount of 1,3-PDO adsorbed was calculated using Eq.(1). Afterward, 0.5 g of the resin that adsorbed 1,3-PDO was placed in 30 ml ethanol/water mixture at 50% (v/v), sealed and then shaken at 150 rpm, 303 K. Sample were taken at 24 h.

2.4 Analysis

The concentrations of 1,3-PDO and glycerol in aqueous solutions were measured by using HPLC Lichrocart-C18 column (250 mm x 4 mm I.D.) with RI detector. The mobile phase was 5%MeOH and maintained at 0.5 ml/min with an injection volume of 20 µL.

After 48 hour of shaking, equilibrium concentrations of 1,3-PDO (C_e) in solutions were determined and the amount of adsorbed (q_e, g 1,3-PDO/g dry resin) was calculated from Eq. (1).

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{1}$$

where V is the volume of solution (L), C_o , C_e is an initial and equilibrium concentration (g/L), W is the weight of dry resin (g). The equilibrium selectivity ($\alpha_{1,2}$) is defined as follows:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \tag{2}$$

where x_1, x_2 are the mole fraction of components (1) and (2) on the adsorbent surface, whereas y_1, y_2 are the corresponding mole fractions in the liquid phase. It will be assumed that component (1) is the more strongly adsorbed species.

3. Result and discussion

3.1 Effect of initial concentration

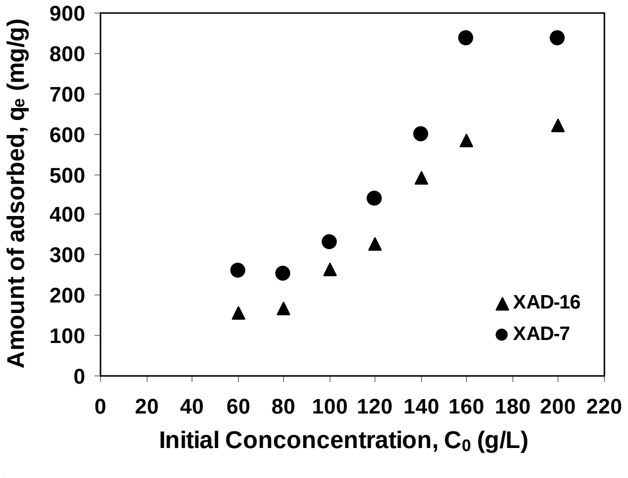

Fig. 1. Adsorption of 1,3-propanediol onto XAD-7 and XAD-16 resins versus initial concentrations.

Fig. 1 illustrates the adsorption of 1,3-PDO by XAD-7 and XAD-16 resins as a function of initial 1,3-PDO concentration. The amount of 1,3-PDO adsorbed were calculated using Eq. (1). It is obvious that favorable adsorption experiments were exhibited by these two polymeric adsorbents for 1,3-PDO with the extent of adsorption increasing as the initial concentration of the adsorbate increased in the aqueous solution. This increase continuously up to 160 g/L and beyond this value, there is no significant change in the amount of adsorbed 1,3-PDO. This plateau represents saturation of the active sites available on the resins for interaction with 1,3-PDO in aqueous solution in range of 160-200 g/L. Maximum experimental adsorption capacity of 1,3-PDO at 160 g/L onto XAD-7 and XAD-16 was 835.96 and 584.61 mg of 1,3-PDO/ g dry resin, show that the XAD-7 resin was suitable for 1,3-PDO adsorption from aqueous media. Moreover, the maximum experimental adsorption capacity of 1,3-PDO onto XAD-7 and XAD-16 resins in this study were higher than H-ZSM-5 zeolite adsorbent (11), which gave a capacity of 91.3 mg 1,3-PDO/ g zeolite. This is due to preferential adsorption of 1,3-PDO with non-ionic characteristic of resin.

3.2 Adsorption isotherms

The amount of 1,3-PDO adsorbed per gram of the resin (q_e) against the 1,3-PDO equilibrium concentration had been plotted in Fig. 2. The Langmuir and Freundlich models can be linearized (shown in Table 1), and then the fitting parameters were determined graphically by linear regression (shown in Table 2). From these figures it can be seen that the adsorption data for 1,3-PDO onto these two polymeric adsorbents are similar. It is quite obvious that the Freundlich model is better fitted than Langmuir model for all of the isotherm, supported by the lowest mean relative deviation value (Δq) (Table 2). The value of K_F and n of 1,3-PDO adsorbed on XAD-7 are much higher than those on XAD-16. All correlation coefficient R^2 for the XAD-16 resin is larger than 0.932 and those for the XAD-7 resin is less than 0.887. These results indicate that the adsorption mechanism of 1,3-PDO on XAD-7 and XAD-16 resin may be different.

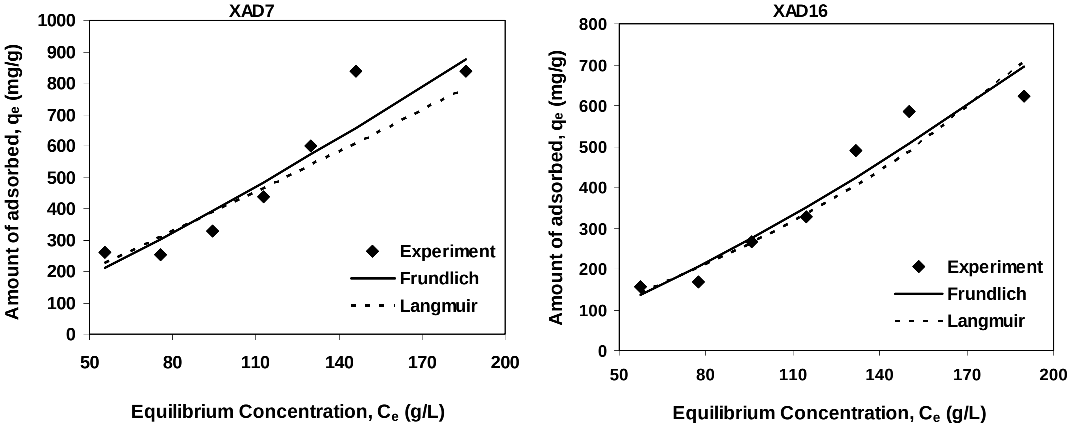

Fig. 2. 1,3-PDO equilibrium adsorption isotherm of XAD-7 and XAD-16 resin. Fitting to Langmuir and Freundlich models are shown together with these experimental data points.

Table 1. Isotherm models

Name	Equation	Linear form	Capacity term
Freundlich model	$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	k_F and n, fitting parameter
Langmuir model	$q_e = \frac{K_L a_L C_e}{1 + a_L C_e}$	$\frac{1}{q_e} = \frac{1}{K_L a_L C_e} + \frac{1}{K_L}$	k_L and a_L , fitting parameter

Table 2. Fitting parameters of models

Langmuir model				
Adsorbents	k_L (mg/g)	a_L (L/mg)	R^2	Δq (%)
XAD-7	-12500	-3.176E-07	0.843	4.531
XAD-16	-1000	-2.183E-06	0.932	3.044
Freundlich model				
	k_F (mg/g)	n (L/g)	R^2	Δq (%)
XAD-7	5.038E-05	0.8445	0.8872	3.743
XAD-16	4.800E-05	0.7371	0.9425	2.087

The different characteristics of isotherms observed for the XAD-7 and XAD-16 resins can be ascribed to the different hydrophobicities of the two types of resins. Van der waals force is normally dominant force for the adsorption from the aqueous phase onto a hydrophobic adsorbent. However, the electrostatic attraction has been important for molecules with certain functional groups. Therefore, the dominant factor for adsorption of 1,3-PDO onto XAD-16 resin is van der waals force while that on the XAD-7 resin may be the cooperation of hydrophobic interaction and electrostatic attraction (12).

3.3 Effect of binary components (1,3-PDO and glycerol) in solution

The adsorption isotherm of 1,3-PDO in single and binary component in aqueous solution onto the two resins at 303K are compared in Figure. 3. Interestingly, 1,3-PDO equilibrium adsorption on XAD-7 resin in binary system shows a significant increasing in the adsorption capacity of 1,3-PDO in the range of 80-140 g/L but reduction between 140-160 g/L, whereas the adsorption onto the XAD-16 resin is different. Moreover, for binary component using XAD-16 gave better adsorption capacity than XAD-7. The reason for the differences in 1,3-PDO adsorption onto the resins is complex. Furthermore, the precise role-played by the polar group, the aromatic center is uncertain. In case of selectivity (data not shown) in binary system, the selectivity of 1,3-PDO/glycerol on these two resins were calculated from Eq. (2). Although, the selectivity of 1,3-PDO from XAD-7 was approximately six times higher than XAD-16 but, interestingly, in binary components, the adsorption capacity of 1,3-PDO at 160 g/L onto XAD-16 was higher than XAD-7. This indicated that for binary system, XAD-16 was more favorable in adsorption of 1,3-PDO over than XAD-7. Next desorption ability of most resins were investigated.

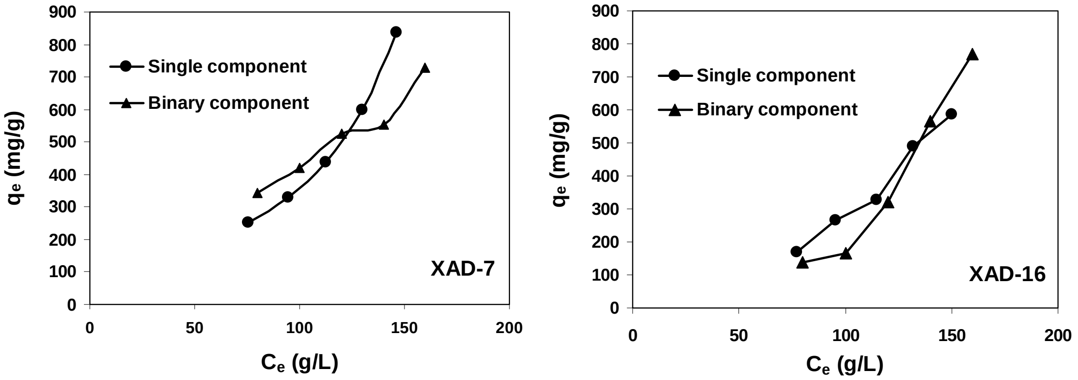

Fig. 3. Comparison of the experimental single equilibrium adsorption data (●) with binary equilibrium adsorption data (▲) of 1,3-PDO onto XAD-7 and XAD-16 resins.

Table 3 shows the desorption yield (%) of 1,3-PDO from the XAD-7 and XAD-16 resins using ethanol solution. It is discovered that desorption yield of 1,3-PDO from XAD-16 was higher than XAD-7 resin for both single and binary component. This can be explained that XAD-7 resin has high affinity for the 1,3-PDO adsorption, therefore 1,3-PDO elution from the resins seem to be very difficult. In binary system, table 4 showed that mass of 1,3-PDO desorption from XAD-16 was in line with adsorption and was higher than those from XAD-7. So, we can conclude that XAD-16 promised to adsorb 1,3-PDO from synthetic mixture over than XAD-7 resin.

Table 3. Desorption yield (%) of 1,3-PDO from XAD-7 and XAD-16 resins at 24 hours.

	Desorption yield (%)	
Resins	Single component	Binary components
XAD-7	61.88	80.91
XAD-16	80.63	85.13

Table 4. Mass of adsorption at 160 g/L and desorption of 1,3-PDO from XAD-7 and XAD-16 resins.

	Adsorbed mass of 1,3-PDO (mg)		Desorbed mass of 1,3-PDO (mg)	
Resins	Single component	Binary components	Single component	Binary components
XAD-7	835.96	726.68	517.29	587.96
XAD-16	584.61	770.05	471.37	655.54

Conclusions

The results in the present study showed that the polymeric resins had good adsorption capacity than another adsorbent (zeolite). Experimental equilibrium adsorption data were fitted well by Freundlich model. In single component system, the XAD-7 showed good favorable for 1,3-PDO adsorption than XAD-16 resin. However, in binary component system at 160 g/L of initial concentration of 1,3-PDO, the efficiency of 1,3-PDO adsorption of XAD-16 was higher than XAD-7. Although the selectivity of 1,3-PDO onto XAD-7 resin was six times higher than the XAD-16 resin. From these results, it could be concluded that the adsorption of 1,3-PDO using polymeric resins is an alternative method for separation of 1,3-PDO from aqueous solution.

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The 18th Thailand Chemical Engineering and Applied Chemistry Conference

(TICHE 17 th)

20-21 October 2008, The Jomtien Plam Beach Hotel, Chonburi, Thailand

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Adsorption of 1,3-propanediol from model mixture of fermentation broth using polymeric resins

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Abstract Two polymeric resins were used to adsorb 1,3-PDO from model mixture of fermentation broth. The equilibrium adsorption isotherm of 1,3-PDO with non-ionic polymeric resins , PTTCH1 and PTTCH2, were investigated for 1,3-PDO adsorption in binary system. The adsorption equilibrium data indicated that the amount of 1,3-PDO adsorbed (q_e) at 160 g/L onto PTTCH1 and PTTCH2 were 835.96 and 584.61 mg 1,3-PDO per g dry resin, respectively. The equilibrium adsorption data were adequately characterized by Freundlich model. Moreover, the amount of 1,3-PDO adsorbed onto PTTCH1 and PTTCH2 and desorption yield (%) between binary and multiple component system have been compared at 160 g/L of initial concentration of 1,3-PDO. The influence of other components in aqueous solution on 1,3-PDO adsorption shows the higher amount of 1,3-PDO adsorbed and 1,3-PDO selectivity than binary system in both resins, in contrary, the 1,3-PDO desorption yield (%) drastically reduced.

1. Introduction

Nowadays, conversion of glycerol into high value product such as 1,3-propanediol (1,3-PDO) is a big challenge. 1,3-PDO has been considered a specialty chemical, which is one of interest as a feedstock for biodegradable polymer, especially for polyester production. 1,3-PDO can be produced via chemical and fermentation processes. In recent years, the crisis of petroleum resources have an impact on the price of petroleum based products, therefore, 1,3-PDO fermentation using glycerol(from biodiesel production) as substrate has been successfully revived since fermentation process is favorable for environmental protection, renewable and involving with cheap raw materials (1-4).

There have been several processes for 1,3-PDO separation from fermentation broth, which still have serious limitations. Because 1,3-PDO has low volatility and strong hydrophilic characteristics in aqueous solutions, therefore, the recovery of 1,3-PDO from fermentation broth is difficult. Conventional distillation processes (5) applied to the separation of product from dilute aqueous solution requires a substantial energy input which accounts for high cost of the final product. Several other methods including a liquid-liquid extraction (6) and a phase separation method (7) have also been proposed, however, no appropriate extractant with a higher mass distribution coefficient has been found for the strong hydrophilic character of 1,3-PDO. Up until now, the separation of 1,3-PDO have been focused to achieve better separation value and easy operation. Since adsorption is easy to operate and has low maintenance cost, and several adsorbents are available for use. Therefore, it is interesting to use adsorption process for 1,3-PDO separation (8-11).

The aim of this study is to focus on the use of non-ionic polymeric resin for the separation of the non-ionic 1,3-PDO from model mixture of fermentation broth. The polymeric resins were chosen because they have both hydrophobicity and hydrophilicity which is a characteristics of 1,3-PDO. Also the influence of component in aqueous solution and ability of 1,3-PDO desorption from resins were investigated in detail.

2. Materials and methods

2.1 **Materials** The resins used in experiments were PTTCH1 and PTTCH2. PTTCH1 is a non-ionic aliphatic acrylic polymer, which derives its adsorptive properties from its macroreticular structure (containing both a continuous

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polymer phase and a continuous pore phase), high surface area and aliphatic nature of its surface. PTTCH2 is rigid, non-ionic, crosslinked macroreticular copolymers, with high surface area and aromatic nature of its surface.

The feed material in multiple system was a mixture of 1,3-PDO, glycerol, acetic, and butyric acid, which corresponds to a typical composition in the fermentation broths from our laboratory. 98% 1,3-PDO and 99% glycerol were purchased from Acros Organic Co. and Ajax Finechem respectively.

2.2 **Analysis** The concentrations of 1,3-PDO and glycerol in aqueous solutions were measured by using HPLC Lichrocart-C18 column (250 mm x 4 mm I.D.) with RI detector. The mobile phase was 5%MeOH and maintained at 0.5 ml/min with an injection volume of 20 µL. After 48 hour of shaking, equilibrium concentrations of 1,3-PDO (C_e) in solutions were determined and the amount of adsorption (q_e, g 1,3-PDO per g dry resin) was calculated from Eq. (1).

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where V is the volume of solution (L), C_o , C_e is an initial and equilibrium concentration (g/L), W is the weight of dry resin (g). The equilibrium selectivity ($\alpha_{1,2}$) is defined as follows:

$$\alpha_{1,2} = \frac{x_1}{x_2} \cdot \frac{y_2}{y_1} \quad (2)$$

Where x_1, x_2 are the mole fraction of components (1) and (2) on the adsorbent surface, whereas y_1, y_2 are the corresponding mole fractions in the liquid phase. It will be assumed that component (1) is the more strongly adsorbed species.

2.3 **Equilibrium adsorption experiments** Adsorption experiments were carried out at 303 K. The wet beads of resin (approximately 0.5 g dry weight) was introduced into a series of 150 ml conical flasks containing 30 ml aqueous solution with known concentrations. Firstly, the binary component equilibrium adsorption was determined using the initial concentrations (C_0) of 1,3-PDO solution from 60 to 200 g/L. Secondly, multiple components equilibrium adsorption and selectivity were investigated using the initial concentration of 1,3-PDO, glycerol, acetic acid, and butyric acid at 160, 0.7273, 2.5455 and 21.8182 g/L respectively. The flasks were then completely sealed and placed in an incubator shaker with shaking speed at 150 rpm for 48 h, which was sufficient for system equilibration. Each of equilibrium concentrations of the solutions were measured using HPLC.

2.4 **Elution** After the adsorption experiment, 0.5 g of the resin that adsorbed 1,3-PDO was placed in 30 ml of 50% (v/v) ethanol/water ratio and then was shaken at 150 rpm, 303 K. Samples were taken at 24 h.

3. Result and discussion

3.1 **Adsorption isotherm** The adsorption isotherm of 1,3-PDO at initial concentration 60 to 200 g/L with PTTCH1 and PTTCH2 resins are shown that in Figure 1. As shown in the experimental results, there exists a type II isotherm, which is typical of physisorption on microporous solid, which correspond to both completion of monolayer coverage and filling of the micropores by capillary condensation. The rest of the curve (160-200 g/L of equilibrium concentration) would then correspond to normal multilayer formation. Maximum experimental adsorption capacity of 1,3-PDO at 160 g/L onto PTTCH1 and PTTCH2 that were 835.96 and 584.61 mg of 1,3-PDO/ g dry resin respectively, revealed that the PTTCH1 resin was suitable for 1,3-PDO adsorption from aqueous media. Moreover, the maximum experimental adsorption capacity of 1,3-PDO onto PTTCH1 and PTTCH2 resins in this study were higher than H-ZSM-5 zeolite adsorbent at batch condition (8), which gave a capacity of 91.3 mg 1,3-PDO/ g zeolite. This is due to preferential adsorption of 1,3-PDO with non-ionic characteristic of resin and so on the basis that “like attracts like” in aqueous media.

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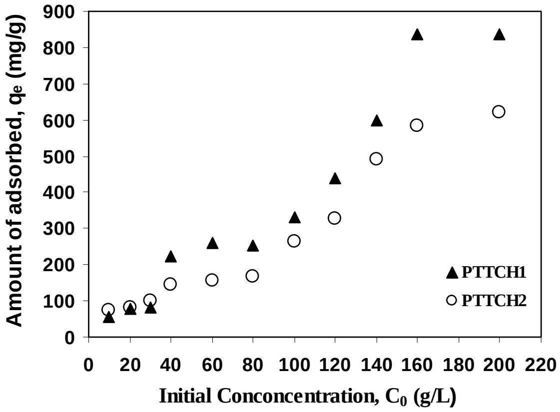

Figure 1 Comparison of adsorption isotherm of 1,3-PDO between PTTCH1 and PTTCH2 resins.

3.2 **Model fitting** Next, the isotherm equilibrium data are analyzed using either Langmuir or Freundlich equilibrium equation. The Langmuir equation can be written in the following form:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} \tag{4}$$

where K_L and a_L are the Langmuir constants. Moreover, the empirical Freundlich equation is given below by Eq (5)

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F and n are the Freundlich constant characteristic of the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The linear plot of 1/ q_e versus 1/ C_e and log q_e versus log C_e for the Langmuir and Freundlich isotherm model are shown, respectively in Figure 2 to 3. The Langmuir and Freundlich constants are determined from the intercept and slope of the plot and presented in Table 1. It is quite obvious that the Freundlich model is better fitted than Langmuir model for the entire isotherm, supported by the lowest mean relative deviation value (Δq). The value of K_F and n of 1,3-PDO adsorbed on PTTCH1 are much higher than those on PTTCH2 thus, the PTTCH1 more suitable for 1,3-PDO adsorption than PTTCH2 resin. All correlation coefficient R^2 for the PTTCH2 resin is larger than 0.932 and those for the PTTCH1 resin is less than 0.887. These results indicate that the adsorption mechanism of 1,3-PDO on PTTCH1 and PTTCH2 resin may be different (12).

Table 1 Fitting parameters of models

Langmuir model				
Adsorbents	K_L (mg/g)	a_L (L/mg)	R^2	Δq(%)
PTTCH1	-12500	-3.176E-07	0.8430	4.531
PTTCH2	-1000	-2.183E-06	0.9323	3.044
Freundlich model				
Adsorbents	K_F (mg/g)	n (L/g)	R^2	Δq(%)
PTTCH1	5.038E-05	0.8445	0.8872	3.743
PTTCH2	4.800E-05	0.7371	0.9425	2.087

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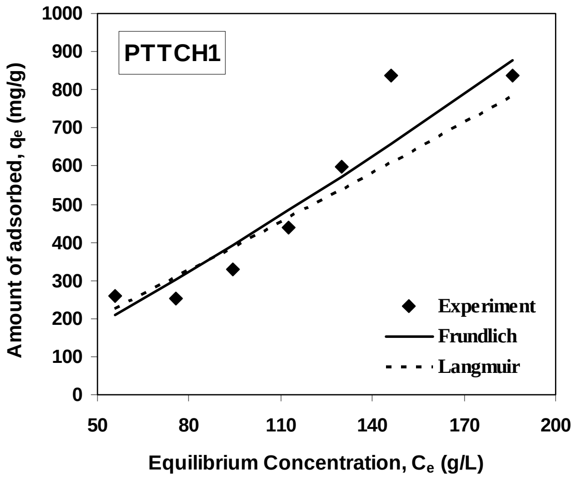

Figure 2 1,3-PDO equilibrium adsorption isotherm of PTTCH1 resin. Fitting to Langmuir and Freundlich models are shown together with these experimental data points.

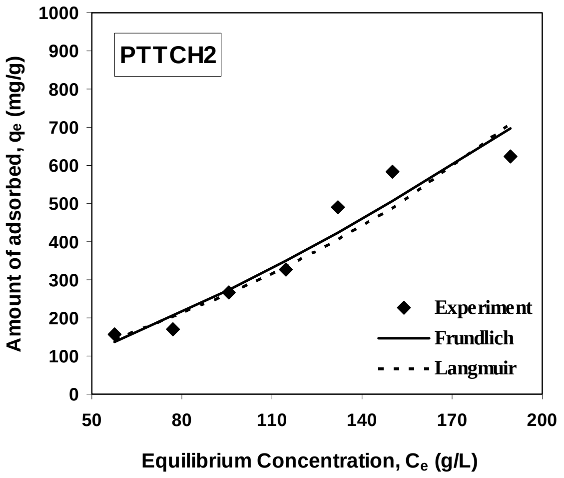

Figure 3 1,3-PDO equilibrium adsorption isotherm of PTTCH2 resin. Fitting to Langmuir and Freundlich models are shown together with these experimental data points.

3.3 **Effect of other component in aqueous mixture** From previous results, it was found that the initial concentration of 1,3-PDO at 160 g/L gives the highest adsorption value, q_e. So in this experiment, the amount of 1,3-PDO adsorbed onto PTTCH1 and PTTCH2 between binary and multiple component system have been compared at 160 g/L for investigating the influence of other components in aqueous solution. Interestingly, from Figure 4 to 5, the results showed that the amount of 1,3-PDO adsorbed in multiple system onto two resins were higher than binary system. It can be explained that the other components in aqueous solution affect to 1,3-PDO adsorption, which reduced the 1,3-PDO-water interaction and then the 1,3-PDO molecule has more independence. So, the 1,3-PDO can be easily bind and adsorbed on surface resins. Moreover, in multiple component system, the value of 1,3-PDO selectivity of PTTCH1 resin was approximately two times higher than PTTCH2 (data not shown). This indicated that, for multiple system, PTTCH1 was more favorable in adsorption of 1,3-PDO over than PTTCH2. Next desorption ability of both resins were investigated.

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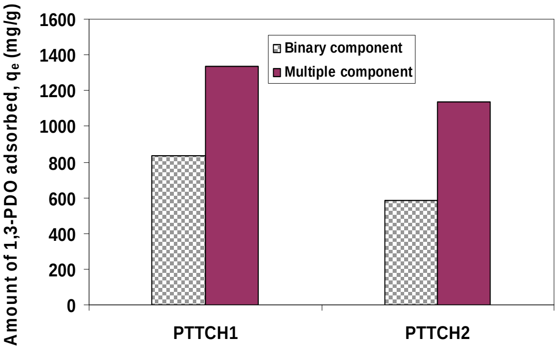

Figure 4 The comparison of the amount of 1,3-PDO adsorbed onto two resins between binary and multiple component system at 160 g/L of initial concentration of 1,3-PDO.

Figure 5 shows the desorption yield (%) of 1,3-PDO from the PTTCH1 and PTTCH2 resins using 50% (v) ethanol solution. It is discovered that desorption yield of 1,3-PDO from PTTCH2 was higher than PTTCH1 resin in binary component. It can be explained that PTTCH1 resin has high affinity for the 1,3-PDO adsorption, therefore 1,3-PDO elution from the resins seem to be very difficult. Interestingly, the desorption yield of 1,3-PDO onto PTTCH1 and PTTCH2 in binary system were 62 and 81%, respectively, while they were 33 and 25%, respectively in multiple system. Therefore, the other components (glycerol, acetic, and butyric acid) adsorbed onto resins affect to the reduction of desorption yield. This observation demonstrates a significant effect of other component on desorption, and the results may be related to the interfering effect of other components on the hydrophobic interaction and electrostatic attraction.

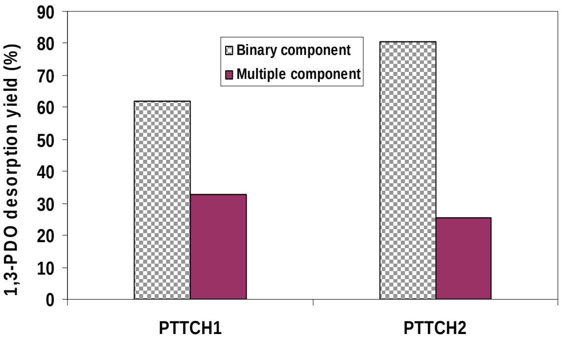

Figure 5 The comparison of the 1,3-PDO desorption yield (%) of PTTCH1 and PTTCH2 resins between binary and multiple component system.

4. Conclusions

The results in the present study showed that the polymeric resins had good adsorption capacity than another adsorbent (zeolite) in batch equilibrium adsorption experiment. The experimental equilibrium adsorption data were fitted well by Freundlich model. In binary component system, the PTTCH1 showed good favorable for 1,3-PDO adsorption than PTTCH2 resin. Moreover, in multiple component system, the selectivity of 1,3-PDO onto PTTCH1 resin was two times higher than the PTTCH2 resin, i.e, the efficiency of 1,3-PDO adsorption of PTTCH1 was higher than PTTCH2. From these results, it could be concluded that the adsorption of 1,3-PDO using polymeric resins is an alternative method for separation of 1,3-PDO from aqueous solution.

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